Figure 5

PCB 28

A  $F_{AW_{od}}$
$F_{AW_{ad}}$
$F_{WD}$
$F_{AD}$
$F_{DEGR}$
$F_{SINK}$
$F_{TURB}$

$F_{D_{total}}$
$F_{SINK}$
$F_{DEGR}$
$F_{RED_{od}}$
$F_{RED_{ad}}$
$F_{WS_{od}}$
$F_{WS_{ad}}$

$[\text{ng m}^{-2} \text{y}^{-1}]$
Results and discussion

Figure 6

$F_{HBM}$ PCB 28

$n g \cdot m^{-3} \cdot s^{-1}$
Results and discussion

Figure 8

A  PCB 28

B  PCB 168

BLACK when abs(Smooth flux) > abs (turbulent inflow flux)
Results and discussion
### APPENDIX A: Contaminant concentrations

#### Table A.1 Contaminant forcing

<table>
<thead>
<tr>
<th>Parameter</th>
<th>PCB Concentration</th>
<th>Range</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{W}$ ($\text{ng m}^{-3}$)</td>
<td>Particulate concentration in the atmosphere</td>
<td>0.01 $10^{-1}$ to 0.01 $10^{-1}$ $\text{ng m}^{-3}$</td>
<td>Mediterranean</td>
</tr>
<tr>
<td>$C_{b}$ ($\text{ng m}^{-3}$)</td>
<td>PCB rain concentration in the atmosphere</td>
<td>0.021 $10^{-2}$ to 0.194 $10^{-2}$ $\text{ng m}^{-3}$</td>
<td>Mediterranean</td>
</tr>
<tr>
<td>$C_{p}$ ($\text{ng m}^{-3}$)</td>
<td>PCB total concentration in the sediment</td>
<td>0.45-140 $\text{ng m}^{-3}$</td>
<td>Mediterranean</td>
</tr>
<tr>
<td>$C_{adj}$ ($\text{ng m}^{-3}$)</td>
<td>PCB total concentration in the deep sediments</td>
<td>0.58 $10^{-2}$-2.5 $10^{-2}$ $\text{ng m}^{-3}$</td>
<td>Mediterranean</td>
</tr>
</tbody>
</table>

#### Table A.2.1 Equations used to evaluate phase speciation of contaminant concentrations

<table>
<thead>
<tr>
<th>Concentration ($\text{ng m}^{-3}$)</th>
<th>Derivation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{W, tot}$</td>
<td>PCB Total concentration in the water column</td>
</tr>
<tr>
<td>$C_{W, diss}$</td>
<td>PCB truly dissolved concentration in the water column</td>
</tr>
<tr>
<td>$C_{W, DOC}$</td>
<td>Concentration of PCB sorbed to colloids</td>
</tr>
<tr>
<td>$C_{W, part}$</td>
<td>Concentration of PCB sorbed to particles</td>
</tr>
<tr>
<td>$C_{W, phys}$</td>
<td>Concentration of PCB sorbed to “physical” particles in the water column</td>
</tr>
<tr>
<td>$C_{W, bio}$</td>
<td>Concentration of PCB sorbed to “biological” particles in the water column</td>
</tr>
<tr>
<td>$C_{W, sed}$</td>
<td>PCB Total concentration in the SML</td>
</tr>
<tr>
<td>$C_{W, sed}$</td>
<td>PCB Truly dissolved concentration in the interstitial water in the SML</td>
</tr>
<tr>
<td>$C_{W, DOC}$</td>
<td>PCB concentration bound to DOC in the SML</td>
</tr>
</tbody>
</table>
### Results and discussion

<table>
<thead>
<tr>
<th>$C_{\text{res}}$</th>
<th>PCB concentration bounded to particles in the SPM</th>
<th>$C_{\text{res}}^\text{diss} = K_{\text{res}} \cdot (C_{\text{res}} - C_{\text{res}}^\text{diss})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>($I = NP$) refers to the number of water layers, where I is the bottom water layer and NP the surface water layer. Concentrations for sediments are expressed in bulk volume, except when the volume is added (then expressed in interstitial water volume).</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Derivation</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{OC}$</td>
<td>Partition coefficient of the chemical between the dissolved organic carbon and the finely dissolved phases</td>
<td>$K_{OC} = 0.1 \times 10^{11}$</td>
</tr>
<tr>
<td>$K_{OC}$</td>
<td>Octanol water partition coefficient</td>
<td>Values of 298 K ($K_{OC, 298}$) obtained from (Hawker and Connell, 1988). Temperature dependence: $K_{OC} = K_{OC, 298} \times 10^{(\Delta H/R)(1/T_{W} - 1/298)}$ (Schwarzenbach et al., 2003). Using $R = 4.19 \times 10^{-2}$ K mol$^{-1}$, the universal gas constant, $K_{OC}$ is the enthalpy of phase change interval water and air, assumed 33 $^\circ$C for all PCBs. $T_{W}$ is the water temperature, computed in the hydrodynamic sub-model.</td>
</tr>
<tr>
<td>$K_{OC}$</td>
<td>Distolved organic carbon concentration</td>
<td>$2.10 \times 10^{10}$ ng m$^{-3}$</td>
</tr>
<tr>
<td>$BCF$</td>
<td>Bioconcentration factor, ratio between the dissolved and phytoplankton uptake modeled using a two compartment system: fast adsorption to the phytoplankton surface ($BCF_s$) and diffusion into the matrix ($BCF_d$) (Di Vento and Dachs, 2002). BCF = $BCF_s + BCF_d$</td>
<td>Predicted values at equilibrated conditions: $\text{log}^{10}(\text{BCF}) = 6.4 - 0.2 \times 10^{8.0 - 0.915} \times 10^{8.0 - 0.915} \times 10^{8.0 - 0.915}$</td>
</tr>
<tr>
<td>$BCF$</td>
<td>Temperature dependence (Schwarzenbach et al., 2003): BCF = $BCF_{\text{eq}} \times (T_{W}/298)^{0.770}$</td>
<td>$R = 8.31$ J mol$^{-1}$ K$^{-1}$ is the universal gas constant, $\Delta H$ (1 mol$^{-1}$) is the enthalpy of phase change.</td>
</tr>
</tbody>
</table>
### Results and discussion

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Symbol</th>
<th>Value</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_{w}^{\text{phys}}$</td>
<td>Unitary mass fraction of organic matter in TON (µg m⁻³)</td>
<td>(µg m⁻³)</td>
<td>0.1-1</td>
<td></td>
</tr>
<tr>
<td>$F_{w}^{\text{bio}}$</td>
<td>Unitary mass fraction of organic carbon in TSM (ng m⁻³)</td>
<td>(ng m⁻³)</td>
<td>0.4</td>
<td>Value in between typical percentages of organic carbon in aerosol particles and sediment resuspended particles.</td>
</tr>
<tr>
<td>$F_{w}^{\text{bio}}$</td>
<td>Unitary mass fraction of organic matter in TSM (ng m⁻³)</td>
<td>(ng m⁻³)</td>
<td></td>
<td>The TSM is defined as the total particulate organic matter in the water column: $F_{w}^{\text{bio}}$</td>
</tr>
<tr>
<td>TSM (ng m⁻³)</td>
<td>Concentrations of &quot;physical&quot; total suspended matter in the water column</td>
<td>(ng m⁻³)</td>
<td></td>
<td>see APPENDIX C</td>
</tr>
<tr>
<td>TSM (ng m⁻³)</td>
<td>Concentrations of &quot;biological&quot; total suspended matter in the water column</td>
<td>(ng m⁻³)</td>
<td></td>
<td>see APPENDIX C</td>
</tr>
</tbody>
</table>

#### Surface Mixed Sediments Layer (S MLSL)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
<th>Symbol</th>
<th>Value</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{G,\text{org}}$</td>
<td>Partition coefficient of the chemical movement between the dissolved organic carbon and the freely dissolved phase in the S MLSL</td>
<td>(mol m⁻³)</td>
<td>$10^{-12}$</td>
<td>(Fedy et al., 1999)</td>
</tr>
<tr>
<td>$K_{G,\text{org}}$</td>
<td>Partition coefficient of the chemical movement between the particulate and the truly dissolved phase in the S MLSL</td>
<td>(mol m⁻³)</td>
<td></td>
<td>(Fedy et al., 1999)</td>
</tr>
<tr>
<td>$K_{G,\text{org}}$</td>
<td>Partition coefficient of the chemical movement between the particulate and the truly dissolved phase in the S MLSL</td>
<td>(mol m⁻³)</td>
<td></td>
<td>(Oikarinen et al., 2001)</td>
</tr>
<tr>
<td>$K_{G,\text{org}}$</td>
<td>Partition coefficient of the chemical movement between the particulate and the truly dissolved phase in the S MLSL</td>
<td>(mol m⁻³)</td>
<td></td>
<td>(Oikarinen et al., 2001)</td>
</tr>
<tr>
<td>$F_{W,\text{org}}$</td>
<td>Unitary mass fraction of organic carbon in the interstitial water of the S MLSL</td>
<td>(µg m⁻³)</td>
<td>$10^{-6}$</td>
<td>(Fedy et al., 1999)</td>
</tr>
</tbody>
</table>

The amount of phytoplankton accounts for the total particulate organic matter in the water column (Gedan et al., 1997), thus the BCP is referred to mass of organic matter: $F_{w}^{\text{bio}}$.
### Results and discussion

<table>
<thead>
<tr>
<th>Process</th>
<th>Flux equation [ng m(^{-2}) s(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Gaseous absorption</td>
<td>(F_{\text{gas}} = k_{\text{gas}}(C_{\text{aq}}/F))</td>
</tr>
<tr>
<td>2. Volatilization</td>
<td>(F_{\text{vol}} = k_{\text{vol}} C_{\text{aq}}^{\text{vol}})</td>
</tr>
<tr>
<td>3. Dry deposition</td>
<td>(F_{\text{dep}} = v_{\text{dep}} C_{\text{p}})</td>
</tr>
<tr>
<td>4. Wet deposition</td>
<td>(F_{\text{wet}} = v_{\text{wet}} C_{\text{p}})</td>
</tr>
<tr>
<td>5. Sinking flux (flux of particle-bound contaminants in the water column)</td>
<td>(F_{\text{sink}} = k_{\text{sink}}(C_{\text{p}}^{\text{sink}}/C_{\text{p}}^{\text{sink}}))</td>
</tr>
<tr>
<td>6. Degradation flux in the water column</td>
<td>(F_{\text{deg}} = k_{\text{deg}} C_{\text{p}}^{\text{deg}})</td>
</tr>
<tr>
<td>7. Diffusion from the interstitial water of the sediments to the water column</td>
<td>(F_{\text{interstitial}} = D_{\text{interstitial}}(C_{\text{sed}}^{\text{interstitial}}/C_{\text{sed}}^{\text{interstitial}}))</td>
</tr>
<tr>
<td>8. Diffusion from the water column to the interstitial water of the sediments</td>
<td>(F_{\text{diff}} = D_{\text{diff}}(C_{\text{sed}}^{\text{diff}}/C_{\text{sed}}^{\text{diff}}))</td>
</tr>
<tr>
<td>9. Sediment re-suspension flux</td>
<td>(F_{\text{resusp}} = k_{\text{resusp}}(C_{\text{sed}}^{\text{resusp}}/C_{\text{sed}}^{\text{resusp}}))</td>
</tr>
<tr>
<td>10. Deposition of contaminants from the re-suspended sediments</td>
<td>(F_{\text{dep}} = k_{\text{dep}} C_{\text{sed}} )</td>
</tr>
<tr>
<td>11. Burial flux</td>
<td>(F_{\text{burial}} = k_{\text{burial}} C_{\text{sed}})</td>
</tr>
<tr>
<td>12. Degradation flux in the sediments</td>
<td>(F_{\text{deg}} = k_{\text{deg}} C_{\text{sed}}^{\text{deg}})</td>
</tr>
<tr>
<td>13. Pore water diffusion from deep sediments to SMEL</td>
<td>(F_{\text{pore}} = (D_{\text{pore}}/C_{\text{sed}}^{\text{pore}})(C_{\text{sed}}^{\text{pore}}/C_{\text{sed}}^{\text{pore}}))</td>
</tr>
<tr>
<td>14. Pore water diffusion from SMEL to deep sediments</td>
<td>(F_{\text{pore}} = (D/\Delta C_{\text{sed}})(C_{\text{sed}}^{\text{deep}}/C_{\text{sed}}^{\text{deep}}))</td>
</tr>
</tbody>
</table>

---

**APPENDIX B: Formulation of contaminant fluxes**

Table B.1 Flux equations for the different processes in the contaminants sub-model.
### Results and discussion

| 15 | Biological flux from deep sediments to OGC | $F_{\text{BIO, OGC}} = (U_{\text{in}} + G_{\text{in}} + G_{\text{out}})^{\text{T}}$ |
| 16 | Biological flux from SMSS to deep sediments | $F_{\text{BIO, SMSS}} = (D_{\text{in}} + G_{\text{in}})$ |

**Table B.2 Parameters used in flux equations**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Derivation</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{\text{aw}}$ [m s$^{-1}$]</td>
<td>Total advection mass transfer velocity</td>
<td>Calculated in the traditional manner, as the result of the transfer through two films at each side of the air water interface: $h_{\text{aw}} = h_{\text{a}} + h_{\text{w}}$, $k_{\text{aw}}$ is calculated to account for the different diffusion coefficients of POPs. Effect of wind speed on $k_{\text{aw}}$ as suggested in (Nightingale et al., 2006). Wind data acquired from the ECMWF 40 Years Re-Analysis for the whole year 2003.</td>
</tr>
<tr>
<td>$u_{10}$ [m s$^{-1}$]</td>
<td>Wind speed</td>
<td></td>
</tr>
<tr>
<td>$H^*$</td>
<td>Dimensionless Henry's constant</td>
<td>$H^* = H^*(T_{\text{water}}) = R(8.31 \text{ J mol}^{-1} \text{ K}^{-1})$; universal gas constant. $T_{\text{water}}$: water temperature computed by the model in the surface water layer.</td>
</tr>
<tr>
<td>$H$ [J mol$^{-1}$]</td>
<td>Henry’s law constant</td>
<td>Values at 298 from (Brunner et al., 1996). Temperature dependence (Schwarzenbach et al., 2003): $H = H_0 \exp(\Delta H_{\text{vap}}/R(1/T_{\text{water}} - 1/298))$. Being $\Delta H_{\text{vap}}$ the enthalpy of phase change between water and air, assumed 25 $10^3$ for all PCBs. Salinity dependence (Klumpp et al., 2003): $H_{\text{salin}} = H_0 \exp(\delta \text{ Salin}/0.585)$. salin [psu] is salinity, given by the model</td>
</tr>
</tbody>
</table>

#### 3. Dry deposition

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Derivation</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_D$ [m s$^{-1}$]</td>
<td>Dry deposition velocity of aerosol particles</td>
<td>$2 \times 10^2$ m s$^{-1}$</td>
</tr>
</tbody>
</table>

#### 4. Wet deposition

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Derivation</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p$ [m s$^{-1}$]</td>
<td>Precipitation rate</td>
<td>6h data acquired from the ECMWF 40 Years Re-Analysis, for the whole year 2003</td>
</tr>
</tbody>
</table>

#### 5. Sinking

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Derivation</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$w_s$ [m s$^{-1}$]</td>
<td>Settling velocity of water column particles</td>
<td>$1.73 \times 10^{-3}$ m s$^{-1}$</td>
</tr>
</tbody>
</table>
## Results and discussion

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_{OM}$</td>
<td>Vertical flux of organic matter collected at the bottom</td>
</tr>
<tr>
<td>$\Gamma_{OC}$</td>
<td>Vertical flux of organic carbon collected at the bottom</td>
</tr>
<tr>
<td>$\text{chl}_a$</td>
<td>Chlorophyll-(a) concentration in the water surface</td>
</tr>
<tr>
<td>$\text{NZ}$</td>
<td>Number of water layers considered in the model</td>
</tr>
<tr>
<td>$\text{TSM}^{\text{vol}}$</td>
<td>Concentration of &quot;biological&quot; total suspended matter</td>
</tr>
</tbody>
</table>

### 6. Degradation in water column

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$h_i$</td>
<td>Depth of the considered water layer</td>
</tr>
<tr>
<td>$k_{bio}$</td>
<td>Degradation rate in the water column</td>
</tr>
</tbody>
</table>

### 7 and 8. Diffusion sediments-water

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{WS}$</td>
<td>Sediment-water diffusion coefficient</td>
</tr>
<tr>
<td>$\phi_{sed}$</td>
<td>Porosity of the SNSL</td>
</tr>
</tbody>
</table>

### 9 and 10. Resuspension flux and desorption of contaminants from the resuspended particles

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_{res}$</td>
<td>Amount of particles per unit area and layer that resuspended</td>
</tr>
<tr>
<td>$\delta_{SM}$</td>
<td>Thickness of the SNSL</td>
</tr>
<tr>
<td>$\text{SM}_{dry}$</td>
<td>SNSL dry weight per volume</td>
</tr>
<tr>
<td>$\phi_{SM}$</td>
<td>Porosity of the SNSL</td>
</tr>
<tr>
<td>$\rho_{sed}$</td>
<td>Dry density of the SNSL</td>
</tr>
<tr>
<td>$K_{res}$</td>
<td>Partition coefficient of the chemical between the particulate and the truly dissolved</td>
</tr>
</tbody>
</table>

---

(See APPENDIX C for details.)
Results and discussion

<table>
<thead>
<tr>
<th>Subscript</th>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{pc,ad}$</td>
<td>Phase in the SMIML</td>
<td>-0.74</td>
</tr>
<tr>
<td>$C_{ad}$</td>
<td>Mass fraction of organic carbon in the SMIML</td>
<td>0.044</td>
</tr>
</tbody>
</table>

### 11. Burial flux

- $w_b$ [m s$^{-1}$]: Burial velocity
  - 1.93 $10^{-3}$ m s$^{-1}$
- $T_{max}$ [m]: Maximum of the SMIML
  - 0.01 m

### 12. Degradation flux in the sediments

- $k_{d,ad}$ [s$^{-1}$]: Degradation rate in the SMIML
  - 0.01
- $D_h$ [m$^3$ s$^{-1}$]: PCB molecular diffusivity in water
  - $10^{-10} M^2 s^{-1}$
- $D_d$ [m$^2$ s$^{-1}$]: Diffusion coefficient
  - $1.7 (w_b, 100 * 3600 * 24 * 365)$
- $d$ [m]: Distance between the centers of two sediment layers
  - 0.01

### 13 and 14. Diffusion deep sediments-SMIML

13 and 14. Diffusion deep sediments-SMIML

### 14 and 15. Biodiffusion deep sediments-SMIML

14 and 15. Biodiffusion deep sediments-SMIML

APPENDIX C: Equations to model the Total Suspended Solids in the water column

The concentration of total suspended solids (TSS, ng m$^{-3}$) is computed at each time step and at each water vertical layer as the sum of a "physical" TSS (1SM$^{phys}$, ng m$^{-3}$), which accounts the atmospheric aerosol inputs and the resuspension of particles from the sediments, and a "biological" TSS (TSIM$^{bio}$, ng m$^{-3}$), representing the total particulate organic matter in the water column:

1SM$^{phys}$ = 1SM$^{bio}$ + 1SM$^{phys}$
where $i$ is the water layer level, from 1 (bottom) to $N$ (surface).

$\text{TSM}_{\text{dry}}$ is affected by the aerosol inputs from rain and continuous dry deposition, by the resuspension of particles from the sediments, and inside the water column by sinking and turbulent diffusive transport:

$$\frac{d(\text{TSM}_{\text{dry}})}{dt} = h(15\text{M}_{\text{w}} \times \nu) \left(15\text{M}_{\text{w}} + \gamma_{\text{ss}} + 15\text{M}_{\text{w}} \times \nu \times \text{w}_{\text{dr}} + 15\text{M}_{\text{w}} \times \text{w}_{\text{dr}} \times \text{b}_{\text{ss}} \times \text{t}_{\text{ss}} \text{r}_{\text{ss}})$$

where $h$ (m) is the depth of the water layer, $\text{TSM}_{\text{tot}}$ is the total suspended matter in air, assumed constant and equal to $30 \times 10^3$ ng m$^{-2}$ (Seinfeld and Pandis, 1998), $\nu$ (2 $\times$ $10^3$ m s$^{-1}$ (Seinfeld and Pandis, 1998)) the dry aerosol deposition velocity, $15\text{M}_{\text{w}}$ the total suspended particles in rain, computed proportional to the particle washout ($7 \times 10^3$ (Horvath et al., 2005)) and $\text{TSM}_{\text{dry}}$ ($\text{TSM}_{\text{tot}} - \text{W}_{\text{dr}}$ $\text{TSM}_{\text{tot}}$). $\text{w}_{\text{dr}}$ (m s$^{-1}$) is the precipitation rate obtained from the ECMWF as 6h reanalysis and $\text{w}_{\text{dr}}$ (m s$^{-1}$) the water column particles settling velocity, assumed constant and equal to $1.72 \times 10^3$ m s$^{-1}$ (Currier et al., 2000).

The last term accounts for the resuspension flux of particles from the sediments; $\text{p}_{\text{ss}}$ (ng m$^{-2}$ s$^{-1}$) is the amount of particles per unit area and time that resuspend. This term is obtained as the 10% of the total suspended matter in the Sediment Mixed Active Layer; $\text{p}_{\text{ss}} = 0.1 \times \text{SSML} \times \text{f}_{\text{w}}$ (0.1/365x3.24x3.600) (Schwanz-Feinbolch et al., 2003). Finally, the thickness of the SMSL ($\text{t}_{\text{ss}}$) porosity ($\phi_{\text{ss}}$) and dry sediments density ($\rho_{\text{ss}}$) have been assumed 0.01 m, 0.85 and $3 \times 10^3$ ng m$^{-3}$ respectively (typical values for Schwanz-Feinbolch et al., 2003).

The total suspended “biological” matter is assumed to equal the particulate organic matter (POM ng m$^{-3}$). The particulate organic carbon (POC ng m$^{-3}$) is assumed the 30% of the POM (Hedges et al., 2002), and also proportional to the chlorophyll-a amount (chloro ng m$^{-3}$) with a ratio of $3 \times 10^3$ ng m$^{-3}$ (Jorgensen et al., 2000).

$\text{TSM}_{\text{dry}} - \text{POC} = 2 \times \text{chloro} \times 10^3 + 0.003$

In this, $\text{TSM}_{\text{dry}}$ is considered constant throughout the water column, forced temporally by the chlorophyll-a amount (ng m$^{-3}$) in the surface, obtained from temporal interpolation of monthly means 2003 from the SEAWIFS satellite. Finally, the transport equation (turbulent mixing) is additionally applied to $\text{TSM}_{\text{dry}}$, but not to $\text{TSM}_{\text{dry}}$.

References in APPENDIX

Results and discussion


Gustafsson, O., Giesbrecht, P. M. and Bueseler, K. O. 1997. Settling removal rates of PCBs into the northwestern Atlantic derived from 238U/236Th disequilibria. Environmental Science and Technology 31 (17), 3544-3550.


Results and discussion


Results and discussion


3.3.3 Major issues and conclusions of chapter 3.3.2

A pioneering 1-D dynamic coupled hydrodynamic-contaminant model has been developed and applied to a station in the Mediterranean continental shelf environment of 50m depth. It allows to evaluate the short-term temporal variability of contaminants at different depths of the water column and to assess the importance of the turbulent mixing versus other processes affecting POPs in the water column, i.e. sinking and degradation. Additional features such as the consideration of two kind of particles (physical and biological) or the consideration of the contaminant in three phases: dissolved-DOC-particulate are also introduced. Results are consistent with measurements reported in pristine open-sea regions but the validation is limited by the scarcity of vertical profiles and time-series.

The combined effect of turbulent and other water column fluxes yield a surface enriched – depth depleted – benthic layer enriched region distribution. The surface layer presents a significant short-term variability, highly dependent of precipitation pulses and other atmospheric forcings. Therefore atmospheric deposition controls the surface waters, delimited by the turbulent layer, which is strong seasonally dependent (major extent in winter). Deep waters are more constant and the bottom 5 m are highly influenced by contaminated sediments.

In the atmospheric side, wet deposition yearly integrated fluxes are dominant, followed by volatilization. However, predominance of wet deposition fluxes is related to the high precipitation rates of the studied region, otherwise diffusive air-water exchange would dominate. At the other extreme of the water column, the diffusion of contaminants from the sediment interstitial waters to deep waters plays a decisive role. Conversely, degradation fluxes can be important in the mid-depths, where turbulent and sinking fluxes are close to 0.

The simulation of the 1-D model highlights the role of the turbulent processes in determining the POP distribution and variability in the water column. In short, turbulent fluxes of contaminants strengthen the upward diffusion of sediment entrained contaminants and determine the extent to which inputs from the atmosphere mix into the water column. When compared to sinking their different contribution is seen in the turbulent surface layer, where sinking tends to overcome the turbulent for highly hydrophobic compounds. Close to the bottom they have similar magnitudes, so that sinking compensates the movement of pollutants coming from the highly contaminated sediments.

The influence of a major sinking, as seen in the more hydrophobic contaminants is noted in the decrease of absolute vertical concentration gradients. This explains a more homogeneous mixing of those contaminants in the surface region delimited by the turbulent layer.
The configuration of the developed 1-D dynamic model allows an easy extrapolation to 3D versions, or coupling to an ecological model. The separated treatment of the POC and DOC permits to further assess the role of microorganisms, using the detailed analysis of the Carbon Cycle performed in the Introduction section 1.6. On the other hand, the model gives the basis to examine what controls and supports the POP concentrations in the food web. Accordingly, preliminary results of the 1-D dynamic model applied to a 10m water column show a strong influence of sediments in all the water column, which may be representative of shallow aquatic environments.
4 GENERAL CONCLUSIONS

Here are shown the overall conclusions and novelties of this PhD-thesis. It should be noted that in previous chapters (3.2.2.4, 3.2.3.7 and 3.3.3) have been presented the partial conclusions of each of the foremost contributions of this work.

Methodological contribution of the PhD-thesis:

- It has been developed a series of models of increasing complexity (0D spatially resolved at steady state-1D dynamic), each one useful to examine different aspects relating the atmosphere-ocean exchange dynamics of POPs. Models have been applied to PCBs and PCDD/Fs but are easily extrapolated to other POPs with well-known physicochemical properties.
- Satellite retrieved parameters have been coupled for the first time to environmental box models describing the fate of POPs.
- The spatial and seasonal variability of mass transfer coefficients has been accounted and modelled in function of available satellite parameters (dry deposition velocity gaseous washout, air-water mass transfer coefficient, etc.). It contrasts with the consideration of constant mass transfer coefficients in most models. Also the spatial variability of the organic carbon fraction in aerosols and the dominant aerosol type over the oceans has been modelled function of retrieved optical parameters from satellites.
- An hydrodynamic model have been coupled to the POPs model in a Fortran environment to examine the sort-term variability and the effect of water column turbulence.

Development and application of the maximum reservoir capacity ratio (MRC) over the global oceans:

- This ratio identifies regions where POPs tend to be retained in surface water when the system is in equilibrium. It results highly variable spatially and seasonally, which justifies the use of spatially resolved models.
- It has been shown that settling of particle-bound compounds deviates significantly the system from the equilibrium state. Indeed it is foreseen that non-fugacity driven processes may be very important and their contribution is highly dependent on biogeophysical properties of the media and chemical properties of the compounds.
- The comparison of MRC values in surface oceans and soils indicates that gradients between them, maximum in high latitudes and highly seasonal, may exert an important influence on global POP cycling. Low gradients in low latitudes may justify a major recycling between land and ocean, yielding higher long-range atmospheric transport (LRAT).
Evaluation of atmospheric deposition fluxes and sinks of Persistent Organic Pollutants at the global oceans, spatially and seasonally resolved:

- It has been proven an important variability in the fluxes, in particular for the wet deposition fluxes. Furthermore, estimated atmospheric deposition fluxes are in agreement with measurements in a factor between 1 and 2.
- Diffusive air-water exchange is the predominant input route for POPs found primarily in the gaseous phase. Dry deposition is minor but can be important in dust influenced areas and in remote oceanic regions where marine aerosol is important. Finally, wet deposition is the most efficient removal mechanism in short-term precipitation periods.
- Sinking of particle-bound compounds plays a major role in the dynamic of POPs on the global scale, especially in areas of high biomass and for highly hydrophobic compounds. In deep-water formation regions subduction of POPs dominates over sinking fluxes.

Evaluation of atmospheric deposition fluxes of total organic carbon to the global oceans, spatially and seasonally resolved:

- Estimated fluxes of aerosol organic carbon give important numbers, much higher than the ones modelled from emissions inventories and which generally assume constant dry deposition velocities.
- Estimated fluxes of gaseous organic carbon, not considered so far in global carbon budgets, represent important numbers, in agreement with the important role of air-sea exchange and wet gaseous deposition of POPs. However those fluxes need experimental validation and air-water exchange of organic carbon is an unexplored area which needs further research.

Evaluation of the role of turbulent mixing of water masses on the distribution of Persistent Organic Pollutants

- It has been developed the first comprehensive analysis of the role of turbulent mixing of water masses on the distribution of Persistent Organic Pollutants and their comparison to other water column fluxes.
- The interplay of turbulent, sinking and degradation fluxes yield profiles of POPs in the water column with an enrichment of contaminants in the surface and deep waters and a depletion in mid-waters.
- Turbulence is responsible for the upward diffusion of pollutants coming from the sediments, compensated by sinking fluxes, of similar magnitude. In the surface waters turbulence magnifies or diminishes the sinking of contaminants.
- The atmospheric deposition affects the surface region delimited by the highly seasonal
turbulent layer. There, a significant variability is encountered, especially driven by the wet deposition flux.

Further research:

- Coupling of an ecological model to the 1D dynamic hydrodynamic-contaminants model developed in this PhD-thesis. It may alter the results obtained since this coupling may primarily affect sinking fluxes, which have proven to play a significant role.
- Better parameterization of sediment-based fluxes, especially the parameters related to resuspension fluxes. Also accurate comparison of sediments and atmospheric contributions to the distribution of Persistent Organic Pollutants in the water column.
- Use of the developed models to predict the effect of the modification of the distribution of biomass in the surface oceans induced by the Climate Change.
Next it is shown the bibliography from the “Introduction” section and from the comments of the scientific contributions. The references of each of the scientific contributions are presented in the pertaining chapters.


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6 ANNEXES

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6.3 Publications and related activities during the PhD

**Scientific publications in referred journals**


Lohmann, R., **Jurado, E.** Pilson, M. E. Q., Dachs, J. 2006. Oceanic deep water formation as a sink of persistent organic pollutants, Geophysical Research Letters, 33, L12607, doi:10.1029/2006GL025953. *editors have selected this paper as an “AGU Journal Highlight” and articles’s abstract was also covered by EOS in the July 2006 25 issue*


Publications in non-referred journals


Oral presentations


Jurado E. 2005. Atmospheric deposition of Persistent Organic Pollutants (POPs) and aerosol carbon to global oceans. Seminar in Inland and Marine Waters Unit in IES-JRC. June 10. Ispra, Italy.


**Poster presentations**


**Other relevant activities**

