Supplementary Information

Implementation of a 3D Coupled Hydrodynamic and Contaminant Fate Model for the PCDD/Fs in Thau Lagoon (France): The Importance of Atmospheric Sources of Contamination

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1. Implementation of the contaminant fate model for PCDD/Fs in Thau lagoon: equations and parameters

1.1 Partitioning of contaminant in water and sediment

In water organic chemicals are either bound to the particulate phase (C^{part}), purely dissolved (C^{diss}) or bound to the dissolved organic carbon DOC (C^{DOC}). Therefore, the total concentration of an organic contaminant in the water column C^T can be described as the sum of these three phases:

$$C^T = C^{diss} + C^{DOC} + C^{part} \quad (1)$$

A common way to describe the particle affinity of an organic contaminant in water is given by the partition coefficient K_d , defined as:

$$K_d = \frac{C^{part}/m}{C^{diss}} \quad (2)$$

where m is the suspended particulate matter concentration in mass dry weight per volume [M dw L^{-3}]. This relationship presupposes that the contaminant has a linear sorption isotherm and it is a good approximation for low concentrations of contaminant. Similarly, the phase bonded to dissolved organic carbon (DOC) can be expressed as:

$$K_{DOC} = \frac{C^{DOC}/DOC}{C^{diss}} \quad (3)$$

K_d is derived from the fraction of organic carbon for suspended solids or sediments, f_{OC} and the organic-carbon partition coefficient, K_{OC}:

$$K_d = f_{OC} \cdot K_{OC} \tag{4}$$

In the Thau lagoon model the f_{OC} was set equal to 0.046 while the sediment DOC was set to 10^{10} ng m^{-3} (Mesnage et al., 2007) and the water DOC is dependent on the POC.

For PCDD/Fs values of K_{OC} and K_{DOC} are calculated using an empirically derived relation that describes the partitioning as a function of the octanol-water partition coefficients K_{ow} (Persson et al., 2005):

$$\log K_{iOC} = A \cdot \log K_{ow} + B \tag{5}$$

Values of A and B depend on the congener and can be found in Table 2. For PCDDs and PCDFs the temperature dependence of K_{ow} is obtained from an empirical relationship (Paasivirta et al.,1999):

$$\log K_{ow} = A_{ow} + \frac{B_{ow}}{T} \tag{6}$$

The same approach is used for the partitioning in the sediments compartment, where the total concentration of the chemical is expressed as: $C_{sed}^{T} = C_{sed}^{part} + C_{sed}^{DOC} + C_{sed}^{diss}$. The dissolved concentration in the sediment is the product of the dissolved concentration in the interstitial water as $C_{\text{int}\,w}^{diss}$ or $C_{\text{int}\,w}^{DOC}$ and the sediment porosity ϕ_{sed}.

$$C_{sed}^{diss} = \phi_{sed} \cdot C_{\text{int}\,w}^{diss} \tag{7}$$

$$C_{sed}^{DOC} = \phi_{sed} \cdot C_{\text{int}\,w}^{DOC}$$

For both, the sediment and the water compartment, the partitioning of the compound between the three phases can be expressed as a function of the total concentration (Farley et al., 1999):

$$C^{diss} = \frac{C_T}{\phi + \phi \cdot K_{DOC} \cdot DOC + K_d \cdot m} \tag{8}$$

$$C^{DOC} = \frac{K_{DOC} \cdot DOC \cdot C_T}{\phi + \phi \cdot K_{DOC} \cdot DOC + K_d \cdot m} \tag{9}$$

$$C^{part} = \frac{K_d \cdot m \cdot C_T}{\phi + \phi \cdot K_{DOC} \cdot DOC + K_d \cdot m} \tag{10}$$

where ϕ in the water compartment is equal to 1, while the sediment porosity of Thau lagoon was set to 0.85 in accordance with values reported by Metzger et al. (2007).

1.2 Atmospheric fluxes

The exchange of organic pollutants such as PCDD/Fs between atmosphere and water surface occurs by means of three main processes: diffusive gas exchange between the atmospheric and water boundary layer, dry deposition of particle bound pollutant, and wet deposition during rainfall.

- Diffusive exchange

The diffusive air-water exchange flux F_{AW} [M·L^2/ T] is represented as (Westerterp *et al.* 1984):

$$F_{AW} = k_{AW}\left(\frac{C^{air}}{K_{GL}} - C^{diss}\right) \tag{11}$$

where C^{air} and C^{diss} are the gas-phase and the dissolved (liquid) concentrations [M L $^{-3}$], respectively. K_{GL} is the dimensionless gas-liquid distribution coefficient, $K_{GL} = C_G^i / C_L^i$, and is calculated from the Henry's law constant using:

$$K_{GL} = \frac{H}{R \cdot T} \tag{12}$$

where R is the universal gas constant 8.314 10^{-3} kJ (mol·K)$^{-1}$ and T is the temperature [K]. For PCDD/Fs the temperature dependence is obtained from (Brunner 1990):

$$\ln H = A_h - \frac{B_h}{T} \tag{13}$$

where the values of the coefficient A_h and B_h are given in Table 2.

The mass transfer coefficient k_{AW} is described by following equation:

$$k_{AW} = \left(\frac{1}{k_G \cdot K_{GL}} + \frac{1}{k_L}\right)^{-1} \tag{14}$$

where and k_G and k_L are the mass transfer coefficients [L T^{-1}] in the air and the water films, respectively. The liquid phase mass transfer coefficient, k_L, [m d^{-1}] is calculated from the mass transfer coefficient of CO_2 in the water side k_{LCO_2}, which is a function of the wind speed at 10 m height, u_{10} [m s^{-1}] (Nightingale *et al.* 2000, Dachs *et al.* 2002):

$$k_{LCO_2} = 0.061 \cdot u_{10} + 0.24 \cdot u_{10}^2 \tag{15}$$

$$k_L = k_{LCO_2} \left(\frac{Sc}{600} \right)^{-0.5} \tag{16}$$

where Sc is the Schmidt number of the pollutant and 600 accounts for the Schmidt number of CO_2 at 298 K. The Schmidt number is defined as:

$$Sc = \frac{\mu}{D \cdot \rho} \tag{17}$$

where ρ and μ are the density and viscosity of the fluid respectively while D is the coefficient of molecular diffusion of the dissolved compound. The temperature dependence of the diffusion coefficient in water is calculated with following correlation by Wilke and Chang (1955):

$$D_L = \frac{7.4 \cdot 10^{-8} (\alpha MW)^{0.5}}{\mu \cdot V_b^{0.6}} \cdot T \tag{18}$$

where T is the temperature of the solvent [K] and μ is its viscosity [cP], V_b [cm^3 mol^{-1}] is the molar volume of the organic compound at its normal boiling point, MW is the molecular weight [g/mol] of solvent and α is the association factor of the solvent, α=2.6 for organic solutes diffusing into water (Perry and Chilton 1984). D_L is given in cm^2s^{-1}.

The gas phase mass transfer coefficient [L T^{-1}] of Eq (14) is calculated using the mass transfer coefficient for water, k_{G,H_2O}, which can be obtained from the wind speed (Schwarzenbach *et al*., 2003):

$$k_{G,H_20} = 0.2u_{10} + 3 \cdot 10^{-3} \tag{19}$$

and then

$$k_G = k_{G,H_20} \left(\frac{D_G}{D_{G,H_20}} \right)^{0.67} \tag{20}$$

where D_G and D_{G,H_2O} refers to the diffusion coefficients in the gas phase (air) of the chemical and water, respectively. An empirical correlation that has been extensively used to estimate the diffusion coefficients in air as a function of temperature is the one presented in Fuller et al. (1966):

$$D_G = \frac{10^{-3} \cdot T^{1.75} \left(\frac{MW_{Air} + MW_B}{MW_{Air} \cdot MW_B} \right)^{1/2}}{P\left(\left[\sum (\upsilon)_{Air} \right]^{1/3} + \left[\sum (\upsilon)_B \right]^{1/3} \right)^2} \quad (21)$$

where T is the temperature [K], P is the pressure [atm], MW are the molecular weights of air (28.8) and the organic compound, and υ are the atomic diffusion values. The diffusion coefficient of water in air is calculated as:

$$D_{G,H_2 0}(m^2 / s) = 1.2365 \cdot 10^{-9} T^{1.75} \quad (22)$$

- Dry aerosol deposition

The dry deposition flux F_d [M $L^{-2}T^{-1}$] from the atmosphere to the surface may be estimated from the particle deposition velocity (v_d, L T^{-1}) and the pollutant concentration in the aerosol phase [M L^{-3}] as (Swackhamer *et al*. 1999):

$$F_d = C_{aerosol} \cdot v_d \quad (23)$$

Particle deposition velocity depends on aerosol size distribution and atmospheric turbulence, which is influenced by wind speed. In coastal areas the velocity usually ranges from 1 10^{-3} to 8 10^{-3} m s^{-1} (Nho-Kim et al., 2004). Studies on PCDD/Fs dry deposition report particle deposition velocities between 4 10^{-4} and 5.2 10^{-3} m s^{-1} see Table 1. A value of 1.5 10^{-3} m s^{-1} was assumed in our model.

Table 1. Reported values for dry deposition velocity.

Dry deposition velocity [m s^{-1}]	Area	Reference
0.002	urban	Koestner and Hites 1992
0.0014-0.0023	rural	Ogura et al. 2001
0.0004-0.0008	urban	Moon et al 2005
0.0015-0.0035	urban	Correa et al. 2006
0.0032-0.0052	rural	Shih et al 2006

- Wet deposition

Wet deposition flux, F_w is calculated from the product of the precipitation rate Pr [L/T] and the contaminant concentration in rain water C_{rain} [M L^{-3}], which includes both the dissolved and particulate phases (Swackhamer et al., 1999; Van Ry et al., 2000) as:

$$F_w = C_{rain} \cdot \mathrm{Pr} \quad (24)$$

C_{rain} is the product of the concentration in the atmosphere and a scavenging ratio W_T, (Jurado et al., 2004):

$$C_{rain} = W_T \cdot C_{atmosphere} \tag{25}$$

and W_T is estimated as (Bidleman 1988; Ligocki et al., 1985a,b):

$$W_T = W_G(1-\varphi) + W_P \cdot \varphi \tag{26}$$

where W_G and W_P are the gas and particle washout ratios, respectively, and φ(dimensionless) is the fraction of aerosol-bound compound to total atmospheric concentration, i.e.

$$\varphi = \frac{C_{aerosol}}{C_{aerosol} + C_{gas}} \tag{27}$$

The gas washout ratio, W_G, has been estimated using the Henry's law constant as:

$$W_G = \frac{1}{K_{GL}} = \frac{R \cdot T}{H} \tag{28}$$

Values for measured W_P reported in literature vary between 10^4-10^5 (Eitzer and Hites 1989; Koester and Hites 1992; Ogura et al., 2003). Therefore an average value of 5 10^4 has been used in our model.

1.3 Water column and sediment fluxes

-Settling

Contaminants bound to particles settle through the water column and are deposited at the sediment surface. The particles sinking is given by the product of the settling velocity w_{se} and the concentration of the contaminant in the particulate matter in the water column

$$F_{SINK} = w_{se} \cdot C_W^{\ part} \tag{29}$$

In the model we assume a settling velocity of 1.73 10^{-5} (Carrer et al., 2000).

- Resuspension

Resuspension is the entrainment of bottom sediments to the water column that occurs whenever the shear stress exerted on the sediment exceeds a critical value. This process can cause remobilisation of contaminant bound to sediment particles through desorption.

The flux of contaminant into the water column associated to resuspension is represented by following equation (Schwarzenbach et al., 2003):

$$F_{res} = \mu_{res}\left(\frac{C^{part}}{m} - K_d C^{diss}\right) \quad (30$$

μ_{res} is the amount of particles per unit area and time that resuspend, which is multiplied by the fraction of contaminant that is desorbed from the resuspended particles (inside the parenthesis).

- Sediment accumulation and burial

Burial is the vertical downward movement of sediment particles that accumulate at the sediment-water interface due to the continuous deposition of settling sediments. The burial flux is obtained from the burial velocity w_{bu} and the concentration of contaminant in the particles that are buried:

$$F_{bu} = w_{bu} C_{sed}^{part} \quad (31)$$

According to values presented in Schmidt et al. (2007) for Thau Lagoon the burial velocity was set to 8 10^{-11} m s^{-1}.

-Sediment-water diffusion

The diffusive flux at the sediment-water interface can be represented with a sediment-water exchange rate coefficient k_{ws} [L/T] (Farley et al., 1999):

$$F^{W/S} = k_{ws}(C_{sed}^{diss+DOC} - C^{diss+DOC}) \quad (32)$$

k_{ws} is obtained from the effective diffusion coefficient D_L [L^2 T^{-1}] of the contaminant divided by the distance between the centre of the sediment surface layer and the bottom water column layer. For POPs, D_L is calculated from the Wilke-Chang correlation (Logan 1999);

$$D_L = \frac{7.4 \cdot 10^{-12} T (2.6 \cdot 18)^{0.5}}{\mu \cdot V_b^{0.6}} \quad (33)$$

- Diffusive fluxes within the sediment

A similar approach as presented in Eq. (32) can be used to describe diffusion flux equation within the sediment:

$$F_{diff} = -\frac{D_{eff}}{dz}(C_{sed_2}^{diss+DOC} - C_{sed_1}^{diss+DOC}) \quad (34)$$

where dz [L] is the distance between the centre of the two sediment layers. D_{eff} [L^2 T^{-1}] accounts for the longer path that the diffusing molecules must follow in a porous media

compared to diffusion in water. Therefore, the effective diffusion coefficient is represented as the ratio of the molecular diffusion coefficient D_L and the square of tortuosity θ:

$$D_{eff} = \frac{D_L}{\theta^2} \tag{35}$$

θ [L L^{-1}] represents the ratio of the average distance a molecule must travel in a porous media to go around solid particles over the direct distance. Based on empirical tortuosity-porosity observations Boudreau (1997) has proposed following relation:

$$\theta^2 = 1 - 2 \cdot \ln(\phi_{sed}) \tag{36}$$

- Biodiffusion and bioirrigation

The biological reworking of sediments by the activity of benthic organisms results in the displacement and mixing of particles and pore water. It is considered a diffusive process when the sediment motion is random in direction and time and when the distance of displacement and the time between mixing events are short compared to the scale of the system. Also, biodiffusive transport is more likely to be important for strongly adsorbing species with low solubility. The biodiffusion equation is similar to the diffusion equation but involves the total concentration in the sediment:

$$F_{biodiff} = \frac{D_B}{H}\left(C^T_{sed2} - C^T_{sed1}\right) \tag{37}$$

D_B is the biodiffusion coefficient (L^2 T^{-1}) and may be correlated to the burial velocity w_b by means of an empirical relationship (Boudreau, 1997):

$$D_B = 15.7 \cdot w_b^{0.69} \tag{38}$$

where D_B is in cm^2 yr^{-1} and w_b is in cm yr^{-1}. Therefore, D_B was set to 1.91 10^{-11} m s^{-1}.

1.4. Degradation

In this model degradation fluxes are represented as a first order reaction model:

$$F_{\deg r} = k_{\deg r} \cdot C^{diss} \tag{39}$$

where C^{diss} is the concentration of the contaminant in dissolved form and k_{degr} is the degradation rate resulting from hydrolysis, biodegradation and photodegradation.

The degradation rate k_{degr} depends on the compartments where the contaminant is located (sediments or water column) and can be calculated from half life times

$$t_{1/2} = \frac{\ln 2}{k_{\deg r}} \tag{40}$$

Values of k_{degr} are given it Table 2.

2. Physicochemical parameters of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans

The specific physico-chemical parameters for the PCDD/Fs family, as well as literature references are given in Table 2.

Table 2. Model parameters

Parameter		Range	Ref
MW	Molecular weight [g/mol]	PeCDD : 356.4 OCDD : 460 TCDF : 306 PeCDF : 340.42 HxCDF : 374.87	
MV	Molar volume [cm^3/mol]	PeCDD : 296.5 OCDD : 359.2 TCDF : 275.6 PeCDF : 289.1 HxCDF : 310	
H	Henry (Pa m^3/mol) values $\ln H = A_h - B_h / T$	Ah Bh PeCDD :7.94 1089 OCDD :8.34 1009 TCDF :8.01 1598 PeCDF :7.13 1275 HxCDF :7.16 1124.14	Paasivirta et al. 1999
K_{ow}	Octanol water partition coefficient in the water column (temperature dependant) [-] $\log K_{OW} = A_{OW} + B_{OW}/Tw$ with T_W [K] water temperature, computed by the hydrodynamic sub-model	A_{OW} B_{OW} K_{OW} 298 PeCDD : 3.206 1212.646 1.8770E+7 OCDD : 3.536 1745.08 2.4524E+9 TCDF : 3.092 1040.42 3.8170E+6 PeCDF : 2.940 1206.398 9.6893E+6 HxCDF : 3.045 1368.185 4.3124E+7	Paasivirta et. al. 1999
K_{OC}	Partition coefficient between organic carbon and water [m^3 ng^{-1}] $\log K_{OC} = A_{OC} \log K_{OW} + B_{OC}$	A_{OC} B_{OC} PCDD : 0.88 0.53 PCDF : 0.95 -0.19	Persson 2005
k_{degr}	Degradation rate [1/s]	Water Sediment PeCDD : 2.6742 10^{-8} 1.9254 10^{-10} OCDD : 2.4372 10^{-9} 1.4811 10^{-10} TCDF : 3.0085 10^{-8} 3.5007 10^{-10} PeCDF : 1.4586 10^{-8} 3.8508 10^{-10} HxCDF : 6.8765 10^{-9} 4.0232 10^{-10}	Sinkkonen and Paasivirta 2000

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