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### Abstract

Phthalate acid esters (PAEs) which are mainly anthropogenic molecules with endocrine disrupting effects in animals and humans, have been detected in terrestrial and aquatic environments. However, little is known about their distribution in the Mediterranean Sea, mainly because of analytical difficulties and the high possibility of ambient sample contamination. Here, we report the optimization of an existing protocol for the determination of PAEs in seawater and freshwater samples, as well as the first estimation of the source and distribution of phthalates acid esters (PAEs) in coastal waters from the NW Mediterranean Sea. By passing 1 L of sample through glass cartridges packed with 200 mg of Oasis HLB and eluted with 6 mL of ethyl acetate followed by gas chromatography and mass spectrometry (GC/MS) analyses, the recoveries for DMP, DEP, DPP, DiBP, DnBP, BzBP, DEHP and DnOP were 101, 98, 115, 110, 99, 98, 103 and 95%, respectively, with acceptable blank values (below 0.4–4.0% of the masses measured in different seawater samples). By using this method, we detected PAEs in the Marseilles coastal area, offshore (2000 m depth) and in the Rhone River with total concentrations ranging from 75.3 ng/L offshore in surface water to 1207.1 ng/L a few meters above the bottom of the Marseilles Bay. High concentrations were also observed in deep waters offshore (310.2 ng/L) as well as in the Rhone River (615.1 ng/L). These results suggest that Marseilles urban area, Rhone River and sediment are potential sources of PAEs in the areas studied.

In the Rhone River, DEHP was the most abundant PAE (66.1%) followed by DiBP (20.5%) and DnBP (6.6%), whereas a gradual change was observed in the plume of the river with increasing salinity. In the Marseilles Bay, DiBP was the most abundant PAE at the surface (47.3% of total PAEs) followed by DEHP (22.7%) and DnBP (19.1%), whereas DnBP was predominant (38.6%) a few meters above the bottom. By contrast, DEHP was the dominant species in the first 50 m (66.9–76.7%) offshore followed by DnBP (10.9–15.2%), whereas DnBP was the most abundant (57.0–72.6%) followed by DEHP (20.1–33.1%) in the deepest waters. This study suggests that in addition to direct PAEs injection in marine waters, different processes regulate PAE distribution in Mediterranean Sea including photochemical oxidation reactions, bacterial degradation and possible diffusion following release from marine litter near the bottom.

Keywords : Phthalates, DEHP, DMP , Dissolved organic matter, Endocrine disruptors

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