Dynamic passive sampling of POPs in surface seawater along a South Atlantic Ocean east-to-west transect

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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 South Atlantic Ocean, 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 used to measure the freely dissolved concentrations of polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), polycyclic aromatic hydrocarbons (PAHs) and their oxy- and nitro-derivates, polybrominated diphenylethers (PBDEs) and novel brominated flame retardants (NBFRs).

A dynamic passive sampling (DPS) device, consisting of an electrically driven large volume water pump coupled to a passive sampler exposure cell to enhance the sampling rate of trace organic compounds, was installed on board of RV Meteor cruising from Cape Town, South Africa, to Rio de Janeiro, Brazil, 1-18 March 2016. Temporally and spatially integrated concentrations of POPs in surface seawater in five stretches covering 34°S/17°E-25°S/38°W were derived. One sampling stretch was covered in approximately three and a half days during which the vessel cruised between 830 and 1450 km. Sampling of POPs was performed using four Altesil silicone rubber sheets (7×28×0.05 cm, exposed surface area of ~780 cm^2). For each stretch two Altesil silicone rubbers (~390 cm^2) were extracted with acetonitrile and analyzed on GC/MS-MS or LC/MS-MS. The sampling rate Rs ranged from 17 to 95 L d^{-1} and sampled volume from 51 to 336 L. In general, sampling rate is estimated from a model by Rusina et al. [1] $R\text{s}=B\times M^{0.47}$, where B is an exposure specific parameter, derived from dissipation of performance reference compounds.

The majority of the targeted compounds were found in the first stretch off South Africa. The derived freely dissolved concentrations of PCBs and OCPs were in the lower pg L^{-1} range, or close to the limit of quantification, which was one order of magnitude lower. Only HCB and PeCB were found in all stretches ranging from 0.80 to 3.06 pg L^{-1}. No spatial trends of POPs concentrations were observed. Only 3 out of 17 cyclodiene pesticides were found in quantifiable concentrations: heptachlor (0.12–2.45 pg L^{-1}), cis-heptachlor epoxide (0.28–0.59 pg L^{-1}) and

endosulfan sulphate (estimated ~1 pg L^{-1}). No clear spatial trend was observed for cyclodiene pesticides, as for PCBs and OCPs. PAH concentrations were found in the lower ng L^{-1} range, with the sum of 29 monitored PAHs (including 2 similar substances) ranged 3.1–4.5 ng L^{-1}. The highest concentrations were found in the last cruise stretch off Brazil, with phenanthrene accounting for almost half of the sum. Again, no spatial trends were observed. The sum of oxy-PAHs was in the lower ng L^{-1} range, while all nitro-PAHs were <0.05 ng L^{-1}. The sum of freely dissolved concentrations of NBFRs ranged 4–161 pg L^{-1} with 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE) as the most abundant species (2–72 pg L^{-1}). Nevertheless, the NBFRs showed a spatial trend, with the highest concentrations found near South Africa (161 pg L^{-1}), decreasing along the east-to-west transect (4–27 pg L^{-1}) and increasing again west of 30°W (35 pg L^{-1}). The sum of freely dissolved concentrations of PBDEs ranged 0.8−5.3 pg L^{-1}, with the same spatial distribution as for NBFRs i.e., starting with the highest concentration near South Africa (5.3 pg L^{-1}), decreasing along the transect (0.8−2.3 pg L^{-1}) and rising again west of 30°W (3.6 pg L^{-1}). Congeners BDE47, BDE 99 and BDE 100 dominated in the PBDE pattern.

[1] Rusina T.P., Smedes F., Kobližková M., Klánová J. (2010) Environ. Sci. Technol. 44,362-367