Dynamic passive sampling of POPs in surface seawater along a South Atlantic Ocean east-to-west transect and across the Black Sea

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Methods

Preparation of silicone passive samplers:

- Soxhlet extraction of silicone in ethylacetate for 40 hours (Altesil, 7 × 28 cm, thickness: 0.5 mm) → to remove oligomers and impurities
- Homogeneous dosing of performace reference compounds (PRCs) → H_2O:MeOH (1:1; V:V)
- PRCs: D10-Biphenyl, PCB 1, PCB 2 , PCB 3, PCB 10, PCB 14, PCB 30, PCB 50, PCB 55, PCB 78, PCB 104, PCB 145, PCB 204

Exposure of silicone passive samplers:

South Atlantic Ocean

- Dynamic passive sampling in a South Atlantic Ocean on board of RV Meteor:
- Cape Town, South Africa → Rio de Janeiro, Brazil
- Seawater was sampled at least 400 km from the coast
- 5 stretches: 34°S/17°E → 25°S/38°W
- Length: 830-1450 km per stretch
- Time period of sampling: ~3.5 days per stretch
- Exposed surface: ~780 cm^2 (4 sheets)

Black Sea

- Dynamic passive sampling in the Black Sea on board of RV Mare Nigrum
- Odessa, Ukraine → Batumi, Georgia → Constanta, Romania
- Also coastal seawater was sampled
- 4 stretches: 46°N/30°E → 41°N/41°E → 44°N/28°E
- Lenght: 280-1300 km per stretch
- Time period of sampling: ~4 days per stretch
- Stationary samples: 27-32 days of deployment
- Exposed surface: ~580 cm^2 (3 sheets)

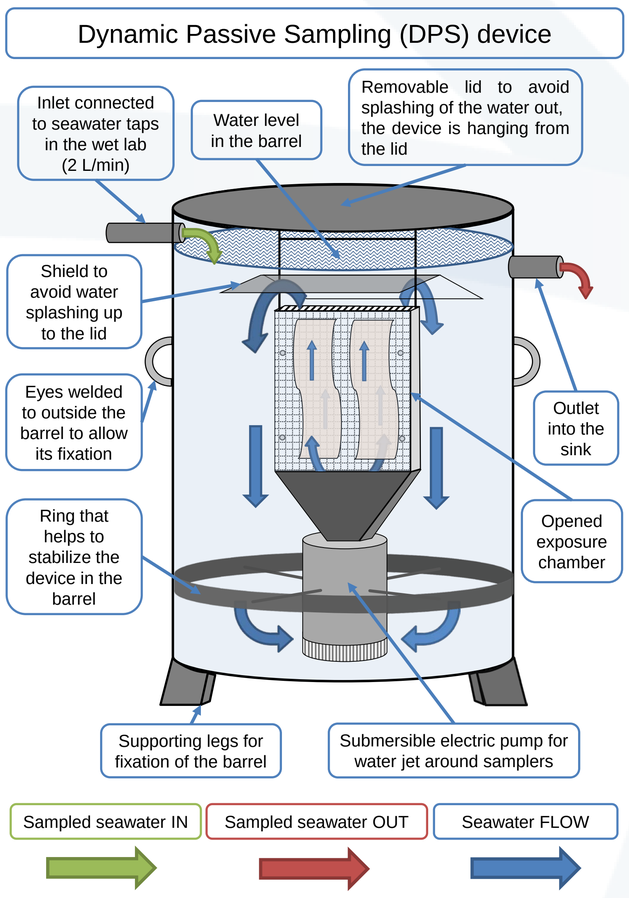
Processing and analysis:

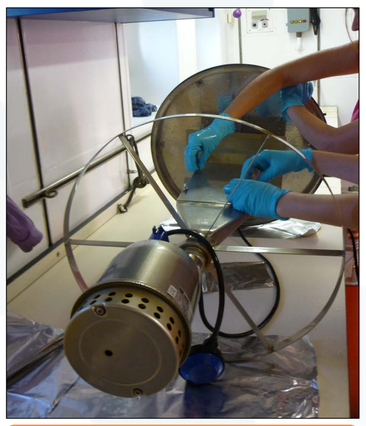
- Soxhlet extraction 8 h → Acetonitrile or Methanol (250 mL)
- Non-destructive clean-up → 10% water deactivated silica gel
- *GC-MS/MS* → OCPs, NBFRs, PAHs, Substituted PAHs
- Destructive clean-up → 44% H_2SO_4 silica gel
- *GC-MS/MS* → OCPs, PBDEs, PCBs

Introduction

For several decades, persistent organic pollutants (POPs) have been emitted to seawater from rivers, atmosphere or released to the sea from ship transportation, coastal or offshore infrastructures. Their concentrations only slowly decrease in the oceans around the world following measures to stop or reduce their emission. The aim of the study was to contribute to the characterisation of environmental exposure to POPs in a South Atlantic Ocean (SAO) and the Black Sea (BS), indicate spatial pollution trends and, in combination with air pollution data, contribute to identification of the direction of air–sea exchange.

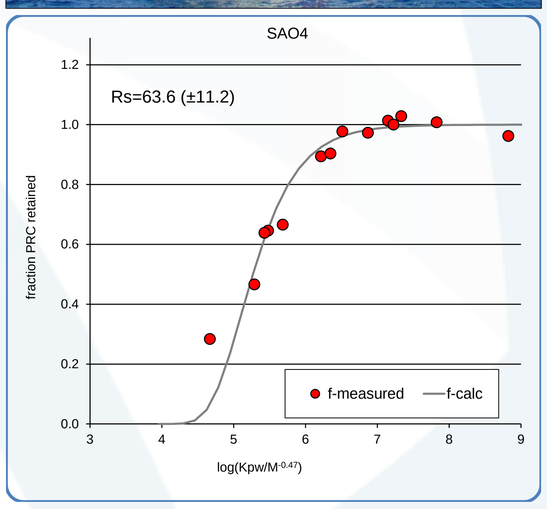
A passive sampling method was applied for monitoring of hydrophobic POPs, such as polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), polycyclic aromatic hydrocarbons (PAHs), polybrominated diphenylethers (PBDEs) and novel brominated flame retardants (NBFRs) (Lohmann et al., 2017). The freely dissolved concentrations were derived since they are suitable for assessment of POPs deposition from or volatilisation to the gas phase in the atmosphere.





- **South Atlantic Ocean**
- Sampling rate: 17–95 L/d
- Sampled volume: 51–336 L
- **Black Sea**
- Sampling rate: 31-82 L/d (DPS), 14-32 L/d (Stat.)
- Sampled volume: 112-343 L (DPS), 381 – 869 L (Stat.)

Sampling rate R_s estimated from a model by Rusina et al. (2010) $R_s = B \times M^{-0.47}$, where B is an exposure specific parameter derived from dissipation of performance reference compounds



Conclusions

South Atlantic Ocean:

The majority of the targeted compounds were found in the first stretch off South Africa. Freely dissolved concentrations of PCBs and OCPs were found in lower units of pg L^{-1}. Spatial trend was observed for heptachlor, cis-heptachlor epoxide, α-endosulfan and endosulfan sulfate, where the partial fractions changed. Heptachlor and cis-heptachlor epoxide were more abundant off South Africa. However, with changing longitude (SAO1 → SAO5) α-endosulfan and endosulfan sulfate were more prevailing. PAHs showed similar concentrations (units of ng L^{-1}) along the whole cruise with deviation among stretches ≤30%. The sum of PBDEs ranged 0.7-4.8 pg L^{-1} and with prevailing BDE-47. NBFRs were in the range 3.7-147 pg L^{-1} with BTBPE as the most abundant. Spatial trend was observed for PBDEs and NBFRs, where the highest concentrations were found off South Africa, decreasing along the east-to-west transect and increasing again west of 30°W.

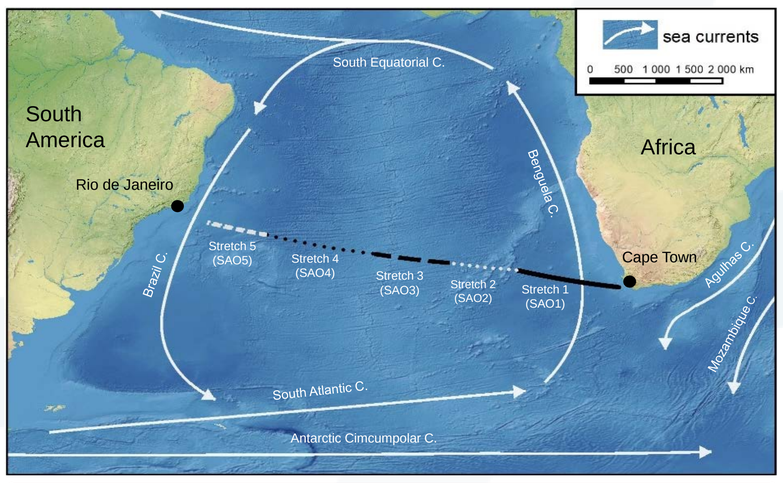
Black Sea:

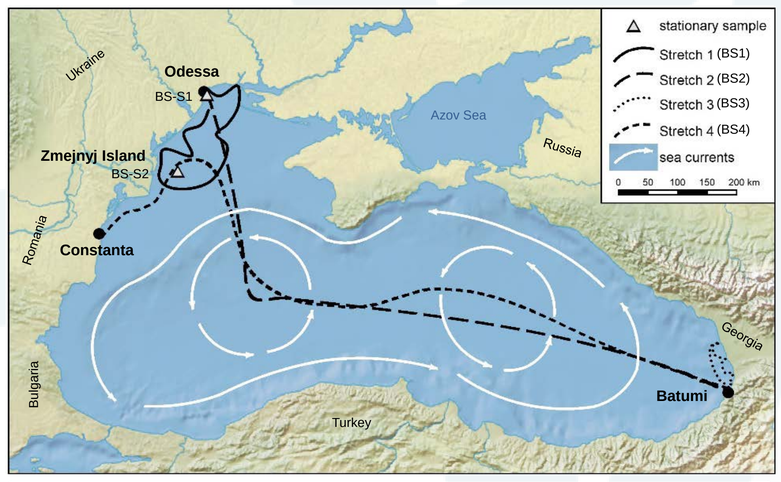
The most compounds were found in the Ukrainian territorial waters (BS1, BS-S1, BS-S2). Freely dissolved concentrations of PCBs were in the range 10.1-63.4 pg L^{-1} with dominance of PCB-28. The sum of OCPs ranged between 26.1-219 pg L^{-1}. A spatial trend was observed for DDTs. The predominance of p,p'-DDD was found close to the coasts. On the other hand, p,p'-DDE was prevailing in the open sea. The sum PBDEs and NBFRs ranged between 0.1-1.1 pg L^{-1} and 0.7-12.4 pg L^{-1}, respectively. PBDEs, α- and β-TBECH showed the same spatial pattern for all stretches. In case of other NBFRs, which were found in all stretches, relative fractions of syn-DP and HBB increased in following stretches in comparison to a-DP and PBT.

Comparison:

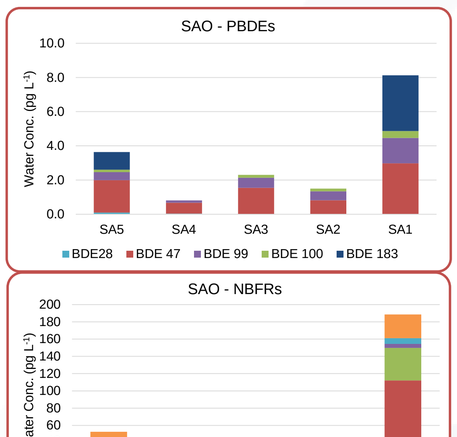
The comparison of both cruises showed two orders of magnitude higher concentrations of PCBs and OCPs in the BS. On the other hand, NBFRs were found in the SAO two orders of magnitude higher. The same distribution pattern was found for PBDEs (BDE 47 > BDE 99 > BDE 100). However, a different NBFRs pattern occured. For the SAO BTBPE > BEHTBP > DBDPE and for the BS a-DP > PBT > BTBPE.

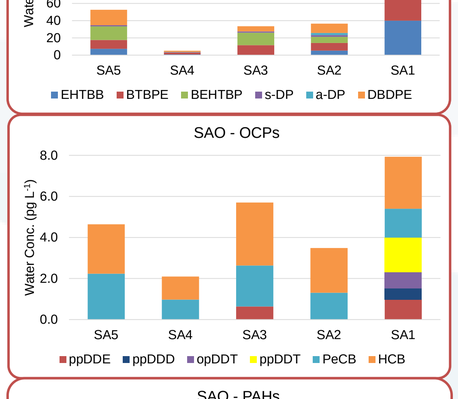
Results

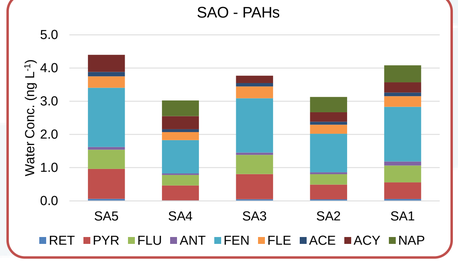




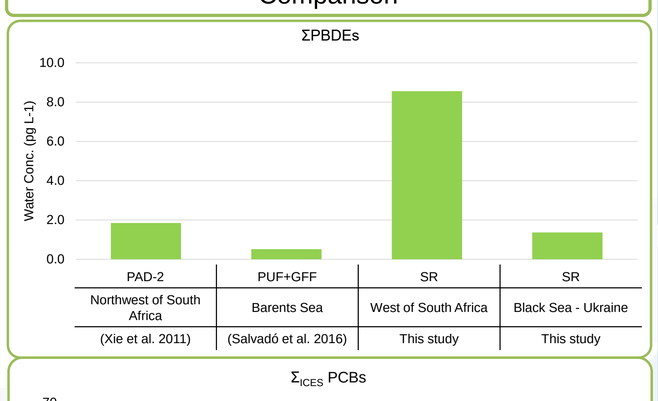
South Atlantic Ocean (SAO) | Black Sea (BS)

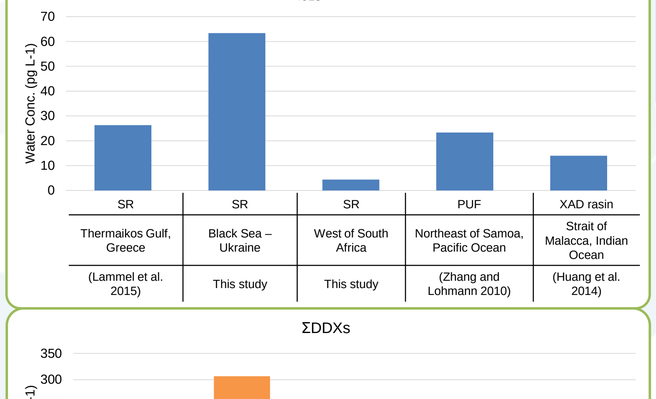


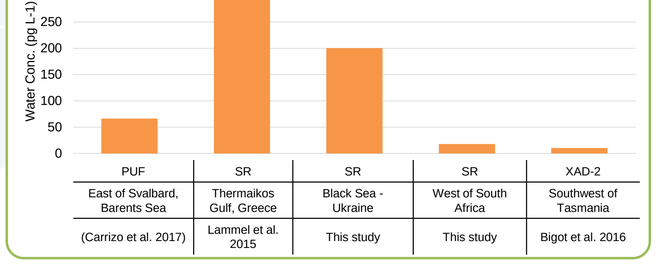


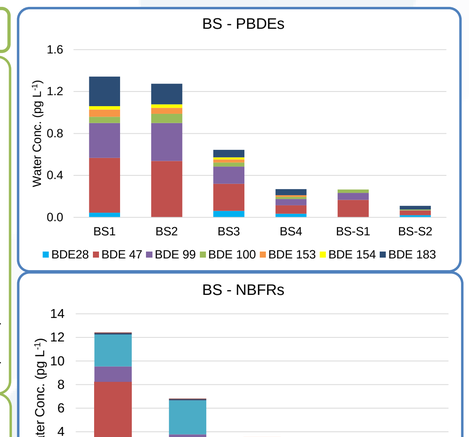


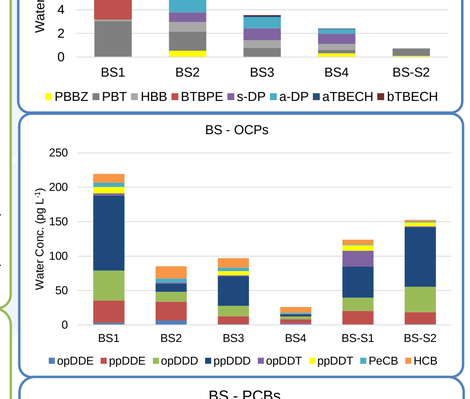
Comparison

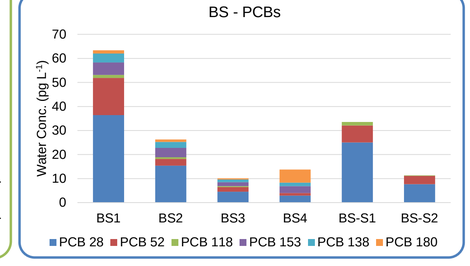












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