A Review of Accidental Release Simulated Case Studies on Dispersion and Bioaccumulation of PCB and CBz Persistent Pollutants in Riverbeds

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PolyChlorinated Biphenyls (PCB) and PolyChlorinated Benzenes (CBz) are two categories of persistent organic pollutants (POP) difficult to be removed from wastewaters and environment. Such very toxic pollutants present a low biodegradability but a high bioaccumulation capacity in biota and sediments, as higher as the number of chlorine atoms in the molecule is larger. Being very stable, their removal in conventional chemical-biological wastewater treatment plants (WWTP) is incomplete, leading to frequent oversteps of the admissible limits in effluents. If the discharge contains a low-level pollutant load, such a problem apparently seems not to be so critical due to the fast pollutant dispersion over a relatively short section of the river. However, repeated accidental discharges can turn into a serious pollution problem due to the high mobility and persistence of PCB and CBz in the aquatic environment. The study illustrates, by comparing previously solved but also new case studies of accidental release scenarios, and by using a combined dispersion-bioaccumulation dynamic model, how such POP releases can become dangerous on a long term due to the moving pollution front effect propagated downstream the river as soon as the aquatic phase-exchange equilibrium tends to be reached in the critical discharge section. The comparison points out relations between pollutant properties and its bioaccumulation capacity, highlighting similarities in the fate of heavy CBz and PCB. Some rough indices are proposed for assessing the pollution degree of the river section.

Keywords: PCB, chlorinated benzenes, river pollution, bioaccumulation

Aquatic environment pollution with toxic persistent compounds resulted from industrial processes represents one of the highest concern of the modern society. Particularly, the POP resulted as by-products or produced for various industrial uses, are a class of stable pollutants difficult to be removed from wastewaters by means of classical treatment methods. Among them, the PCB and CBz are characterized by a very low biodegradability, high toxicity and high bioaccumulation capacity in the environment.

PCB compounds, with C_{12-15}H_{10-12}Cl_{1-10} formula and two biphenyls in molecule, are a class of POP including 209 congeners, from which ca. 140 have been manufactured as commercial mixtures of viscous liquids. The coplanar PCB present toxicity comparable to those of dioxins, altering the transcription of genes in the living cells. The increase of the chlorine content leads to an easier bioaccumulation of PCB in biota and sediments, a lower biodegradability, and a lower solubility in water but higher in lipids. PCB are low volatile and very stable (with halflife-time of 10-30 years), with a high toxicity including the carcinogen and mutagen effect on fauna. Their resistance to thermal, biological or chemical degradation leads to a high mobility and persistence, i.e. a long-range transport and residence times, negatively affecting the dispersion area and inducing long-term environment degradation. PCB have extensively been used in various industries, being synthesized on a large scale and discharged in the environment without any precaution until 80’s when their production has been ban and their use restricted in most of the countries [1]. Despite of that, PCB inevitably persist in the environment, and inherently appear as by-products in the production of pesticides, insecticides, or chlorinated aromatics. In spite of intensive researches on PCB treatment methods (physical, chemical, or biological), their removal is costly and incomplete, continuing to be present in traces in wastewaters (where the EU threshold is of 1 ng L^{-1}), sludge (EU threshold of 800 ng gdw^{-1}), sediments, industrial wastes and levigates from waste deposits [2].

CBz are a class of persistent hydrophobic POP widely distributed in the environment due to their long history of use in industry, agriculture and households, such as insecticides, pesticides, deodorizers, soil fumigants, disinfectants, solvents, precursors for the production of dyes and silicone coatings [3]. CBz pollutants, of C_{6-8}H_{10-12}Cl_{1-6} formula, include 12 possible representatives. Even if their bioaccumulation capacity is lower than of PCB, the CBz still present a severe contamination potential of the environment (i.e. high indices Log K_{ow} > 5 and Log(BCF) >2-3, see below sections). The toxicity of CBz, especially of pentachlorobenzene (QCBz) and hexachlorobenzene (HCBz), for the human health and environment is comparable to those of PCB and dioxins (EU threshold in water is of 0.4-3.2 ng L^{-1} for QCBz and HCBz and of 0.4-10 μg L^{-1} for other CBz).

The current EU and international regulations recommend measures to control the waste stocks and industrial discharges containing CBz, while their use is subjected to regulations and restrictions in most of the industrialized countries, due to their high toxicity and frequent accidental releases in the environment (HCBz was banned from use in the US from 1966). Unfortunately, CBz inevitably appear as by-products in the production of chlorinated organics, while their removal in classical WWTP is difficult and
suffers from some inconveniences (e.g. a max. 60% removal yield for TCBz and HCBz [3]). If the released amounts of such contaminants are quite small, concentrations in effluents of ca. 1-2 μg L⁻¹ for DCBz-TCBz are close to the admissible limits, and the pollutant may quickly be dispersed over a small-size section of the river. The pollution problem seems to be in this case limited. However, for heavy CBz and PCB or frequent POP releases, the pollution can turn into a serious pollution problem due to the "moving pollution front" effect propagated downstream the river as the "moving pollution problem" seems to be in this case limited. For these cases, it is questionable what effect can have such an incomplete treatment of POP in WWTP on a long term on the whole riverine area.

The scope of this paper is to illustrate the high pollution potential of the river of a low-level but frequent accidental discharge of PCB and CBz from a WWTP. By using a combined advective-dispersive dynamic model (including the phase-exchange, bioaccumulation terms in biota and sediments, pollutant biodegradation and evaporation), it is proved how such situations can become dangerous on a long term. Simulations of various release scenarios include previously solved case studies [2,3] but also new accidental release cases of two other PCB pollutant.

A comparative analysis of all simulated case studies points out the direct relationship between the pollutant physical properties / structure (number of benzene rings and chlorine in molecule) and its bioaccumulation potential. For PCB concerning their high pollution potential in the aquatic environment. Some rough indices are proposed to assess the pollution degree of the river section. Finally, the model proves how a low level but frequent discharge of POP can turn into a serious pollution problem due to the "moving pollution front" effect propagated downstream the river as soon as the aquatic phase-exchange equilibrium tends to be reached in the critical discharge section.

Pollutant dispersion and bioaccumulation model

In order to simulate the pollutant fate downstream a release point located in the river middle (x=y=z=0), a 2D advective-dispersive dynamic model has been adopted [2-6]. Prediction of the pollutant concentration field c(x,y,t) in water is made by using the following mass balance:

\[
\frac{\partial c_w}{\partial t} + v_x \frac{\partial c_w}{\partial x} + v_y \frac{\partial c_w}{\partial y} = D_x \frac{\partial^2 c_w}{\partial x^2} + D_y \frac{\partial^2 c_w}{\partial y^2} + \sum \gamma_i \ ; \quad (1)
\]

\[
\frac{\partial c_w}{\partial y} = 0 , \text{ (for } y = 0) \ ; \quad c_w (x, 0, t) = c_{w0} , \text{ (for } x = 0) \ ;
\]

where:

- \( c_w \) = pollutant concentration in water;
- \( x \) = longitudinal distance from source;
- \( y \) = lateral distance from middle-river;
- \( z \) = vertical distance from water surface;
- \( B \) = river half-width; \( h \) = river depth;
- \( \omega \) = water-mean velocity in the flow direction;
- \( D_x = \text{apparent lateral dispersion coefficient} \ ;
- \( t \) = time.

The terms \( \gamma_i \) account for reaction or phase transport rates leading to disappearance (uptake) or appearance (clearance) of the pollutant in the river by various mechanisms such as: evaporation/runoff, biodegradation, uptake or clearance by/from biota, sediments or suspended solids. Such a model is based on several simplificatory assumptions: i) a small size discharge source (of negligible jet effects), with a continuous release flow-rate \( Q_w \) including the pollutant flow-rate \( Q_p \); ii) contaminant release time in the riverine pathway is much longer than the travel time \( T_r = \omega / \omega_w \) in the control section, from the source to a receptor located at a relevant distance \( x_{max} > 20d \) \ ; \( d = 2h(2B) / (2B + h) \); iii) an uniform longitudinal flow with a constant flow-rate \( Q_w \) and velocity \( \omega_w \) over the analysed time interval; iv) a prismatic river-geometry with an approximately constant rectangular cross-section; v) quasi-constant water quality parameters (temperature, dissolved oxygen, pollutant concentration before the release point \( c_{w0} \) ) averaged over the analysed time interval; vi) negligible adsorption/desorption of the pollutant from the river to suspended solids (others than biota or sediments; supplementary pollutant exchange rates \( \Sigma_r \) can be added if necessary); vii) an advection which dominates dispersion in the longitudinal direction \( (D_x = 0) \); viii) a fully mixed contaminant plume over the river depth; ix) a constant lateral dispersion coefficient \( (D_y) \) that includes the lateral turbulent mixing and diffusion; ix) a value of \( D_y = 0.06hw_x \) is adopted following the recommendations of Fischer [7]).

By assuming that pollutant biodegradation occurs only in the water (index 'w'), the inter-phase exchange dynamics of the contaminant can usually be satisfactorily represented by a pseudo first-order kinetics, of the form:

\[
\frac{dc_w}{dt} = -k_d c_w - k_{ev} c_w - \sum k_{we} F_e c_e + \sum k_{ew} F_w c_w , \quad (3)
\]

where:

- \( \text{index 'e'} \) denotes the phases in contact with the water, i.e. biota 'b' or sediments 's';
- \( F_\text{e} = \text{ratio of two phase quantities being in contact referred to the water volume}. \)

The pollutant biodegradation in the water is included in the \( r_d \) term, while its evaporation through the river surface in the term \( r_{ev} \). The last two terms in (3) account for the pollutant uptake (\( r_u \)) and clearance rates (\( r_c \)). The pollutant bioaccumulation mass balances can be derived similarly:

\[
\frac{dc_b}{dt} = k_{wb} c_w - k_{bw} c_b ; \quad c_b|_{x=0} = c_{b0} (x, y, 0) = 0 \ ; \quad (4)
\]

\[
\frac{dc_s}{dt} = k_{ws} c_w - k_{sw} c_s ; \quad c_s|_{x=0} = c_{s0} (x, y, 0) = 0 . \quad (5)
\]

The thermodynamic models are based on the partition coefficients \( K_p \) of the pollutant between every two phases at equilibrium, that is [8]: \( K_p = k_p / k_p \rightarrow c^* / c^* \ ; \quad (\text{where: } i, j = \text{the phases in contact, i.e. water ('w'), aquatic fauna and plants (biota 'b'), sediments and sludge ('s'), suspended solids, air/aerosols; } k_p = \text{uptake rate constant of the pollutant from phase i to phase j} \ ; \quad k_p = \text{clearance rate constant of the pollutant from phase j to phase i} \ ; \quad c^* = \text{concentration of the pollutant in the phase i} \ ; \quad (c^* \text{ denotes the equilibrium value}) \). The coefficients \( k_p, k_p \) are determined experimentally or, when no such data are available, they are correlated with the structural characteristics or properties of the pollutant, such as the \( K_w \) (octanol-water partition coefficient of the pollutant) or \( S_a \) (aqueous solubility of the chemical). A review of such correlations is given for POP [9], and for PCB [2]. Common notations used for the partition coefficients are: \( \text{BCF} = K_{ow} / (\text{lab studies}) \ ; \quad \text{BASF} = K_{ow} / \text{partition coefficient of the pollutant} \ ; \quad \text{oc} \text{index denotes the water to organic carbon partition} \). The equilibrium
evaluations are looking for the pollutant amounts distributed among compartments of a multi-phase environment, and ignore the dynamics of the dispersion / accumulation process [8,10]. It is to observe that mass balance (3) leads at limit \((t \to \infty)\) to the equilibrium conditions, i.e. \(K_{\text{we}} = k_{\text{we}} / k_{\text{ew}}\) or all the phases in contact (if biodegradation and evaporation are neglected).

To solve the model (1-3) a combined numerical-analytical procedure has been used. By choosing a time discretization step of \(\Delta t = 1\) day, evolution of the 2D field of concentrations in the river (perfect mixing being considered over the river depth) can be obtained by considering the pollutant dispersion at quasi-stationarity (dcw / dt = 0) over one integration step, the release time being longer than the travel time in the river control section:

\[
C(x,y,t) = \left(C_{\text{fond}} \frac{Q}{Q + Q_{\text{ef}}} + C_{\text{disp}}(x,y) \right) \times \exp(-k_{M}t) \times \frac{k_{M} - (1 - \exp(-k_{M}t))}{k_{M}} ;
\]

\[
k_{M} = k_{d} + k_{w} + k_{wb}F_{b} + k_{s}F_{s} ;
\]

\[
k_{d} = k_{d}F_{b}c_{b} + k_{s}F_{s}c_{s} .
\]

(6)

where:

- \(C_{\text{disp}}\) = dispersed pollutant concentration;
- \(C_{\text{fond}}\) = pollutant concentration before the release point;
- \(k_{M}\) = the apparent McKinney rate constant;
- \(k_{d}\) = the apparent clearance rate of pollutant from the phases in contact with the water;

\(c_{\text{disp}} = \text{dispersed pollutant concentration};\)

\(c_{\text{fond}} = \text{pollutant concentration before the release point};\)

\[k_{M} = \text{the apparent McKinney rate constant};\]

\[k_{d} = \text{the apparent clearance rate of pollutant from the phases in contact with the water};\]

\[k_{i} = \text{biodegradation (first-order) rate constant};\]

\[k_{ev} = \text{evaporation (first-order) rate constant}.\]

The \(k_{i}\) constant has been constructed by considering quasi-constant concentrations of pollutant in biota and sediments over one time-step, taken at the previous values \(c_{i}(x,y,t-\Delta t)\) for every river location. To get the analytical solution of (4-5), the pollutant concentrations in water for each spatial location downstream the release point are kept constant over one time-step, \(c_{w}(x,y) = c_{w}(x,y,t)\), while the initial conditions are those at the end of previous time-step:

\[
c_{w}(x,y,t) = \frac{k_{\text{we}}c_{w}(x,y)}{k_{\text{ew}} + c_{w}(x,y) \exp(-k_{\text{ew}}t)} + c_{\text{disp}}(x,y) \exp(-k_{d}t) ; \quad t = 0, b,s
\]

(7)

The solving procedure starts from the known initial conditions of the river phases and WWTP discharge. Then, by successively evaluating the phase concentration fields (6-7) with the chosen time-increment, one finally obtains the dynamics of the pollutant distribution in water \(c_{w}(x,y,t)\), biota \(c_{b}(x,y,t)\), and sediment \(c_{s}(x,y,t)\).

Release scenarios and fate of CBz and PCB

Simulation of accidental release scenarios and individual pollutant fate in the control river section (ca. 2000 m downstream the release point) accounts for CBz with 2-6 Cl in molecule (dichlorobenzene DCBz, trichlorobenzene TCBz, tetrachlorobenzene TeCBz, QCBz, HCBz) and for PCB with 3-6 Cl in molecule (PCB31 = 2,4',5 trichlorobiphenyl; PCB52 = 2,2',5,5' tetrachlorobiphenyl; PCB101 = 2,2',4,5,5'

<table>
<thead>
<tr>
<th>Table 1</th>
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<tbody>
<tr>
<td><strong>INPUT DATA FOR THE SIMULATION MODEL OF THE POLLUTANT FATE IN THE RIVERINE PATHWAY</strong></td>
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<tr>
<td><strong>River topological/water data</strong></td>
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<tr>
<td>Symbol</td>
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<td>(y)</td>
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<tr>
<td>(z)</td>
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<td>(Q)</td>
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<tr>
<td>(w_{x})</td>
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<td>(D_{y})</td>
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<tr>
<td>(F_{b})</td>
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<tr>
<td>(F_{s})</td>
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</table>

(a) Fischer’s correlation [7]; (b) EU regulations set PCB limits in the environment to 800 ng (g dw)\(^{-1}\) (in sediment, sludge), 0.1-2 μg (g ww)\(^{-1}\) (in food and feed) [5,14,15]. The high chlorinated CBz limits are usually assimilated to PCB; ww= wet weight; dw= dry weight; (c) the average biota density \(\rho_{b} = 1000 \text{ kg/m}^{3}\) and volumetric fraction in water \(y_{bw} = 10^{-4}\) (plants, fauna) have been adopted following the Mackay [8] and NEHC [10] case studies; (d) \(\sigma_{s}=0.1m\) is the active sediment depth [10]; of density \(\rho_{s} = 1500 \text{ kg/m}^{3}\).
Fig. 1. HCBz pollutant concentration in the river longitudinal axis, in water, biota and sediment, downstream the discharge point after 1 day (up), 250 days (middle) and 1000 days (down) of continuous release. The discharged pollutant flow-rate is of $8 \times 10^{-5}$ kg/s (ca. 2100 ng/L at source).

Fig. 2. PCB-101 pollutant concentration in the river longitudinal axis, in water, biota and sediment, downstream the discharge point after 1 day (up), 250 days (middle) and 1000 days (down) of continuous release. The discharged pollutant flow-rate is of $7.5 \times 10^{-8}$ kg/s (ca. 2.1 ng/L at source).

pentachlorobiphenyl; PCB137 = 2,2',3,4,4',5 hexachlorobiphenyl.

The input data, including the river characteristics and the constant flow rates are presented in table 1. For a better comparison, a contaminant level at source of ca. 2.1 μg L$^{-1}$ for CBz and of 2.1 ng L$^{-1}$ for PCB was adopted, being close to the admissible limits of these pollutants in surface waters. The bioaccumulation and physical properties of CBz and POP are presented in tables 2 and 3. It is to observe that values of Log(BCF) > 2-3 and Log($K_{ow}$) > 4.5-5.5 clearly indicates a high bioaccumulation and biomagnification potential of such POP in the environment [11-13].

Following such indices, the contaminants can be lumped in moderate persistent (DCBz, TCBz), high persistent (TeCBz) and very high persistent (QCBz, HCBz, PCB). For the first lump, the values of biodegradation constant ($k_d$ = 0.02-0.06 h$^{-1}$) and evaporation rate constant ($k_{ev}$ = 0.015-0.046 h$^{-1}$) are moderate. Oppositely, the most persistent POP (QCBz, HCBz, PCB) present low values of these constants ($k_d$ and $k_{ev}$ of $10^{-3}$-$10^{-6}$ h$^{-1}$). The same trend is confirmed by an increase in the uptake rate constants in biota and sediments, values varying from Log($k_{ws}$) = 2.4-2.8 and Log($k_{wb}$) = 1.2-3.8 for (DCBz, TCBz) until Log($k_{ws}$) = 3-4.5 and Log($k_{wb}$) = 2.5-3.8 for (QCBz, HCBz, PCB).

Simulations are performed for every mentioned POP over ca. 250 days of continuous pollutant release, because experimental investigations on fish reported bioaccumulation times of 15-256 days until the equilibrium is reached [12]. The obtained concentration fields in water biota and sediments after 1 day, 250 days and 1000 days are presented in figure 1 for HCBz and in figure 2 for PCB101. Even if both pollutants present 6 Cl in molecule, it is to observe that, at a certain moment, the pollution front (where concentrations are close to the equilibrium,
overstepping the regulation thresholds) is of ca. three times closer to the source for PCB than for CBz, as expected due to the higher bioaccumulation potential of PCB (see the partition constants $K_{BCF}$, $K_{W}$, $K_{OW}$ in tables 2-3). On a long-term, the situation becomes dramatic due to the low biodegradability and high bioaccumulation capacity of such POP, the pollution front continuing to move down the river as soon as the equilibrium is reached.

This moving-front effect can be better pointed-out by plotting in figure 3-4 the axial concentrations in the riverbed Table 2

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Significance</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M$</td>
<td>pollutant molecular weight (g mol$^{-1}$)</td>
<td>147.0</td>
</tr>
<tr>
<td>$S_w$</td>
<td>solubility in water at 22-25°C (mg L$^{-1}$)</td>
<td>100</td>
</tr>
<tr>
<td>$P_v$</td>
<td>vapor pressure at 20°C (mm Hg)</td>
<td>0.0013</td>
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<tr>
<td>$H$</td>
<td>Henry’s constant at 20°C (Pa m$^3$ mol$^{-1}$)</td>
<td>1.40</td>
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<tr>
<td>$k_{BCF}$</td>
<td>water-fish uptake rate constant (L kg$^{-1}$)</td>
<td>1.074</td>
</tr>
<tr>
<td>$k_{BCF}$</td>
<td>fish-water exchange rate constant (L kg$^{-1}$)</td>
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</tr>
<tr>
<td>$k_{BCF}$</td>
<td>predicted water-bioa concentration factor (L kg$^{-1}$)</td>
<td>2.08</td>
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<tr>
<td>$k_{BCF}$</td>
<td>measured water-bioa concentration factor (L kg$^{-1}$)</td>
<td>1.95</td>
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<tr>
<td>$k_w$</td>
<td>water-sediment uptake rate constant (L kg$^{-1}$)</td>
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<tr>
<td>$k_{w}$</td>
<td>sediment-water clearance rate constant (d$^{-1}$)</td>
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<td>$k_{w}$</td>
<td>water-sediment bioaccumulation factor (L kg$^{-1}$)</td>
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<td>$k_{w}$</td>
<td>octanol to water partition coefficient, 15°C (m)</td>
<td>3.4</td>
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<tr>
<td>$k_{OC}$</td>
<td>organic carbon to water partition coefficient (L kg TOC$^{-1}$)</td>
<td>2.92</td>
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<tr>
<td>$k_{OCE}$</td>
<td>evaporation constant through water surface (d$^{-1}$)</td>
<td>0.046</td>
</tr>
</tbody>
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This moving-front effect can be better pointed-out by plotting in figure 3-4 the axial concentrations in the riverbed for (y=0), downstream the release point (x > 0) for all CBz and PCB and for all the phases in contact after 250 days of release. The comparative results reveal that phase-equilibrium is reached over a section close to the source as smaller as the pollutant persistence is higher (i.e. over 500-600m for CBz and 50-300m for PCB). Besides, the pollutant loads in biota and sediments (overstepping critical thresholds) are much higher for heavy CBz (TeCBz, QCBz, HCBz) and heavy PCB (PCB101, PCB137), as underlined in Table 3.

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Fig. 3. CBz concentrations along the river longitudinal axis in water, biota and sediment, downstream the source, after 250 days of release ($8 \times 10^{-5}$ kgCBz/s, 2100 ng/L at source) [3]. Legend: 1= 1,2DCBz; 2= 1,3DCBz; 3= 1,4DCBz; 4= 1,3,5TCBz; 5= 1,2,4TCBz; 6= 1,2,3,4TeCBz; 7= 1,2,3,4TeCBz; 8= 1,2,3,5TeCBz; 9= 1,2,4,5TeCBz; 10= QCBz; 11= HCBz

Fig. 4. PCB concentrations along the river longitudinal axis in water, biota and sediment, downstream the source, after 250 days of release (discharged flow-rate of $7.5 \times 10^{-8}$ kg/s, ca. 2.1 ng/L at source). Legend: 1= PCB31; 2= PCB52; 3= PCB101; 4= PCB137

Fig. 5. Pollutant mass concentration dynamics along the river longitudinal axis ($y=0$) in water, biota and sediment downstream the source, after 250 days and 1000 days of continuous release. (Left) Chlorobenzenes: TCBz, TeCBz, HCBz; the discharged pollutant flow-rate is of $8 \times 10^{-5}$ kg/s, ca. 2100 ng/L at source. (Right) Chlorobiphenyls: PCB52 (- - - ) and PCB101 (-). The discharged pollutant flow-rate is of $7.5 \times 10^{-8}$ kg/s (ca. 2.1 ng/L at source)

Table 4

| Pollutant | $lg K_{ow}$ | $BCF$ (L kgww$^{-1}$) | $c_b / c_w | h_{x=0}$ (at source) (L kgww$^{-1}$) | x-distance (m) from source to get $0.9(c_b / c_w | h_{x=0}$) | x-distance (m) from source to get $0.1(c_b / c_w | h_{x=0}$) |
|-----------|-------------|------------------------|----------------------------------------|---------------------------------|---------------------------------|
| DCBz      | 3.35-3.44   | 1.2-3.3x10$^3$         | 1.2-3.3x10$^3$                         | 332                             | >2000                           |
| TCBz      | 4.4-4.5     | 1.2-2.0x10$^3$         | 1.2-2.0x10$^3$                         | 354                             | >2000                           |
| TeCBz     | 4.5-4.6     | 1.6-5.1x10$^6$         | 1.6-5.1x10$^6$                         | 364                             | >2000                           |
| QCBz      | 5.06        | 5.4x10$^7$             | 5.4x10$^7$                             | 366                             | 1810                           |
| HCBz      | 5.60        | 1.9x10$^8$             | 1.9x10$^8$                             | 366                             | 1078                           |
| tri-CB    | 5.52        | 5.62x10$^7$            | 5.62x10$^7$                            | 370                             | >2000                           |
| tetra-CB  | 5.92        | 4.89x10$^4$            | 4.89x10$^4$                            | 246                             | 646                            |
| penta-CB  | 6.50        | 2.51x10$^3$            | 1.55x10$^3$                            | 84                              | 324                            |
| hexa-CB   | 6.98        | 7.58x10$^3$            | 2.31x10$^3$                            | 14                              | 60                             |
by the axial plots of the moving front over 250-1000 days in figure 5.

Pollutant fate similarities between heavy CBz and tri-/teta-CB can be better pointed out by evaluating for instance the bioaccumulation in biota level after 250 days of continuous pollutant release, at source (x=0) and over the pollution front. The comparative results, presented in table 4, reveal that phase-equilibrium near the pollution source tend to be reach faster for light POP (CBz and tri-CB) and slower for heavy POP (penta-CB and hexa-CB). However, the pollutant loads in biota is as higher as its molecular mass (i.e. corresponding to a higher chlorine and phenyl content leading to higher $\lg K_{ow}$ constants) and distributed closer to the source. For instance, while the pollution front corresponding to $[90-100\% \text{ of } (c_{cb}/c_{cw})_{x=0}]$ cover ca. 330-370m from the source for light POP, the front longitudinal length becomes dramatically smaller for heavy POP (up to 14m for hexa-CB). The situation is the same for the larger length becomes dramatically smaller for heavy POP (up to 370m from the source for light POP, the front longitudinal length becomes dramatically smaller for heavy POP (up to 14m for hexa-CB). The situation is the same for the larger length becomes dramatically smaller for heavy POP (up to 370m from the source for light POP, the front longitudinal length becomes dramatically smaller for heavy POP (up to 14m for hexa-CB). The situation is the same for the larger

Conclusions

By using a relative simple dispersion-bioaccumulation model, it is possible to predict the negative effects of accidental discharges of POP on a riverbed (water, sediment and biota) over long time intervals. The model is quite flexible, and can be easily extended to account for variations in flow-rates and pollutant loads, or various riverbed sections. In the case of CBz and PCB, the model can point-out the long-term risk of a low-level but frequent pollutant release, due to the low biodegradability and high bioaccumulation capacity of such POP in biota and sediments. The risk is increasing exponentially with the chlorine and phenyl content in molecule, and as their persistence in the environment. Thus, similar fate and bioaccumulation behaviour have been found between heavy CBz (QCBz, HCBz) and medium PCB (tri-/teta-CB). Simulations also prove that a longer release interval (more than 15 days) leads to reaching the phase-equilibrium in the discharge section and then to a continuous moving-down of the pollution front, the riverbed being slowly point-out the long-term risk of a low-level but frequent discharge of POP on a riverbed (water, sediment and biota) over long time intervals. The model is quite flexible, and can be easily extended to account for variations in flow-rates and pollutant loads, or various riverbed sections. In the case of CBz and PCB, the model can point-out the long-term risk of a low-level but frequent pollutant release, due to the low biodegradability and high bioaccumulation capacity of such POP in biota and sediments. The risk is increasing exponentially with the chlorine and phenyl content in molecule, and as their persistence in the environment. Thus, similar fate and bioaccumulation behaviour have been found between heavy CBz (QCBz, HCBz) and medium PCB (tri-/teta-CB). Simulations also prove that a longer release interval (more than 15 days) leads to reaching the phase-equilibrium in the discharge section and then to a continuous moving-down of the pollution front, the riverbed being slowly

Acknowledgment. Partial support from the CNCSIS national research grant “A nonlinear approach to conceptual design and safe operation of chemical processes” (2008-2011) is acknowledged.

References

8. MACKAY, D., Multimedia environmental models - The fugacity approach, Boca Raton: Lewis Publ, 2001
10. NEHC, Ex-ORISKANY Artificial Reef Project, Prospective Risk Assessment Model (PRAM 1.4c), Navy Environmental Health Center, SPAWAR Systems Center, San Diego, 2006
14. NAGPAL, N.K., Water quality criteria for PCBs, Technical Appendix, Ministry of Environment, Lands and Parks, British Columbia (Canada), 1992
18. VAN WIJK, D., THOMPSON, R.S., DE ROOIJ, C., GARNY, V., LECLUX, A., KANNE, R., Environmental Monitoring and Assessment, 97, 2004, p. 87
25. DERCÖVA, K., VRANA, B., BALFI, S., Chemosphere, 38, 1999, p. 1391

Manuscript received: 28.1.2008