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Organic polar pollutants in surface waters of inland seas

Anna Orlikowska *, Kathrin Fisch, Detlef E. Schulz-Bull

Leibniz Institute for Baltic Sea Research, Warnemünde, Germany

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ABSTRACT

Available data about contamination by polar substances are mostly reported for rivers and near-shore waters and only limited studies exists about their occurrence in marine waters. We present concentrations and distribution of several polar pesticides and UV-filters in surface waters of three inland seas, the Baltic, Black and Mediterranean Sea. Many of the investigated compounds were below detection limits, however, those found in off-shore waters raise a concern about their persistence and possible adverse effect on the ecosystem.

Despite a longstanding EU-wide ban we were able to detect atrazine in the Mediterranean and the Baltic Sea. Concentrations in the Black Sea were substantially higher. Runoff from agricultural and urban areas was the main transport route to marine ecosystems for investigated compounds, though irgarol in Mediterranean waters was attributed to intense maritime traffic. 2-Phenylbenzimidazole-5-sulfonic acid was the only UV-filter detected in marine waters, while benzophenone-4 was observed in the estuaries. Occurrence of UV-filters was seasonal.

Many organic substances used as pesticides, biocides or in personal care products and in various industrial products can be classified as polar pollutants. Their persistence depends on environmental conditions and is highly variable (Mackay et al., 2006; Santos et al., 2012). The combination of wide-spread use and hydrophilic character have resulted in their frequent detection in the natural waters (Jurado et al., 2014; Loos et al., 2009; Munaron et al., 2012). The main route of polar pollutants to enter surface water is via runoff from places of application (e.g. fields, urban areas) but also indirect input through sewerage effluents (Loos et al., 2013; Reemtsma et al., 2006; Rodil et al., 2008; Wittmer et al., 2010). Herbicides, biocides and some other polar contaminants pose a toxicological threat to aquatic ecosystems (EC, 2003, 2013; Giger et al., 2009; LeBaron et al., 2008; PAN, 2015; Tsui et al., 2014). For many, however, the risk associated with their occurrence in aquatic, especially marine, environment is still unknown.

Inland seas, such as the Black Sea, the Baltic Sea and the Mediterranean Sea are particularly susceptible to pollution due to many anthropogenic activities within their large catchment areas. Coastal zones, especially areas around large cities, ports and estuaries, show high contamination levels, while open waters are less affected by hazardous substances (Bakan and Büyükgüngör, 2000; HELCOM, 2010; Kostianoy and Kosarev, 2008; UNEP/MAP, 2012). Data about contamination by polar substances is scarce and is mostly reported for rivers and near-shore waters (Carafa et al., 2007; Fent et al., 2010; Loos et al., 2009; Munaron et al., 2012; Nödler et al., 2014; Readman et al., 1993). This precludes reliable understanding of their distribution, fate and effect in marine ecosystems. Therefore, the aim of our work was to estimate current concentration levels and distribution of various classes of polar organic pollutants in the Black Sea, the Baltic Sea and the Mediterranean Sea. Special interest was put on the fate of pollutants in the upper water layer of the open sea.

Water samples from the Mediterranean and Black Seas were collected during cruise MSM33 with R/V Maria S. Merian in November 2013. Surface water samples from the Mediterranean were taken along cruise transects (Fig. S1) directly from the vessel's clean water supply system. In the northern and the central Black Sea (Fig. S2), discrete water samples from the surface and selected depths were taken via rosette Niskin water sampler. Water samples from the Baltic Sea (Fig. S3) were collected during three cruises in February (AL430), May (EMB69) and June (EMB76) 2014. Samples from AL430 were collected via the vessel's clean water supply system, while samples from EMB69 and EMB76 were taken via rosette Niskin water sampler. Additional samples were taken from German Baltic Sea estuaries in May and June 2014 (Fig. S3). Pre-cleaned 2 L amber glass bottles were used to collect water. Samples from MSM33 and from EMB76 were pre-concentrated by solid-phase extraction (SPE) on board the ship. Samples collected during AL430 and EMB69 were stored in the dark at 4 °C until SPE in the laboratory, no longer than two weeks after collection.

Prior to extraction, samples were divided into two 1 L subsamples for repeated determination. Each sample was spiked with 1 mL of 5 ng mL^{-1} internal standard mixture and the pH was adjusted to 2 with 5 M HCl (VWR, Germany). Sample enrichment was achieved on a Chromabond Easy extraction cartridge (3 mL, 200 mg, Marchery-Nagel GmbH, Germany) conditioned with 4 mL acetone (Promochem, Germany) and 4 mL LC/MS-grade water (VWR, Germany). The sample

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* Corresponding author.
E-mail address: anna.orlikowska@io-warnemuende.de (A. Orlikowska).

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was loaded onto a cartridge via filtration unit with a glass-fiber filter (GF/F, 0.7 μm, Whatman) with a flow rate of 25 mL min^{-1}. After sample enrichment, each cartridge was rinsed with 4 mL acidified (pH 2) LC/MS-grade water and gently dried. The extraction cartridges with the samples from MSM33 and EMB76 were wrapped in aluminum foil and stored at −20 °C until analysis. Polar substances were eluted with 4 mL acetone/methanol (*v*/*v*, 1/1) and 6 mL methanol/13% $NH_{3(aq)}$ (*v*/*v*, 97/3). The extract was evaporated to dryness with clean air at a 45 °C water bath (Turbo-Vap LV, Zymark, USA) and reconstituted in 1 mL methanol/water (*v*/*v*, 1/1) for analysis with liquid chromatograph-tandem mass spectrometer (LC-MS/MS) (Thermo Fisher Scientific, Germany). Chromatographic separation was performed using a reverse-phase Kinetex C-18 column (2.6 μm, 50 × 2.1 mm, Phenomenex, Germany) with a guard column. The mobile phase consisted of A: water (LC/MS-grade) with 0.1% acetic acid and B: methanol with 0.1% formic acid. A gradient elution program with the flow rate of 250 mL min^{-1} was used. Sample injection volume was 10 μL. The system operated in selected reaction monitoring (SRM) mode. Two characteristic fragments of the precursor molecular ion ($[M + H]^+$ or $[M - H]^-$) were monitored. The most abundant transition (based on peak area and signal to noise ratio) was used for quantification, whereas the second ion was used for confirmation. Each sample was measured in triplicate. The method detection limits (LOD) are given in Table 1. Instrument control, data acquisition and evaluation were performed with Xcalibur software (Thermo Fischer Scientific). For details of analytical method and study sites see supplementary materials.

Surface waters of the Black Sea, the Mediterranean Sea as well as the Baltic Sea and its estuaries, were analyzed for polar pesticides (18 pesticide and 3 transformation products), UV-filters (11 compounds), disinfectant (triclocarban), bisphenol A, and nonylphenoxyacetic acid (Table 1, supplementary materials). Results showed that even though the investigated compounds are extensively used worldwide, many of them were below detection limits during our study (Table 1). Bisphenol A (BPA), used to manufacture plastics and resins, and triclocarban, a disinfectant added to many consumer products, were always below detection limits; probably due to rapid biodegradation of BPA in natural waters (Kang et al. (2006) and references therein) and effective removal (97–98%) of triclocarban in waste water treatment plants (WWTPs) (Halden (2014) and references therein). Nonylphenoxyacetic acid (NPE_1C), a transformation product of nonylphenol polyethoxylate (NP_nEO) surfactants, was detected in estuarine samples (<1.0–32.2 ng L^{-1}) but not in marine waters. NPE_1C was among the most abundant contaminants in European rivers (Giger et al., 2009; Loos et al., 2009; Loos et al., 2010). The use of NP_nEO surfactants was restricted in many counties, including EU countries (EC, 2003; Giger et al., 2009), to reduce the environmental risk of their toxic metabolites. The low levels of NPE_1C in this study could reflect implemented ban of use of NP_nEO surfactants.

Table 1
Summary of analytical results of polar pollutants in water samples of Mediterranean Sea, Black Sea, Baltic Sea and estuaries of the German Baltic coast. (Frequency of detection, mean value and standard deviation calculated from samples above limit of detection (LOD), maximal concentration.)

Compound		Mediterranean Sea (N = 34)			Black Sea (N = 74)			Baltic Sea (N = 75)			Estuaries Baltic coast (N = 21)		
	LOD (ng L^{-1})	Freq (%)	Mean ± sd (ng L^{-1})	Max (ng L^{-1})	Freq (%)	Mean ± sd (ng L^{-1})	Max (ng L^{-1})	Freq (%)	Mean ± sd (ng L^{-1})	Max (ng L^{-1})	Freq (%)	Mean ± sd (ng L^{-1})	Max (ng L^{-1})
Triazine compounds													
Atrazine	1.2	18	1.4 ± 0.1	1.5	100	40.5 ± 3.1	50.7	100	1.9 ± 0.3	2.6	48	3.0 ± 2.1	7.6
Simazine	1.5	n.d.			100	9.4 ± 0.6	10.9	95	2.3 ± 0.4	3.5	52	3.4 ± 1.5	5.8
Terbuthylazine	1.0	3		9.2	100	1.1 ± 0.2	1.7	83	1.1 ± 0.5	3.8	86	140 ± 255	1111
Terbutryn	1.0	n.d.			n.d.			n.d.			38	3.0 ± 3.4	10.5
Irgarol	0.5	100	2.5 ± 0.6	3.6	5	1.0 ± 0.6	1.8	n.d.			5		1.9
Desisopropylatrazine	1.5	n.d.			86	1.6 ± 0.2	1.8	n.d.			43	3.1 ± 0.8	4.6
Desethylatrazine	1.5	n.d.			100	2.9 ± 0.4	4.2	n.d.			24	1.9 ± 0.4	2.5
Other pesticides													
Chloridazon	0.5	3		1.6	100	3.9 ± 0.3	4.9	100	4.3 ± 1.3	7.4	95	10.9 ± 27.6	126
CMD	1.0	n.d.			n.d.			100	2.8 ± 1.8	8.9	100	8.2 ± 7.3	32.9
Chlorotoluron	1.0	3		3.8	n.d.			8	1.8 ± 0.6	2.7	62	14.5 ± 29.3	136
Diuron	1.0	n.d.			n.d.			9	2.4 ± 0.4	2.9	67	13.2 ± 23.0	107
Isoproturon	0.8	n.d.			n.d.			13	0.9 ± 1.3	6.6	100	9.4 ± 12.8	60.7
Bentazone	1.0	n.d.			n.d.			3	1.1 ± 0.0	1.1	100	15.5 ± 47.2	221
2,4-D	0.5	n.d.			n.d.			100	1.8 ± 0.5	3.2	76	4.1 ± 4.7	19.6
MCPA	1.0	n.d.			n.d.			n.d.			95	8.2 ± 9.7	36.3
Dichloroprop	1.5	n.d.			n.d.			n.d.			n.d.		
Mecoprop	1.0	n.d.			n.d.			n.d.			71	3.8 ± 2.6	9.7
Metamitron	1.5	n.d.			n.d.			n.d.			n.d.		
Metribuzin	1.5	n.d.			n.d.			n.d.			n.d.		
Metazachlor	1.3	n.d.			n.d.			5	1.9 ± 0.4	2.5	57	6.6 ± 6.7	27.0
Pendimethalin	2.5	n.d.			n.d.			n.d.			n.d.		
UV-filters													
PBSA	1.0	n.d.			3	1.8 ± 0.7	2.3	24	1.5 ± 0.7	3.4	62	29.0 ± 38.9	170
BP-1	1.0	n.d.			n.d.			n.d.			5		2.5
BP-2	1.5	n.d.			n.d.			n.d.			n.d.		
BP-3	5.0	n.d.			n.d.			n.d.			n.d.		
BP-4	1.0	n.d.			n.d.			n.d.			48	63.2 ± 61.9	226
4-MBC	5.0	n.d.			n.d.			n.d.			n.d.		
EHMC	5.0	n.d.			n.d.			n.d.			n.d.		
OC	5.0	n.d.			n.d.			n.d.			n.d.		
OD-PABA	5.0	n.d.			n.d.			n.d.			n.d.		
Et-PABA	5.0	n.d.			n.d.			n.d.			n.d.		
4-DHB	5.0	n.d.			n.d.			n.d.			n.d.		
Others													
Bisphenol A	50	n.d.			n.d.			n.d.			n.d.		
Triclocarban	5.0	n.d.			n.d.			n.d.			n.d.		
Nonylphenoxyacetic acid	1.0	n.d.			n.d.			n.d.			67	7.5 ± 7.9	32.2