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Transfer of lipid molecules and polycyclic aromatic hydrocarbons to open marine waters by dense water cascading events

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ABSTRACT

Settling particles were collected by a set of moored sediment traps deployed during one year in the western Gulf of Lion along Cap de Creus and Lacaze-Duthiers submarine canyons and on the adjacent southern open slope. These traps collected particles during periods of pelagic settling and also during events of deep water flushing by dense shelf water cascading (DSWC). Analyses of lipid biomarkers (*n*-alkanes, *n*-alkan-1-ols, sterols and C_{37}-C_{38} alkenones) and polycyclic aromatic hydrocarbons (PAHs) showed much higher transfer of terrestrial lipids and PAHs to open deep waters during DSWC than in the absence of cascading. The area of highest lateral fluxes was mostly located at 1000 m depth but also at 1500 m depth and extended along the canyons and to the adjacent slope. Higher fluxes were observed near the bottom (30 m above bottom; mab) than at intermediate waters (500 mab) which is consistent with the formation and sinking of dense water over the continental shelf, and its transport through the canyons towards the continental slope and deep basin. DSWC involved the highest settling fluxes of terrestrial lipids and PAHs ever described in marine continental slopes and the pelagic domain, as illustrated by peak values of C_{23}-C_{33} odd carbon numbered alkanes (405 ng m^{-2} d^{-1}), C_{22}-C_{32} even carbon numbered alkan-1-ols (850 ng m^{-2} d^{-1}), β-sitosterol + sitostanol (4800 ng m^{-2} d^{-1}) and PAHs (55 μg m^{-2} d^{-1}). The algal lipids also showed higher transfer to deep waters during DSWC but to a lower extent than the terrigenous compounds. However, the C_{37}-C_{38} alkenones constituted an exception and their settling fluxes were not influenced by DSWC. The lack of influence of the DSWC on the C_{37}-C_{38} alkenone settling is consistent with absence of haptophyte algal inputs from the continental shelf and reinforces the reliability of these molecules for palaeothermometry and palaeoproductivity measurements in pelagic systems.

1. Introduction

About 20–30% of the global marine primary production occurs in continental margins (Wollast, 1991). Massive amounts of terrestrial organic carbon are also deposited in these areas, which are key sites for the global burial of organic carbon in marine sediments (Hedges and Keil, 1995; Goñi et al., 1997; Sanchez-Vidal et al., 2013). In continental margins the transfer of organic matter to deep environments occurs either through pelagic settling of biogenic particles generated in the photic zone or by lateral transport (advection) of materials accumulated in shallower sites due to storms, convection currents and internal waves (Sleath, 1987; Stastna and Lamb, 2008; Sanchez-Vidal et al., 2012).

Recently, the role of submarine canyons has been outlined (Canals et al., 2006; Puig et al., 2014; Rumin-Caparros et al., 2016). Canyons may funnel large volumes of sediment and organic matter from the shallow continental shelf to the deep margin and basin (Estournel et al., 2005; Canals et al., 2009; Palanques et al., 2012; Pasqual et al., 2013; Posamentier et al., 1988). They experience occasional sediment gravity flows which may be triggered by mass failure, river flooding or dense shelf water cascading (DSWC), a type of current that is driven by seawater density contrast (Palanques et al., 2006, 2009; Puig et al., 2008). The role of DSWC in the transport of sedimentary material, pigments, amino acids, lignin and organochlorine compounds has recently been investigated (Canals et al., 2006; Palanques et al., 2006, 2009; Puig et al., 2008; Pasqual et al., 2011; Salvadó et al., 2012a; Salvado et al., 2013), but the general significance of this process in the transport of

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lipid biomarkers and anthropogenic compounds such as polycyclic aromatic hydrocarbons (PAHs) needs still to be elucidated.

Lipids in the marine environment are derived from a variety of sources, like biota, fluvial and eolian inputs and resuspension of sedimentary material. These compounds encompass *n*-alkanes, *n*-alkan-1-ols, sterols and C_{37}-C_{38} alkenones and constitute mixtures that contain information on the sources of organic materials accumulated in the sediments (Grimalt and Albaiges, 1990; Grimalt et al., 1990; Peulve et al., 1996; Zhu et al., 2011). These compounds are integrated into larger particles through biotic processes (grazing, algal mat formation, molting) and abiotic processes (adsorption, flocculation, agglomeration), which ease their transfer to deep sea environments (Grimalt et al., 1990; Peulve et al., 1996).

PAHs are pollutants of priority concern due to their toxicity and their continuous release into the environment as consequence of human activities (Fernández et al., 1999; Van Metre et al., 2000; Mesquita et al., 2014, 2016), e.g. forest fires, petroleum production and fossil fuel combustion (Broman et al., 1988; Lipiatou et al., 1993; Bouloubassi et al., 2006; Bosch et al., 2015). Atmospheric deposition and/or sorption on biotic and abiotic particles in seawater are two major processes for PAH incorporation into deep marine environments (Dachs et al., 1999, 2002; Ko et al., 2003; Lin et al., 2016). Yet, PAH transport from surface to deep waters has only been addressed in few studies, which is in contrast with the large body of data on sedimentary PAH worldwide. In this context, no previous study has considered the significance of the mechanisms associated to DSWC for PAH transport to deep marine environments.

Overall, the qualitative and quantitative composition of lipid molecules and PAHs may be useful to elucidate the associations between sources and predominant transport modes to deep water environments. They may also allow assessing the role of submarine canyons and the significance of DSWC in comparison to the mechanisms not related to water density contrast, either pelagic or continental.

DSWC is a significant high-energy process in the Gulf of Lion (GoL), namely in its westernmost end, particularly through the Cap de Creus canyon (CCC) (Canals et al., 2006; Palanques et al., 2008, 2012; Sanchez-Vidal et al., 2008; Pasqual et al., 2010). Accordingly, moorings equipped with automated sediment traps were deployed in nine sites of the western GoL following the physiography of the most active submarine canyons in the area regarding sediment transfer, namely CCC and Lacaze-Duthiers canyon (LDC) and in the adjacent southern open slope (SOS) (Fig. 1). Traps were set between 300 m and 1900 m of water depth and settling particles were sampled between October 2005 and October 2006 at fortnightly intervals. Two DSWC events occurred during this period with two deep-reaching cascading pulses in January and March-April 2006. Thus, this sediment trap experiment offered the possibility to study the transfer of lipid molecules and PAH to the deep margin and basin both during DSWC and in the absence of cascading. The present study is aimed to analyze the spatial and temporal variability of the deposition these compounds for assessment of the role of DSWC and the submarine canyons in their transport to the deep sea.

1.1. Study area and sediment trap deployment

1.1.1. Oceanographic setting

The GoL is a micro-tidal, river-dominated continental and margin that extends from Cap Croisette (northeast) to Cap de Creus (southwest) in the northwestern Mediterranean Sea (Fig. 1). The continental shelf has a crescent shape with a maximum width of about 70 km and a well-defined shelf edge around 150 m deep (Got and Aloisi, 1990). This shelf-edge is deeply incised by twelve main submarine canyons that coalesce into two principal valleys on the deep continental slope and rise.

The GoL is fed by several small rivers (Tech, Têt, Agly, Aude, Orb, Hérault, Vidourle) along its western shoreline. These rivers are subject to a Mediterranean regime with short and intense flash-flood events (Serrat et al., 2001). The Rhône River, in the eastern part of the GoL, provides 90% of the total freshwater and approximately 94% of the total sediment input, mainly during snowmelt in spring (Pont et al., 2002; Bourrin and Durrieu de Madron, 2006).

The general circulation pattern within the GoL is dominated by the Northern Current (NC), which flows south-westward along the continental slope and outer shelf as a part of a cyclonic circulation of the western Mediterranean Sea (Millot, 1990) (Fig. 1). The NC is associated with a permanent shelf-slope density front separating less-saline shelf waters, with continental influence, from saltier and denser open-sea waters, which constrains shelf-slope exchanges and advection of suspended matter (Durrieu de Madron et al., 1999). Biological production is characterized by a spring bloom that lasts generally until May and it is initiated by the increase of insolation and thermal stratification (Bosc et al., 2004; Rigual-Hernandez et al., 2012). Secondary blooms appear in summer and are linked to upwelling or river nutrient inputs (Lefevre et al., 1997; Campbell et al., 2013).

Extreme wind-driven processes (marine storms and dense-water currents) are responsible of most of the sediment resuspension and export of suspended sediment and associated elements from the shelf, primarily at the southwestern end of the GoL (Palanques et al., 2006; Durrieu de Madron et al., 2008). Submarine canyons represent the preferential pathway as the incision of their heads and upper courses into the shelf makes them interacting with near-bottom shelf flows and thus favoring their capability to capture and funnel shelf water and sediment basinward (Monaco et al., 1990). Recent observations from the GoL highlighted the importance of DSWC in particular in exporting large amounts of water and sediment to the deep margin and basin (Canals et al., 2006; Palanques et al., 2012; Pasqual et al., 2013).

1.1.2. Sediment trap deployment

Nine instrumented moorings were deployed in the GoL area (northwestern Mediterranean Sea) along the axes of the Lacaze-Duthiers canyon (LDC) and CCC. The water column depths selected for the moorings were 300 m (upper canyon, CCC300 and LDC300), 1000 m (middle canyon, CCC1000 and LDC1000) and 1500 m (lower canyon, CCC1500 and LDC1500). Another mooring was deployed at the confluence of the canyons (1900 m, CCC1900) and on the adjacent southern open slopes (1000 m and 1900 m depth, SOS1000 and SOS1900, respectively) (Fig. 1). Each mooring was equipped with a sequential-sampling sediment trap that was installed at 30 m above bottom and one Aanderaa current meter (RCM7/8/9) at 5 m above bottom. At mid-water over LCD1000 another trap was installed at 500 m above bottom (LDC1000 (500 m)). The results are always reported by reference to the location acronym (CCC, LDC and SOS) and water column depth of the mooring site. Each trap (PPS3 Technicap cylindrical trap with a 0.125 m^2 opening) was equipped with 12 cups (250 ml).

1.1.3. Dense shelf water cascading during sediment trap deployment

Two major DSWC events occurred from early January to late March 2006. Temperature decrease and current speed increase at CCC1000 peaked at the onset of each cascading event (Sanchez-Vidal et al., 2008), e.g. 100 cm s^{-1} in early January and 60 cm s^{-1} in late March 2006. High current speeds were recorded at CCC300 and LDC300 (up to 100 cm s^{-1}) during these episodes. At 1000 m depth the current velocity increases reached up to 70 and 50 cm s^{-1} in CCC and LDC, respectively. In CCC1500 current speeds were in the range of 10–35 cm s^{-1} during DSWC. High velocities were also recorded at the intersection of CCC and LDC (1900 m) as well as outside the canyons (50 and 30 cm·s^{-1} at SOS1000 and SOS1900).

These events also involved temperature decreases of 2 °C at 300 m depth and 1 °C at 1000 m depth. At SOS1000 and SOS1900 the observed temperatures decreased by 0.8 °C and 0.1 °C, respectively. In CCC1500 temperatures decreased only by 0.3 °C and no significant change was observed at 1900 m depth. These temperature measurements indicate that