Results and discussion

Figure 24  Depth-time distribution of the total water concentration for PCB 180 and for a water column of 10 m depth. the temporal evolution of the wind speed is also shown.

In this case the distribution of contaminants is driven by a combination of atmospheric and sediments inputs. The recycling from the sediments is highly controlled by wind-generated turbulence and also rain-generated turbulence. It contrasts with the 50 m column depth, where atmospheric inputs clearly control the distribution of contaminants in the first 20 m (see Figure 3 in chapter 3.3.2). Indeed, attention should be paid in shallow aquatic environments, where all organisms of the water column may present higher loads of pollutants, affected by the recycling of the sediments and the atmospheric inputs.
3.3.2 Scientific contribution:

Fate of persistent organic pollutants in the water column: does turbulent mixing matter?

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FATE OF PERSISTENT ORGANIC POLLUTANTS IN THE WATER COLUMN:
DOES TURBULENT MIXING MATTER?

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Abstract

The effect of vertical turbulent mixing on the dynamics of Persistent Organic Pollutants has long been overlooked and its role is still hardly understood. Here we present the first comprehensive analysis of the role of turbulent diffusion on the distribution of these contaminants and its interplay with sinking fluxes. To this end, a 1D dynamic coupled hydrodynamic-contaminant model has been developed and applied to a Mediterranean continental shelf environment. The hydrodynamic sub-model is adapted from COHERENS, the contaminant sub-model is an improvement from the BIODEP model and considers the contaminant in 3 states: dissolved-colloidal-particle. The simulation highlights the role of the turbulent processes in determining the POP distribution and variability in the water column. In short, turbulent flux of contaminants strengthens the upward diffusion of sediment entrained
Results and discussion

Contaminants and determines the extent to which inputs from the atmosphere mix into the water column. It acts in parallel with degradation and sinking fluxes, the combined effect yielding a surface enriched - depth depleted - benthic layer enriched region distribution, which presents similarities to reported experimental measures.

Keywords: PUPs, PCNs, turbulence, hydrodynamic model, contaminant model, sinking

1. Introduction

The oceans play an important role in controlling the environmental transport, fate (or air-sea exchanges) and sinks of persistent organic pollutants (POPs) at regional and global scales (Wania and Mackay, 1996; Dachs et al., 2002). The occurrence of these hydrophobic and semivolatile compounds is of special concern due to their ubiquity, toxicity and accumulation in food webs (Jones and de Voogt, 1999). It has been demonstrated that water-column processes have a strong impact on the air-sea exchange of POPs, since their efficient removal from the mixed surface water layer reduces the volatilization rates (Dachs et al., 1999; Scheringer et al., 2004). However, there is a scarcity of vertical flux measurements of POP associated with sinking particles. Nevertheless, there is a complex interplay of processes controlling the vertical transport of contaminants in the water column (Schulz-Bull et al., 1988; Dachs et al., 1997; Gustafsson et al., 1997; Dachs et al., 1999). On the other hand, marine sediments have been hypothesized to become a pool of contaminants available for mixing throughout the water column, especially during poorly stratified periods (Baker et al., 1991; Berglund et al., 2001; Bogdan et al., 2002, Ko et al., 2003). From the above, the POPs transformations and fate in water column need to be more adequately parameterized in particular for shallow water bodies and the ocean shelf zone.
Results and discussion

Namely, POP water column processes are: partitioning onto colloidal and particulate matter with the sinking of particulate-bound contaminants, degradation of dissolved compounds, incorporation to trophic chains and transport of contaminants due mixing of water masses by turbulent diffusion and vertical advection. Among them, the influence of mixing of waters masses by turbulent diffusion on POPs distribution has usually not been considered in environmental models (Mackay, 2001; Ullrich et al., 2002; Palm et al., 2004). The reason deals, apart from the intrinsic complexity to model highly variable turbulent fluxes, that most models assume that vertical mixing within the surface layer is fast, and therefore, it is not the kinetic limiting process. In deeper layers and in the open ocean the vertical movement of water due to turbulent diffusion is often assumed negligible due to the disparity between horizontal and vertical scales, which generates much lower vertical diffusivities compared to horizontal diffusivities. Furthermore, it is assumed that vertical fluxes of POPs with settling particles dominate over other removal processes (Ullrich et al., 2002; Wania and Daly, 2002).

The traditional approach to model POPs in the water column is to consider two well-mixed boxes during stratification periods (which would be the permanent case for oceans, and temporarily for coastal-lakes-marginal seas) and one well-mixed the rest of the time (Schwarebasch et al., 2003; Meijer et al., 2006). The extreme number of 0D models for these hydrophobic organic compounds (Wania and Mackay, 1996, Scheringer et al., 2000, Dall-Valle et al., 2003, Dues et al., 2005) contrasts with the lack of spatially and temporally resolved models, with the exception of the recently developed coastal lagoon model for herbicides (Caruffi et al., 2006), but its chemical behavior differs from the POPs, and the recent one reported for HCH by Ilyin et al. (2006), but not applied to chemicals with higher hydrophobicities and thus stronger interactions with particles and sediments.

Here we develop a 1D dynamic coupled hydrodynamic-contaminant model to analyze the influence of vertical mixing on the distribution of POPs in the water column. The effect of seasonal dynamics of phytoplankton on POPs fate has been also considered. Such a 1D dynamic model for POPs consists in a novelty, since no similar models are known in the literature. Using a 1D instead of a 3D version is
adequate for open sea areas, where the atmospheric transport is the prevalent route for the introduction of contaminants (Tolosa et al., 1997). Furthermore, it avoids the difficulties associated with providing time-series of boundary conditions, reduces computation time and prepares a simpler model variant which after verification gives the option to lately easily extend it to 3D model version using the COHERENS framework. The model has been applied to a buoy station located in the Mediterranean continental shelf, where strong seasonal stratification occurs and its effects can be investigated.

Particular attention is given to answer the following questions: (i) the role played by vertical turbulent mixing on the distribution and variability of POPs in the water column; (ii) the extent to which atmospheric and sediment inputs diffuse in the water body; (iii) the importance of turbulent diffusion versus other processes that also take place in the water column, such as sinking of particle-bound contaminants and degradation of dissolved contaminants; (iv) the validity of estimated profiles by the 1D dynamic model comparing results to literature.

2. Model description

2.1. Model design

The model consists in a 1D dynamic coupled hydrodynamic-contaminant model applied to the water column and forced with seasonal phytoplankton abundance. The water column is subdivided into a number of discrete layers and the concentrations do vary in time and space. The structure of the model and its physical part is based on COHERENS (http://www.unimom.ac.be/coherens), a complex 3D/1D hydrodynamic finite difference model for coastal seas which is freely available for scientific purposes (Luyten et al., 1999; Luyten et al., 2003). Its hydrodynamic performance has been verified in various environments like the North Sea and Suez di Goro (Ungiesser et al., 2002, Marinov et al., 2006). Changes introduced here mainly concern the introduction and coupling of a contaminants module into the program structure of COHERENS. In addition, the model includes a suspended particulate matter (TSM) as an individual compartment, because of its key role in the re-distribution of POPs in marine
Results and discussion

Due to its 1D nature, the model presented is adequate for areas in which horizontal concentration variations can be disregarded and where bottom deep currents can be assumed negligible. According to the 1D parameterization, horizontal advection and diffusion transports are neglected and just the transport of substances by vertical turbulent diffusion and advection by sinking are considered. For that reason the model is not suitable for regions of deep water formation and down/up-welling advection zones where the vertical fluxes should be considered (Lohmann et al., 2008). However, the 1D approach is adequate to assess the objectives listed above.

The present model has been applied to a buoy station in the Mediterranean continental platform (44N, 141 - open North Adriatic), in a location without strong anthropogenic influences and with an average depth of 50m. At these depths internal water mixing is mainly generated by atmospheric forcing at the air-sea interface, being tidal friction unimportant. Since the northern Adriatic basin is subject to strong forcing functions, it produces a clear seasonality in the ecosystem (Zavattelli et al., 2008), consequently results are adequate to evaluate the temporal variation of contaminants dynamics. The model is written and implemented in FORTRAN and it has been discretized in 50 vertical layers (NZ=50) and time step of 60 s. A linear interpolation has been applied to recalculate the forcing functions with hourly frequency.

2.2. Hydrodynamic modeling

The hydrodynamic part of the model solves the 1D equations of momentum (adopting the Boussinesq approximation and vertical hydrostatic equilibrium), continuity, temperature and salinity. Further, all vertical eddy viscosity and diffusivity coefficients in the momentum and scalar equations are evaluated by classical two-equation turbulence closure scheme. For a detailed description of the hydrodynamic momentum, scalar and turbulent model equations, the reader should refer to COHERENS (Luyten et al., 1999).
Results and discussion

The state variables of the hydrodynamic sub-model are temperature, salinity and eddy diffusion coefficients. The forcing consists in meteorological conditions obtained from 6h measures provided by reanalyses from the European Center for Medium Weather Forecast (ECMWF, http://www.ecmwf.int/): air temperature at 2m, wind speed and direction at 10m, precipitation rate, cloud cover, relative humidity. They are referred to the whole year 2003 and to the buoy location (44N, 14E). Besides, this hydrodynamic part was initialized using a constant profile for temperature (1°C at 1m) and a constant rate of salinity with depth \( S(x) = S_0 \left( 1 + 0.5 \frac{(x-k)}{30} \right) \), where \( k = 1, 2, \ldots, NZ \).

2.3. Contaminant modeling

The contaminants sub-model, coupled to the hydrodynamic sub-model, is based on the BODIP model described elsewhere (Meyer et al., 2006) and contains all the equations that describe the compounds partitioning, boundary and internal related fluxes. The contaminant part has been completely incorporated in the original CUBI/URANS model framework. Considered state variables are the total concentration in the open water \( C_w(t) \) (ng m\(^{-2}\)) and the total concentration in the surface mixed sediment layer \( C_{sml}(t) \) (ng m\(^{-2}\)), the latter expressed as bulk volume. Thus the model not only considers contaminant processes in the water column but as well in the sediments surface mixed layer. In particular, 7 representative polychlorinated biphenyls (PCBs) (PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 153, PCB 180) have been chosen as the contaminants of study.

Atmospheric and deep sediments concentrations are considered as the drivers of the contaminants sub-model, hence the contaminant forcing data consists of PCB measured concentrations in rain (Mandolakis and Stephanou, 2004), atmospheric (gas/particulate) (Mandolakis and Stephanou, 2002) and deep sediments (Moert et al., 2001) (see Table A.1 in Appendix), representative of pristine open sea Mediterranean. Their choice is hampered by the scarcity of data for atmospheric PCB concentrations in the offshore Mediterranean. Forcing concentrations have been assumed yearly constant, not influenced by processes in the water column. Finally, initial concentrations in the
Results and discussion

Simulations are homogeneous $10^{-9}$ ng m$^{-3}$ in the water column and $10^{5}$ ng m$^{-3}$ in the sediments, but this does not impact the final results because the model was consequently rerun for few years under same forcing conditions until two consecutive years yielded equal results.

In the water column Persistent Organic Pollutants are modeled either as truly-dissolved form ($U_{doc}$ [ng m$^{-3}$]), sorbed to colloids ($U_{doc}$ [ng m$^{-3}$]) or to suspended solids ($U_{suspended}$ [ng m$^{-3}$]). A similar three-phase approach has also been considered in the sediments:

\[ U_{sed}^{T} = U_{sed}^{B} + U_{sed}^{DOC} + U_{sed}^{suspended} \]  \hspace{1cm} [1] \\
\[ U_{sed}^{i} = C_{sed}^{i} + U_{sed}^{DOC} + U_{sed}^{suspended} \]  \hspace{1cm} [2]

where $i$ is evaluated water layer (1: bottom water layer, N: surface water layer).

This phase separation determines the dynamics of the organic compound in the system: dissolved POPs are bioavailable since they can be incorporated by passive diffusion to the biota, POPs sorbed to particles can be deposited by gravity; POPs sorbed to colloidal material can not sink and diminish the accumulation of contaminants in trophic chains. In either phase they are subject to diffusion because of turbulence of water masses. Furthermore, the phase separation depends on the physicochemical properties of the contaminant, abundance and typology of organic matter in the media, and other properties of the surrounding media, being temperature one of the most controlling factors. Assuming equilibrium at all times between the phases, previous equations can then be rewritten as:

\[ C_{doc}^{T} = C_{doc}^{B} + (1 + K_{DOC} \cdot DOC) \cdot RCF \cdot TSM^{phys}POM^{phys} + RCF \cdot TSM_{sed}^{phys}POM^{phys} \]  \hspace{1cm} [3] \\
\[ C_{sed}^{T} = C_{sed}^{B} + (1 + K_{DOC} \cdot DOC) + K_{sed} \cdot TSM_{sed}^{phys}POM^{phys} \]  \hspace{1cm} [4]

where DOC (ng m$^{-3}$) is the dissolved organic carbon concentration and TSM$^{phys}$ and TSM$^{phys}$ (ng m$^{-3}$) the concentration of total suspended matter in the water column in the so-called “physical” and “biological” particles respectively, $\phi_{sed}$ [0-1] the porosity of the SMPL, $f_{SOM}^{phys}$ [0-1] and $f_{SOM}^{phys}$ [0-1] the unitary mass fraction of organic matter in the physical and biological TSM. DOC has been assumed constant, but the TSM has been determined at each time and depth point in the contaminants sub model. In particular, TSM$^{phys}$ accounts the atmospheric aerosol inputs and the resuspension of
Results and discussion

particles from the sediments with a fraction of organic matter of 0.1, while $1NM^{\text{bulk}}$ represents the total particulate organic matter in the water column from biological origin. Then $f_{\text{net, bulk}}$ is in fact $1NM^{\text{bulk}}$ has been considered constant all the water column forced to follow the temporal variation of chlorophyll-a amount in the surface. The porosity is assumed 0.85. $K_{\text{col}}$ and $K_{\text{col,diss}}$ ($m^3 ng^{-1}$) are the partition coefficients of the chemical between the colloidal and the truly dissolved phases, $K_{\text{diss}}$ ($m^3 ng^{-1}$) is the partition coefficient of the chemical between the particulate and the truly dissolved phase and $BCF$ ($m^3 ng^{-1}$) is the bioconcentration factor, i.e. the ratio between dissolved and phytoplankton PTH concentration at equilibrium. Moreover, BCF has been assumed to be correlated to the colloidal-water partition coefficient and modeled using a two compartment system (Del Ventis and Haers, 2002). All previously named partition coefficients are function of the water temperature, taken from the outputs of the hydrodynamical part of the model. Derivations and values of the previous parameters are shown in detail in the Table A.2.1 and A.2.2 in the Appendix section. The 1NM modeling is explained in Appendix C.

Apart from the fluxes of contaminants that take part in the water column, we have considered as well the processes that occur in the SMSL, and boundary fluxes with surrounding media such as atmosphere and deep sediments. In particular, the following processes are considered (see Figure 1): atmospheric exchange, i.e. diffusive gaseous absorption and volatilization, gaseous and particle-bound wet deposition (rain), dry particle deposition; internal water column processes, i.e. sinking of particle-bound contaminants, turbulent diffusion, degradation and sorption to DOC and suspended particles; fluxes between the SMSL and the water column, i.e. resuspension and diffusion from the pore water; and finally fluxes between the SMSL and the deep sediments such as burial, pore water diffusion and biodiffusion (generated by biological reworking of sediments).

The fluxes between atmosphere and water are based in parameterizations described elsewhere (Duclos et al., 1999, Jurado et al., 2004, Jurado et al., 2005). Sinking fluxes in each layer of the water body are computed as the sum of the sinking of contaminants bounded to “physical” particles and to
Results and discussion

“Biological” particles. The former is characterized by a constant settling velocity, the latter is assumed to be proportional to the flux of organic matter collected in the bottom (Barnes et al., 1994). The sediment-water exchanges follow largely (Schwarzenbach et al., 2003; Jacob et al., 2005). Tables with the equations and parameter values for each of the processes are available in the Appendix section (see Table B.1 and Table B.2).

The time-dependent concentrations in each water layer \( i \) and as well as the sediment concentrations are estimated based on the mass balance approach, i.e. change = inputs - outputs - transformations:

\[
\begin{align*}
\frac{dC_{\text{ss}}^i}{dt} &= (\text{I} \cdot h_i) \left( F_{\text{AW,ss}} \cdot F_{\text{AW,ss}} + F_{\text{WD}} + F_{\text{DIR}} + F_{\text{SG,ss}} \cdot F_{\text{SG,ss}} + F_{\text{SG,ss}} \cdot F_{\text{SG,ss}} + F_{\text{RES,ss}} \cdot F_{\text{RES,ss}} \cdot F_{\text{RES,ss}} \cdot F_{\text{RES,ss}} \right) \\
&+ F_{\text{RES,ss}} \cdot F_{\text{RES,ss}} \cdot F_{\text{RES,ss}} \cdot F_{\text{RES,ss}} 
\end{align*}
\]  

where \( h_i \) (m) is the depth of the evaluated water layer, \( F_{\text{AW,ss}} \) (ng m\(^{-2}\) s\(^{-1}\)) the gaseous diffusive absorption flux, \( F_{\text{WD,ss}} \) (ng m\(^{-2}\) s\(^{-1}\)) the wet deposition flux, \( F_{\text{RES,ss}} \) (ng m\(^{-2}\) s\(^{-1}\)) the sediment resuspension flux, \( F_{\text{SG,ss}} \) (ng m\(^{-2}\) s\(^{-1}\)) the settling flux (physcial and biological) associated with water layer \( i \), \( F_{\text{DIR,ss}} \) (ng m\(^{-2}\) s\(^{-1}\)) the degradation flux in the water layer \( i \), \( F_{\text{RES,aw}} \) (ng m\(^{-2}\) s\(^{-1}\)) the diffusive flux from SML to the water column, \( F_{\text{SS,aw}} \) (ng m\(^{-2}\) s\(^{-1}\)) the sediment resuspension flux, \( F_{\text{SS,ss}} \) (ng m\(^{-2}\) s\(^{-1}\)) accounts the desorption of contaminants from the resuspended sediments. The units of sediments fluxes refer to the bulk volume of the SML (interstitial water volume + solids volume), this is why \( g_{\text{ss}} \) is used as a conversion factor. In the previous formula \( F_{\text{AW,ss}}, F_{\text{WD,ss}}, F_{\text{SG,ss}}, F_{\text{DIR,ss}} \) are only accounted if \( i = \text{NL (surface)} \), \( F_{\text{SS,ss}}, F_{\text{SS,aw}}, F_{\text{SS,aw}}, F_{\text{SS,ss}} \) are only accounted if \( i = \text{1 (bottom water column)} \).

For the SML, the following differential equation is used:

\[
\begin{align*}
\frac{dC_{\text{sm}}}{dt} &= (\text{I} \cdot h_{\text{sm}}) \left( F_{\text{SG,sm}} \cdot F_{\text{SG,sm}} + F_{\text{DIR,sm}} + F_{\text{SG,sm}} \cdot F_{\text{SG,sm}} + F_{\text{SG,sm}} \cdot F_{\text{SG,sm}} + F_{\text{RES,sm}} \cdot F_{\text{RES,sm}} \cdot F_{\text{RES,sm}} \cdot F_{\text{RES,sm}} \right) \\
&+ F_{\text{RES,sm}} \cdot F_{\text{RES,sm}} \cdot F_{\text{RES,sm}} \cdot F_{\text{RES,sm}} 
\end{align*}
\]  

where \( h_{\text{sm}} \) is the thickness of the SML (assumed 0.01m), \( F_{\text{RI}} \) (ng m\(^{-2}\) s\(^{-1}\)) the burial flux, \( F_{\text{RES,sm}} \) (ng m\(^{-2}\) s\(^{-1}\)) flux of pure water diffusion from deep sediments to SML, \( F_{\text{SS,sm}} \) (ng m\(^{-2}\) s\(^{-1}\)) flux of pure
Results and discussion

Water diffusion from SML to deep sediments, $F_{\text{diff},\text{SML}}$ (ng m$^{-2}$ s$^{-1}$) biodiffusion flux from deep sediments to SML, $F_{\text{diff},\text{SML}}$ (ng m$^{-2}$ s$^{-1}$) biodiffusion flux from SML to deep sediments, $F_{\text{deg,\text{SML}}}$ (ng m$^{-2}$ s$^{-1}$) the degradation flux in the sediments.

Turbulent diffusive transport have been additionally applied into contaminant equations through parameters driven by the hydrodynamical sub-model. To note, by turbulent flux is understood as the flux of contaminants generated by turbulent diffusion in the body of water, not the molecular diffusivity. In short, turbulent flux is evaluated by the model through the Fick 1st and 2nd laws:

$$F_{\text{turb}} = \nabla \cdot (\rho D \nabla C)$$

where $\nabla$ (v) accounts for the vertical dimension and $D$ (m$^2$ s$^{-1}$) the turbulent diffusivity.

3. Results and discussion

Using the same climate conditions repeatedly (January 2003 - December 2003), the model was run for several “years” (i.e., repetitions of the standard year) until the results of two consecutive years were equal. This represents a “long-term steady state” situation where concentrations and fluxes vary throughout the year, but not between years. Hence it ensures that model outcomes are independent of initial values. A typical 1-year simulation takes about 2h in a Pentium IV 500MHz PC. Results presented here are extracted from the last year of model integration.

3.1. Hydrodynamic model results

Vertical-temporal distributions of water temperature and eddy diffusivity, obtained from the hydrodynamic module, are shown in Figure 2. They are useful to better understand the fate of the POPs. Figure 2A shows the spring-summer thermocline, typical of temperate climate, promoted by the large gradients of temperature between surface and deep waters. Vertical modeled diffusivities (Figure 2B) are in the range of 0.01 – 0.1 m$^2$ s$^{-1}$. Higher values are located close to the surface and they are largely shear driven, since the wind stress at the surface is a primary mixing agent, although significant
Results and discussion

Another factor that plays an important role in mixing is the precipitation events. Together, these higher superficial values conform the so-called turbulent layer or in an ocean situation the Oecane Mixed Layer. Diffusivities at deeper water layers are lower by one order of magnitude. The model is able to reproduce a seasonal trend: strong mixing, i.e., high values of vertical diffusivity, during winter and minimum values during the formation of the seasonal thermocline, where the vertical stratification inhibits turbulence.

3.2. Contaminants distribution: water body regions

Figure 3 shows the temporal variability in the vertical profiles for a low and a highly hydrophobic PCB. To note, the hydrophobicity of PCBs, linked to the tendency to sorb to particles, is one of the most determinant physicochemical properties determining their fate. Three regions can be distinguished. Deep water does show a huge influence from the contaminated sediments, mainly due to sediment diffusion of chemicals from the interstitial waters to deep waters. Conversely, the surface waters are extremely sensible to atmospheric inputs with peaks of concentrations due to atmospheric wet deposition. The extent to which atmospheric entrained contaminants mix in the water is highly seasonal and it follows the shape of the turbulent layer, which encloses the part of the water column with higher eddy diffusivity coefficients. The layer in the mid-depth water has low concentrations and they are reasonably constant all year round. The occurrence of these regions, differs from traditional model approaches of two regions during stratification periods in warm months and one the rest of the year, each one being well mixed internally (Schwarzenbach et al., 2003; Meijer et al., 2006). Besides, the more volatile and less hydrophobic congeners (Figure 3A) present stronger vertical and temporal concentration gradients than the more hydrophobic one (Figure 3B).
The seasonal averaged vertical variability of all PCB congeners in the water column is depicted in Figure 4, which clearly shows that variability can be ten fold in surface waters while in sediments and mid-water column remain close to a constant value. More volatile and less hydrophobic congeners are subject to stronger seasonal trends temporal gradients. The high surface variability (Figure 4A) is linked to atmospheric forcings, i.e input of contaminants due to precipitation pulses, influence of higher temperatures during the summer, influence of high wind speeds. During summer, volatilization losses depletes compounds, but higher temperatures in the water column favor an enrichment of compounds in the dissolved phase. In addition, the spring and autumn phytoplankton blooms increase the particulate-bound PCBs during those periods, noted especially in the bottom water layer (Figure 4C), where atmospheric influence has been diluted.

3.3. Influence of forcing POP fluxes

The vertical water column boundaries are the lower part of the atmosphere and the surface mixed sediment layer (SMXL). The magnitude and variability of exchange with those external environments have a direct impact on the entire water column. Atmospheric-based fluxes are far more variable than the sediments ones. Still, the magnitude of the sediment-based fluxes is greater, influenced by the high POP concentrations in the sediments compared to the ones in the water column and supported by sinking fluxes.

Concerning POPs transfer through water surface, the wet deposition and diffusive fluxes are dominant (see Figure 5A). The figure displays only PCB 28 but the importance of wet deposition fluxes was found for all the studied PCBs in the present exercise. The volatilization flux shows to be major for the lower chlorinated compounds. However, the representation of those accumulated fluxes hides the intrinsic seasonality and time variability. For example, volatilization is stronger during warm periods, and wet deposition acts like pulses, generally major from September to January but still highly
Results and discussion

Random. Finally, degradation and dry deposition fluxes can be assumed negligible in the surface boundary layer.

At the other extreme of the water column, the diffusion of contaminants from the sediment interstitial waters to deep waters plays a decisive role (Figure 31), especially for the low chlorinated PCBs. They exceed atmospheric input fluxes by more than one order of magnitude and are responsible of introducing amounts of contaminants to the water column, compensated mainly by the sinking fluxes. Conversely, other fluxes such as reuspension of particle-sorbed contaminants appear not to be so important as diffusion from sediments. Nevertheless, in shallow water columns, reuspension may be important due to wind driven turbulence. Finally, the mass balance in the NML, shows that contaminants are introduced from deep sediments mainly through biodiffusion.

3.4. Internal fluxes: turbulent, sinking and degradation fluxes

The discussion of the internal contaminant fluxes in the water column covers turbulent, sinking and degradation fluxes. They determine the extent of the forcing fluxes described before. The turbulent flux between two layers acts leading to eliminate the concentration gradients and is composed in fact by two fluxes acting in parallel and with opposite signs. The sense of the net flux is determined by the concentration gradient: it goes from the higher to the lower concentration layer. This net flux may be zero if the concentration distribution is completely homogeneous (dC/dz=0). In the water column, this picture gets more complicated if we think that each water layer is affected by the turbulent fluxes not from one but from two adjacent layers. The total net turbulent flux, resulting from adding the fluxes from the “interior” and “superior” layers, may then result positive when it creates an increase of the amount of chemical, and vice versa. It is represented in Figure 6 for PCB38 but the discussion covers all PCBs in concern. The turbulent fluxes show a high variability, especially close to the surface. In deep waters the total net turbulent fluxes are almost always positive and are the highest due to the important gradients of contaminant between sediments and water column. In the mid-depth, fluxes of
Results and discussion

total net turbulence are virtually negligible. Despite their complexity and extreme variability, net turbulent fluxes can be visualized as acting upward in the hitherto region and acting downward close to the surface, except for periods of output of contaminants (favoring by highly windy periods, no rain, and hot periods). On the other hand, turbulent fluxes are greater for the more volatile compounds, since they are associated to major concentration gradients.

The sinking fluxes (physical and biological), depicted in Figure 7 for a highly hydrophobic PCB, result from the settling of particle-bound contaminants. They are favored by lower temperatures, by higher concentrations of particles and in some cases by turbulent mixing. Superimposed to the figure is shown the precipitation pulses for year 2003. Rain entrains particles and pollutants that fall in the water column and leave a significant “path” in the observed depth-temporal plot. For a lower chlorinated PCB a significant decrease of those fluxes would be noted.

The individual effect of sinking and turbulent flux is difficult to discern since they both depend on a same variable, the PCB concentration. However, the former acts only to particle-sorbed contaminants, in contrast to turbulent mixing which affects also dissolved and colloidal sorbed contaminants. What should be kept in mind is that the distribution of contaminants in the three water column regions is result of the interplay of sinking and turbulent fluxes. If sinking did not exist, the contaminated sediment-influenced deep waters would not find a barrier to diffuse upward and also atmospheric inputs would penetrate less in the water column; if turbulent fluxes did not exist, contaminants introduced from the sediments would not move upward through the water column. Furthermore, the influence of a major sinking in the contaminants distribution is noted in the decrease of absolute vertical concentration gradients. Among other reasons, the downward force of turbulent fluxes is diminished. This explains a more homogeneous mixing and as well major values in the surface region for PCB 180 (Figure 7B), and it is responsible of higher concentration values in the mid-depth waters. Figure 8 shows whether sinking or turbulent flux dominates the vertical transport on a temporal and spatial scale. As can be seen the sinking fluxes tend to overcome turbulent fluxes in the poorly
Results and discussion

Stratified periods and in the so-called turbulent layer. On the other hand, sinking is more important for the more chlorinated PCBs. However, this graph masks the fact that in the benthic region the magnitude of both fluxes is similar, their different contribution becomes important close to the surface, where turbulent fluxes can be more than ten times the sinking ones. In the mid-depths their magnitude is minimum, since the amount of contaminants is nearly zero. Due to such low values of sinking and turbulent fluxes in this region, contaminants coming from the atmosphere may not diffuse downward when reaching the boundary.

Chemical and biological degradation of contaminants is generally not significant when compared to sinking and turbulent fluxes. Yet, for lower chlorinated compounds and between 30-40m it is dominant (see Figure 9).

3.5. Comparison of model results to experimental trends

To assess the adequacy of the model in predicting trends, estimated concentrations and sinking fluxes have been compared preferentially with measurements performed in the central Mediterranean. A detailed validation of the results obtained presents the difficulty that profiles and time series of PCB concentrations in the Mediterranean are scarce, if not nonexistent (Tolosa et al., 1997).

Concentrations found here are among the ranges defined as background concentrations defined by OSPAR commission (OSPAR, 2004) and are of the same order of magnitude to levels detected in open Mediterranean waters (Tolosa et al., 1997) and in different stations of the western Mediterranean continental shelf (Dachs et al., 1997). However, they are about one order of magnitude lower than the measured in the north-western coastal Mediterranean (García-Flor et al., 2005) and in Adriatic Sea samples collected between 1976-1987 in the Rijeka Bay from (Picer and Picer, 1992, Picer, 2000) or in Venice (Monet et al., 2005), which are recognized as quite polluted zones. This is due to the fact that these measures are found close to coastal areas, under the influence of human activities, instead atmospheric and sediments inputs used here are more representative of pristine open-sea regions.
Measured concentrations at different depths show lowest values in deepest samples, highest values close to the surface (Ichahs et al., 1997; Schulz-Bull et al., 1998; García-Flor et al., 2005). Such vertical profiles agree with our results, in which surface waters (in this case 0-20m) are enriched in PUFs by a factor of five in comparison to deep waters. Furthermore, temporal variability detected here, function of the depth, is consistent to the measured trends: mixed surface short-term variability (García-Flor et al., 2005) and low variability close to the sediments, due to the fact that the capacity of sediments to accumulate PUFs is so large (Dalla Valle et al., 2005). However, the bottom water column values have seen to vary in shallower depths than the studied in this modeling exercise and mainly related to storms that originate high resuspension events (Hornbeakle et al., 2004).

Mass settling fluxes determined by sediment traps at different depths in the Western Mediterranean such as the Alboran Sea (Ichahs et al., 1997), the Lacaze-Duthiers Canyon (Fowler et al., 1998) and Lake Superior (Baker et al., 1991) demonstrate that particulate PUF fluxes vary both temporally and vertically. Seasonally, they fluctuate by one order of magnitude, co-varying with the general cycles of primary productivity in surface waters and with the maximum flux occurring in non-stratified periods. Besides, the depth profile presents maximum close to the surface layers, a posterior decrease with depth and finally an increase close to the bottom. Finally, it has been highlighted in various articles (Baker et al., 1991, Morrison et al., 2000, Bogdan et al., 2002; Hornbeakle et al., 2004) the importance of physical turbulence generating resuspended particles which cause mass settling fluxes to increase. These observations agree with temporal and vertical trends found in sinking fluxes in our modeling exercise. However, the amount of benthic fluxes seems to be underestimated in the model. This could be attributed to the intrinsic limitations of using a 1D model, when extrapolating to 3D lateral advective transport would originate a major amount of resuspended particles and higher sinking fluxes could be expected close to the bottom.

4. Conclusions
In order to evaluate the role of turbulent mixing a novel 1D coupled hydrodynamic-contaminant model has been developed and applied to a 50 m water column. It is the first time that turbulent fluxes and its interplay with other processes is explicitly assessed. Results are consistent with measured vertical and temporal PUC profiles. Furthermore, on a short-term basis, it approximates better the POPs associated variability in surface and enrichment in deep waters than the classical approach of two well-mixed box model approach for stratified periods and one for non-stratified periods.

Turbulent vertical diffusion is essential to explain the temporal variability of POP concentrations and the extent to which atmospheric and sediment inputs mix in the water column. It acts in parallel with other internal water fluxes, i.e. degradation and sinking fluxes, the combined effect yielding a surface enriched – mid-depth depleted – benthic layer enriched distribution. Deep water show a huge influence from the contaminated sediments, mainly due to sediment diffusion of chemicals from the interstitial waters to deep waters. Conversely, the surface waters are extremely sensitive to atmospheric inputs with pulses of concentrations due to atmospheric wet deposition. The extent to which atmospheric entrained contaminants mix in the water is highly seasonal and it follows the shape of the turbulent layer, deeper in autumn-winter, shallower in summers. The layer in the mid-depth water has low concentrations and they are reasonably constant all year round.

Turbulent fluxes and sinking of particle-bound contaminants overcome the degradation fluxes. As a general trend, sinking has been proven the dominant flux for the more hydrophobic compounds and especially in the non-stratified periods. Sinking favors the homogeneous contaminant distribution in the surface region and it is responsible of higher concentration values in the water column not affected by atmospheric or contaminant inputs (the bottom waters).

Finally, model results show the necessity to reconsider the existing sampling strategies, accounting for the important vertical gradients close to the sediments, and the seasonal variations and short-term variability in the surface (atmospheric) influenced region.
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Supporting information available

Further details on methodology to estimate contaminants speciation and related processes are found in Appendix A and B respectively. The modeling of the Total Suspended Matter (TSM) is given in Appendix C.

References


Results and discussion


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Figure Legends

Figure 1: Fluxes of POPs accounted in the 1D coupled hydrodynamce-contaminant model.

Figure 2: Depth-time distribution of modeled water temperature (fig. 2A) and eddy diffusivity (fig. 2B) in the water column.

Figure 3: Depth-time distribution of the total concentration in the water column for PCB 28 (fig. 3A) and PCB 153 (fig. 3B).

Figure 4: Time series of the total concentration and for all PCB congeners at different depths of the water column: surface (fig. 4A), mid-water column (fig. 4B), bottom water column (fig. 4C).

Figure 5: Accumulated yearly fluxes for PCB28 at the surface (fig. 5A) and at the bottom water layer (fig. 5B). In positive value are represented the input fluxes, in negative value the output fluxes.

Figure 6: Depth-time distribution of the net turbulent flux for PCB 28.

Figure 7: Depth-time distribution of the sinking flux (phytase / biological) for PCB 153. The profile of proeptoration pulses is superimposed.

Figure 8: Comparison between dominant turbulent inferior and sinking fluxes for PCB 28 (fig. 8B) and PCB 153 (fig. 8A). In black absolute sinking flux dominates, in white absolute turbulent inferior flux dominates.

Figure 9: Yearly accumulated fluxes for PCB28 at different depths of the water column.
Results and discussion

Figure 1
Results and discussion

Figure 2

A Temperature $T_\text{w}$

B Eddy Diffusivity ?

[Graph showing temperature and eddy diffusivity]
Results and discussion

Figure 3
Figure 4

A  surface layer

B  25cm depth

C  bottom layer

PCB 28
PCB 52
PCB 101
PCB 118
PCB 138
HCB 118
HCB 160