# Leaching of Organic Compounds from Microrubber Under Conditions Simulating the Sea Surface and the Deep Sea

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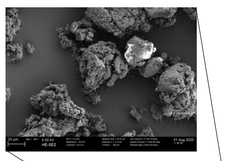
## Test materials

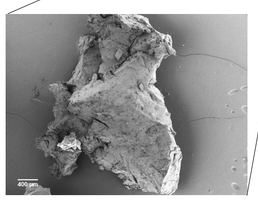


**CMTT: Cryo-milled tire tread:**
Average size: 179 ± 89 µm

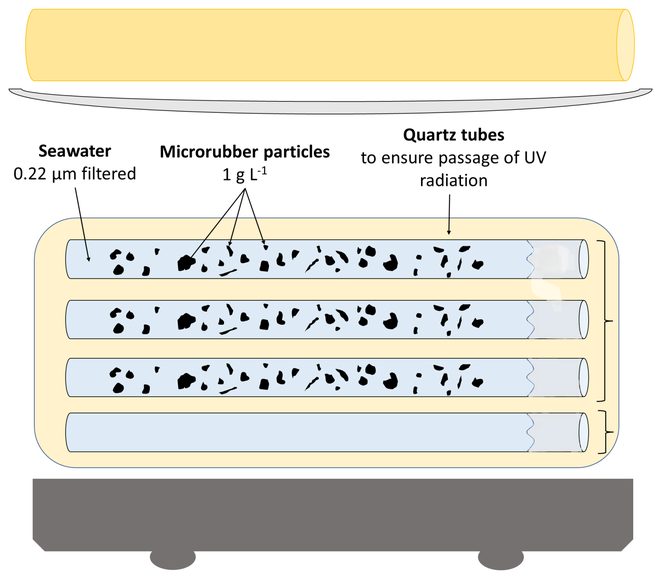
**Crumb rubber:**
Average size: 3 ± 1 mm

**VCR: virgin crumb rubber**

**WCR: weathered crumb rubber**
(exposed ≥ 12 months at the sea surface)

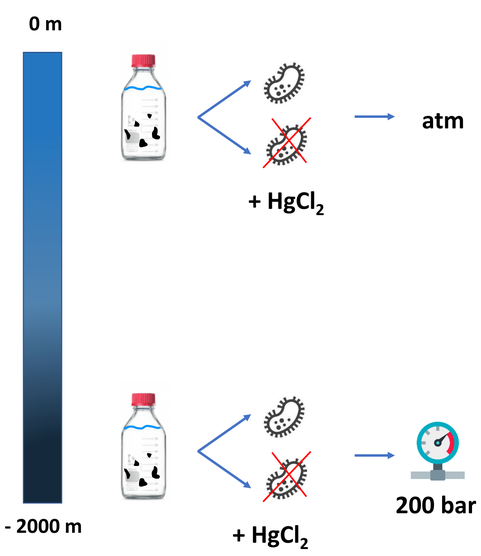


## i. Artificial sunlight exposure




**+ dark conditions for comparison**

## ii. High hydrostatic pressure vs. Atmospheric pressure




## Leachate analysis

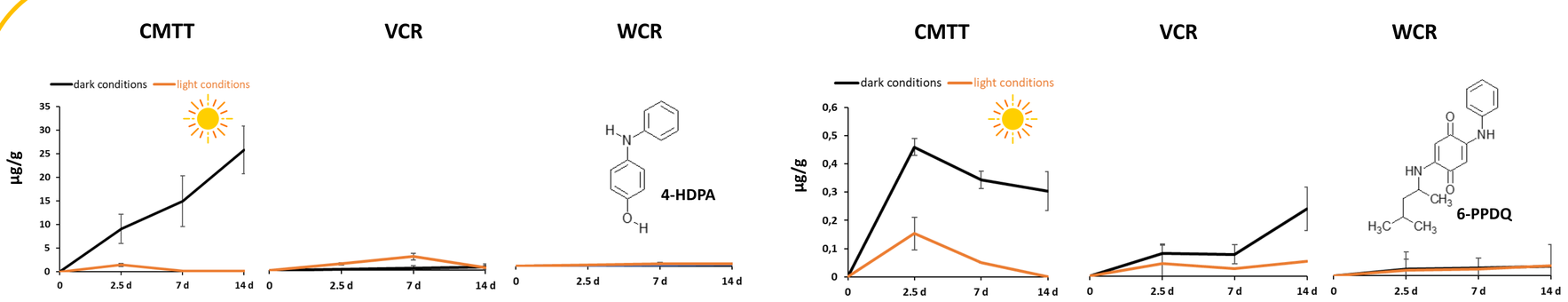
UPLC-HRMS

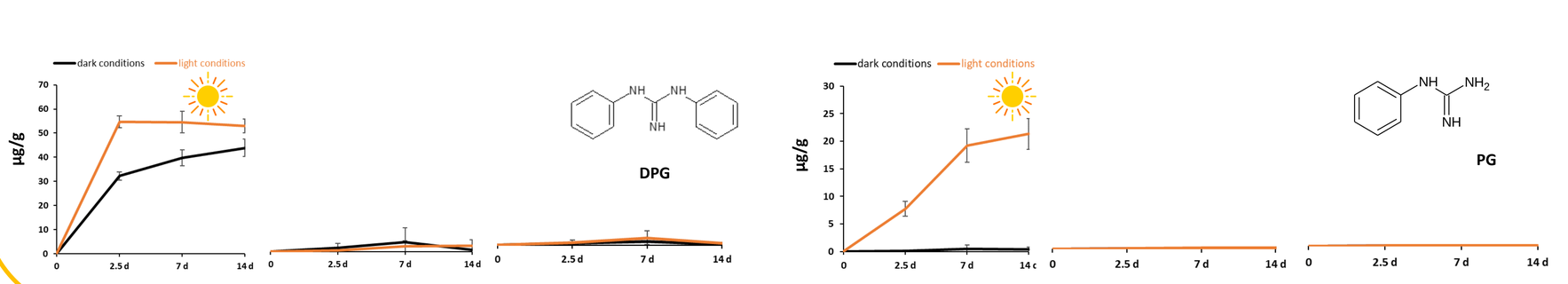
Tire related chemicals (not exhaustive):

- **4-HDPA**: 4-hydroxydiphenylamine
- **6-PPDQ**: N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine quinone
- **DPG**: 1,3-diphenylguanidine
- **PG**: phenylguanidine

Dissolved organic carbon (data not presented here)

**Nutrients** ($NO_3$, $SiOH_4$, $PO_4$)




- **19 target compounds** detected in leachates of all tested materials. These consist of **vulcanization accelerators** and **antioxidants** used in the tire industry
- Overall higher concentrations found in CMTT leachates rather than VCR and WCR due to **particles properties**
- **Higher amount** of vulcanization accelerators **released under artificial sunlight** (e.g., DPG) promoting the **formation** of related **transformation products** (PG + 23 new compounds)
- **Antioxidants degradation products** (4-HDPA and 6-PPDQ) **readily photodegraded** under artificial sunlight compared to dark conditions

Foscari & Schmidt et al., submitted

## CMTT: Cryo-milled tire tread

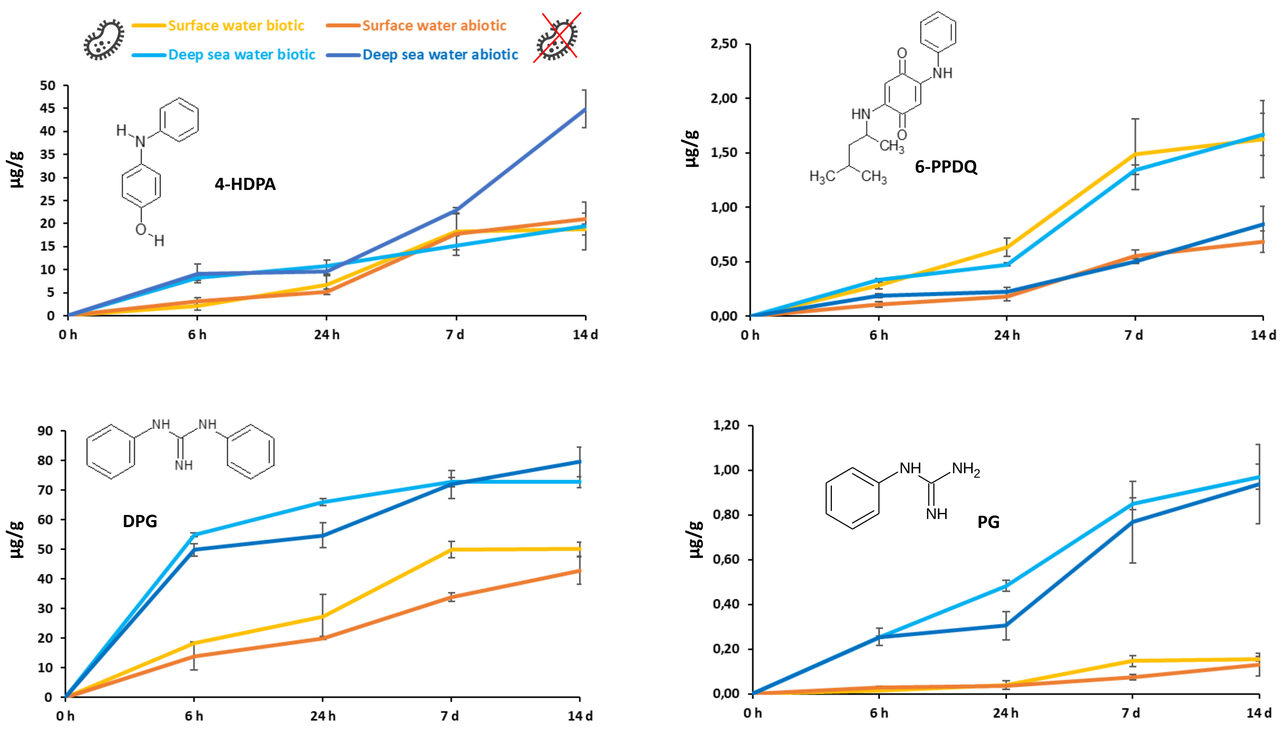



Table 1: Mean nutrient concentrations (in µM) in test samples and seawater controls.

| | $NO_3$ | $SiOH_4$ | $PO_4$ |
|---|---|---|---|
| Seawater control biotic atm | 0.51 | 3.91 | 0.01 |
| Seawater control abiotic atm | 0.46 | 5.44 | 0.02 |
| Seawater control biotic 200 bar | 9.10 | 11.90 | 0.44 |
| Seawater control abiotic 200 bar | 8.72 | 31.81 | 0.45 |
| CMTT biotic atm | 0.50 | 3.83 | 0.03 |
| CMTT abiotic atm | 0.45 | 4.94 | 0.01 |
| CMTT biotic 200 bar | 6.51 | 12.46 | 0.25 |
| CMTT abiotic 200 bar | 7.07 | 30.46 | 0.38 |
| VCR biotic atm | 0.54 | 1.99 | 0.03 |
| VCR abiotic atm | 0.50 | 4.93 | 0.05 |
| VCR biotic 200 bar | 8.42 | 10.81 | 0.39 |
| VCR abiotic 200 bar | 7.14 | 28.82 | 0.41 |
| WCR biotic atm | 0.57 | 3.60 | 0.75 |
| WCR abiotic atm | 0.54 | 4.21 | 0.99 |
| WCR biotic 200 bar | 9.03 | 11.47 | 0.99 |
| WCR abiotic 200 bar | 9.04 | 33.18 | 1.41 |

- Higher chemical release in CMTT samples compared to VCR (e.g., DPG max. 3.75 µg/g) and WCR (DPG max. 2.31 µg/g) samples
- No clear trend for 4-HDPA, but general increase in concentrations in time under all conditions
- Biotic conditions seem to increase release of 6-PPDQ → **biotransformation processes** of parent compounds?
- DPG & PG: **high hydrostatic pressure favors leaching** compared to atmospheric pressure
- $NO_3$ and $SiOH_4$ concentrations higher in deep seawater samples, in accordance with characteristics of surface and deep-sea water masses of the Mediterranean (oligotrophic sea)
- For $PO_4$ the same trend was observed, but with significantly higher values in WCR samples → $PO_4$ release from biofilm that formed during natural weathering of WCR?

**Background**: Tires are commonly made of styrene-butadiene-rubber (SBR) and butadiene rubber (BR) and can contain high amounts of filling agents, vulcanization agents (e.g., 1,3-diphenylguanidine, benzotriazoles and benzothiazoles) and other additives, such as zinc (Wagner et al., 2018). Currently, a widely used antioxidant, N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6-PPD) and its derivative 6-PPD quinone (6-PPDQ) receive growing attention, since a study reported 6-PPDQ to induce acute mortality in juvenile coho salmon (*Oncorhynchus kisutch*) (Tian et al., 2021). While tire particle leaching studies have been performed for freshwater environments, dedicated studies on the release of tire related chemicals that consider marine environment conditions have not been published, yet. Therefore, our objective was to investigate the leaching behavior of three different tire materials in natural seawater when exposed to artificial sunlight or high hydrostatic pressure to simulate processes expected to occur when tire particles reach the marine environment.

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Foscari A., Schmidt N., Seiwert B., Herzke D., Sempéré R., Reemtsma T., submitted. Leaching of chemicals and DOC from tire particles under simulated marine conditions.
Tian Z., Zhao H., Peter K.T., Gonzalez M., Wetzel J., Wu C., Hu X., Prat J., Mudrock E., Hettinger R., Cortina A.E., Biswas R.G., Kock F.V.C., Soong R., Jenne A., Du B., Hou F., He H., Lundeen R., Gilbreath A., Sutton R., Scholz N.L., Davis J.W., Dodd M.C., Simpson A., McIntyre J.K., Kolodziej E.P., 2021. A ubiquitous tire rubber–derived chemical induces acute mortality in coho salmon. Science (1979) 371, 185–189.
Wagner S., Hüffer T., Klöckner P., Wehrhahn M., Hofmann T., Reemtsma T., 2018. Tire wear particles in the aquatic environment - A review on generation, analysis, occurrence, fate and effects. Water Res 139, 83–100.