Plastic-associated chemicals – are plastics a sink or source of organic chemicals to the North Pacific Ocean?

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Background and rationale of our Project MICRO-FATE based on expedition SO268/3 (Figure 1, www.ufz.de/micro-fate)

- Sorbed chemicals particles are relevant in addition to the for comprehensive assessments of the fate and potential effects of plastics (Bucci and Rochman, 2021)
- Plastics might represent a vector for long-range transport of sorbed chemicals (Gouin 2021)
- But equilibration with the surroundings might be faster than the particle transport – to be assessed in MICRO-FATE
- Some polymers have high sorption capacity for hydrophobic organic compounds (HOCs)
- Following sufficiently long exposure times, the plastics and surrounding seawater are expected to approach equilibrium partitioning
- There are two processes that are expected to occur in parallel:
  (1) additives from the production process are present in the newly emitted plastic and leach the environment
  (2) plastics are initially low in levels of environmental pollutants and sorb HOCs from the environment
- Assuming that 80 % of all marine plastic are exposed for >4 y (Koelmans et al., 2016), pollutants in the plastics are expected to be close to equilibrium partitioning

Research questions:

- What are the levels and patterns of pollutants in the surface seawater, at greater depths in the water column and in the sediment from the SONNE transit SO268/3?
- Does plastic litter aged in the marine environment show higher effects than the corresponding original material?
- Can we simulate environmental weathering artificially in the laboratory? Does the relevance of different endpoints vary over time and location?

Hypothesis: The diverse chemical mixture sorbed from the seawater leads to higher effects of the field-weathered plastic than the original new product

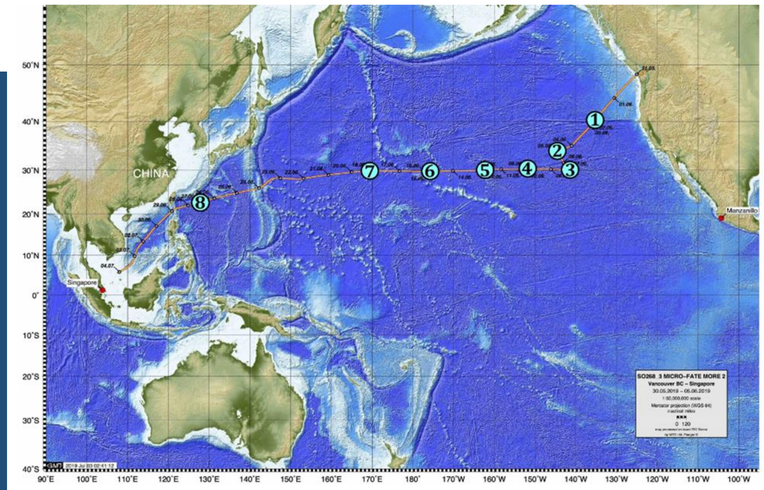


Figure 1. Track of expedition SO268/3 on research vessel SONNE with major sampling stations.

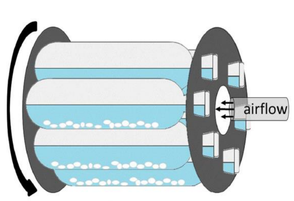
Material and Methods

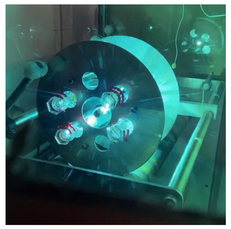
1. Characterization of chemicals

- Media sampled on SO268/3
- (1) surface seawater while steaming
  (2) water from four depths at stations
  (3) sediments
  (4) floating plastic items
- Water extraction: Large-Volume Solid Phase Extraction (LV-SPE) on board (sorbent: HR-X)
- Sediment extraction: Accelerated Solvent Extraction (ASE)
- Plastic extraction: ultrasound-assisted extraction (UAE)
- Chemical analysis of ~750 chemicals: liquid/gas chromatography (LC/GC) coupled to high-resolution mass spectrometry (HRMS, Orbitrap Q-Exactive Thermo Fisher)

2. Characterization of mixture effects

- Plastic extraction: ultrasound-assisted extraction (UAE)
- Weathering experiments: plastic pieces in artificial seawater were exposed to strong UV light (OSRAM HTC 400) for 8 d (~65 d outdoors)
- Treatments in UV light (UV) and dark controls (DC)
- Extraction of water phase: SPE (enrichment factor 200)





Weathering wheel (Gewert et al. 2018)

- Mixture effects in cell-based bioassays
- (1) AhR (aryl hydrocarbon receptor) for dioxin-like compounds
  (2) AREc32 assay for oxidative stress
  (3) peroxisome proliferator activated receptor gamma (PPARγ) indicative of the presence of obesogenic compounds
  (4) ERα assay for estrogenic compounds
- AhR data shown here

Results and Discussion

1. Characterization of chemicals

- Preliminary results show 140-150 quantifiable compounds in our samples (LC-HRMS, Figure 2)
- Quality assurance/control (QA/QC): peak identification, blank/background, detection limits (Rojo Nieto et al. in preparation)

Figure 2. Preliminary overview of the chemicals in seawater

2. Characterization of mixture effects in the AhR assay

- Solvent and procedural controls did not show any relevant induction
- Diverse results either proved or disproved the hypothesis above (Rummel et al. in preparation)
- Field-weathered plastics in many cases showed higher AhR induction than the new product (Figure 3 a) and b)
  → noodle cup, green jerry can, black fishing buoy, white vessel, black food tray, silicon tube
  → the plastics from the North Pacific may have served as a passive samplers, accumulating HOCs inducing AhR
- New products showed higher effects in some cases
  → most active sample: the new eel trap was the most potent inducer of AhR
  → indicates presence of high amounts of dioxin-like compounds as plastic additives
  → already leached out from the field-weathered eel traps
- Solvent extracts of UV-weathered plastics often induced lower effects than the DCs (Figure 3 c)
  → eel trap, coffee lid, noodle cup, silicon tube
  → substances may have leached out from the plastics into the artificial sea water
- AhR inducers were enriched in leachates concentrated on SPE
  → coffee lid, noodle cup, blue jerry can and black fishing buoy
- Blue barrel: UV-treated plastic and leachate induced higher effects than the DC
  → potential degradation products of the additives may have induced AhR

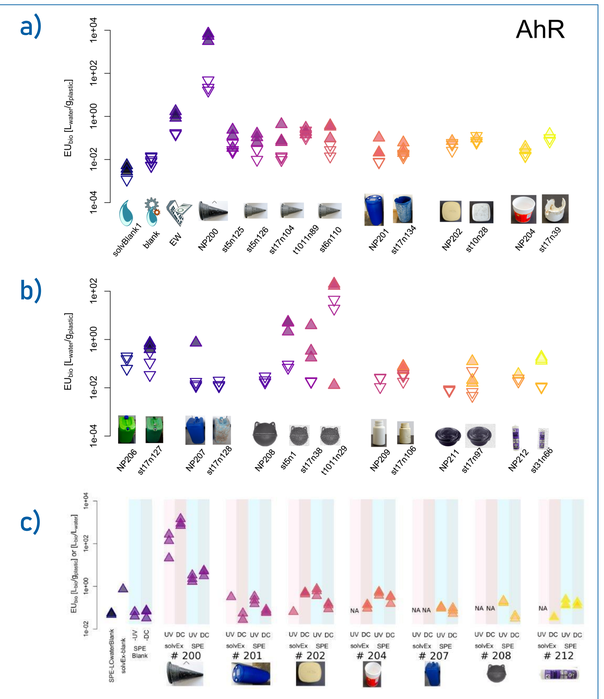


Figure 3. AhR assay: a) and b) field-weathered plastic vs. corresponding new product. c) artificial weathering

Preliminary conclusions

1. Characterization of chemicals

- In very remote regions and the deep sea, diverse pollutants are still detectable
- Ultra-trace levels require very thorough QA/QC

2. Characterization of mixture effects in the AhR assay

- Plastics can be a source and sink of HOCs to the North Pacific Ocean
- Underlines the relevance of weathering under marine conditions for marine plastic debris and its potential to leach substances of concern into the environment.

References

Bucci and Rochman, 2021 (NA SETAC meeting 2021, ISSN 1087-8939)
Gouin 2021 (doi 10.1186/s43591-021-00016-w)
Koelmans et al., 2016 (doi 10.1021/acs.est.5b06069)
Gewert et al. 2018 (doi 10.1021/acs.estlett.8b00119)

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