

## Bioaccumulation Dynamics of a PCB Low-level Discharge in a Riverine Pathway Downstream the Release Point

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The low biodegradability and high persistence in environment of POPs (persistent organic pollutants), and especially some of them such as PCBs (polychlorinated biphenyls), make their removal difficult and incomplete in conventional wastewater treatment plants (WWTP). A low-level quasi-continuous release of such pollutants in rivers, fluctuating around or beyond the admissible levels, is a quite common problem especially for discharges from large industrial plants. 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 pathway, i.e. over a few dozen meters downstream the WWTP release point. However, this problem can turn into a serious one if the pollutant is a POP, even for small concentrations in the WWTP effluent, due to their known high bioaccumulation capacity in biota and sediments. For this last case, the paper illustrates, by means of a relatively simple dynamic model and two case studies, how the dispersion and bioaccumulation critical zone of a PCB near the release point tends to move slowly downstream.

*Key words:*

Pollutant dispersion, bioaccumulation, PCB, river pollution

### Introduction

Environmental pollution, especially pollution of waters with toxic persistent compounds from industrial processes that display a very low biodegradability and a high dispersion degree, represents one of the greatest concerns of modern society. Particularly, POPs resulted as by-products or produced for various industrial uses, are a class of very stable pollutants and are very difficult to remove from wastewaters by means of classical treatment methods. Among them, the PCBs present an environmental and human health concern, even if appearing in very low mass concentrations ( $\text{ng L}^{-1}$ ).<sup>1</sup> PCBs are characterized by low solubility in water but much higher in lipids, low volatility, and high stability (with half-life-time of 10–30 years), with high toxicity (including the carcinogenic and mutagenic effect on fauna) and bioaccumulation capacity in an aquatic environment. Their resistance to thermal, biological or chemical degradation lead to high mobility, i.e. long-range transport and residence times, negatively affecting the dispersion area and inducing long-term environmental degradation.

PCBs have extensively been used in various industries, as hydraulic and dielectric fluids, plasticis-

ers in paints and cements, as casting agents, adhesives, water-proofing, vaseline, fire-proofing, railway sleepers, or for production of insecticides, pesticides, solvents etc. They have been synthesized on a large scale (millions of tons) and discharged in the environment without any precaution until the 80's. However, due to increased concerns regarding their toxicity and persistence, PCB production has been banned in the USA since 1977.<sup>1,8</sup> Eventually, PCB production, processing and distribution has been prohibited in almost all industrial countries since the late 1980s,<sup>9,2</sup> although some use continued in closed units such as capacitors and transformers.<sup>8</sup> Nevertheless, PCBs inevitably persist in the environment and remain a focus of attention. Moreover, these POPs inherently appear as by-products in the worldwide production of various chlorinated organics such as pesticides, insecticides, or chlorinated aromatics, continuing to be present in wastewaters, sediments and industrial wastes, sludges from WWTPs, and in the levigates from the industrial waste deposits.<sup>1–5</sup>

From the chemical point of view, PCBs are a class of organic chlorinated compounds with the general formula  $\text{C}_{12}\text{H}_{10-x}\text{Cl}_x$  and with 1 to 10 chlorine atoms attached to the biphenyl. Among 209 congeners of PCBs, ca. 140 have been manufactured as commercial mixtures of viscous liquids. The coplanar PCBs present toxicity comparable to

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those of dioxins, by altering the transcription of genes in the living cells. The increase of the chlorine content in the PCB molecule will lead to an easier bioaccumulation in biota and a lower biodegradability and solubility in water.

While the EU regulations sets PCB limits in the aquatic environment to  $1 \text{ ng L}^{-1}$  (water),  $800 \text{ ng g}^{-1}$  dw (in sediments, sludge), the wastewaters and waste sludge from some WWTP can sometimes present significant loads, up to  $2 \text{ } \mu\text{g L}^{-1}$  (water),<sup>3</sup>  $10 \text{ } \mu\text{g g}^{-1}$  dw (sludge),<sup>6</sup>  $31 \text{ } \mu\text{g g}^{-1}$  dw (sediment),<sup>7–8</sup> while the waste and levigates can present even higher PCB contents depending on the waste type (more than  $50 \text{ } \mu\text{g g}^{-1}$  dw).<sup>9</sup> These current loads are however much lower than the pollution levels of the rivers and lakes with PCBs before the year 1985.<sup>7</sup>

New EU regulations and national programs impose urgent action for reducing the POP presence in the environment. Moreover, EU and international commissions set PCB maximum levels for food and feed ( $0.1\text{--}2 \text{ } \mu\text{g g}^{-1}$  ww),<sup>8,10</sup> and recommend regulations to control the waste stocks and industrial discharges. As a result, intensive research and a large number of contributions have been published over the last decade, reporting remarkable progress in PCB treatment methods. These approaches may be separated into three categories: physical, chemical, and microbial (biological).

Physical PCB removal methods are usually expensive and include: incineration at high temperatures (up to  $1200 \text{ }^\circ\text{C}$ ), with the risk of producing dioxins when insufficient quantities of oxygen are used;<sup>11</sup> ultrasound leading to polluted water thermolysis and PCB oxidation;<sup>12</sup> irradiation with gamma rays and PCB decomposition to chloride and aromatic hydrocarbons; Corona electrical discharges in water with producing oxidant radicals.<sup>13–14</sup> Other methods, such as those based on absorption (on polymers, ash from coal-burning, activated carbon)<sup>15–17</sup> or selective extraction, are less economic due to the very large quantities of water to be treated and due to low PCB concentrations in wastewaters.

The chemical methods aim at oxidising or reducing the PCB to simpler molecules, of higher biodegradability, and more rarely to substitute the chlorine. Among these are:<sup>18</sup> chlorine substitution by PEG (polyethyleneglycols) from liquid wastes (with PEG/KOH/Al),<sup>19–20</sup> electrolytic reduction in aqueous solutions;<sup>21</sup> photochemical reduction (with UV, or visible light)<sup>22</sup> or photocatalytic oxidation (UV, cat.  $\text{TiO}_2$ ) in aqueous solutions (even if it might generate toxic by-products such as dioxins or dibenzofurans);<sup>23</sup> oxidation with ozone, hydrogen peroxide, peroxides,<sup>2,24</sup> sometimes combined with biotreatment;<sup>25–27</sup> neutralization (with  $\text{NaHCO}_3$ )<sup>28</sup> and others. A special class of methods is the catalytic oxidative-reductive decomposition of PCBs, such as: ho-

mogeneous catalysis in Fenton system,<sup>29–30</sup> sometimes combined with biological treatment, with the disadvantage of increasing the Fe concentration in water;<sup>31–34</sup> heterogeneous catalysis on zeolites in an oxidative environment (in the presence/absence of UV); heterogeneous catalysis in Fenton system with Fe-ions included in the zeolite/silicates structure;<sup>35–36</sup> heterogeneous catalysis in water environment (with oxides,<sup>23</sup> with Pd/C/hydrogen<sup>37</sup>), or in solvents (Pd/Fe);<sup>38–39</sup> heterogeneous catalysis at high temperatures in a reductive environment (Cu/Pd, Pd/C, Ni/C at  $300 \text{ }^\circ\text{C}$ ;<sup>40</sup> Ni–Mo/ $\text{Al}_2\text{O}_3$  hydrodechlorination  $230\text{--}290 \text{ }^\circ\text{C}$ <sup>41</sup>), or oxidation at high temperatures ( $\text{V}_2\text{O}_5/\text{WO}_3\text{--TiO}_2$  catalysts,  $180\text{--}300 \text{ }^\circ\text{C}$ ).<sup>11</sup>

The biological methods use specialized microorganisms (adapted in the Lab) to biodegrade PCBs based on a reductive dechlorinating mechanism.<sup>3,4,6,42–51,90</sup> However, frequent problems arise when transferring a successful laboratory strain to a natural biological water treatment system, or due to the high selectivity in dechlorinating only of some POP structures. Trials to use some peroxidases in the presence of  $\text{H}_2\text{O}_2$  can improve the removal yields.<sup>52–53</sup>

Irrespective of the used method, introduction of a supplementary wastewater (or sludge) treatment step for large discharged flow-rates is very costly. On the other hand, PCB neutralisation from waste is difficult, their removal in WWTPs is problematic and incomplete, while the use of classical treatment methods are unsatisfactory. Application of conventional chemical-biological water treatment can remove max. 45 % of PCBs, while addition of Fenton's reagent in the chemical step can yield a max. of 51 % removal.<sup>31–32</sup> Even if an adapted sludge is used, the effluents from WWTP can sometimes still contain  $1.4\text{--}4.3 \text{ ng L}^{-1}$  PCBs (and  $0.4\text{--}1.5 \text{ } \mu\text{g L}^{-1}$  PAHs in the Montreal area<sup>54</sup>), or  $250 \text{ ng L}^{-1}$  (Thessaloniki area<sup>3</sup>). Usually, such discharges are quickly dispersed in the large surface waters, however the PCB presence in the WWTP effluents still remains an open issue due to their long-lasting capacity in the environment.

Difficulties in removing PCBs from urban, agricultural sewerage or industrial discharges when the treatment possibilities are limited can periodically lead to overstepping of the maximal POP admissible limits in the riverine discharge section. If the released amounts of PCBs are quite small, the mass concentrations in the WWTP effluent (ca.  $1\text{--}5 \text{ ng L}^{-1}$ ) can be close to the admissible limits, and the pollutant may be dispersed quickly over a small-size section of the river, downstream the WWTP release point. The pollution problem seems to be in this case very limited. However, if such a situation persists, it is questionable as to what effect can the incomplete treatment of PCBs have on wastewaters and on the riverine area in the long term.

By using a relatively simple dynamic model applied to a case study, this paper investigates how the low levels of pollutant loads in the WWTP discharges, quickly dispersed over a small section near the release point, can become dangerous for the whole riverine waterway if the pollutant is very persistent (such as the POPs/PCBs). In other words, it is to investigate the pollution potential of such low-level but frequent POP discharges due to the “moving pollution front” effect propagated downstream the river over long time intervals, as soon as the aquatic phase-exchange equilibrium tends to be reached.

Such a problem is important for the case of frequent WWTP discharges, when the low quantities of the released pollutant appear not rising critical situations due to their fast dispersion over a relatively small section of the river. The very low level but rather continuous pollution problem is however suspected to turn into a serious one if the pollutant belongs to the POP class, due to their very high bioaccumulation capacity in biota and sediments, very low biodegradability and long-term persistence in the aquatic environment. Exemplifications with two case studies of accidental release of PCB-101 and PCB-52 highlight the increased pollution potential of higher chlorinated PCBs (e.g. PCB-101 vs. PCB-52) due to their high bioaccumulation capacity in the environment.

### Pollutant dispersion and bioaccumulation models in the riverine pathway

Pollutant fate in a surface water control section is characterized from two main points of view: i) partition of the discharged pollutant among various phases when a quasi-equilibrium state is reached, and ii) the dynamics of the pollutant dispersion in water and bioaccumulation in sediments, biota, or volatilisation in air after the pollutant release until the quasi-equilibrium tends to be reached.

The equilibrium (or thermodynamic) models are based on using partition coefficients  $K_{ij}$  of the pollutant between every two phases in contact, that is:

$$\left. \frac{dc_i}{dt} \right|_s = -k_{ij}c_i^* + k_{ji}c_j^* = 0 \Rightarrow K_{ij} = \frac{k_{ij}}{k_{ji}} = \frac{c_j^*}{c_i^*}, \quad (1)$$

where:  $i, j$  = the phases in contact, i.e. water (index ‘w’), aquatic fauna and plants (biota ‘b’), sediments and sludge (‘s’), suspended solids, air/aerosols;  $r_u = k_{ij}c_i$  = uptake rate of the pollutant from phase  $i$  to phase  $j$ ;  $r_c = k_{ji}c_j$  = clearance rate of the pollutant from phase  $j$ ;  $c_i$  = concentration of the pollutant in the phase  $i$ ;  $t$  = time; index ‘s’ also denotes the steady-state; superscript ‘\*’ denotes the equilibrium value. The coefficients  $K_{ij}$  are determined experimen-

tally or, when no such data are available, they are correlated with the structural characteristics or properties of the pollutant, such as the  $K_{ow}$  (octanol-water partition coefficient of the pollutant) or  $S_w$  (aqueous solubility of the chemical). Table 1 presents some empirical (QSAR-type) correlations of rate constants  $k_{ij}$ ,  $k_{ji}$  and  $K_{ij}$  for the PCB pollutant case. The common notations used for the partition coefficients are: BCF =  $K_{wb}$  (Lab studies), BAF =  $K_{wb}$  (in field studies), BSAF =  $K_{wb}/K_{ws}$ ,  $K_{oc}$ ,  $K_{ws}$ ,  $K_{doc}$  (‘oc’ index denotes the water to organic carbon partition; ‘doc’ denotes the water to dissolved organic carbon partition).

When the pollutant is discharged in surface waters, several stationary models can predict its distribution among phases. For instance, in the compartmental approach, four levels of modelling can be used:<sup>55–56</sup> a closed system at equilibrium and thermodynamic steady-state with no chemical reactions (Level I); an open system at equilibrium and thermodynamic steady-state with chemical reactions (Level II); an open system not at equilibrium while at thermodynamic steady-state with chemical reactions (Level III); an open system not at equilibrium and not at thermodynamic steady-state with chemical reactions (Level IV).

In order to facilitate the calculus especially for situations close to equilibrium, Mackay and Paterson<sup>57</sup> replaced concentrations  $c_i$  (mol m<sup>-3</sup>) in the phase  $i$  by the product  $c_i = f Z_i$ . The introduced ‘fugacity’  $f$  (Pa) represents a measure of the ‘escaping tendency’ of the chemical from a particular phase, and it has the same value irrespective of the phases in contact at equilibrium. The use of fugacity capacity  $Z_i$  (mol Pa<sup>-1</sup> m<sup>-3</sup>) of phase  $i$  presents the advantage of being easily correlated with the pollutant and phase characteristics, such as temperature, vapour pressure, Henry constant, solubility, density, lipid content in biota,  $K_{ow}$ ,  $K_{oc}$ ,  $K_{doc}$ , etc.<sup>55</sup> Thus, the following compartmental (integral) models can predict the partition or distribution among phases of a quantity ( $n_T$ , mol) or of a continuous flow-rate ( $Q_c$ , mol d<sup>-1</sup>) of released pollutant:

$$f = \frac{n_T}{\sum_i Z_i V_i}, \quad (\text{Level I model})$$

$$f = \frac{Q_c}{\sum_i Z_i V_i K_i} = \frac{Q_c}{\sum_i D_{Ai} + \sum_i D_{Ri}}, \quad (\text{Level II model})$$

$$f_i = \frac{Q_c + \sum_j (D_{ji} f_j)}{\sum_i (D_{ij} + D_{Ai} + D_{Ri})}, \quad (\text{Level III model}) \quad (2)$$

$$Z_i V_i \frac{df_i}{dt} = Q_c(t) - f_i \sum_j (D_{ij} + D_{Ai} + D_{Ri}) + \sum_j (D_{ji} f_j), \quad (\text{Level IV model})$$



where:  $V_i$  = the volume of the phase or compartment  $i$  ( $\text{m}^3$ );  $K_i$  = advection or any additional first-order rate constant occurring within phase or compartment  $i$  ( $\text{d}^{-1}$ );  $D_{Ai}$  = advective transport in the phase or compartment  $i$  ( $\text{mol d}^{-1} \text{Pa}^{-1}$ );  $D_{Ri}$  = reaction process in the phase or compartment  $i$  ( $\text{mol d}^{-1} \text{Pa}^{-1}$ );  $D_{ji}$  = the transport coefficient from compartment  $j$  into compartment  $i$  ( $\text{mol d}^{-1} \text{Pa}^{-1}$ ). Based on the fugacity approach, Mackay *et al.*<sup>58</sup> developed the compartmented/multi-phase and multi-segment QWASI model to predict the pollutant fate in lakes or rivers, based on a series of well-mixed inter-connected water sections (boxes, Fig. 1). The model is able to even reproduce, for a large number of boxes, the river nearly plug flow,<sup>55</sup> being solved algebraically for steady-state conditions or numerically for dynamic conditions.

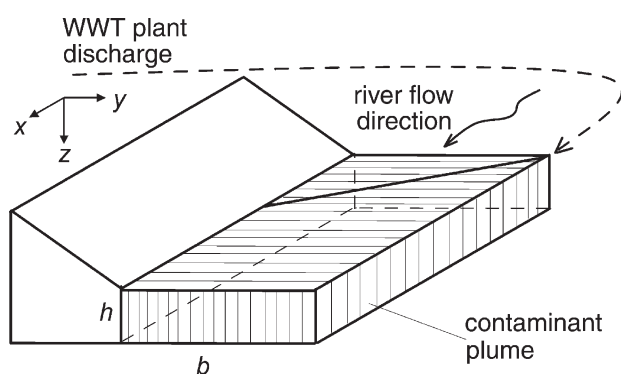


Fig. 1 – Schematic representation of the control section of the riverine pathway contaminated with a pollutant release from a WWT-plant (in a multi-segment model representation; the small size release point is located in the middle of the river)

Alternatively, the classical formulation of the pollutant dispersion models in the riverine pathways (or surface waters) is based on the differential mass balance for an infinitesimal element of the river. By considering a turbulent field, the concentration and velocity in any point fluctuate around the mean values, i.e.  $c = \bar{c} + c''$  and  $w = \bar{w} + w''$ . The general differential model is written for the mean values  $\bar{c}$  and  $\bar{w}$  in a turbulent motion, accounting for the advective, diffusional, phase transfer, accumulation and reaction terms:

$$\begin{aligned} & \frac{\partial \bar{c}}{\partial t} + \frac{\partial (\bar{c} \bar{w}_x)}{\partial x} + \frac{\partial (\bar{c} \bar{w}_y)}{\partial y} + \frac{\partial (\bar{c} \bar{w}_z)}{\partial z} = \\ & = \frac{\partial}{\partial x} \left( \bar{D}_x \frac{\partial \bar{c}}{\partial x} \right) + \frac{\partial}{\partial y} \left( \bar{D}_y \frac{\partial \bar{c}}{\partial y} \right) + \frac{\partial}{\partial z} \left( \bar{D}_z \frac{\partial \bar{c}}{\partial z} \right) + \sum_i r_i, \quad (3) \end{aligned}$$

where:  $\bar{c}$  = pollutant concentration at the moment  $t$  in the location  $(x, y, z)$ ;  $\bar{w}_x, \bar{w}_y, \bar{w}_z$  = fluid velocities over movement directions;  $\bar{D}_x, \bar{D}_y, \bar{D}_z$  = mass dispersion coefficients;  $r_i$  = reaction rates responsible

to the pollutant degradation in the river or characterizing the inter-phase exchanges. The adopted dispersion model can be of various complexity, according to the pollution source and river characteristics: dynamic or stationary models, one-dimensional 1D (accounting for only longitudinal direction  $x$ ), bi-dimensional 2D (longitudinal and lateral directions  $x, y$ ), tri-dimensional 3D (longitudinal, lateral, and vertical directions  $x, y, z$ ).<sup>59–61</sup> Particular models have also been developed to simulate the surface or submerge releases in the river (in the form of jets or plumes), and the transient zones where the jet energy is progressively diminished until its velocity becomes practically the same with that of the river.<sup>62</sup> These models are usually solved numerically by imposing initial and limit conditions specific to the pollution source (continuous or intermittent) and river topology. Even if more precise than the fugacity compartmental approach, the differential transport models meet difficulties with including changes in the flow volume, velocity, or river width or depth, requiring separate solutions for different river sections. However, advanced modelling can account for moving (time-dependent) boundary conditions of the dispersion region in (3), corresponding to variable discharges and distributed concentrations over river width/borders, thus allowing to couple subsequent river sections over simulation by means of flux continuation conditions.<sup>91</sup> Even if such complex differential models require a significant computational effort to simulate dynamic cases, numerical solutions can offer a sufficiently accurate representation of the pollutant dispersion with even including several phenomena, such as: absorption/desorption of gases/pollutant from/to atmosphere through the river surface; chemical and biological pollutant degradation; interaction with multiple receptors from the aquatic environment; pollutant adsorption in suspended solids, sediments, or living organisms.

A reduced version of the differential models, adopted in the present study, can offer a rapid simulation of the pollutant dispersion downstream a small-size continuous release point (see Fig. 1). The dynamic bi-dimensional advective-dispersive model is of the form:

$$\begin{aligned} & \frac{\partial c}{\partial t} + w_x \frac{\partial c}{\partial x} = D_y \frac{\partial^2 c}{\partial y^2} + \sum_i r_i; \\ & \frac{\partial c}{\partial y} = 0, \text{ for } y = 0; \\ & c = 0, \text{ for } y = b; \\ & c = c_0, \text{ for } x = 0, y = 0, \end{aligned} \quad (4)$$

where:  $y$  = lateral distance from middle-river;  $b$  = river half-width;  $w_x$  = water-mean velocity in the flow direction;  $D_y$  = apparent lateral dispersion coefficient. The accounted reaction or phase transport rates  $r_i$  lead to disappearance or appearance of the pollutant in the river (e.g. pollutant evaporation/runoff, biodegradation, uptake or clearance by/from biota, sediments, suspended solids, river-bed). Such a model is based on several simplification assumptions:<sup>63–64</sup>

i) a small-size discharge source, with a continuous release flow-rate ( $Q_{ef}$ ) including the pollutant flow-rate ( $Q_c$ ), and located in the middle of the river ( $x, y, z$ ) = (0, 0, 0); the release water temperature and dissolved oxygen (DO) are approximately the same with those of the river; the discharge presents a negligible jet effect in the dispersion region (corresponding to small Froude numbers);<sup>62</sup>

ii) contaminant release time in the riverine pathway is much longer than the travel time ( $\bar{t} = x/w_x$ ) in the control section, from the source to a receptor located at a relevant distance (analysed control length must be of  $x_{\max} \geq 20(d_e)$  to fulfill the nearly plug-flow hypothesis, where  $d_e = 2h(2b)/(2b + h)$ );<sup>65</sup>

iii) a uniform longitudinal flow with a constant flow-rate ( $Q$ ) and velocity ( $w_x$ ) over the analysed time interval (obtained from mediated recorded data);

iv) a prismatic river-geometry with an approximately constant rectangular cross-section, of width  $b$  and depth  $h$ ;

v) quasi-constant water quality parameters (temperature, pH, DO, pollutant mass concentration before the release point  $\gamma_{fond}$ ), averaged over the analysed time interval;

vi) negligible adsorption/desorption of the pollutant from the river to suspended solids (others than biota or sediments); if these are proved to be important, a supplementary pollutant exchange rate must be added to the mass balance term  $\sum_i r_i$ ;

vii) an advection which dominates dispersion in the longitudinal direction ( $D_x = 0$ );

viii) a fully mixed contaminant plume over the river depth (i.e. vertically homogeneous water concentration field);

ix) a constant lateral dispersion coefficient ( $D_y$ ) that includes the lateral turbulent mixing and diffusion; a value of  $D_y = 0.06 h w_x$  is adopted following the recommendations of Fischer<sup>66</sup>).

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

$$\begin{aligned} \frac{d\gamma_w}{dt} &= r_d + r_u + r_c = \\ &= -k_d \gamma_w - \sum k_{we} \Psi_e \gamma_w + \sum k_{ew} \Psi_e \xi_e, \end{aligned} \quad (5)$$

where: index 'e' denotes the phases in contact with the water, i.e. biota ('b'), sediments ('s'), or air ('a');  $\Psi_e$  = the ratio of quantities from the two phases being in contact (referred to the water volume). At limit, for  $t \rightarrow \infty$ , the thermodynamic constraints are fulfilled, i.e.  $K_{we} = k_{we}/k_{ew}$  for all the phases in contact. The last two terms in (5) account for the bioaccumulation kinetics in the phases 'e', i.e. the pollutant uptake and clearance rates. As another observation, more accurate rate expressions can also be considered for the biodegradation term ( $r_d$ ), as for instance the Monod-type kinetic models reported in the literature (see Table 1 for PCB data).<sup>46,51</sup>

### Case study: PCB pollutant fate downstream a low-level continuous release source

In order to study the dispersion and bioaccumulation dynamics of a persistent pollutant in a riverine pathway, a continuous low-level release of a PCB (i.e. PCB-101 or PCB-52 in this analysis) in the effluent of an industrial WWTP has been considered (incompletely removed by the chemical and biological treatment steps).

The input data, including the river characteristics and the constant flow rates are presented in Table 2. The continuous pollution source has been considered in the following alternatives: a) a constant mass flow-rate of  $Q_c = 1.5 \cdot 10^{-7}$  (kg s<sup>-1</sup>), leading to a mass concentration in the river (at source, after mixing) of 4.09 ng L<sup>-1</sup>; b) a constant flow-rate of  $Q_c = 0.5 \cdot 10^{-7}$  (kg s<sup>-1</sup> PCB) leading to a PCB concentration in the release point (after mixing) of 1.42 ng L<sup>-1</sup>. In both cases, the WWTP effluent flow-rate ( $Q_{ef}$ ) and the pollutant concentration in the river before the release point ( $\xi_{ef}$ ) have been kept at constant values.

The water characteristics in the river control section (of  $x_{\max} = 1000$  m) are considered stationary, at their annual average values, that is (Table 2): temperature (15 °C), pH (7.5), DO (9 mg L<sup>-1</sup>), river flow-rate ( $Q$ ), water velocity ( $w_x$ ), riverbed sizes ( $b, h$ ), biota ( $\Psi_b$ ) and sediment ( $\Psi_s$ ) content of the river, loads in suspended solids, ions and other components.

The released PCB-101 (2,2',4,5,5' penta-chlorobiphenyl) or PCB-52 (2,2',5,5' tetra-chlorobiphenyl) are two of the most persistent POPs (see the characteristics in Table 2, compared to the other PCBs presented in Table 1). PCB-101 presents low solu-

Table 1 – Typical values and correlations of the partition coefficients and bioaccumulation kinetic parameters for PCBs in the aquatic environment

Correlation	Observations	Reference																								
<i>Water(w) – biota(b) biphasic system:</i> <sup>a</sup>	$BCF \left[ \frac{\text{L}}{\text{kg ww}} \right] = K_{wb} = \frac{\zeta_b^* [\text{g kg}^{-1} \text{ ww}]}{\gamma_w^* [\text{g L}^{-1}]} = \frac{k_{wb} [\text{L d}^{-1} \text{ kg}^{-1} \text{ ww}]}{k_{bw} [\text{d}^{-1}]}$																									
$BCF = \varphi K_{ow}$ ; $BCF = 86/S_w$ $\log BCF = 0.542 \log K_{ow} + 0.124$ $\log BCF = 0.85 \log K_{ow} - 0.70$ $\log BCF = n \log K_{ow} + b$ , with various parameter values such as: $[n, b] = [0.907, -0.361], [0.837, -0.77], [1.16, -0.75], [0.85, -0.7], [0.542, 0.124]$	– fish, biota/organic pollutant (water) system; $\varphi$ = lipid content of the receptor organism (vol. fraction); usually $\varphi = 0.048$ (for fish); $K_{ow}$ = octanol-water partition coefficient of the pollutant; <sup>(b)</sup> $S_w$ = aqueous solubility of the chemical (mol m <sup>-3</sup> )	Mackay <sup>55,72</sup> Mackay and Fraser <sup>73</sup>																								
$\log BCF = 0.909 \log K_{ow} + 0.874$ $\log k_{wb} = 0.122 \log K_{ow} + 2.192$ $\log k_{bw} = -0.791 \log K_{ow} + 2.972$	– fish/PCB (water) system	Tolls and Sijm <sup>74</sup>																								
$\log BCF = 0.79 \log K_{ow} - 0.40$ , for $\log K_{ow} \leq 6.5$ $\log BAF = 1.07 \log K_{ow} - 0.21$	– aquatic organism/nonionic organics (EPA model)	Suter II <i>et al.</i> <sup>75</sup>																								
$\log BCF = 0.91 \log K_{ow} -$ $-1.975 \log (6.8 \cdot 10^{-7} K_{ow} + 1) - 0.786$	– fish/PCB,OCP (water) system; <sup>c</sup> $\zeta_f = 1.6 \div 7.6 \text{ ng g}^{-1} \text{ ww}$ ; $\gamma_w = 0 \div 6 \text{ ng L}^{-1}$ ; PCB# 28, 52, 101, 118, 138, 153	Verweij <i>et al.</i> <sup>76</sup>																								
$BCF = 2050 \div 7580$	– fish/PCB (water) system; $\zeta_f = 40 \div 826 \text{ ng g}^{-1} \text{ ww}$ ; $\gamma_w = 1 \div 10 \text{ ng L}^{-1}$	Bremle <i>et al.</i> <sup>7</sup>																								
$\log BCF = 1.085 \log K_{ow} - 3.770$ , for $\log K_{ow} < 6.4$ $\log BCF = 0.343 \log K_{ow} + 0.913$ , for $\log K_{ow} \geq 6.4$	– clams, phytoplankton/pesticide & herbicide POPs (water) system; $\zeta_b = 0 \div 100 \text{ } \mu\text{g kg}^{-1} \text{ ww}$ ; tested POPs: <sup>c</sup> atrazine, simanzine, terbuthylazine	Carafa <i>et al.</i> <sup>68</sup>																								
$\log BCF = \begin{cases} 0.50 \text{ for } \log K_{ow} < 1 \\ 0.77 \log K_{ow} - 0.70 + \sum F_i, \\ \text{for } \log K_{ow} = 1-7 \\ -1.37 \log K_{ow} + 14.4 + \sum F_i, \\ \text{for } \log K_{ow} > 7 \\ 0.50, \text{ for } \log K_{ow} > 10.5 \end{cases}$	– fish/nonionic compounds; the correction factors $F_i$ (between $-1.65$ and $2$ ) are chosen in accordance to the pollutant chemical structure	Suter II <i>et al.</i> <sup>75</sup>																								
$\log BCF = 0.76 \log K_{ow} - 0.52$	– fish/nonionic compounds (water) system	Lopes <i>et al.</i> <sup>77</sup>																								
$\log BCF = 0.16 \div 5.92$ (experimental; 122 nonionic compounds) $\log BCF = 2.69 \div 5.92$ (experimental; 36 PCB compounds)	– fish/nonionic compounds (water) system; individual $BCF$ experimental values for 122 compounds from which 36 PCBs	Liu <i>et al.</i> <sup>78</sup>																								
<table border="1" style="display: inline-table; vertical-align: top;"> <thead> <tr> <th>PCB chlorine positions</th> <th>IUPAC#</th> <th><math>k_{wb}</math></th> <th><math>k_{bw}</math></th> </tr> </thead> <tbody> <tr> <td>2,5-di</td> <td>9</td> <td>920</td> <td>0.066</td> </tr> <tr> <td>2,2',5-tri</td> <td>18</td> <td>950</td> <td>0.048</td> </tr> <tr> <td>2,4',5-tri</td> <td>31</td> <td>890</td> <td>0.021</td> </tr> <tr> <td>2,2',5,5'-tetra</td> <td>52</td> <td>740</td> <td>0.015</td> </tr> <tr> <td>2,3',4',5-tetra</td> <td>70</td> <td>420</td> <td>0.010</td> </tr> </tbody> </table>	PCB chlorine positions	IUPAC#	$k_{wb}$	$k_{bw}$	2,5-di	9	920	0.066	2,2',5-tri	18	950	0.048	2,4',5-tri	31	890	0.021	2,2',5,5'-tetra	52	740	0.015	2,3',4',5-tetra	70	420	0.010	– fish/PCB (water) system; $\zeta_f = 0 \div 2510 \text{ } \mu\text{g g}^{-1} \text{ ww}$ ; $\gamma_w = 0.2 - 50 \text{ } \mu\text{g L}^{-1}$ ; $k_{wb}$ (L d <sup>-1</sup> kg <sup>-1</sup> ww); $k_{bw}$ (d <sup>-1</sup> )	Bruggeman <i>et al.</i> <sup>79</sup>
PCB chlorine positions	IUPAC#	$k_{wb}$	$k_{bw}$																							
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$\log BAF = 4.7 \div 6.8$ (L kg <sup>-1</sup> ) $k_{wb} = 90 - 7000$ (L h <sup>-1</sup> kg <sup>-1</sup> dw); $k_{bw} = 0.001 - 0.006$ (h <sup>-1</sup> )	– blue mussel/PCB (water) system; individual parameter values for PCB# 31, 49, 153	Björk and Gilek <sup>80</sup>																								
$k_{wb} = 33$ (L h <sup>-1</sup> kg <sup>-1</sup> ww); $k_{bw} = 0.005$ (h <sup>-1</sup> )	– fish/PCB 52 (water)/sediment system; $\zeta_f = 0 \div 0.5 \text{ } \mu\text{g g}^{-1} \text{ ww}$ ; EEDP <sup>81</sup> $\gamma_w = 0.05 - 0.5 \text{ } \mu\text{g L}^{-1}$ ; $\zeta_s = 0 - 1.5 \text{ } \mu\text{g g}^{-1} \text{ dw}$																									
$k_{bw} = 0.005 - 0.029$ (d <sup>-1</sup> )	– fish/PCB (water) system; $\zeta_f = 0 - 100 \text{ ng g}^{-1} \text{ ww}$ ; individual $k_{bw}$ values for PCB# 18, 28, 44, 52, 66, 101, 105, 118, 128, 138, 153, 187, 189, 195, 206, 209	Fisk <i>et al.</i> <sup>69</sup>																								

Table 1 (continued)

Correlation	Observations	Reference
$k_{wb} = 380 \text{ (L d}^{-1} \text{ kg}^{-1} \text{ ww)}$ ; $k_{bw} = 0.018 \text{ (d}^{-1}\text{)}$	– fish/PCB 70 (water) system; $\zeta_f = 0 \div 20 \text{ } \mu\text{g g}^{-1} \text{ ww}$ ; $\gamma_w = 2\text{--}10 \text{ } \mu\text{g L}^{-1}$	Opperhuizen <i>et al.</i> <sup>82</sup>
$k_{wb} = 12.2 \text{ (L h}^{-1} \text{ kg}^{-1} \text{ ww)}$ ; $\log BCF = 0.76 \log K_{ow} - 0.23$ $\log BCF = 0.542 \log K_{ow} + 0.124$ $\log BCF = -0.508 \log S_w + 3.41$	– $k_{wb}$ for fish/tetra-CB (water) system; BCF for various POPs <sup>c</sup> ; $S_w$ = aqueous solubility of the chemical ( $\mu\text{mol L}^{-1}$ )	Neely <sup>83</sup>
<i>Water(w) – sediment(s) biphasic system:</i>	$K_{ws} \left[ \frac{\text{L}}{\text{kg dw}} \right] = \frac{\zeta_s^* [\text{g kg}^{-1} \text{ dw}]}{\gamma_w^* [\text{g L}^{-1}]} = \frac{k_{ws} [\text{L d}^{-1} \text{ kg}^{-1} \text{ dw}]}{k_{sw} [\text{d}^{-1}]}$	
$K_{ws} = wK_{oc} = w(0.41 K_{ow})$ ; $K_{oc} \left[ \frac{\text{L}}{\text{kg organic carbon}} \right] = \frac{\zeta_{s,o}^*}{\gamma_w^*}$ ; $K_{oc} \left[ \frac{\text{L}}{\text{kg organic carbon}} \right] = \frac{\zeta_{s,o}^*}{\gamma_w^*} \approx K_{ow}$	– organic compound (water)/sediment system; $K_{oc}$ = the sediment organic carbon – water partition coefficient; Nagpal <sup>8</sup> $\zeta_{s,o}^*$ = equilibrium concentration in sediment based upon organic carbon content; $w$ = organic matter content in sediment (mass fraction); usually $w = 0.04$	Mackay <sup>55</sup>
$\log K_{ws} = 0.715 \log K_{ow} = 1.29$ ; $BSAF = \frac{\zeta_b^* [\mu\text{g g}^{-1} \text{ lipid}]}{\zeta_s^* [\mu\text{g g}^{-1} \text{ organic carbon}]} = \frac{K_{wb}}{K_{ws}} = 0.1\text{--}80$	– PCB, PAH <sup>c</sup> (water)/sediment system; individual $K_{ws}$ and BSAF values (fish) for PCB# 28, 52, 101, 118, 138, 153	Verweij <i>et al.</i> <sup>76</sup>
$k_{sw} \text{ (slow)} = 0.0014\text{--}0.0043 \text{ (h}^{-1}\text{)}$ ; $k_{sw} \text{ (rapid)} = 0.09\text{--}0.25 \text{ (h}^{-1}\text{)}$ ; $BSAF = \frac{\zeta_b^* [\mu\text{g g}^{-1} \text{ lipid}]}{\zeta_s^* [\mu\text{g g}^{-1} \text{ organic carbon}]} = \frac{K_{wb}}{K_{ws}} = 1.1\text{--}2.65$	– PCB (water)/aquatic biota/sediment system; individual $k_{sw}$ and BSAF values (fish) for PCB# 44, 49, 52, 66, 70, 87, 95, 97, 99, 101, 105, 110, 118, 128, 138, 153, 156, 170; $\zeta_b = 330\text{--}5000 \text{ } \mu\text{g kg}^{-1} \text{ lipid}$ ; $\zeta_s = 250\text{--}2400 \text{ } \mu\text{g kg}^{-1} \text{ TOC}^a$	You <i>et al.</i> <sup>84</sup>
$k_{ws} = 27600 \text{ (L d}^{-1} \text{ kg}^{-1} \text{ dw)}$ ; $k_{sw} = 2.6 \text{ (d}^{-1}\text{)}$	– fish/PCB 52 (water)/sediment system; $\zeta_f = 0 \div 0.5 \text{ } \mu\text{g g}^{-1} \text{ ww}$ ; EEDP <sup>81</sup> $\gamma_w = 0.05 \div 0.5 \text{ } \mu\text{g L}^{-1}$ ; $\zeta_s = 0 \div 1.5 \text{ } \mu\text{g g}^{-1} \text{ dw}$	
<i>Overall biodegradation constant: <math>k_d [\text{d}^{-1}]</math></i>		
$k_d = 10^{-4}\text{--}10^{-1} \text{ (h}^{-1}\text{)}$ ; $k_{evap} = 10^{-3}\text{--}3 \cdot 10^{-2} \text{ (h}^{-1}\text{)}^{(d)}$	– bacterial cultures ( <i>Pseudomonas stutzeri</i> )/PCB (water) system; $\gamma_w = 0 \div 90 \text{ } \mu\text{g L}^{-1}$ ; individual $k_d$ values for PCB# 4–10, 15–19, 22, 24–28, 32, 33, 40–42, 44–46, 48–49, 51–53, 55–56, 60, 63, 64, 66–67, 70–72, 74, 76, 84, 91–92, 97	Dercova <i>et al.</i> <sup>70</sup>
$k_d = 0.42\text{--}8 \text{ (h}^{-1}\text{)}$	– bacterial cultures ( <i>Alcaligenes sp.</i> JB1)/PCB (water) system; $\gamma_w = 0.5 \div 25 \text{ } \mu\text{g L}^{-1}$ ; $\zeta_b = 0.007 \div 2 \text{ } \mu\text{g L}^{-1}$ ; individual $k_d$ values for PCB# 40, 52, 54, 100, 101, 119, 121, 128, 136 (from Monod kinetics)	Commandeur <i>et al.</i> <sup>51</sup>
$k_d = 0.02\text{--}0.04 \text{ (d}^{-1}\text{)}$	– microbial cultures ( <i>Bacillus megaterium</i> )/PCB (sludge) system; $I_s = 0.04 \div 45 \text{ } \mu\text{g g}^{-1} \text{ dw}$ ; individual $k_d$ values for Aroclor# 1242, 1248, 1254, 1260	Nakhla <i>et al.</i> <sup>47</sup>
$k_d \approx 0.04\text{--}4.5 \text{ (h}^{-1}\text{)}$	– bacterial cultures ( <i>Burkholderia sp.</i> LB400, <i>Pseudomonas fluorescens</i> F113pcb and F113::1180)/PCB (water) system; $\gamma_w = 0.94 \div 1.63 \text{ mg L}^{-1}$ (from Monod kinetics)	Rein <i>et al.</i> <sup>46</sup>
$k_d \approx 0.005\text{--}0.1 \text{ (y}^{-1}\text{)}$	– natural process in surface waters (PCB/water system); $\gamma_w = 0.94 \div 1.63 \text{ mg L}^{-1}$	NEHC <sup>56</sup>

<sup>a</sup> BCF values are derived from conventional laboratory studies, while BAF are BCF values derived from field studies;<sup>75</sup> ww = wet mass (of biota); dw = dry mass (of sediment); superscript (\*) indicates the equilibrium value; TOC = total organic carbon;

<sup>b</sup>  $K_{ow}$  values for 205 PCB congeners are given by Eisler and Belisle<sup>85</sup> and NEHC;<sup>56</sup> experimental values for some PCBs are given by various contributors;<sup>46,72,76,84,86,87,88</sup> values and correlations of BCF with  $K_{ow}$  for a large number of chemicals are given by Devillers *et al.*<sup>89</sup>

<sup>c</sup> PCB = polychlorinated biphenyls; OCP = organochlorine pesticides; POP = persistent organic pollutants; PAH = polycyclic aromatic hydrocarbons;

<sup>d</sup>  $k_{evap}$  = overall rate constant of PCB evaporation in air from water system.

Table 2 – Input data for the simulation model of the pollutant fate in the riverine pathway

(a) River topological/water data			(b) Pollution source data		
Symbol	Significance	Value	Symbol	Significance	Value
$x$	longitudinal flow-direction ( $x = 0$ at pollutant release location)	$0 \leq x \leq x_{\max} = 1000$ (m)	$Q_c$	discharged pollutant/ contaminant flow-rate	$1.5 \cdot 10^{-7}$ (kg s <sup>-1</sup> ), or $0.5 \cdot 10^{-7}$ (kg s <sup>-1</sup> )
$y$	lateral distance from mid-river ( $y = 0$ ) to a lateral receptor	$0 \leq y \leq b$	$Q_{ef}$	discharged water flow-rate (at $x = 0$ ) (average)	$2.5$ (m <sup>3</sup> s <sup>-1</sup> )
$z$	vertical distance from the water surface ( $z = 0$ )	$0 \leq z \leq h$	$\gamma_{ef}$	pollutant concentration in the discharged water (average, before mixing)	$\gamma_{ef} = Q_c / Q_{ef}$
$b$	river half-width	$50/2$ (m)	$\gamma_{fond}$	pollutant concentration before the release point	$0.1$ ng L <sup>-1</sup> (average)
$\bar{h}$	average river depth in the control section	$\bar{h} = (Q + Q_{ef}) / (2bw)$	$\gamma_o$	pollutant concentration at the re- lease point ( $x = 0$ ) after mixing; $(Q\gamma_{fond} + Q_c) / (Q + Q_{ef})$	$4.09$ ng L <sup>-1</sup> or $1.42$ ng L <sup>-1</sup>
$Q$	river average flow-rate	$35$ (m <sup>3</sup> s <sup>-1</sup> )	$\gamma_{\max}$	max allowable PCB concentration in the river	$1$ ng PCB L <sup>-1</sup>
$w_x$	river mean velocity in the flow direction	$0.2$ (m s <sup>-1</sup> )	$\gamma(x, y, t)$	2D dynamic concentration field of the pollutant, downstream the release point (avg. on the depth)	dispersion model solution (kg m <sup>-3</sup> )
$D_y$	lateral dispersion coefficient	$D_y = 0.06 hu =$ $4.5 \cdot 10^{-2}$ (m <sup>2</sup> s <sup>-1</sup> )			
(c) PCB pollutant characteristics					
Symbol	Significance	Value (Reference)			
		PCB-101 (penta-CB)	PCB-52 (tetra-CB)		
$k_d$	overall biodegradation rate constant (average)	$1.3 \cdot 10^{-5}$ (d <sup>-1</sup> ) <sup>a</sup>	$2.74 \cdot 10^{-4}$ (d <sup>-1</sup> ) <sup>a</sup>		
$k_{wb}$	water-biota overall uptake rate constant	$966$ (L d <sup>-1</sup> kg <sup>-1</sup> ww) <sup>b</sup>	$740$ (L d <sup>-1</sup> kg <sup>-1</sup> ww) <sup>b</sup>		
$k_{bw}$	biota-water clearance rate constant	$0.0038$ (d <sup>-1</sup> ) <sup>b</sup>	$0.015$ (d <sup>-1</sup> ) <sup>b</sup>		
$\log(BCF)$	water-biota bioconcentration factor	$5.4$ (L kg <sup>-1</sup> ww) <sup>c</sup>	$4.69$ (L kg <sup>-1</sup> ww) <sup>c</sup>		
$k_{ws}$	water-sediment overall uptake rate constant	$5823$ (L d <sup>-1</sup> kg <sup>-1</sup> dw) <sup>d</sup>	$3256$ (L d <sup>-1</sup> kg <sup>-1</sup> dw) <sup>d</sup>		
$k_{sw}$	sediment-water clearance rate constant	$0.0624$ (d <sup>-1</sup> ) <sup>d</sup>	$0.1032$ (d <sup>-1</sup> ) <sup>d</sup>		
$\log(K_{ws})$	water-sediment bioconcentration factor	$4.97$ (L kg <sup>-1</sup> dw) <sup>d</sup>	$4.50$ (L kg <sup>-1</sup> dw) <sup>d</sup>		
$\Psi_b$	biota content of river relatively to the water	$5 \cdot 10^{-5}$ (kg ww L <sup>-1</sup> water) <sup>e</sup>	$5 \cdot 10^{-5}$ (kg ww L <sup>-1</sup> water) <sup>e</sup>		
$\Psi_s$	active sediment content of river relatively to the water	$4.7 \cdot 10^{-2}$ (kg dw L <sup>-1</sup> water) <sup>f</sup>	$4.7 \cdot 10^{-2}$ (kg dw L <sup>-1</sup> water) <sup>f</sup>		
$\log(K_{ow})$	octanol to water partition coefficient	$6.5$ (g)	$5.92$ (g)		
$\log(K_{oc})$	organic carbon to water partition coefficient	$4.94$ (g)	$4.65$ (g)		
$\log(K_{doc})$	dissolved organic carbon to water partition coefficient	$5.36$ (g)	$4.79$ (g)		
$M$	pollutant molar mass	$326.43$ (g mol <sup>-1</sup> )	$291.99$ (g mol <sup>-1</sup> )		
$S_w$	solubility in water	$26.1$ (μg L <sup>-1</sup> ) <sup>g</sup>	$66.7$ (μg L <sup>-1</sup> ) <sup>g</sup>		
$p_v$	vapour pressure	$2.96 \cdot 10^{-3}$ (Pa) <sup>g</sup>	$2.08 \cdot 10^{-2}$ (Pa) <sup>g</sup>		
$H$	Henry's constant	$37$ (Pa m <sup>3</sup> mol <sup>-1</sup> ) <sup>g</sup>	$91$ (Pa m <sup>3</sup> mol <sup>-1</sup> ) <sup>g</sup>		

<sup>a</sup> See Table 1 and reference NEHC;<sup>56</sup> complex correlation with temperature, pH, DO (dissolved oxygen).<sup>b</sup> See Table 1 and correlations of Tolls & Sijm<sup>74</sup> (PCB101) and Bruggeman *et al.*<sup>79</sup> (PCB52);  $k_{bw}$  was derived to fulfill the relationship  $BCF = k_{wb} / k_{bw}$ ;<sup>c</sup> See Table 1 and experimental value of Liu *et al.*<sup>78</sup> (PCB101) and Bruggeman *et al.*<sup>79</sup> (PCB52);<sup>d</sup> See Table 1 and correlations of You *et al.*<sup>84</sup>;  $K_{ws}$  was computed from  $K_{ws} = K_{wb} / BSAF$  relationship by using the experimental  $K_{wb}$  and  $BSAF$  values;  $k_{ws}$  was derived to fulfill the relationship  $K_{ws} = k_{ws} / k_{sw}$ ;<sup>e</sup> the average biota density  $\rho_b = 1000$  kg m<sup>-3</sup> and volumetric fraction in water  $y_{bw} = 10^{-4}$  (plants, fauna) have been adopted following the Mackay<sup>55</sup> and NEHC<sup>56</sup> case studies;<sup>f</sup>  $\delta_s = 0.1$  m is the active sediment depth;<sup>56</sup>  $\rho_s = 1500$  kg m<sup>-3</sup>;<sup>g</sup> NEHC.<sup>56</sup>



bility and vapour pressure, low biodegradability (small  $k_d$ ), but high bioaccumulation potential in biota and sediments (large  $k_{wb}$  and  $k_{ws}$ ) compared to their small clearance rates (small  $k_{bw}$  and  $k_{sw}$ ). A value of  $\log(BCF) = 5.4 \gg 2-3^{67}$  and  $\log(K_{ow}) = 6.5 > 5.0-5.5^{68-69}$  clearly indicates a pollutant with high bioaccumulation and biomagnification potential. Concerning PCB-52, even if not exhibiting such a severe contamination potential, its  $\log(BCF) = 4.69$  and  $\log(K_{ow}) = 5.92$  still indicates a highly persistent pollutant with a significant environmental hazard index.

To simply prove the long-term danger of the highly persistent PCB in the aquatic environment, various simulations of its dispersion-bioaccumulation scenarios have been performed, by considering the fate model (4-5) and including lumped biota (fauna and plants) and sediments, that is:

$$\frac{d\gamma_w}{dt} = -k_d\gamma_w - k_{wb}\Psi_b\gamma_w - k_{ws}\Psi_s\gamma_w + k_{bw}\Psi_b\zeta_b + k_{sw}\Psi_s\zeta_s \quad (6)$$

where  $\gamma_w$  (g L<sup>-1</sup>),  $\zeta_b$  (g kg<sup>-1</sup> ww),  $\zeta_s$  (g kg<sup>-1</sup> dw) are the PCB mass concentrations in water, biota and sediment respectively. The rate constants in the previous relationship have been considered at values that correspond to the river average parameters of Table 2. The PCB evaporation and the exchange terms with the suspended solids have been neglected due to their small contributions (for small concentrations  $k_{evap} \ll 0.001$  d<sup>-1</sup>).<sup>70</sup>

The numerical solution of the formulated dispersion-bioaccumulation model (4,6) strongly depends on the pollution source and river parameter variability. By considering constant river and WWTP effluent flow-rates of stationary characteristics, and only first-order reaction/exchange rates, a combined numerical – analytical solution can be derived. To simulate the pollutant fate over ca. 1000 days, a time discretization uniform step of  $\Delta t = 1$  day has been adopted. During one integration step, the pollutant dispersion can be considered at quasi-stationary state ( $d\gamma_w/dt \approx 0$ ), the contaminant release time being longer than the travel time ( $\bar{t} = x/w_x$ ) in the river control section (of ca. 1000 m downstream the source). Thus, the analytical solution of model (4) can be obtained in the form:<sup>63,64,71</sup>

$$\gamma_w(x, y, \bar{t}) = \left( \gamma_{fond} \frac{Q}{Q + Q_{ef}} + \gamma_{disp}(x, y) \right) \exp(-k_M \bar{t}) + \frac{k_c}{k_M} (1 - \exp(-k_M \bar{t}));$$

$$\gamma_{disp}(x, y) = \frac{Q_c}{(Q + Q_{ef})\pi} \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{2n-1} \cdot \exp\left(-n^2 \frac{\pi^2 D_y}{b^2} \frac{x}{w_x}\right) \cos\left(n_1 \frac{\pi}{b} y\right); \quad n_1 = \frac{2n-1}{2}; \quad (7)$$

$$k_M = k_d + k_{wb}\Psi_b + k_{ws}\Psi_s;$$

$$k_c = k_{bw}\Psi_b\zeta_b + k_{sw}\Psi_s\zeta_s,$$

where:  $k_M$  = the apparent McKinney rate constant;<sup>64</sup>  $k_c$  = the apparent clearance rate of pollutant from the phases in contact with the water. The  $k_c$  constant has been constructed by considering quasi-constant concentrations of PCB in biota and sediments over one time-step, being taken at the previous values, i.e.  $\zeta_b(x, y, t - \Delta t)$  and  $\zeta_s(x, y, t - \Delta t)$  for every river location. The initial and limit conditions used in obtaining the solution (7) are those indicated in eq. (4). It is to observe that, the dispersion term in (7) tends to decrease to zero for large residence times  $\bar{t} \rightarrow \infty$  when only phase-exchange terms remain significant.

The bioaccumulation dynamics were considered during the integration of the dispersion model, by incrementing the PCB concentrations in biota and sediments for every time-step according to the dynamic model:

$$\frac{d\zeta_b}{dt} = k_{wb}\tilde{\gamma}_w - k_{bw}\zeta_b; \quad \zeta_b|_{t=0} = \zeta_b(x, y, 0) = 0;$$

$$\frac{d\zeta_s}{dt} = k_{ws}\tilde{\gamma}_w - k_{sw}\zeta_s; \quad \zeta_s|_{t=0} = \zeta_s(x, y, 0) = 0. \quad (8)$$

To derive an analytical solution of (8), the PCB mass concentrations in water for each spatial location of the river downstream the release point are kept constant over one time-step, at values corresponding to the current time step [i.e.  $\tilde{\gamma}_w(x, y) = \gamma_w(x, y, t)$ ], while the initial conditions correspond to the end of the previous step. Thus, the solution of model (8) becomes:

$$\zeta_b(x, y, t) = \frac{k_{wb}\tilde{\gamma}_w(x, y)}{k_{bw}} (1 - \exp(-k_{bw}t)) + \zeta_{b,o}(x, y) \exp(-k_{bw}t);$$

$$\zeta_s(x, y, t) = \frac{k_{ws}\tilde{\gamma}_w(x, y)}{k_{sw}} (1 - \exp(-k_{sw}t)) + \zeta_{s,o}(x, y) \exp(-k_{sw}t); \quad (9)$$

For long bioaccumulation times  $t \rightarrow \infty$  the solution (9) tends to reach the phase equilibrium limits, that is  $BCF = K_{wb} = k_{wb}/k_{bw} = \zeta_b^*/\gamma_w^*$  and  $K_{ws} = k_{ws}/k_{sw} = \zeta_s^*/\gamma_w^*$ . It is to mention that, experimental investigations for PCB bioaccumulation in

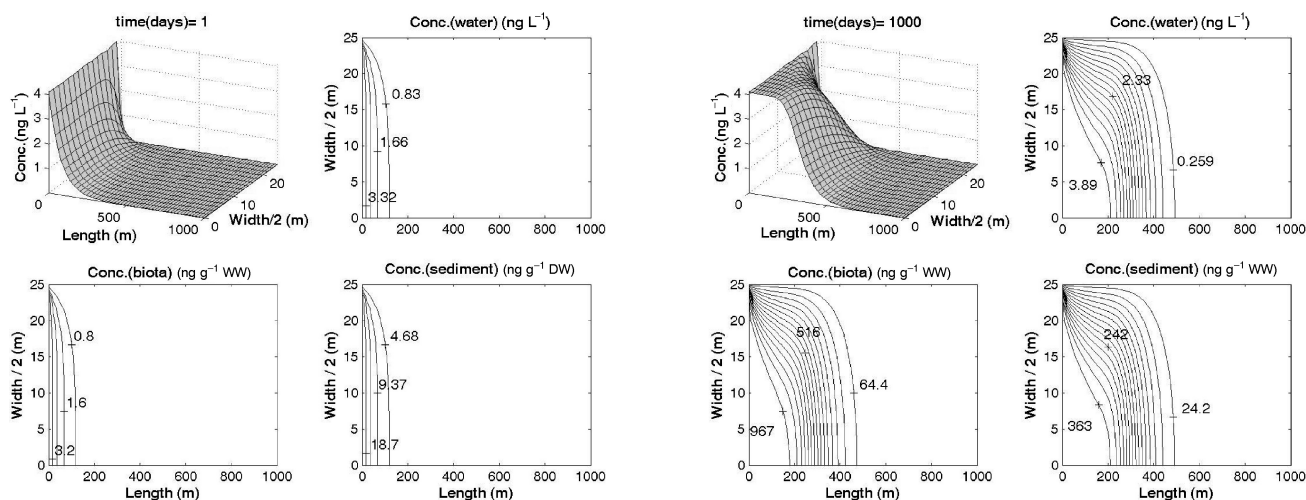


Fig. 2 – Pollutant (PCB 101) concentration field dynamics in the river, biota and sediment, downstream the release point: after one day of continuous release (left); after 1000 days of continuous release (right), for a discharged pollutant flow-rate of  $Q_c = 1.5 \cdot 10^{-7} \text{ kg s}^{-1}$

fish reported transient times between 15 and 256 days to reach the equilibrium after exposure to different pollutant concentrations.<sup>68</sup>

The solving procedure starts from the initial conditions of the river phases and WWTP discharge. Then, by successively evaluating the phase concentration fields (7) and (9) for every time-increment, one finally obtains the dynamic evolution of the PCB distribution in water  $\gamma_w(x,y,t)$ , biota  $\zeta_b(x,y,t)$ , and sediment  $\zeta_s(x,y,t)$  on a long term.

By considering the input data and model parameters of Table 2, simulation of PCB release in the alternative of a constant contaminant flow-rate of  $Q_c = 1.5 \cdot 10^{-7} \text{ (kg s}^{-1}\text{)}$ , leads to the concentration fields of Fig. 2 (plots after 1 day and 1000 days release time for PCB-101 pollutant). Axial PCB concentrations in the riverbed (for  $y = 0$ ), downstream the release point ( $x > 0$ ), are displayed in Fig. 3 for all the phases in contact, comparatively for PCB-101 and PCB-52 contaminant cases. It is to observe that, after 1 day of discharge, the critical pollution front is located very close to the source; practically, after more than 100–200 m downstream the PCB concentration in the river is below the threshold ( $1 \text{ ng L}^{-1}$  in water). However, even if the discharge load is quite modest (ca.  $4 \text{ ng L}^{-1}$  at source), the situation tends to change dramatically in the long term due to the PCB low degradability and high bioaccumulation capacity. Thus, after 1000 days of continuous release, the phase-equilibrium is practically reached over 200–300 m downstream the source (the critical thresholds being exceeded in water and biota, see Fig. 3 plots), and the pollution front continue to move down river. In such a way, by applying the simulation model, it is quite easy to predict the negative effects of such a

PCB low-level release over much longer time intervals. It is also to observe that the PCB-101, with a higher persistence capacity, always exhibits higher concentrations in the polluted area in all phases, even if the affected river section is smaller compared to the PCB-52 case.

Simulation of the PCB release is repeated in the alternative of a smaller released contaminant flow-rate of  $Q_c = 0.5 \cdot 10^{-7} \text{ (kg s}^{-1}\text{)}$  (i.e. 1/3 of the previous case), under the same river conditions of Table 2. Simulations lead to predict similar concentration fields and axial PCB concentration profiles in water, biota and sediment phases, at levels of approx. 1/3 of those presented in Fig. 3. The conclusions are similar, even if the pollution is of a re-

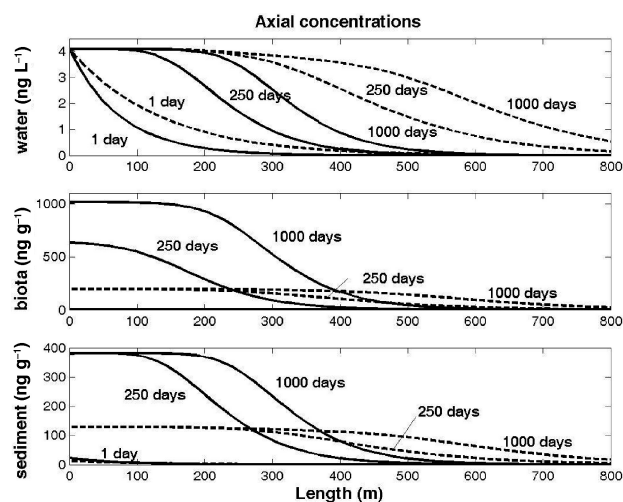


Fig. 3 – PCB101 (-) and PCB52 (---) mass concentration (ratio) dynamics along the river longitudinal axis ( $y = 0$ ) in water, biota and sediment downstream the release point (for a discharged pollutant flow-rate of  $Q_c = 1.5 \cdot 10^{-7} \text{ kg s}^{-1}$ ; ca.  $4 \text{ ng L}^{-1}$  PCB at source)

duced level in water (ca.  $1.5 \text{ ng L}^{-1}$ ) and the equilibrium concentrations are smaller, exceeding the regulation thresholds in biota and sediments only for PCB-101 case. In conclusion, an even lower level accidental release in the river is still of high concern due to the significant negative effects of the very persistent POPs including the tendency of the pollution-front to move downstream in a long term.

## Conclusions

A reduced 2D model, combining the spatial dispersion with the bioaccumulation dynamics, can be a worthy instrument to quickly simulate the pollutant transport and its fate in a riverine pathway, downstream a small-size contamination source. The model can easily reproduce stationary but also dynamic contamination conditions by means of suitably chosen integration time-step and inter-phase exchange kinetic terms. The model seems to be quite flexible, and can easily be extended to account for variations in flow-rates and pollutant loads by keeping their quasi-stationarity over one integration step (i.e. over  $\Delta t = 1$  day in this example). However, more precise solutions that account for complex biodegradation processes and multiple receptors over the river sections require application of more elaborate numerical integration procedures to solve the partial differential equation mass balances.

The model can be coupled with a statistical analysis associated to the accidental release of a pollutant, in order to derive the risk contours downstream the river in various release scenarios that concern discharges from a WWTP with incomplete treatment of certain pollutants.<sup>64</sup>

In the approached case study, a PCB (relevant PCB-101 or PCB-52) is released in the effluent of a WWTP due to its incomplete removal by classical treatment. The dispersion and fate of this POP pollutant in the riverbed can be easily simulated under various release scenarios. It is proved that, even for a low level quasi-continuous pollution (ca.  $1.4\text{--}4 \text{ ng L}^{-1}$  compared to  $1 \text{ ng L}^{-1}$  threshold in the water), the quick dispersion of the pollutant over a small-size river section is not without risk and can become a real danger over the long-term. Such a result is explained by the POP's very low biodegradability and high bioaccumulation capacity in biota and sediments that make their presence in aquatic environments very long. Simulations also prove that a longer release interval (more than 15 days) leads to reaching of the phase-equilibrium in the discharge section (near the source) and then to a continuous moving-down of the pollution front. As a result, the

entire riverbed can be slowly but continuously contaminated by means of the pollution propagation effect. As the persistence potential is higher (e.g. PCB-101 compared to PCB-52), the more severe are the contamination effects over a longer term.

As a general conclusion, in the case of a river polluted with POPs even at a very low level, it is risky to consider that only a small section of the river is contaminated and only near the release point. Such a simulation model can offer a longer-term perspective on the effects of such a quasi-continuous release on various river compartments.

Even if only two POPs have been approached in the presented case study, the pollutant fate and WWTP-effluent risk analysis can be applied to a larger category of contaminants if the model parameters are suitably set (based on experimental data or on QSAR predictions). Supplementary terms can easily be accounted for, such as pollutant adsorption in various organisms and riverbed compartments, or volatilisation through the water-surface. The analysis can be repeated if necessary in various river sections. In this case, the flux continuity boundary conditions among successive sections, and the travel times through the succeeding media, should be explicitly accounted in the model.

The predictions offered by such a pollutant dispersion/bioaccumulation model, coupled with those of the WWTP, can offer a base to simulate various plant failure scenarios and a consequence analysis. Such evaluations can be used to derive site-specific risk assessments, can support failure prevention measures, WWTP optimization and risk management, and can indicate suitable monitoring locations of river pollution.

## Nomenclature

- $b$  – river half-width, m
- $BCF = K_{wb}$  – bioaccumulation partition constant (water to biota),  $\text{L kg}^{-1}$
- $c_i$  – pollutant concentration in the phase  $i$ ,  $\text{mol L}^{-1}$
- $D_x, D_y, D_z$  – mass dispersion coefficients over Cartesian directions,  $\text{m}^2 \text{ s}^{-1}$
- $D_{Ai}$  – advective transport in the phase or compartment  $i$  (eq. 2),  $\text{mol d}^{-1} \text{ Pa}^{-1}$
- $D_{Ri}$  – reaction process in the phase or compartment  $i$  (eq. 2),  $\text{mol d}^{-1} \text{ Pa}^{-1}$
- $D_{ji}$  – transport coefficient from compartment  $j$  into compartment  $i$  (eq. 2),  $\text{mol d}^{-1} \text{ Pa}^{-1}$
- $f$  – fugacity, Pa
- $F$  – correction factors in empirical correlations of BCF (Table 1)
- $h$  – average river depth, m
- $k_d$  – biodegradation rate constant,  $\text{d}^{-1}$

- $k_M$  – pollutant removal overall rate constant (i.e. McKinney constant),  $d^{-1}$
- $k_{ij}$  – rate constant of the pollutant transfer from phase  $i$  to phase  $j$ ,  $d^{-1}$ ,  $d^{-1} \text{ kg}^{-1}$
- $K_{ij}$  – partition coefficient,  $L \text{ kg}^{-1}$
- $K_i$  – advection or any additional first-order rate constant occurring within phase or compartment  $i$ ,  $d^{-1}$
- $K_{doc}$  – water to dissolved organic carbon partition coefficient of the pollutant,  $L \text{ kg}^{-1}$
- $K_{oc}$  – water to organic carbon partition coefficient of the pollutant,  $L \text{ kg}^{-1}$
- $K_{ow}$  – octanol-water partition coefficient of the pollutant
- $l$  – length, m
- $M$  – molar mass,  $\text{g mol}^{-1}$
- $n_T$  – pollutant quantity, amount of substance, mol
- $p_v$  – vapour pressure, Pa
- $Q$  – river average flow-rate,  $\text{m}^3 \text{ s}^{-1}$
- $Q_c$  – discharged pollutant/contaminant flow-rate,  $\text{mol d}^{-1}$ ,  $\text{kg s}^{-1}$
- $Q_{ef}$  – discharged water flow-rate,  $\text{m}^3 \text{ s}^{-1}$
- $r$  – reaction or inter-phase transport rate,  $\text{mol L}^{-1} \text{ d}^{-1}$ ,  $\text{g L}^{-1} \text{ d}^{-1}$
- $S_w$  – solubility in water,  $\text{g L}^{-1}$
- $\bar{t}$  – fluid residence time in the control section ( $\bar{t} = x/w_x$ ), s
- $t$  – time, s, d
- $V_i$  – volume of the phase or compartment  $i$ ,  $\text{m}^3$ , L
- $(x, y, z)$  – Cartesian directions of the analysed system ( $x$  = longitudinal;  $y$  = lateral;  $z$  = vertical directions), m
- $y_{bw}$  – biota volumetric fraction in water
- $Z_i$  – fugacity capacity of phase  $i$  ( $c_i = f Z_i$ ),  $\text{mol Pa}^{-1} \text{ m}^{-3}$
- $w_x, w_y, w_z$  – fluid superficial velocities over movement directions,  $\text{m s}^{-1}$
- $w$  – organic mater content in sediment (mass fraction, %)

### Greeks

- $\Delta t$  – time increment, s, d
- $\gamma_{ef}$  – pollutant mass concentration in the discharged water,  $\text{g L}^{-1}$
- $\gamma_{fond}$  – pollutant mass concentration in the river before the release point,  $\text{g L}^{-1}$
- $\zeta$  – mass ratio,  $\text{g kg}^{-1}$
- $\delta_s$  – active sediment depth, m
- $\varphi$  – lipid content of the receptor organism (vol. fraction), %
- $\rho_b$  – biota density,  $\text{kg m}^{-3}$
- $\rho_s$  – sediment density,  $\text{kg m}^{-3}$
- $\Psi_e$  – ratio of phase 'e' quantity (volume) to the water volume,  $\text{kg L}^{-1}$

### Index

- a – air
- b – biota
- c – clearance
- d – degradation
- e – equivalent, or environment phase
- evap – evaporation
- f – fish
- max – maximum
- o – initial, or referring to the organic content
- s – sediment, or stationary
- u – uptake
- w – water

### Superscript

- \* – equilibrium value
- $\bar{\quad}$  – mean value

### Abbreviations

- BAF – partition constant water to biota (in field studies)
- BCF – partition constant water to biota (in Lab studies)
- BSAF – partition constant biota to sediment
- DO – dissolved oxygen
- dw – dry weight
- H – Henry's constant
- OCP – organochlorine pesticides
- PAH – polycyclic aromatic hydrocarbons
- PCB – polychlorinated biphenyls
- POP – persistent organic pollutants
- QSAR – quantitative structure – activity relations
- TOC – total organic carbon
- UV – ultraviolet light
- WWTP – wastewater treatment plant
- ww – wet weight

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