The role of dense shelf water cascading in the transfer of organochlorine compounds to open marine waters

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Abstract

Settling particles were collected by an array of sediment trap moorings deployed along the Cap de Creus (CCC) and Lacaze-Duthiers (LDC) submarine canyons and on the adjacent southern open slope (SOS) between October 2005 and October 2006. This array collected particles during common settling processes and particles transferred to deep waters by dense shelf water cascading (DSWC). Polychlorobiphenyls (PCBs), dichlorodiphenyltrichloroethane and its metabolites (DDTs), chlorobenzenes (CBzs) –pentachlorobenzene and hexachlorobenzene- and hexachlorocyclohexanes were analyzed in all samples. The results show much higher settling fluxes of these compounds during DSWC than during common sedimentation processes. The area of highest deposition was located between 1000 and 1500 m depth and extended along the canyons and outside them showing their channelling effects but also overflows of dense shelf water from these canyons. 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 close to the continental shelf and main displacement through the slope by the bottom. DSWC involved the highest settling fluxes of these compounds ever described in marine continental slopes and pelagic areas, e.g. peak values of PCBs (960 $ng·m^{-2}·d^{-1}$), DDTs (2900 $ng·m^{-2}·d^{-1}$), CBzs (340 $ng·m^{-2}·d^{-1}$) and lindane (180 $ng·m^{-2}·d^{-1}$).

Introduction

Organochlorine compounds (OCs), such as polychlorobiphenyls (PCBs) and chlorinated pesticides, constitute a group of persistent organic pollutants of worldwide concern due to their toxic effects.[1,2] Their high lipophilicity, hydrophobicity, chemical stability and resistance to biological degradation have led to the accumulation of these compounds in biological tissues and their biomagnification through to the food chain.[3,4] These compounds are also susceptible of long-range atmospheric transport to remote areas such as polar regions[5], mountain lakes[6,7] and marine environments[8].

OCs can enter into the marine environment by effluent discharges, atmospheric deposition, runoff and other means.[8] Once in the water column association to particulate matter, transport and settling play an important role in their transfer from surface to deep waters and sediments.[9] Particle settling is also favoured by biological processes involving incorporation into the food web, organism migration, vertical mixing, formation of large particles such as fecal pellets, organic matter aggregation, and others.

Besides these mechanisms, other hydrodynamic processes induce lateral (cross-slope) transport from continental shelves to the adjoining environments.[10-12] This is the case of the Gulf of Lion (GoL) where a major mechanism controlling shelf-deep ocean exchange is dense shelf water cascading (DSWC). The strongest exchange by this process takes place in the westernmost end of the GoL through the Cap the Creus canyon (CCC)[13,14]. Various studies have described the rapid export of sediment from the shelf and upper slope to deep environments by DSWC events and the role of submarine canyons in funneling the waters generated in these episodes.[15-19]

To date no study has considered the influence of these cascading processes in the transport of OCs from the continental shelf to the deep marine environment. For this purpose, mooring lines with sediment traps were deployed in nine sites of the western GoL following the physiography of the CCC and Lacaze-Duthiers canyon (LDC), the most active in the area regarding sediment transfer. Traps were set between 300 m and 1900 m water depth and settling particles were sampled between October 2005 and October 2006 at fortnightly intervals. Two DSWC events occurred during this period and this experiment offered the possibility to study transfer of OCs to the deep realm both during common settling and intense events. The present study is aimed to analyze the spatial and temporal variability of

OCs deposition in order to assess the role of DSWC and the submarine canyons in the transport of these compounds to the deep sea. Data are also compared with results from previous sediment trap studies that have generally been performed in coastal areas, bays or lakes.[7,20-23].

Results and discussion

Dense shelf water cascading. Two major deep DSWC pulses occurred during early January and late March 2006 (Fig. S1). Strongest temperature drops and current speed peaks occurred at the onset of each cascading period and in late March 2006[17,18], e.g. 60-100 $cm \cdot s^{-1}$ in CCC1000. High current intensities were recorded at CCC300 and LDC300 (up to 95 $cm \cdot s^{-1}$; Fig. S1) during these episodes. At 1000 m depth the intensities reached up to 70 and 50 $cm \cdot s^{-1}$ in CCC and LDC, respectively. In CCC1500 the current intensities were in the range of 10-35 $cm \cdot s^{-1}$ during these events. These intensities were also recorded at the intersect of CCC and LDC (CCC1900 m; Fig. S1) as well as outside the canyons (50 and 30 $cm \cdot s^{-1}$ in SOS1000 and SOS1900).

In the canyons, these episodes also involved temperature decreases down to 2ºC at 300 m depth and 1ºC at 1000 m depth (Fig. S1). In SOS1000 and SOS1900 the observed temperatures decreased down to 0.8ºC and 0.1ºC, respectively. In CCC1500 temperatures decreased down to 0.3ºC and no significant change was observed at 1900 m depth. These temperature measurements and the preferential directions along slope of the DSWC water mass at CCC1900 and SOS1900 stations[18] indicate that dense water reached equilibrium (neutral density contrast) at about 1900 m depth and flowed along the SOS slope following the cyclonic circulation once dense water is no longer constrained by the canyon walls.

DSWC entrained a strong increase of settling particle fluxes. The highest increase was recorded in CCC1000 with total mass fluxes up to 90 $g \cdot m^{-2} \cdot d^{-1}$ (Fig. 2). In the LDC and the SOS the highest fluxes were also observed at 1000 m depth (40 $g \cdot m^{-2} \cdot d^{-1}$). The mid-water LDC trap (500 m above bottom; mab) also showed a total mass flux maximum during DSWC (10 $g \cdot m^{-2} \cdot d^{-1}$) in agreement with the near-bottom trap in the same line (Fig. 2). These values strongly contrasted with those recorded during periods without deep DSWC for which fluxes were lower than 5 $g \cdot m^{-2} \cdot d^{-1}$.

Concentrations and fluxes of organochlorine compounds. *PCBs.* The PCB concentrations (sum of 7 ICES congeners) in the settling particles ranged between 2.7 and 160 $ng \cdot g^{-1}$ (Fig. S2). The highest concentrations were found in the deepest traps deployed in the CCC and LDC (CCC1500, CCC1900 and LDC1500) and in the SOS (SOS1900). The peak values were recorded during November-December 2005 and July-August 2006. Average concentrations in the different sediment trap stations ranged between 16 (CCC1000) and 26 $ng \cdot g^{-1}$ (LDC1000 (500)) (Table 1). The observed concentrations did not increase during DSWC (Fig. S2). These concentration values were lower than those reported in the LDC 20 years ago (31-1500 $ng \cdot g^{-1}$)[24], although in that case they were reported as Aroclor 1254 equivalents.

The observed congener profiles are similar to those found in other marine settling particles, such as the Mediterranean Sea[24-27], the Sargasso Sea[28] and the Arabian Sea.[29] PCB-101 was the highest congener in all samples (Fig. S3). Nevertheless, during DSWC (January-March 2006) a relative enrichment of PCB-153 and PCB-138 was observed in all stations (Fig. S3A) whereas enrichment in the less chlorinated isomers, especially PCB-52 and PCB-101 (Fig. S3B), was found during common sedimentation. This contrast may reflect PCB composition differences between shelf sediment and settling particles. The former, dragged by DSWC, may be depleted in the less chlorinated congeners by long-term dissolution and washing while the latter may better reflect atmospheric deposition[30].

All traps except one, LDC300, showed highest PCB fluxes in the period of DSWC (Table 2; Fig. 2). During these DSWC episodes a maximum flux of 960 $ng \cdot m^{-2} \cdot d^{-1}$ was recorded at CCC1000 station (Table 1). Average PCB deposition fluxes at CCC1000, CCC1500, LDC1000, LDC1500 and SOS1000 sites during DSWC ranged between 63.5 and 570 $ng \cdot m^{-2} \cdot d^{-1}$. These moorings were all located in the 1000-1500 m water column depth range. The trap situated close to the bottom (30 mab) at LDC1000 station exhibited higher fluxes, 400 $ng \cdot m^{-2} \cdot d^{-1}$, than the one at high position (500 mab), 135 $ng \cdot m^{-2} \cdot d^{-1}$ (Table 2). Other average fluxes during DSCW ranged between 24 and 31 $ng \cdot m^{-2} \cdot d^{-1}$ (Table 2).

The average settling fluxes in the period without DSWC ranged between 12 and 160 $ng \cdot m^{-2} \cdot d^{-1}$ and decreased with increasing distance from the mud belt on the shelf (Table 2). According to these results, while PCB settling without cascading occurred in higher intensity closer to the mud belt, deposition during DSWC was dominant in an area between 1000 and 1500 m in agreement with the location of the CCC1000, LDC1000, LDC1500 and SOS1000 sites. This area extends inside and outside the canyons denoting both their channeling effect on the sediments washed by DSWC but also overflows of dense shelf water from these canyons.

Comparison of the average settling fluxes during DSWC and common sedimentation (D/R ratios; Table 2) shows highest values for the moorings in the above mentioned 1000-

1500 m depth sites, involving between 5.3 and 12 times higher fluxes during DSWC. In all the other mooring sites except LDC300 the PCB settling fluxes were also higher during DSCW with D/R ratio values between 1.5 and 4.2. LDC300, the only exception, had an average PCB settling flux during DSWC of 24 $ng·m^{-2}·d^{-1}$ that was similar to that observed in CCC1900 and SOS1900 in the same period. However, during common sedimentation the highest average flux, 160 $ng·m^{-2}·d^{-1}$, was observed in this site close to the mud belt.

Comparison of the settling fluxes during common sedimentation found in the western GoL with those observed in other sites shows values in the same range as those in the Arabian Sea (1988-91; 4017 m)[29], 16 $ng·m^{-2}·d^{-1}$ (13 PCB congeners), the Alboran Sea (1992; 1200 m)[26], 18.5 $ng·m^{-2}·d^{-1}$ (7 ICES PCB congeners), or in the Botnian Sea (1991-93; 115 m)[31], 34 $ng·m^{-2}·d^{-1}$ (68 PCB congeners). However, in other marine areas the observed settling fluxes are much lower, e.g. in the eastern Mediterranean Sea (2001; 186-1426 m)[27], 0.63 $ng·m^{-2}·d^{-1}$ (54 PCB congeners), in the Sargasso Sea (1978-80; 3200 m)[28], 4.3 $ng·m^{-2}·d^{-1}$ (12 PCB congeners), and in the Swedish western coast (1999-01; 125-155 m)[32], 5.5 $ng·m^{-2}·d^{-1}$ (6 PCB congeners). In this context, the observed PCB settling fluxes during DSWC (Fig. 2; Table 2) are the highest ever described in marine continental slopes and open sea areas.

DDTs. The DDT concentrations in the settling particles (sum of 2,4'-DDE, 4,4'-DDE, 2,4'-DDD, 4,4'-DDD, 2,4'-DDT, 4,4'-DDT) ranged between 0.8 and 85 $ng·g^{-1}$ (Table 1). The highest concentrations, 85 $ng·g^{-1}$, were found at SOS1000 in the first fortnight of January 2006. With the exception of this result the DDT concentrations followed rather closely the changes observed for the PCBs. The average concentrations in the different sediment trap stations ranged between 7.0 (CCC300) and 41 $ng·g^{-1}$ (SOS1000) (Table 1). These concentrations are lower than those observed in a sediment trap study performed in the LDC (3.1-64.5 $ng·g^{-1}$) in 1985-86.[24] Nevertheless, the present GoL concentrations are higher than those found in sediment traps deployed in the Alboran Sea (1.9 $ng·g^{-1}$)[26], in the Baltic Sea (8.1 $ng·g^{-1}$)[31] and in the Arabian Sea (4.1 $ng·g^{-1}$).[29]

In all moorings except LDC300 the average total DDT fluxes during DSWC were higher than in the period of common sedimentation (Fig. 2; Table 2). The highest average total DDT fluxes during DSWC, between 60 and 530 $ng·m^{-2}·d^{-1}$, were observed in the moorings located at 1000 m, CCC1000, LDC1000 and SOS1000 (Table 2). In this context, the trap located close to the bottom (30 mab, LDC1000) exhibited higher fluxes, e.g. 190 $ng·m^{-2}·d^{-1}$ than the one at mid-water (500 mab, LDC1000 (500)), e.g. 60 $ng·m^{-2}·d^{-1}$ (Table 2). The moorings located at 1500 m, CCC1500 and LDC1500, defined a second group of high average settling fluxes, 32-33 $ng·m^{-2}·d^{-1}$ (Table 2). The geographic area of high average total

DDT settling during DSWC is about the same as the one observed from PCB deposition during these episodes. The settling fluxes in the moorings at 1900 m, CCC1900 and SOS 1900, ranged between 11 and 17 $ng \cdot m^{-2} \cdot d^{-1}$ during DSWC (Table 2). The average settling fluxes during common sedimentation ranged between 3.6 and 73 $ng \cdot m^{-2} \cdot d^{-1}$, and, as for PCBs, decreased from increasing distance from the mud belt on the shelf (Table 2). However, deposition during DSWC was accumulated in an area between 1000 and 1500 m (CCC1000, LDC1000, LDC1500, SOS1000) both inside and outside the canyons.

The average settling fluxes in the moorings of the above mentioned 1000-1500 m depth sites were between 6.8 and 79 times higher during DSWC than during common sedimentation (Table 2). In all the other mooring sites except LDC300 the DDT settling fluxes were also higher during DSCW than during common sedimentation with D/R ratio values between 2.3 and 4.5. Only in LDC300 the average total DDT flux was lower during DSWC than in the common sedimentation period, D/R ratio 0.16 (Table 2).

The observed DDT settling fluxes during common sedimentation in the GoL are in the same order of magnitude than those found in the Botnian Sea (1991-93; 115 m)[31], 16 $ng \cdot m^{-2} \cdot d^{-1}$, and higher than those observed in the Arabian Sea (1988-91; 4017 m)[29], 0.6 $ng \cdot m^{-2} \cdot d^{-1}$, and in the Alboran Sea (1992; 1200 m)[26], 1.4 $ng \cdot m^{-2} \cdot d^{-1}$. According to these previous studies, the observed DDT settling fluxes during DSWC (Fig. 2; Table 2) are the highest ever described in marine continental slopes and pelagic areas.

The percent ratio 100·(2,4'-DDT + 4,4'-DDT)/(2,4'-DDT + 4,4'-DDT + 2,4'-DDE + 4,4'-DDE + 2,4'-DDD + 4,4'-DDD) can be used to assess whether DDT emission occurred recently or in the past. High ratios involve predominance of the original insecticide and therefore recent applications of it whereas low ratios correspond to predominance of metabolites and indicate older use. In most samples these ratios are below 50% (Fig. S4), in consistency with predominance of older use. In some cases the ratio exceeded 50% which may reflect some contributions of recent applications of the insecticide.

Chlorobenzenes. Total chlorobenzenes (CBzs) encompass the sum of pentachlorobenzene (PeCB) and hexachlorobenzene (HCB). Even though the production of PeCB and HCB was banned globally under the Stockholm Convention (2004), these compounds are still released into the environment as byproducts of the synthesis of several organochlorine solvents and as a result of backyard trash burning and municipal waste incineration.[33] The concentrations of these compounds in the settling particles varied between not detected and 21 $ng \cdot g^{-1}$ in CCC1000 and CCC1500, respectively (Fig. S2). The average concentrations ranged between 3.8 and 6.6 $ng \cdot g^{-1}$ in LDC1000 and CCC1500, respectively

(Table 1). These values correspond to average percentages of 31% and 67 % for PeCB and HCB, respectively, and both compounds showed the same temporal pattern in the sediment trap stations (not shown). The temporal and geographic distribution of these CBzs is very similar to that observed for the PCBs, with the highest concentrations found in the deepest traps. In comparison to other studies, the HCB concentrations (nd-14.5 $ng{\cdot}g^{-1}$; average 3.5 $ng{\cdot}g^{-1}$) are similar to those found in the Baltic Sea (0.49 – 3.4 $ng{\cdot}g^{-1}$; average 1.9 $ng{\cdot}g^{-1}$)[31] and in the LDC in 1985-86 (0.3-3.7 $ng{\cdot}g^{-1}$; average 1.7 $ng{\cdot}g^{-1}$).[24]

Consistently with the trends observed for DDTs and PCBs, all trap stations except LDC300 showed higher deposition fluxes during DSWC (Fig. 2; Table 2). The average deposition fluxes during DSWC ranged between 6.6 and 200 $ng{\cdot}m^{-2}{\cdot}d^{-1}$ and the average fluxes during common sedimentation were 1.3-37 $ng{\cdot}m^{-2}{\cdot}d^{-1}$ (Table 2). This flux range during the period without cascading was found in LDC and is consistent with previous flux measurements, 9.2 $ng{\cdot}m^{-2}{\cdot}d^{-1}$, in this canyon in 1985-86[24]. These values are higher than those observed in the Botnian Sea[31], 3.7 $ng{\cdot}m^{-2}{\cdot}d^{-1}$, as for DDTs and PCBs. The results observed in the GoL show that the deposition fluxes during DSWC are the highest ever reported in the literature.

The highest deposition CBzs fluxes during DSWC were observed at 1000 m depth in CCC, LDC and SOS, 42-200 $ng{\cdot}m^{-2}{\cdot}d^{-1}$ (Table 2). The deposition flux in LDC1000 (500 mab) was also high, 35 $ng{\cdot}m^{-2}{\cdot}d^{-1}$, but a bit lower than at 30 m depth, 95 $ng{\cdot}m^{-2}{\cdot}d^{-1}$. The enhanced settling during DSWC was also recorded at 1500 m depth which showed lower values than in the mooring located at shallower positions, 20-24 $ng{\cdot}m^{-2}{\cdot}d^{-1}$, but still higher than those in the deep mooring sites, 6.6-8.9 $ng{\cdot}m^{-2}{\cdot}d^{-1}$. The moorings at 1000 and 1500 m depth defined a geographic area of highest DSWC CBzs accumulation that is coincident with the area of PCB and DDT accumulation during these events (Fig. 1). Again, the CBzs results showed that the canyons channel the supply of these compounds during DSWC but there was an overflow which resulted into enhanced transfer in the SOS areas.

The DSWC involved higher settling fluxes of CBzs than during common sedimentation. Thus, in the moorings at 1000 m the D/R ratios ranged between 7.9 and 20 (5.7 for the trap at 500 mab). In the moorings at 1500 m these ratios were 9.2 and 13 (CCC1500 and LDC1500, respectively) and in the moorings at 1900 m the ratios were 3.7 (CCC1900) and 6.8 (SOS1900). LDC300 was the only mooring in which the opposite trend was observed and the D/R was 0.21. This differential behavior of this mooring is in agreement with the observations in PCB and DDT sedimentation fluxes. Like in these previous cases, the smaller distance of this mooring from the mud belt on the shelf suggests that during common sedimentation in this area there is a regular deliver of pollutants stored in the mud belt which is also consistent with the enhanced total mass flux recorded in this mooring (Fig. 2).

Lindane. γ-HCH was the only hexachlorocyclohexane isomer detected in most of the samples. The concentrations of lindane in the settling particles varied between not detected (CCC1000, SOS1000) and 11 $ng \cdot g^{-1}$ (LDC1000 500mab, LDC1500) and the average trap concentrations in each mooring ranged between 0.5 and 4.1 $ng \cdot g^{-1}$, the former in CCC300 and the latest in CCC1900 (Fig. S2, Table 1). These concentrations were similar to those found in the Baltic Sea,[31], 3.6 $ng \cdot g^{-1}$ and in the LDC 20 years ago[24], 2.8 $ng \cdot g^{-1}$, but lower than those found in the Alboran Sea[26], 24 $ng \cdot g^{-1}$.

The depositional fluxes of lindane were higher during DSWC, 5.1-98 $ng \cdot m^{-2} \cdot d^{-1}$, than during common sedimentation, 0.6-10 $ng \cdot m^{-2} \cdot d^{-1}$, in all cases except LDC300 (Fig. 2; Table 2). The highest fluxes during DSWC were found in the moorings located at 1000 m depth both in the traps at 30 m depth, 20-90 $ng \cdot m^{-2} \cdot d^{-1}$, and in the trap at 500 m depth, 23.5 $ng \cdot m^{-2} \cdot d^{-1}$ (Table 2). The trap at 1500 m from LDC also showed important fluxes during this event, 14 $ng \cdot m^{-2} \cdot d^{-1}$. In the case of CCC1500 the DSWC deposition flux was smaller and similar to those at 1900 m depth or LDC300, 5.1-6.35 $ng \cdot m^{-2} \cdot d^{-1}$ (Table 2). The deposition fluxes during common sedimentation were much lower 0.6-3.5 $ng \cdot m^{-2} \cdot d^{-1}$, except in LDC300, 10 $ng \cdot m^{-2} \cdot d^{-1}$ (Table 2), the mooring situated closer to the mud belt. This pattern in well in agreement with the flux differences observed for the other OCs.

The fluxes during common sedimentation were higher than the average fluxes observed in the Alboran Sea[26], 4.2 $ng \cdot m^{-2} \cdot d^{-1}$, but lower than those found in the Botnian Sea[31], 34 $ng \cdot m^{-2} \cdot d^{-1}$, and in the LDC in 1985-86[24], 24 $ng \cdot m^{-2} \cdot d^{-1}$. However, the deposition fluxes during DSWC were similar to those from these two last cases and much higher than those recorded in the Alboran Sea[26].

The DSWC involved higher deposition fluxes of lindane than during common sedimentation. Thus, in the moorings at 1000 m the D/R ratios ranged between 12 and 41 (6.7 for the trap at 500 mab). In LDC1500 the ratio was 22. The D/R ratios in the other moorings with higher flux during the DSWC ranged between 3.4 and 9.0. LDC300 was the only mooring in which the opposite trend was observed (D/R = 0.51). These ratios in each of the moorings are well in agreement with the ratios found in PCB, DDT and CBzs.

The role of DSWC in the transport of organochlorine compounds. The two DSWC pulses in early January and late March (Fig. S1) show the capacity of cascading waters to transport OCs over several tens of kilometers offshore in a few days. The first pulse was more intense at the upper reaches of the CCC (1000 m depth) involving peak fortnightly-averaged settling fluxes of 960 ng·m^{-2}·d^{-1}, 630 ng·m^{-2}·d^{-1}, 340 ng·m^{-2}·d^{-1} and 180 ng·m^{-2}·d^{-1} for PCBs, DDTs, CBzs and lindane, respectively (Fig. 2; Table 1). In the LDC, peak settling values were also found at 1000 m depth, 280 ng·m^{-2}·d^{-1}, 110 ng·m^{-2}·d^{-1}, 77 ng·m^{-2}·d^{-1} and 51 ng·m^{-2}·d^{-1}, respectively. In this canyon, DDTs constituted the only exception and the highest settling flux occurred at 300 m depth, not being related to DSWC (Fig. 2; Table 1). On the SOS, peak settling flux also occurred at 1000 m depth and related to DSWC, showing fortnightly-averaged deposition fluxes of 640 ng·m^{-2}·d^{-1}, 2900 ng·m^{-2}·d^{-1}, 100 ng·m^{-2}·d^{-1} and 44 ng·m^{-2}·d^{-1} for PCBs, DDTs, CBzs and lindane, respectively (Fig. 2; Table 1). The second pulse was less intense but again involved a peak settling flux of OCs at 1000 m depth (Fig. 2).

The enhanced settling fluxes of OCs during DSWC were paralleled by increases of total mass flux. Representation of the settling fluxes of OCs and total particulate organic carbon from the fortnightly-averaged samples collected during DSWC and common sedimentation show very strong correlation coefficients (r^2 = 0.94, 0.89, 0.92 and 0.79 for PCBs, DDTs, CBzs and lindane, respectively; Fig. 3). The changes in deposition fluxes are therefore related to the general dynamics of the settling particles in the GoL. Accordingly, during common sedimentation, the observed increase in fluxes of PCBs, DDTs and CBzs in CCC300 and LDC300 during September-October 2006 occurred in parallel to increases of total mass flux. Such increase was caused by sporadic events of shelf and/or canyon-head sediment resuspension[10] due to the increase of waves and western river discharges during these months.[18,34,35].

In this respect, the above mentioned low OCs fluxes in LDC300 during DSWC that were even lower than the fluxes at 1000 m in the same canyon during common sedimentation, e.g. 24 ng·m^{-2}·d^{-1} vs 52-76 ng·m^{-2}·d^{-1} for PCBs, or 12 ng·m^{-2}·d^{-1} vs 20-28 ng·m^{-2}·d^{-1} for DDTs (Fig. 2; Table 2), may have been caused by low particle deposition due to very strong currents at the canyon head during these DSWC episodes.

The overall significance of the enhanced flux deposition due to DSWC episodes can be assessed by calculation of the inventories by integration of the average fluxes during the time intervals in which DSWC and common sedimentation were predominant. The PCB inventories show that deposition during DSWC was more important than during common sedimentation in the mooring sites at 1000 and 1500 m depth, those with highest settling fluxes during DSWC (Table 2). In these sites, the accumulated PCBs during the DSWC episodes represented about 58-80% of the total annual input. In the moorings at 1900 m depth, the settling PCBs during DSWC involved 33-46% of the whole annual budget and in

LDC300 they only involved 5% (Table 2). The lower rate in LDC1000 (500) than in LDC1000, 41% vs 63%, respectively, is consistent with the physical characteristics of the DSWC episodes involving formation and sinking of dense water close to the continental shelf and main displacement through the slope by the bottom.

Similar figures were obtained for DDTs, in which sedimentation during DSWC at 1000 and 1500 m depth involved 60-96% of the annual input, at 1900 m depth 45-58% and at 300 m depth only 5% (Table 2). The inventories of CBzs showed that sedimentation during DSWC was very significant at 1000 m and 1500 m depth, 72-87%, but also at 1900 m depth, 55-69%, and not in LDC300, 7% (Table 2). The same is the case for lindane, with 53-93% in the mooring traps at 1000 and 1500 m depth, 56-75% at 1900 m depth and 14% at 300 m depth (Table 2). In all these cases higher inventories in LDC1000 were found in the trap located at 30 mab depth than at 500 mab depth, e.g. 69% vs 50%, 72% vs 64% and 91% vs 71% for DDTs, CBzs and lindane, respectively, which is consistent with the preferred transport close to the bottom sea as consequence of the formation of dense waters. Representation of the summed inventories of all measured compounds (Table 2) shows an area of highest settling of OCs during DSWC that is related to the morphology of the canyons but that also extends outside them, in the SOS region (Fig. 4).

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Supporting information available

The study area, oceanographic setting, sample collection methods, materials and analytical procedures are described in a Supporting Information section. This information is available free of charge via the internet at http://pubs.acs.org/.

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Table 1. Settling fluxes (ng·m^{-2}·d^{-1}) and concentrations (ng·g^{-1}) of PCBs, DDTs, CBzs and HCHs and total mass (TM; g·m^{-2}·d^{-1}) and organic carbon (TOC; %) in particles collected in sediment traps deployed along the Cap de Creus Canyon (CCC), Lacaze-Duthiers Canyon (LDC) and the Southern Open Slope (SOS). nd = not detected; nq = not quantified.

		TM[c]	TOC	PCBs[d]		DDTs		CBzs		Lindane	
Station		Flux	%	Flux[e]	Conc	Flux	Conc	Flux	Conc	Flux	Conc
CCC300[a]	Max	12.5	2.9	320	30	92	7.5	62	5.1	6.1	0.7
	Min	3.8	1.4	99	21	28	5.5	5.2	1.2	2.0	0.4
	Mean[b]	7.0	1.8	180	25	50	7.0	30	4.2	3.4	0.5
CCC1000	Max	90	2.9	960	51	630	34	340	5.1	180	7.2
	Min	1.1	0.8	28	8.5	11	4.0	nd	nd	nd	nd
	Mean	12	1.3	190	16	100	8.6	57	5.0	26	2.4
CCC1500*	Max	6.3	9.5	120	95	58	36	53	21	18	5.9
	Min	<0.1	1.4	1.4	12	0.6	6.4	nq	nq	0.1	0.6
	Mean	1.3	1.9	28	20	14	10	8.8	6.6	2.7	2.0
CCC1900*	Max	3.2	6.5	82	81	35	28	20	14	19	7.5
	Min	<0.1	1.4	2.6	11	1.0	5.5	0.4	1.0	0.1	0.6
	Mean	0.7	2.1	18	25	6.2	9.3	3.1	5.0	2.5	4.1
LDC300	Max	18	3.5	460	33	350	25	120	9.7	52	6.5
	Min	0.3	1.4	6.4	9.1	3.9	4.4	2.4	2.5	1.7	0.3
	Mean	6.7	1.8	125	19	57	9.5	29	4.8	8.9	1.6
LDC1000	Max	11	4.5	280	46	130	19	77	12	51	11
(500mab)	Min	0.6	1.5	15	14	5.7	7.2	1.4	1.5	1.0	0.6
	Mean	2.9	2.2	80	26	30	10	14	5.2	8.5	3.3
LDC1000*	Max	40	2.3	570	35	260	14	140	5.4	96	6.4
	Min	2.1	1.2	25	11	13	5.3	6.1	2.5	nq	nq
	Mean	6.7	1.5	105	18	42	8.0	20	3.8	12	2.4
LDC1500	Max	12	5.4	270	160	100	49	61	19	45	11
	Min	<0.1	1.4	0.8	2.7	0.3	0.8	0.1	0.3	<0.1	0.1
	Mean	1.4	1.9	30	21	11	8.2	6.3	4.8	3.9	3.1
SOS1000*	Max	34	4.2	640	59	2900	85	100	8.9	44	5.5
	Min	0.2	1.2	3.4	6.5	2.0	3.4	0.6	1.8	nd	nd
	Mean	3.4	1.5	70	20	145	41	13	3.9	6.6	1.9
SOS1900*	Max	5.7	6.5	64	140	41	44	20	17	13	7.4
	Min	<0.1	1.2	1.2	9.8	0.4	7.1	0.2	1.5	<0.1	0.8
	Mean	0.8	1.9	20	18	7.4	8.7	3.3	4.2	2.2	3.8

[a]Sediment trap material was collected fortnightly from mid October 2005 to late October 2006. A maintenance and turnaround was performed in mid April 2006 and no samples were collected during this period. Failure of the sediment traps rotating motor resulted in the absence of samples during the first six months at the CCC300 station and from February to April 2006 in LDC1000. Due to low amounts of collected particles during July 15, 2006 to October 30, 2006 no samples were analyzed in CCC1500, CCC1900 and SOS1900.

[b]Mean concentrations for each specific OC were calculated by as follows:
where i is the indicator of each cup, is the concentration of the OC in cup i, the total mass collected in cup i and n the total number of cups.

[c]Total mass fluxes in each cup: where is the number of days in which the cup was deployed.

[d]7 ICES PCB Congeners

[e]Mean fluxes for each specific OC were calculated by as follows: where is the flux of the OC in cup i and the other variables are defined as above.

Table 2. Mean settling fluxes ($ng \cdot m^{-2} \cdot d^{-1}$) and inventories ($\mu g \cdot m^{-2}$) of organochlorine compounds during the dense seawater cascading episode (D; January-March 2006) and during the period of common sedimentation (R).

		PCBs				DDTs				CBzs				Lindane				OCs[d]			
		Flux		Inventory[a]		Flux		Inventory		Flux		Inventory		Flux		Inventory		Flux		Inventory	
CCC1000	D	570	8.8[b]	51	74[c]	320	13[b]	29	81[c]	200	20[b]	18	87[c]	98	41[b]	8.8	93[c]	1200	12[b]	110	80[c]
	R	65		18		24		6.6		9.9		2.7		2.4		0.66		100		27.5	
CCC1500	D	63.5	4.2	5.7	58	32	4.5	2.9	60	24	9.2	2.2	76	5.5	3.4	0.495	53	125	4.8	11	61
	R	15		4.1		7.0		1.9		2.6		0.71		1.6		0.44		26		7.5	
CCC1900	D	24	1.5	2.2	33	11	2.3	0.99	45	6.6	3.7	0.59	55	5.5	3.9	0.495	56	47	1.9	4.2	39
	R	16		4.4		4.7		1.2		1.8		0.49		1.4		0.385		24		6.6	
LDC300	D	24	0.15	2.2	5	12	0.16	1.1	5	8.1	0.21	0.73	7	5.1	0.51	0.46	14	49	0.23	4.4	5
	R	160		44		73		20		37		10		10		2.75		290		80	
LDC1000 (500)	D	135	2.2	12	41	60	3.0	5.4	50	35	5.4	3.15	64	23.5	6.7	2.1	71	250	2.7	23	48
	R	62		17		20		5.5		6.5		1.8		3.5		0.85		93		25	
LDC1000	D	400	5.3	36	63	190	6.8	17	69	95	7.9	8.55	72	79	33	7.1	91	760	6.3	69	68
	R	76		21		28		7.7		12		3.3		2.4		0.66		120		33	
LDC1500	D	80	6.7	7.2	69	33	9.2	3.0	75	20	13	1.8	81	13	22	1.8	92	150	8.3	13	73
	R	12		3.3		3.6		0.99		1.5		0.41		0.60		0.165		18		4.9	
SOS1000	D	220	12	20	80	530	79	48	96	42	14	3.8	82	20	12	1.8	80	810	27	73	90
	R	18		4.9		6.7		1.8		3.0		0.82		1.7		0.46		30		8.2	
SOS1900	D	31	2.6	2.8	46	17	4.2	1.5	58	8.9	6.8	0.80	69	6.3	9.0	0.57	75	63	3.5	5.7	54
	R	12		3.3		4.0		1.1		1.3		0.36		0.70		0.19		18		4.9	

[a]Inventories during DSWC and common sedimentation were calculated by multiplication of the average fluxes during these two periods by 90 and 275 days, respectively.
[b]D/R ratio of deposition fluxes.
[c]100·D/(R+D) ratio of inventories.
[d]OCs, sum of all measured organochlorine compounds.

Figure captions

Figure 1. Map of the Gulf of Lion (GoL) and location of the sediment trap mooring lines along transects in Lacaze-Duthiers (LDC) and Cap de Creus (CCC) Canyons and in Southern Open Slope (SOS) sites. The arrow highlights the dominant Northern Current (NC). Numbers indicate the water column depths at each site. The traps were deployed at 30 m above sea bottom. In LCD1000 another trap was installed at 500 m above sea bottom.

Figure 2. Deposition fluxes of organochlorine compounds (PCBs, DDTs, CBzs and Lindane; $ng \cdot m^{-2} \cdot d^{-1}$) and total mass (TMF; $g \cdot m^{-2} \cdot d^{-1}$) measured in sediment traps deployed in the Cap de Creus (CCC) and Lacaze-Duthiers (LDC) canyons and in Southern Open Slope (SOS) sites (Fig. 1). See Fig. 1 for details.

Figure. 3. Correlations between fluxes of total organic carbon (TOC; $g \cdot m^{-2} \cdot d^{-1}$) and organochlorine compounds ($ng \cdot m^{-2} \cdot d^{-1}$) in the particles collected with the sediment traps deployed in the Cap de Creus and Lacaze-Duthiers canyons and in Southern Open Slope sites (Fig. 1).

Figure. 4. Inventories ($\mu g \cdot m^{-2}$) of settling organochlorine compounds (sum of PCBs, DDTs, CBzs and lindane) during the DSWC episode (January-March 2003; in red) and during the period of common sedimentation (in orange). The acronyms refer to Cap de Creus (CCC) and Lacaze-Duthiers (LDC) canyons and Southern Open Slope (SOS) sites. Numbers besides the acronyms refer to water column depths.