

POLLUTION IN THE MARINE ENVIRONMENT: PLASTICS, MICROPLASTICS AND ORGANIC POLLUTANTS



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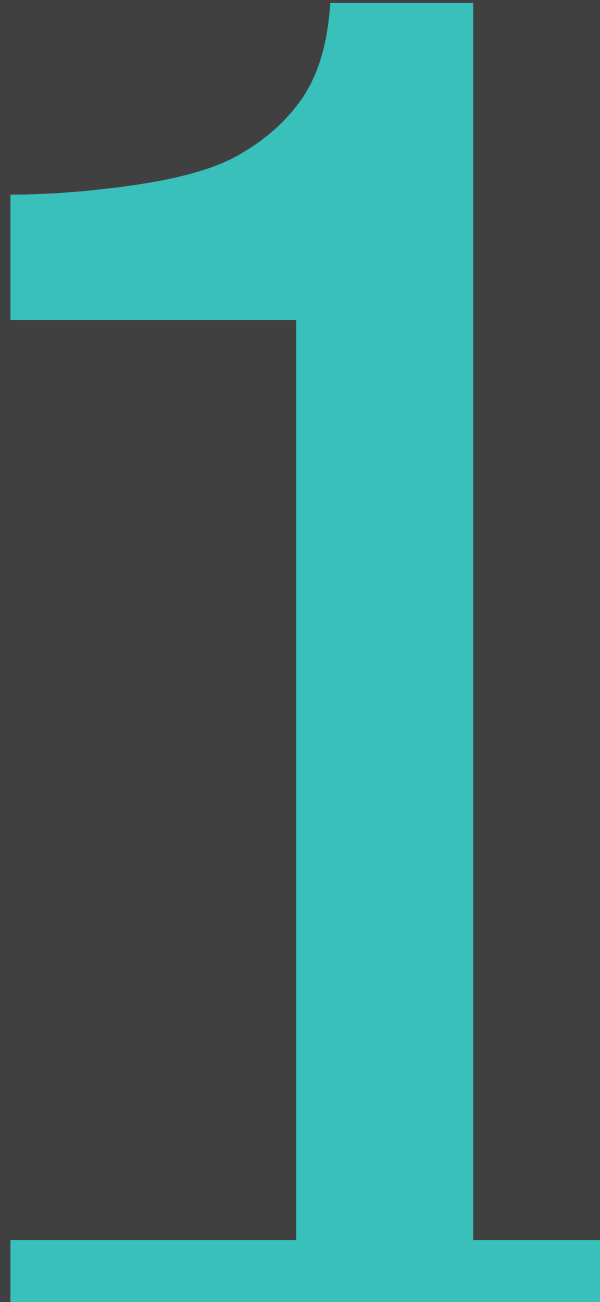


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10th April, 2019



The problem



The known problem

Deficient treatment of plastic waste → plastics reach the ocean



**10 Million tons
of plastics are
thrown out to
the ocean
every year**

The known problem

Deficient treatment of plastics → plastics reach the ocean



1.5 kg/person
are
out to
the ocean
every year

Marine debris (MDs)

MD = Solid material that has been deposited, dumped or abandoned in the coastal environment

Dumping

- Directly by human action
- Through rivers, waste waters, rain and winds
- Boats and ships (accidental loss)



Worrying presence

- Harmful to organisms & human health
- Pollutant transport
- Risk to fishing & sea products

Composition

- Glass
- Metal
- Paper
- **PLASTICS (higher percentage)**

Samples

Selection of samples to study

MDs used: mix of wastes collected during 1-Day sampling
Boat trip near the coast in Santa Pola (Alicante)



Samples

Selection of samples to study



Characterization

- Humidity
- Ash content
- Heating power
- Elemental analysis
 - ✓ Carbon
 - ✓ Nitrogen
 - ✓ Hydrogen
 - ✓ Sulphur
 - ✓ Oxygen
- Ion chromatography
 - ✓ Fluorine
 - ✓ Chlorine
 - ✓ Bromine

Homogeneous



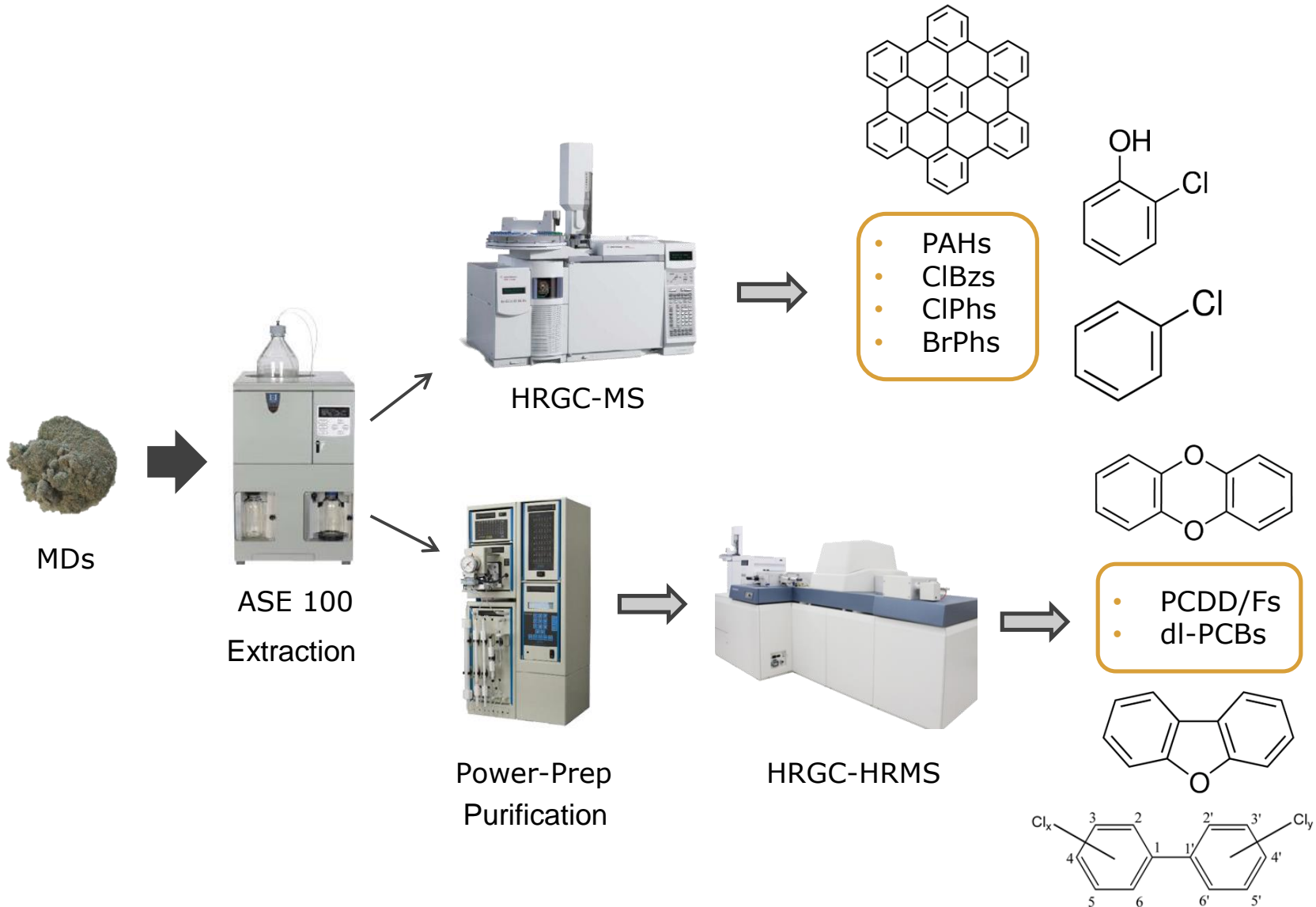
Cryogenic ball mill



Crushed

Analysis

Pollutants in the MDs



Pollutants

Results

- High chlorine content: 1.83 % (taken from saline medium)
- Heating power: 25.6 MJ/kg

Analysis of pollutants

PAHs

Total: 450-500 ng/g_{sample}
Naphtalene: 100 ng/g_{sample}

CIBzs

180-215 ng/g_{sample}
1,2-dichlorobenzene

CIPhs

105 ng/g_{sample}

BrPhs

58-77 ng/g_{sample}

MDs

Not very contaminated

High content of CIBzs.

Values similar to:

- Plant soil
- River sediments

Wooden furniture/pine wood:

- PAHs: 645 ng/g
- CIBzs: not detected
- CIPhs: 100 ng/g

Similar levels of pollutants

Pollutants

Results

PCDD/Fs

1.05 ± 0.15 pg WHO-TEQ/g

Vietman sediment (Tri et al., 2016) → 1.8 pg WHO-TEQ/g, similar to that obtained in this study

PCBs

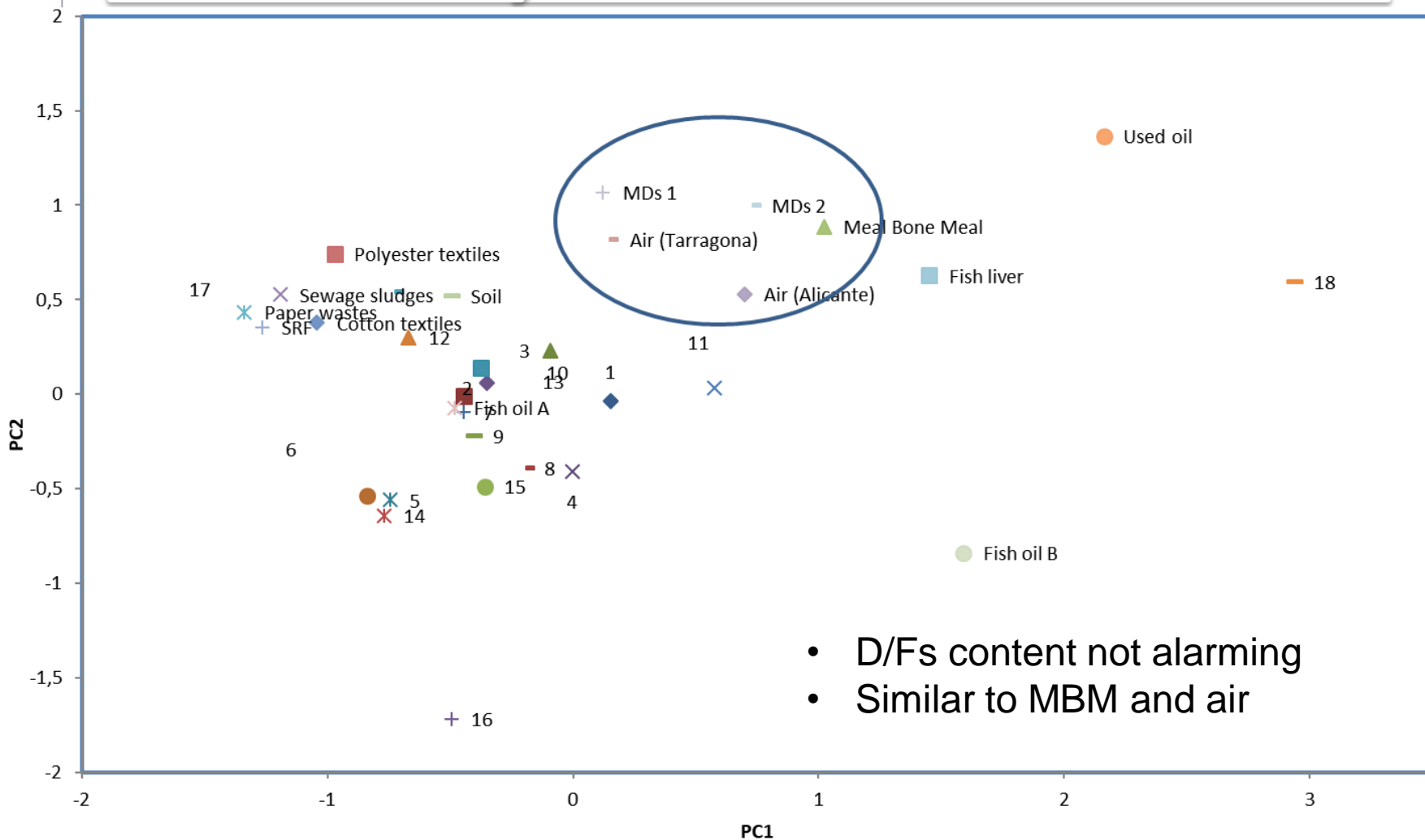
0.46 ± 0.02 pg WHO-TEQ/g

Total toxicity of PCBs represents ca. 30 % of the dioxin-like compounds toxicity.

dl-PCBs contribution very different depending on the sample:
Fish oils → 65 - 80% (Ábalos et al., 2010)
Polyester textiles → 2 % (Moltó et al., 2006)

PCDD/Fs

Comparison congener profile and levels



- D/Fs content not alarming
- Similar to MBM and air

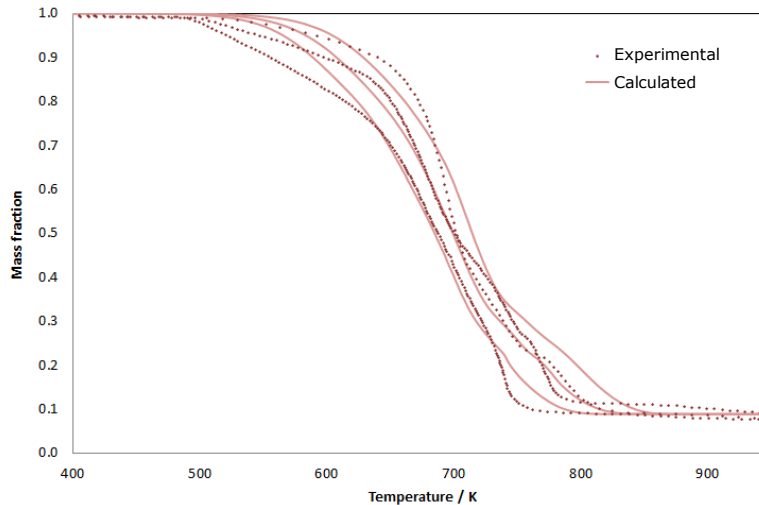
1-MSWI (mass burn-water wall w/hot-side ESP)
 2-MSWI (mass burn-water wall w/ds)
 3-Medical Waste Incinerators (w/o APCD)
 4-Hazardous Waste Incinerators

5-Cement Kilns Burning Haz Waste
 6-Cement Kilns Not Burning Haz Waste
 7-Industrial Oil-Fired Boilers
 8-Industrial/Utility Coal Combustors

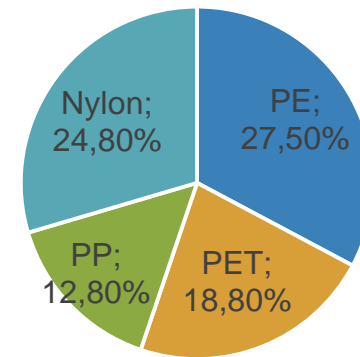
9-Industrial Wood Combustors
 10-Unleaded Gasoline Vehicles (w/ cat. conv.)
 11-Diesel Trucks (tailpipe emissions)
 12-Diesel Trucks (Baltimore Tunnel)

MDs

Thermogravimetry runs

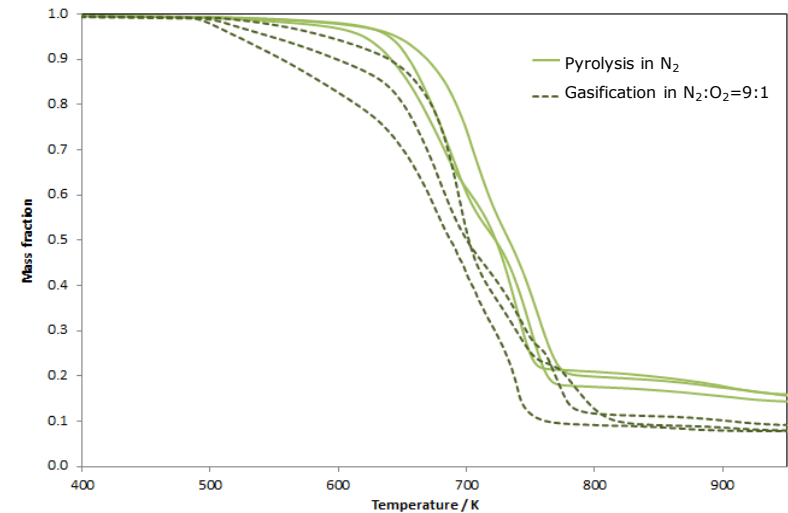


Comparison of thermal decomposition of MD sample with curves obtained for pure components
--> Estimated composition (%)



Comparison N₂ vs. AIR

- O₂ → slight acceleration of the decomposition
- T > 700 K → increased weight loss in the presence of O₂.



Human exposure



How these MDs arrive to humans??

- Main form of exposure to marine pollution: food of marine origin.



Salt as medium of transport of MPs

Microplastics

Materials & methods



SAMPLES STUDIED

- 21 samples of different types, including:
 - Coastal and interior salts (well salt)
 - 2 particle sizes
 - Before and after packaging



Aim: obtain information about the origin of the MPs

200 g salt + 1 L pure water



Centrifuge
1 h



Vacuum filtration.
FILTERS OF 5 μm
pore size

MPs



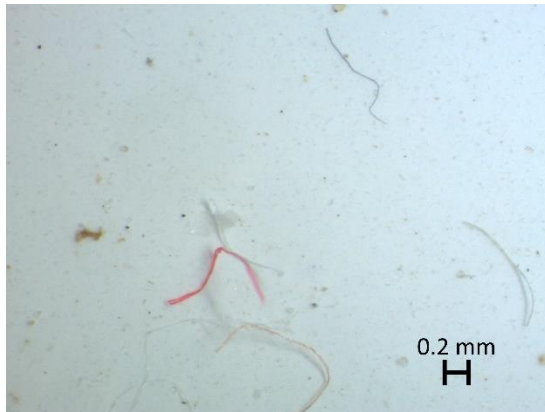
Identification: FTIR



Counting in optical microscope

MPs in salt

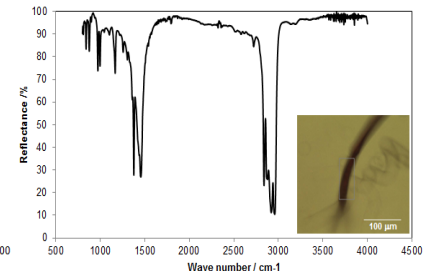
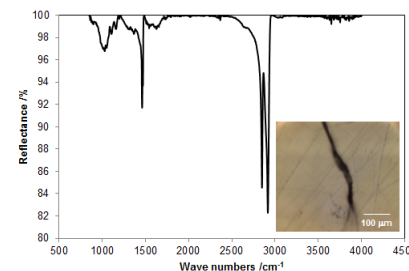
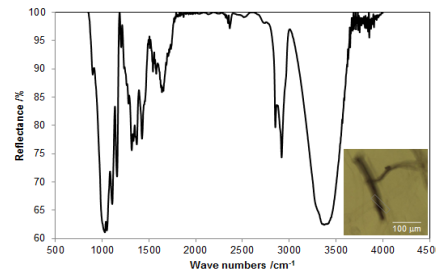
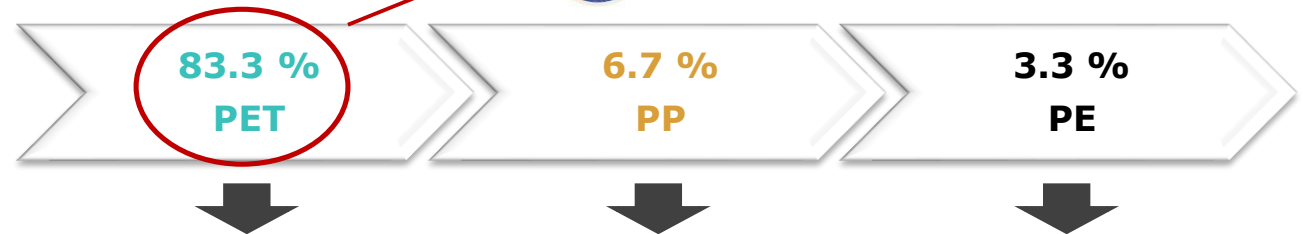
Results



- Majority of MPs: microfibers (not microballs)
- Size: 30 μm – 3.5 mm
- Common colors: black, red, blue, white, transparent



From textiles (PET most used)?



Most used
plastics in
the world

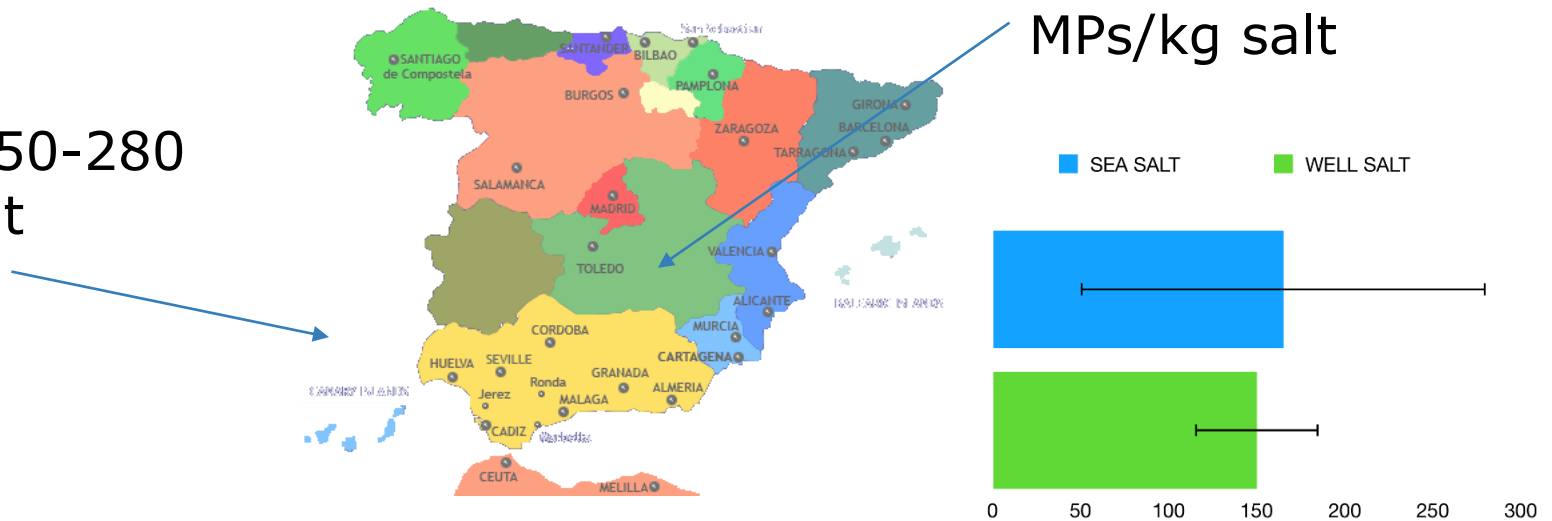
MPs in salt

Results

NO SIGNIFICANT DIFFERENCES IN THE AMOUNTS OF MICROPLASTICS FOUND IN THE DIFFERENT SALTS

Sea salt : 50-280
MPs/kg salt

Well salt: 115-185
MPs/kg salt



Packaging and milling do not influence the amount of MPs found



MPs in salt

To be continued...

- Pollutant content in the microplastics



{solution}



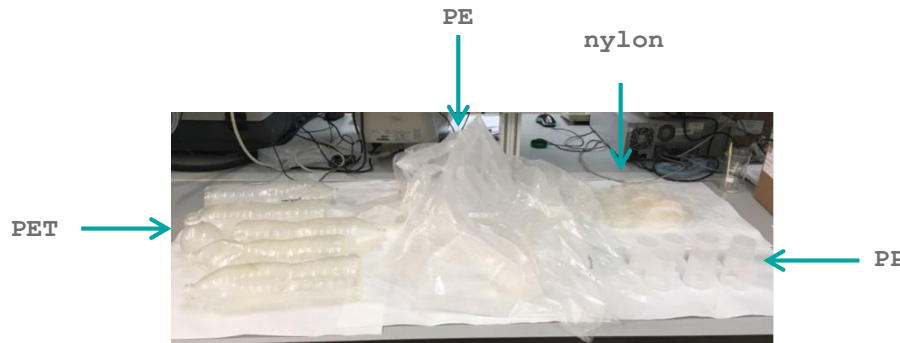
**One possible
treatment**

Treatment

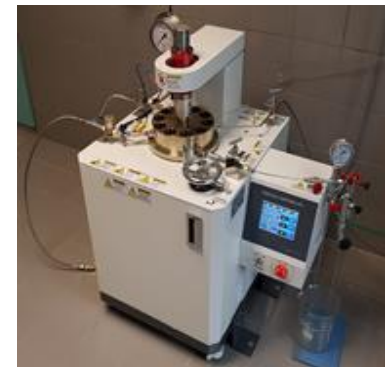
Hydrothermal carbonization HTC

Waste: mix of plastics
Liquid phase: sea water

50 g plastic mix
+
500 mL sea water



heating



High pressure reactor

Operational parameters:

- Final T: 200, 250, 300 °C
- 3 hours
- 3 °C/min
- Pressure: 1.6, 4.0 & 8.6 MPa

Objectives:

- Examine characteristics of final products
- Study feasibility of converting this waste into a good fuel

HTC

Solids obtained



No treatment



Solid HTC 200 °C



Solid HTC 250 °C



Solid HTC 300 °C

Characterization of hydrochars:

- Elemental analysis (C, H, N, S)
- Humidity
- Heating power
- Ion chromatography

Thermal decomposition:

- In air ($N_2:O_2 = 4:1$)
- Heating rates = 5, 10 and 20 °C/min

Solids HTC

Results

Solid after the treatment → more fragile and easy to grind than plastics

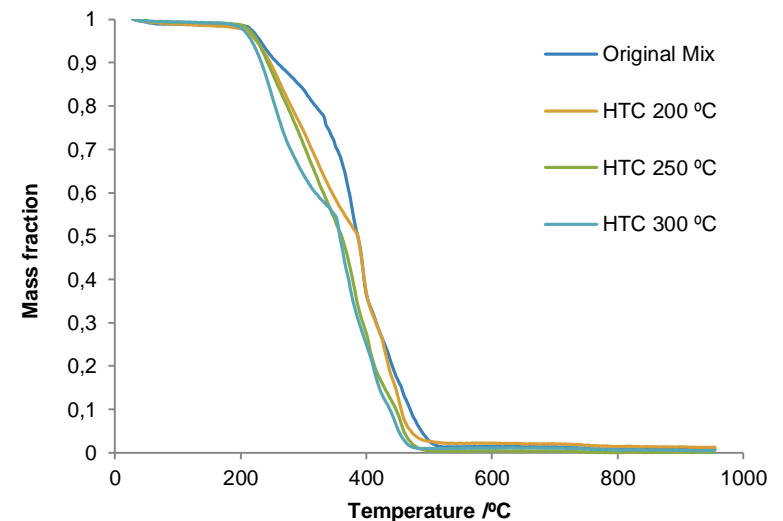
Analysis of the original and HTC solid (wt.%)

	Original	HTC 200 °C	HTC 250 °C	HTC 300 °C
Immediate analysis				
Moisture	2.00	24.5	22.9	28.7
Ash	5.84	6.95	6.20	5.27
NCV (MJ/kg)	35.6	38.3	38.9	39.1
Yield	-	66.7	40.1	37.4
Energy yield	-	71.8	43.7	41.1
Elemental analysis				
C	77.4	79.0	80.1	80.9
H	12.6	11.9	12.6	13.0
N	2.99	0.60	n.d.	n.d.
S	n.d.	n.d.	n.d.	n.d.
O	1.22	1.45	1.14	0.77
Ionic chromatography				
Fluorine (x 10⁻³)	5.34	2.86	1.53	1.07
Chlorine (x 10⁻¹)	4.59	3.17	3.42	4.13
Bromine (x 10⁻⁴)	11.2	0.97	0.81	0.81

*n.d. = not detected

Increasing temperature:

- Hydrochar with more C and less O → Increasing heating power
- Decrease in inorganic anion content



Liquids HTC

Characterization. Pollutants??

- **Inorganic compounds**

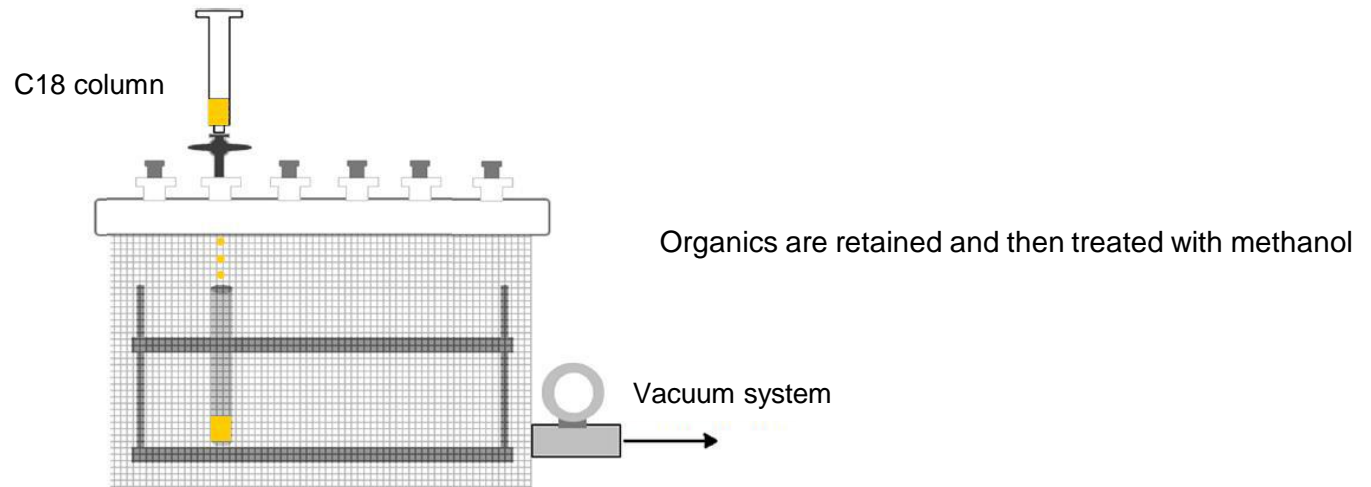


Ion chromatography

- **Organic compounds**



Isolated by C18 column treatment

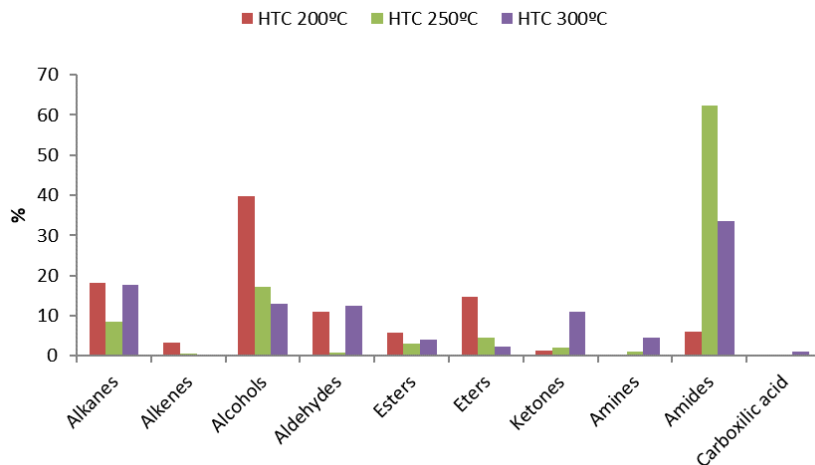


Liquids HTC

Results

	mg/L						
Sample	Fluoride	Chloride	Nitrite	Bromide	Nitrate	Phosphate	Sulfate
HTC 200 °C	0.40	27808	nd	5.72	7.08	7.28	169
HTC 250 °C	0.48	27035	nd	6.16	6.48	5.96	254
HTC 300 °C	0.52	24618	nd	9.16	3.96	3.00	241

n.d = not detected

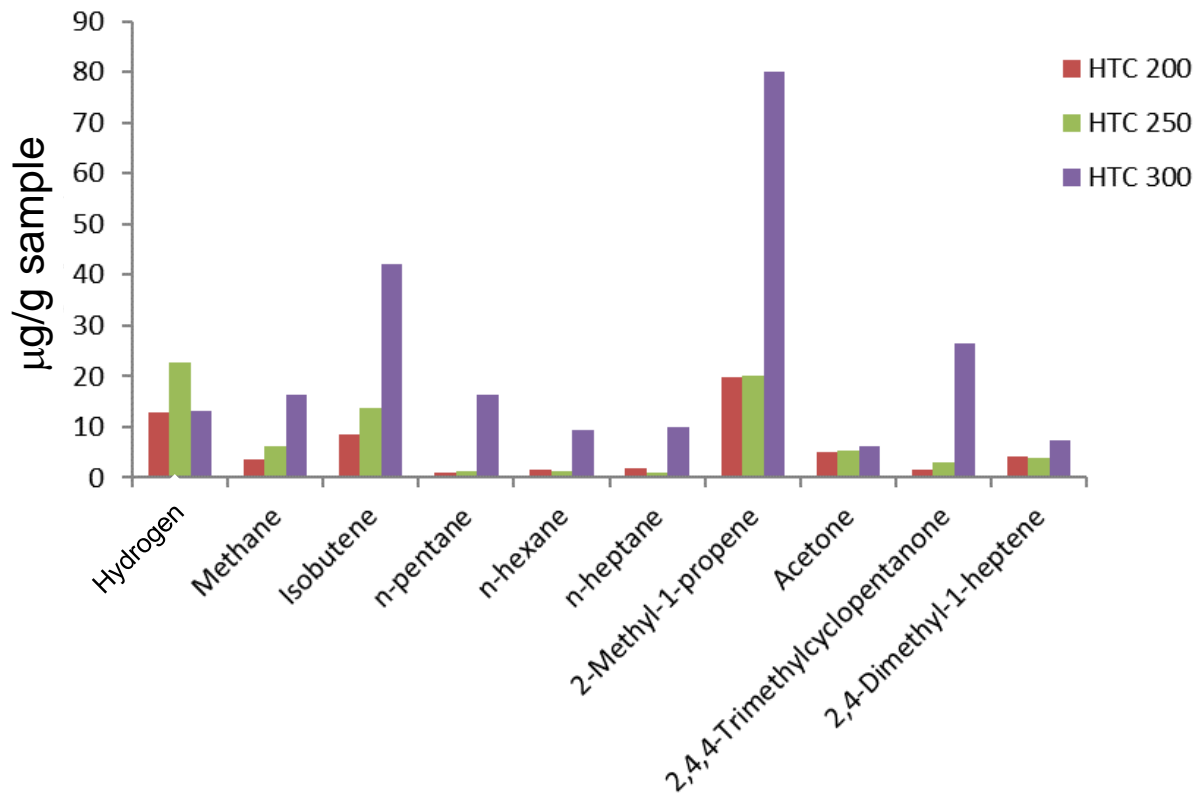


- ✓ Chlorine was the predominant compound in the liquid fraction (sea water).
- ✓ The fluorine, bromine and sulfate content increased as the temperature of the process increased, indicating that these compounds were transferred from the plastic to the liquid.
- ✓ Organic compounds: Amides, alcohols and alkanes are the major compounds.

Gas HTC

Results

- Main light hydrocarbons: isobutene and methane
- Aromatics: Benzene, xylenes
- Others: acetaldehyde and 2-methyl-1-propene



Maximum emission (µg/g):
@ 200 °C → 116
@ 250 °C → 152
@ 300 °C → 822

0.08 % wt.
Very low amount

CONCLUSIONS

Characterization of a real MD sample

Not very contaminated, comparable to other wastes.

Estimated composition from the kinetic model: 27.5 % PE, 24.8% nylon, 18.8% PET, 12.8% PP

Human exposure: Microplastics in table salt

Amount: 50–280 MPs/kg salt

Abundance: 83.3% PET, 6.7% PP, 3.3% PE

No significant differences among all the samples (sea salt vs. well salt; before or after packaging or milling).

Background presence of microplastics in the environment.

HTC treatment of MD

Solid: + C, - O --> + heating power

Inorganic anion content in liquid: + F, +Br, + SO₄²⁻

Amides, alcohols and alkanes formation

Good viability

AKNOWLEDGEMENTS

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Thank you.

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