



Influence of deep water formation by open-sea convection on the transport of low hydrophobicity organic pollutants in the NW Mediterranean Sea

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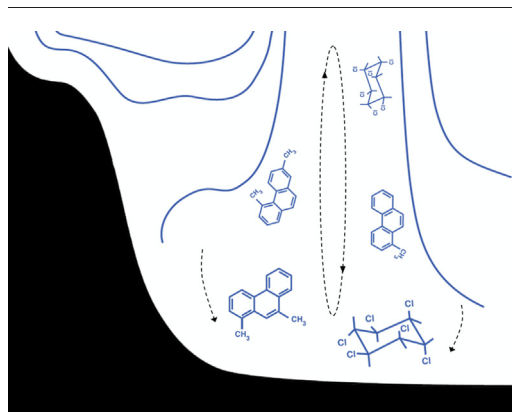
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HIGHLIGHTS

- Lindane is more abundant in the continental rise of the GoL than in the mud belt.
- Open-sea convection accumulates organic compounds in the continental rise.
- Sea convection enhances the transport of low hydrophobic compounds to deep waters.
- The Rhone prodelta is a sink for the river discharged hydrophobic organochlorines.
- Hydrophobic organochlorines and river particles in the GoL show similar distributions.

GRAPHICAL ABSTRACT



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ABSTRACT

The significance of the offshore vertical convection currents in the transport and sinking of water-soluble organic pollutants into marine deep basins has been evaluated. For this purpose, sediment cores were collected in the Gulf of Lion (GoL) at sites between 26 and 2330 m water depth. The top core layers were analyzed for aromatic and aliphatic hydrocarbons and organochlorine compounds. Organic compounds with $\log K_{AW}$ (air water partition coefficient) between -2 and -4 , e.g. lindane, PCB 28, PCB 52, phenanthrene, methylphenanthrenes, dimethylphenanthrenes, C_{14} – C_{23} *n*-alkanes, are found in higher concentrations or exhibit relative concentration increases in the sediments deposited in the continental rise as consequence of the open-sea convection processes associated with the formation of Western Mediterranean Deep Water (WMDW). In contrast, the organic pollutants with intermediate air-water distribution coefficients, $\log K_{AW}$ between -2 and 0 , and high octanol water distribution coefficients ($\log K_{OW} > 6$), e.g. highly chlorinated PCBs, DDTs, DDEs, DDDs, C_{25} – C_{35} *n*-alkanes, and polycyclic aromatic hydrocarbons with molecular weight higher than 200, occur in association to sediment particles, which are mainly transported by the Northern current along the continental shelf forming the mud belt. The Rhône prodelta is therefore the area of the GoL showing the highest concentrations of this group of organic compounds, which are preferentially associated with water particles. Overall, the results show that vertical open-sea convection processes related with offshore formation of WMDW may have an important role in the transport and accumulation of water soluble pollutants to deep marine environments of the GoL (>2000 m water depth).

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1. Introduction

Organic pollutants in marine environments encompass molecules with diverse toxic activities and diverse physical-chemical properties. Some of them have intermediate air-water distribution coefficients, $\log K_{AW}$ between -2 and 0 , and high octanol water distribution coefficients, $\log K_{OW}$ (octanol water partition coefficient) > 6.0 . These properties give them high potential for bioaccumulation and long-range transport (Wania, 2006). They may also sorb to sinking particulate organic matter being eventually transported to deep waters and underlying sediments (Dachs et al., 1999; Fowler and Knauer, 1986; Gustafsson et al., 1997) which constitute their environmental sink. The settling fluxes of these compounds associated with particle sedimentation may be high enough as to modify both the water and atmospheric concentrations in some environments (Dachs et al., 1999; Schenker et al., 2008).

Other marine organic pollutants exhibit low $\log K_{AW}$ coefficients, between -2 and -4 , involving much higher water solubility. The influence of sinking particles in the transport of these compounds to deep water environments is low. According to model calculations deep water formation may increase the transport of these organic pollutants to deep water environments and this mechanism may outweigh the settling removal processes from the surface mixed layer associated with particle sedimentation (Lohmann et al., 2006). Formation of deep water convection is the primary engine of the thermohaline circulation due to gradients in salinity and temperature, and moves surface waters, directly to the deep Ocean (Houpert et al., 2016; Severin et al., 2016, 2017). This mechanism may be relevant for the overall distribution of low hydrophobic organic pollutants in the marine environment but, to the best of our knowledge, no experimental field study has attempted to assess the reliability of these calculations.

In the Gulf of Lion, the sea surface buoyancy loss caused by the same persistent cold and dry winds that form dense water on the shelf (Canals et al., 2006) also causes open-sea convection in the Gulf of Lion (GoL) (Marschall and Schott, 1999; Rhein, 1995; Schröder et al., 2006; Houpert et al., 2016), generating a simultaneous triggering of offshore convection and shelf-water cascading in the region. These processes are important as lead to the formation of Western Mediterranean Deep Water (WMDW), which plays a crucial role in the thermohaline dominated circulation of the Mediterranean Sea. The open-sea convection processes occur in some areas of the continental rise, ca. $42^{\circ}\text{N } 5^{\circ}\text{E}$ (MEDOC Group, 1970; Schott and Leaman, 1991). In this deep area, vertical convection causes mixing of surface water with warmer but saltier Levantine Intermediate water (LIW) and deepening of the mixed layer. In specific years, the open-sea convection reaches the sea floor and forms new deep water that is slightly saltier and warmer than the ambient waters above the bottom, resulting from the mixing of LIW and Western Mediterranean Deep water (WMDM; Font et al., 2007; Palanques et al., 2012). WMDW is formed in these areas, which subsequently sinks and spreads over the western Mediterranean basin below 1900 m depth (Schott and Leaman, 1991; Smith et al., 2008; Martin et al., 2010). The GoL is, therefore, an ideal site to assess the down-load transport of water soluble organic pollutants under the influence of convection processes.

Accordingly, the present study is aimed to assess whether these organic pollutants of low $\log K_{AW}$, the less hydrophobic organic contaminants, exhibit higher occurrence in the GoL sites of formation of open-sea deep water. For this purpose, the sedimentary composition of organochlorine compounds, aliphatic hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) has been determined in diverse sites of the Gulf of Lion (GoL). The results provide an experimental assessment of the significance of offshore deep water formation in the transport and sinking of water-soluble pollutants.

2. Materials and methods

2.1. Sample collection

Superficial sediment cores were collected in the Gulf of Lion between 26 and 2330 m water depth during several oceanic cruises (2005–2008; Table 1, Fig. 1). Most of the samples were collected with box cores in April 2005 on the R/V Endeavor. The sampling areas included in the study were the Rhône prodelta, the Mud Belt along the sediment dispersal system (~ 60 – 80 m depth) and the head of the western canyons, Lacaze-Duthiers (LDC) and Cap de Creus (CCC) submarine canyons. Some samples were also collected along these canyons and in the adjacent southern open slope (SOS) in October 2005 on the R/V Universitatis (multi-cores), in August 2006 on the R/V Tethys II (box-core) and in April 2008 on the R/V L'Europe (box-core). Subsamples from the box-cores were obtained with acrylic glass tubing and stored frozen (-20°C) until being sliced (0.5 cm sections until 5 cm depth and 1 cm sections below) and analyzed in the laboratory. Multicores were sliced on board and also frozen at -20°C . The external part of the sample that was in contact with the sampling tubing was removed to avoid smearing during the extrusion process.

2.2. Analysis

The organochlorine compounds were analyzed in the Rhône prodelta, the Mud Belt and along the CCC, LDC, SOS and Sete Canyons ($n = 65$). The aliphatic hydrocarbons and PAHs were analyzed in superficial sediments ($n = 11$) along the CCC, LDC, SOS and Sete Canyons (Fig. 1).

2.2.1. Aliphatic and polycyclic aromatic hydrocarbons

Freeze-dried sediments (~ 0.5 g, 0 – 0.5 cm) were extracted by sonication with dichloromethane (3×4 mL). The extracts were spiked with *n*-nonadecan-1-ol, *n*-hexatriacontane, *n*-tetracontane and perdeuterated polycyclic aromatic hydrocarbons (PAHs; [$^2\text{H}_{10}$]-anthracene, [$^2\text{H}_{12}$]-benz[*a*]anthracene, [$^2\text{H}_{10}$]-benzo[*b*]fluoranthene and [$^2\text{H}_{10}$]-benzo[*ghi*]perylene) as surrogates. Then, they were nitrogen concentrated to few milliliters and hydrolyzed overnight with 4 mL of 9% KOH in (80:20) methanol-water. The neutral fractions were recovered with *n*-hexane (3×4 mL), nitrogen concentrated to almost dryness and derivatized with bis(trimethylsilyl)trifluoroacetamide. Before sample injection for PAH analyses, 100 μL of an internal standard solution of [$^2\text{H}_{10}$]-pyrene and [$^2\text{H}_{12}$]-perylene in iso-octane was added.

The aromatic compounds were analyzed by gas chromatography coupled to mass spectrometry (GC-MS; Thermo DSQII instrument). The oven temperature program started at 90°C (held for 1 min) and increased to 120°C at $10^{\circ}\text{C} \cdot \text{min}^{-1}$ and then to 310°C at $6^{\circ}\text{C} \cdot \text{min}^{-1}$ where it was held for 25 min. Injector, transfer line and ion source temperatures were 280°C , 270°C , and 250°C , respectively. Helium was the carrier gas (1.0 mL \cdot min $^{-1}$). The injector operated in the splitless mode (0.8 min). Mass spectra were acquired in the electron impact mode (EI, 70 eV ionization energy). PAHs were determined in selected ion recording mode (SIR). The diagnostic ions selected for study were: *m/z* 152, 154, 166, 178, 188, 192, 198, 202, 206, 212, 216, 226, 228, 240, 252, 264, 276, 278, 288, 300, and 302. They were recorded with a dwell time of 70–100 ms and a width of 0.8 a.m.u. (ion windows were chosen according to retention times of standards) (Salvadó et al., 2012c).

The samples were injected onto an HP-5MS column (60 m length, 0.25 mm i.d., 0.25 μm film thickness). This column afforded the analysis of 59 PAHs (see Table S3). PAHs identification was performed by peak matching to retention time to reference standards and comparison to literature retention indices (Benner et al., 1995; Lee et al., 1979). Quantitative data were obtained by the external standard method (EPA mix 16, Dr. Ehrenstorfer). Compounds lacking reference standard were quantified using the response factor of the standard exhibiting the closest retention time. Recoveries for the overall procedure calculated from

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