Long-term Pollutant Fate of Some PAHs and Other Persistent Organic Pollutants in Riverbeds for a Quasi-continuous Release of Low-level

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Persistent Organic Pollutants (POP) are a class of stable pollutants difficult to be removed from wastewaters and environment by classical methods. Among them, the Polycyclic Aromatic Hydrocarbons (PAH), PolyChlorinated Biphenyls (PCB) and PolyChlorinated Benzenes (CBz) are very toxic compounds, presenting a low volatility, biodegradability, and solubility in water. Their high bioaccumulation capacity in the aquatic environment sharply increases with the number of carbon, chlorine atoms, and aromatic rings in the molecule. Such characteristics may lead to an incomplete removal in the wastewater treatment plants (WWTP), their level in effluents being frequently close and sometimes slightly overstepping the admissible limits. By using a dynamic 2D advective-dispersive model with accounting for pollutant inter-phase transport among water, biota, sediment, and air, the paper proves by means of simulated scenarios how such a low level but quasicontinuous release can turn into a serious river pollution problem. A case study exemplifies this comparative analysis of the pollutant fate for some PAHs, PCBs, and CBz-s, by indicating conditions that may lead to the pollutant dangerous accumulation in the riverbed. Model predictions also prove that frequent POP releases around the regulation limits can become dangerous on a long term due to the migration of the pollution front downstream the river as soon as the aquatic phase equilibrium is reached in the discharge section. The risk assessment also points out the importance of considering in the model all the pollutant properties (e.g. volatility and biodegradability) besides the bioaccumulation terms related to the high lg(BCF) and $lg(K_m)$ indices, thus highlighting fate similarities among POPs.

Keywords: POP, PAH, PCB, chlorinated benzenes, river pollution, dispersion, bioaccumulation

POPs are organic compounds that are resistant to environmental degradation through chemical, biological, and photolytic processes. POPs result as by-products from (petro)chemical industry, from power plants or waste incineration, or continue to be produced (even in restricted quantities) for various industrial use. They are a class of stable pollutants, difficult to be removed from wastewaters by means of classical treatment methods in WWTP. Consequently, they have been observed to persist in the environment, to be capable of long-range transport, bioaccumulate in human and animal tissue, biomagnify in food chains, and to have potential significant impacts on human health and environment. POPs include several subclasses, that is PCBs, CBz-s, PAHs, various insecticides and pesticides, and organometallic compounds. Starting from 1995 they began to be systematically investigated through a UN Programme, while the Stockholm Convention on 2001 restricted the POP production worldwide [1]. Unfortunately, any such regulation does not exist in most African countries and unrestricted use and accidental/illegal release in the environment continue unabatedly.

POPs are characterized by a low solubility in water but high in lipids, low-to-medium volatility, and a high molecular mass. POPs with molecular weights lower than 236 g/mol are less toxic, less persistent in the environment, and have more reversible effects than those with higher molecular masses [1]. POPs are frequently halogenated, usually with chlorine, the more chlorine groups a POP has, the more resistant it is to chemical/biological degradation. The high lipo-solubility results in the possibility to pass through biological phospholipid membranes and to bioaccumulate in the fatty tissues of living organisms. POPs are extremely toxic, and exposure can cause death and illnesses including disruption of the endocrine, reproductive, and immune systems, neurobehavioral disorders, and cancers.

PAHs are a sub-class of POPs that are usually formed by the incomplete combustion of organic materials, such as wood or fossil fuels, but are also products in the petrochemical industry. PAH molecules are made up of three or more benzene rings, at least two of which are fused with two neighbouring rings sharing two adjacent carbon atoms. In addition, some PAHs contain heteroatoms such as nitrogen and sulphur. The most toxic members of this class are molecules that have four to seven rings. Among these, benzo[a]pyrene of five unsubstituted aromatic rings is the most studied because of its relatively high environmental levels and high level of toxicity resulting in larger health impact than any other PAH identified in the environment.

In spite of increasingly protection measures, PAH discharges continue to contaminate the environment especially in the industrial area [18]. Due to rapid economic development and urbanization, the aquatic levels of PAHs may be quite significant in certain over-populated locations, for instance being up to $10 \mu g/L$ in Pearl river delta (China, [2]), up to 200 ng/g dw in the bay sediments [3], up to 2700 ng/g dw in sediments and 210 ng/g ww in biota of coastal lagoons [4], and up to 48 $\mu g/L$ in sediments of large harbors [5]. The maximum levels in surface waters imposed by PAH-regulations vary from 10 ng/L [benz(a)anthracene, chlor-naphtalene] to 2.4 $\mu g/L$ for naphthalene. PAHs deposited onto sediments could be

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$$\begin{aligned} decinve-dispersive model in water (w): \\ \begin{aligned} \frac{\partial c_u}{\partial t} &= w_u \frac{\partial c_u}{\partial t} &= D_y \frac{\partial^2 c_u}{\partial t} + \sum_{i=1}^{i} r_i; \\ \frac{\partial c_w}{\partial t} &= (for \ y = 0); \ c_w = 0, (for \ y = B); \ c_w = c_{wo}, (for \ x = 0, \ y = 0) \\ \end{aligned}$$

$$\begin{aligned} &= c_d + c_w + r_e + r_e - -k_d c_w + k_e c_w - \sum_{i=1}^{i} k_{w_i} F_e c_w + \sum_{i=1}^{i} k_{e_i} F_e c_e \\ &= c_{w_i} + c_w + c_w - k_w c_k + \cdot c_k |_{u=0} = c_{w,0}(x, y, 0) = 0 \\ &= dc_u - k_w c_w - k_w c_k + \cdot c_k |_{u=0} - c_{w,0}(x, y, 0) = 0 \\ &= dc_u - k_w c_w - k_w c_k + \cdot c_k |_{u=0} - c_{w,0}(x, y, 0) = 0 \\ &= dc_u - k_w c_w - k_w c_k + \cdot c_k |_{u=0} - c_{w,0}(x, y, 0) = 0 \\ &= (x, y, t) - k_w c_w^2 + c_{w,0}(x, y, y) \times exp(-k_w t) : e^{-h_i x}, \\ &= k_{d_i} + k_w (x_u - c_y^2 / c_i^2) \\ &= dc_u - k_w c_w^2 + c_{w,0}(x, y, y) \times exp(-k_w t) : e^{-h_i x}, \\ &= k_{d_i} + k_w (x_u - c_y^2 / c_i^2) \\ &= dc_u - k_w c_w^2 + c_{w,0}(x, y, y) \times exp(-k_w t) : e^{-h_i x}, \\ &= k_{d_i} + k_w (x_u - c_y^2 / c_i^2) \\ &= dc_u - k_w c_w^2 + c_{w,0}(x, y, y) \times exp(-k_w t) : e^{-h_i x}, \\ &= k_{d_i} + k_w (x_u - c_y^2 / c_i^2) \\ &= dc_u - k_w c_w^2 + c_{w,0}(x, y, y) \times exp(-k_w t) : e^{-h_i x}, \\ &= k_d + k_w - k_w c_w^2 + k_w c_w^2 + c_{w,0}(x, y, y) \times exp(-k_w t) : e^{-h_i x}, \\ &= k_d + k_w - k_w c_w^2 + k_w c_w^2 + c_{w,0}(x, y, x) + c_w^2 - k_w c_w^2 + c_w^$$

Table 1 2D DYNAMIC MODEL FOR DISPERSION AND UPTAKE-CLEARANCE OF POLLUTANTS IN THE RIVERINE PATHWAY [6-8]

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redissolved or re-suspended in association with fine particles becoming bioavailable to aquatic organisms. Despite environmental ubiquity and highly toxicological importance of PAHs, there are few reports regarding the accumulation potential especially for long-term discharges of low levels.

CBz-s are persistent hydrophobic organic compounds 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 [6]. CBz-s include 12 representatives with 1-6 chlorine atoms in the molecule, the bioaccumulation potential in the environment increasing with the chlorine content, corresponding to $\lg(K_{ouv}) > 4-5$ and $\lg(BCF) > 2-3$ (see notations of tables 1-3). The toxicity of penta-CBz and hexa-CBz (HCBz) for the human health and environment is comparable to those of PCB and dioxins. CBz pollutants have been produced in large quantities and discharged in the environment without any precaution until 70-80's, with a production of hundreds of thousands of tones per year. 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)[6]. Unfortunately, CBz-s inevitably appear as by-products in the production of chlorinated organics, while their removal in classical WWTP is difficult and suffers from some inconvenients (e.g. a max. 60% removal yield for TeCBz and HCBz).

The EU thresholds of CBz-s in water are of 0.4-3.2 ng/L for penta-CBz and HCBz, and of 0.4-10 μ g/L for other CBz. However, frequent over-steps of such limits are reported in industrial area, that is up to 13 μ g/L in water, up to 42 μ g/g dw in sludge, and up to 1110 μ g/g TOC in sediments [6]. If an accidental CBz release of low level (of concentrations in effluents being close to the admissible limits) can not have a high impact on the aquatic environment, the pollutant being quickly dispersed over the river section, this may not be the case for the heavy CBz-s, due to the high bioaccumulation potential. Consequently, it is of interest to investigate what effect can have such an incomplete treatment of CBz-s in a WWTP on a long term over the riverine pathway.

PCBs are a class of POPs with the general formula $C_{12}H_{10}$. Cl₂ and with x = 1-10 chlorine atoms attached to the biphenyl. Among the 209 congeners of PCBs, ca. 140 have been manufactured as commercial mixtures of viscous liquids. The coplanar PCBs present toxicity comparable to those of dioxins, the increase of the chlorine content leading to a lower biodegradability and solubility in water, to a higher toxicity, bioaccumulation capacity and persistence in the environment [7].

PCBs are low volatile and very stable, with half-lifetime 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, negatively affecting the dispersion area on a long-term. PCBs 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 banned and their use

Table 2							
CHARACTERISTICS OF SOME PCBs, CBz-s, AND PAH POLLUTANTS USED IN THE COMPARATIVE ANALYSIS OF							
THE POP FATE IN A RIVERINE PATHWAY (ww= wet WEIGHT; dw= dry WEIGHT)							

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	Significance	PAH ⁽⁸⁾			<i>CB</i> z ^(b)			PCB ^(c)		
- Spannel		oapbtolen e	anthracene	henzo[a]	I,2- D€CBa	1,2,4,5- Tof Ba	HCBz	PCB-31 A6-CB1	PCB-52 (terra-CB)	PCB-137 (herea-CB)
М	pollutzut molecular weight (g mol ¹¹)	128.2	178.2	252.5	147.0	215.9	284.8	257.54	291.99	360.88
S_{W}	solubility in water at 22-25% (mg $\rm L^{-1})$	5×10 ⁻³	7.6×10 ⁻²	5×10 ⁻⁴ 9×10 ⁻⁵	100	0.53	6×10 ⁻⁴	8.14×10 ⁻²	6.67×10 ²	9.50×10 [±]
p_{v}	vapor pressure at 20°C (Pa)	11	2,3×10 ⁻²	7.1×10 ⁻⁵	131.7	5.3	1.4×10 ⁻⁴	2.44×10 ⁻²	2.08×10^{-2}	3.43×10 ⁻⁵
× _a	overall biodegradation rate constant $(d^{\prime i})^{\{d\}}$	175.4 (w) 0.03 (s)	35.0 (w) 0.002 (s)	0.5 (w) 0.003 (s)	1.44	0.07	2.9×10 ⁴	1.9×10 ⁻²	2.74×10 ^{:4}	1.0×10 ^{.\$}
k _{nb}	water-fish uptake rate constant (L d $^{+}$ kgww $^{-1}$ \rangle $^{(e)}$	9.97	308	2.3×10 ⁴	284	1.5×10^{4}	1.5×10 ⁵	890	740	1105
× _{bн}	fish-water cleatance rate constant (d ⁻¹) (f)	7.6×10 ⁻²	¢.31	9.42	23	2.3	0.33	1.58×10 ⁻¹	1.51×10 ⁻²	1.45×10 ⁻²
ig(BCF)	water-biota hieconomization factor (L kgww ⁻¹ or, total body) (g)	2.12	2.99	2.3-2.7 3.40	2.08	3.24	4.28	3.75	4.69	5.88
k ₁₁₄₅	water-sediment uptake rate constant (1, d^4 kgdw ⁴) ^(b)	245.3	816.6	3746	260.4	\$50.0	2362.6	226.3	3261	3.28×10^{4}
k _{ser}	sediment -water clearance rate constant $(d^3)^{(j)}$	4.54	0.95	0.13	7.86	3.15	0.71	0.0624	0.1032	0.0624
$lg(K_{WS})$	water-sediment bioconcentration factor (L kgdw ⁻¹) ^(k)	0.73	2 93	4.45	1.52	2.43	3.52	3.56	4.50	5.72
lg(Κ _{σψ})	octanol to water partition coefficient, L5°C	3.34	4.54 4.51	6.06 6.1-6.3	3.4	4.6	5.60	5.52	5.92	6.95
$lg(K_{\alpha c})$	organic carbon to water partition coefficient (L kgTOC-) ^(m)	3.13 3.35	4.33	5.48 5.85	2.92	3.92	3.92	4.63	4.65	6.03
k _{er}	evaporation constant through water surface $(h^4)^{(n)}$	5.50	-2.1×10^{4}	1.4×10 ⁻⁴	0.046	0.002	4x]0 ⁻⁵	D.006	0.092	10 ^{.4}

(a) used references [3,24-29].

(c) [7,8].

(d) for CBz and PCB evaluated from biodegradation experiments [6-8]; for PAH evaluated from the CBz conclusion: $Log(k_{d'}) = 2.8194 - 0.5528 Log K_{opt}$, with $k_{d'}$ in b^4 . (e) for PAH one uses the CBz correlation $lg k_{top} = -3.14526 + 1.24082 lg K_{opt}$, with k_{ud} in $1, b^4$ kg/wv⁻¹.8].

(f) calculated from $k_{bw}=k_{wb}$ / BCF .

(g) $BCF = K_{ob} = c_b^* / c_w^* = k_{wb} / k_{tw}$; experimental values or predicted by $BCF = LK_{ow}$], where L - lipid content of the receptor organism (vol. fraction, L = 0.044 for fish); BCF [L kgww⁴], c_b^* [g kgww⁴], c_w^* [g L⁴], k_{wb} [L d⁴ kgww³], k_{gw} [d⁴].

(h) for CBz and PAH one uses the correlation $Logk_{WS} = 0.93583 + 0.43528 LogK_{OW}$, with k_{WS} in L d⁻¹ kgdw⁻¹; for PCB one uses the definition of K_{WS} ; $K_{WS} = c_s^* / c_w^* = k_{WS} / k_{SW}$; K_{WS} [L kgdw⁻¹], c_s^* [g L⁻¹], k_{WS} [L d⁻¹ kgdw⁻¹], k_{SW} [d⁻¹].

(j) for CBz and PAH k_{SW} is evaluated from K_{WS} value; for PCB is evaluated experimentally [8].

(k) for CBz one uses experimental values; for PCB and PAH one uses the correlation $K_{WS} = LK_{OC}$; L= organic mater content in sediment (wt. fraction, L=0.04) [6-8].

(m) for CBz and PCB one uses experimental values; for PAH one uses the correlation $LogK_{oc} = LogK_{ow} - 0.21$ [30]; $K_{oc} = c_{s,oc}^* / c_{w}^*$; $c_{s,oc}^* =$ equilibrium concentration in sediment based upon organic carbon content; TOC = total organic carbon.

(n) for CBz and PCB one uses experimental values; for PAH one uses the correlation from PCB: $Log(k_{ev}) = -0.5041 + 1.1951Log(p_v)$, with p_v in Pa.

⁽b)[6,27]

River topological/water data			Pollution source data					
Symbol	Significance	Value	Symbol	Significance	Value			
x	longitudinal flow- direction ($x=0$ at pollutant release location)	$\theta \le x \le x_{max} =$ 2000 (m)	Qc	discharged pollutant / contaminant flow-rate	1.5×10^{-6} (kg PAH/s); 7.6 × 10 ⁻⁶ (kg PAH/s); 8 × 10 ⁻⁵ (kg CBz/s) 7 × 10 ⁻⁶ (kg PCB/s)			
У	lateral distance from mid-river ($\nu = \theta$) to a lateral receptor	$0 \le y \le b$	Qef	discharged water flow-rate (at $x = 0$) (average)	2.5 (m ³ s ⁻¹)			
В	river half-width	50/2 (m)	Cef	pollutant concentration in the discharged water (average, before mixing)	$c_{ef} = Q_c / Q_{ef}$			
ħ	average river depth in the control section	$\overline{h} = (Q + Q_{ef})$ $/(2bw_x)$	c _{fond}	pollutant concentration before the release point	.1 ng L ⁻¹ (PAH) ng L ⁻¹ (CBz) 0.1ng L ⁻¹ (PCB)			
Q	river average flow-rate	35 (m ³ s)	c_{ρ}	pollutant concentration in water at the release point after mixing;	40; 200 μg L ⁻¹ (PAH); 2100 ng L ⁻¹ (CBz); 2.1 ng L ⁻¹ (PCB)			
w _x	river mean velocity in the flow direction	0.2 (in s' ¹)		pollutant threshold concepting	ations in water: ^(b)			
D_y	lateral dispersion coefficient ⁽³⁾	$D_y = 0.06 hu =$ 4.5 × 10 ⁻² (m ² s ⁻¹)		anthracene 63 benzopyrene 50	+ μg/L i ng/I.) ng/L			
F_b	biota content of river relatively to the water ^(c)	5×10^{-5} kg ww (L water) ⁻¹	с _{тах}	DCBz 10 TeCBz 10 HCBz 0.4	<u>µg/L.</u> µg/L ng/L			
F_{s}	active sediment content of river relatively to the water ^(d)	$4.7 \times 10^{-2} \text{ kg dw}$ (L water) ⁻¹	-	tri-CB tetra-CB 1 hexa-CB	ng/l.			

Table 3INPUT DATA FOR THESIMULATION MODEL OF THEPOLLUTANT FATE IN THERIVERINE PATHWAY

(a) Fischer's correlation [23].

(b) EU regulations set PCB and CBz limits in the environment to 800 ng (g dw)⁻¹ (in sediment, sludge), 0.1-2 μ g (g ww)⁻¹ (in food and feed).

(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 [11], and NEHC [31] case studies.

(d) $\delta_s + 0.1$ m is the active sediment depth [31], of density $\rho_s = 1500$ kg/m³.

restricted in most of the countries. Despite of that, PCB inevitably persist in the environment, and inherently appear as by-products in the production of pesticides, insecticides, or chlorinated aromatics. The classical treatment in a WWTP is ineffective, while advanced physical, chemical, or biological treatment methods are very costly being not applicable a large-scale [7].

While the EU regulations set PCB limits in the aquatic environment to 1 ng/L in surface waters, and to 800 ng/g dw in sediments and sludge, the wastewaters and WWTP waste sludge, sediments, industrial wastes, and levigates from waste deposits can sometimes present significant loads, up to 2μ g/L (water), 10 μ g/g dw (sludge), 31 μ g/g dw (sediment), while the waste and levigates can present even higher PCB contents depending on the waste type. These current loads are however much lower than the pollution levels of the rivers and lakes with PCBs recorded before 1985 [7].

Despite environmental ubiquity and highly toxicological importance of POPs, there are few reports concerning the accumulation potential especially for long-term discharges of low levels. Recently the researchers comparatively studied the pollution potential of a low-level but frequent discharge of CBz-s from a WWTP in a river [6]. Simulations proved how a small but quasi-continuous release of CBz with higher chlorine content can become dangerous for the whole riverine pathway on a long term (years), due to the "moving pollution front" effect propagated downstream the river as soon as the aquatic inter-phase exchange equilibrium tends to be reached in the critical discharge section. A similar conclusion was derived by [7,8] for POPs of high molecular mass, revealing a similar fate and bioaccumulation process for heavy CBz-s (penta-CBz, hexa-CBz) and for medium PCBs (tri-/tetra-CB). Simulations also proved that an interval of ca. 15 days of quasi-continuous release (even of low level) is enough for reaching the phase-equilibrium in the discharge section, then leading to a moving-down pollution front in the riverbed. The pollution is higher in biota and sediments as the POP is more persistent (i.e. for > 5, and > 3).

The aim of this paper is to extend this analysis by studying the river pollution potential of some PAHs present in discharges at concentrations in the vicinity of regulations limits. Various accidental release scenarios are analysed by using a combined advective-dispersive dynamic model, including the phase-exchange and bioaccumulation terms in biota and sediments together with pollutant biodegradation and evaporation through water surface. A comparative analysis of simulated case studies involving CBz-s and PCB pollutants under similar release conditions, points out the relationship between the pollutant physical properties, its chemical structure and bioaccumulation capacity. The analysis points out that not only the bioaccumulation terms are of importance for a complete risk assessment, but also a holistic approach is necessary by considering all relevant properties of the pollutant, such as its volatility and biodegradability.

Release scenarios and fate of some PAHs, CBz-s, and PCBs

Simulation model

To simulate the pollutant fate downstream a release point located in the middle of a river (x=y=0), a 2D advective-dispersive dynamic model, of moderate complexity, has been adopted [6,9]. Prediction of the pollutant concentration field $c_w(x,y,t)$ in water is made by solving the differential mass balance written for an infinitesimal small section of the river (table 1). The model includes dynamic, convective and diffusional transport terms in the water, but also terms accounting for pollutant reaction, or inter-phase transport rates leading to disappearance (uptake) or appearance (clearance) of the pollutant in the river by various mechanisms such as: evaporation ('ev'), runoff ('p'), biodegradation ('d'), uptake or clearance by/from biota, sediments or suspended solids. Several simplificatory assumptions are presented in the Table 1, while a schema of the inter-phase transport processes is given in figure 1.

By assuming that pollutant biodegradation occurs only in the water (index 'w'), the inter-phase exchange

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Fig. 1. Schema of the inter-phase transport and pollutant degradation in the riverbed

dynamics of the contaminant can usually be satisfactorily represented by a pseudo first-order kinetics, written for every location of the river. The model solution gives the dispersion of the pollutant and its partition among phases at a certain moment, but also the dynamics of the pollutant distribution in water, biota and sediments during the continuous release. The rate constants k_{ii} of the inter-phase transport (from the source phase *i* to the receptor phase *j*, and vice-versa) are related to the partition coefficients K_{ii} $=k_{ij}/k_{ji}$ of the pollutant between every two phases in contact. The thermodynamic equilibrium is reached when the uptake rate $r_{ii} = k_{ij} c_i$, of the pollutant from phase *i* to phase *j*, equals the clearance rate $r_c = k_{ij} c_i$ of the pollutant from phase *j*, that is $K_{ij} = c^* / c^*_i$. The constants K_{ij} 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_{ow} (octanol-water partition coefficient of the pollutant), or S_w (aqueous solubility of the chemical). Maria & Maria [7] present a review of such empirical correlations used to characterize the inter-phase transport for the PCBs, while extended reviews are reported in the literature for most of pollutants [10-17]. The common notations used for the partition coefficients are given in table 2. It is to remark that bioaccumulation capacity is expressed by BCF = K_{uv} , i.e. the water-biota partition coefficient, and by K_{uv} proportional to $K_{\alpha c}$, that is the sediment organic carbon (TOC) to water partition coefficient.

To solve the model for known initial and boundary conditions, a hybrid analytical-numerical procedure was applied [6-8]. It is to observe that a separate analytical solution can be obtained for the stationary dispersion, leading to the $\tilde{c_w}(x,y)$ field, and also for the phase transport leading to the pollutant distribution in biota $\tilde{c}_{b}(x,y,t)$, and sediment $c_{s}(x,y,t)$. Consequently, the solving procedure starts from the known initial conditions of the river phases and discharge characteristics. Then, by keeping a certain trade-off between the solution precision and the required computational time, a small time-step is adopted. Over one integration step, the pollutant concentration in water $c_{w}(x,y,t)$ is evaluated under quasi-steady-state assumptions by using the biota ('b') and sediment ('s') field from the previous time-step $c_a(x,y,t - \Delta t)$ (index 'e' = b,s). Then, the phase transfer equations are applied with known $\tilde{c}_{w}(x,y)$ values for correcting the biota/sediment field of concentration and the time is incremented with one step. The rule is repeated step-after-step until a chosen final time, leading to the dynamics of the pollutant distribution in water, biota, and sediment.

Release scenarios

To simulate various release scenarios of individual pollutants in the control section (ca. 2000 m downstream the release point) of an analysed river, three representatives have been selected from every class of PAHs, CBz-s, and PCBs, of comparable molecular mass and $lg(K_{out})$. The physical and transport properties of these pollutants are presented in table 2. It is to observe that every class includes a light, a moderate heavy, and a heavy compound, that is: I) naphthalene (C₁₀H₈); anthracene (C₁₄H₁₀); benzo[a]pyrene (C₂₀H₁₂); ii) 1,2-dichlorobenzene (DCBz, C₆H₄Cl₂); 1,2,4,5-tetrachlorobenzene (TeCBz, C₆H₂Cl₄); hexachlorobenzene (HCBz, C₆Cl₃); iii) 2,4',5-trichlorobiphenyl (PCB-52, C₁₂H₆Cl₄); 2,2',3,4,4',5-hexachlorobiphenyl (PCB-137, C₁₂H₄Cl₆).

It is to a remark that the solubility in water of CBz-s is higher than those of PAHs and PCBs. The volatility is higher for naphthalene and light CBz-s, as is their biodegradability. Anthracene biodegradability is also higher than those of heavy-PAHs, CBz-s, and PCBs. The values of $\lg(K_{ouv}) > 3.4$ for all considered POPs clearly indicate a high bioaccumulation capacity in the aquatic environment. However, a simple "translation" of conclusions about pollutant fate in the riverine pathway based on only similarity in the $\lg(K_{ouv})$ values is expected not to be applicable when large differences in volatility and biodegradability are also present. Consequently, a holistic approach of the dispersion and transport between phases is necessary based on the adopted model.

The input data, including the river characteristics and the constant flow rates are presented in table 3. For a better comparison among POPs, a pollutant level at source of ca. two-times the admissible levels in surface waters have been adopted (i.e. ca. 200 ng PAH /L, ca. 2000 ng CBz/L, and 2 ng PCB/L)[19].

Simulations are performed for every mentioned POP over ca. 1000 days of quasi-continuous pollutant release, because experimental investigations on fish reported bioaccumulation times of 15-256 days until the equilibrium is reached [20]. The dynamics of the resulted concentration field in water, biota, and sediments reveal the pollutant fate in the riverbed on a long term. For instance the benzopyrene concentration field after 1 day, 250 days, and 1000 days of continuous release is presented in Figure 2, revealing the tendency of reaching the saturation in the vicinity of the source (over ca. 500 m after 1000 days).

The pollution front propagation (where loads are close to the equilibrium) can be better observed by plotting the pollutant concentrations in all phases in contact in the middle of the river, at certain times. Figure 3 displays such



Fig. 2. Dynamics of the benzopyrene concentration in water along the river, downstream the source, after 1 day, 250 days, and 1000 days of continuous release. The average concentration at source is of ca. 200 ng/L, i.e. four-times higher than the

regulations' limit.

an axial concentration profile in water, biota, and sediment for the selected PAHs, CBZ-s, and PCBs after 1000 days of quasi-continuous release. In the PAH case, while naphthalene and anthracene are quickly dispersed in water, reporting relatively low levels in biota and negligible ones in sediment, benzopyrene already reached the equilibrium over a large section of ca. 400-500 m downstream the source, and its level in biota (500 ng/g ww) and sediment (5500 ng/g dw) is very high, overstepping the admissible limits. Such differences in the PAH fates, apparently surprisingly because all selected compounds present high values $lg(K_{ow}) > 3$, can be explained by the differences in the biodegradation and evaporation rate constants especially in the naphthalene case. On a long-term, the situation can become dramatic due the low biodegradability and high bioaccumulation capacity of the heavy POPs (such as benzopyrene), the pollution front continuing to move down the river as soon as the equilibrium is reached near the source.

A similar analysis is repeated for the CBz case, by simulating for every individual pollutant the dynamics of the concentration field in all aquatic phases in contact. The axial concentration profiles in the river, downstream



Fig. 3. PAH (up), CBz (middle), and PCB (down) concentrations along the river longitudinal axis in water, biota and sediment, downstream the source, after 1000 days of continuous release. Concentrations in water at source are ca. two-times higher than the regulations' limits. The discharged pollutant flow rate is of 7.6×10^{-6} kg PAH/s (ca. 200 ng/L at source), of 8.0×10^{-5} kg CBz/s (ca. 2000 ng/L at source), and of 7.0×10^{-8} kg PCB/s (ca. 2 ng/L at source)

the source, are displayed in figure 3 after 1000 days of contaminant release. By comparing the CBz distribution, it clearly appears that heavy contaminants, such as HCBz, already reached the equilibrium and accumulated in the biota and sediments over more than 1000 m downstream the river (ca. 40 mg/g ww in biota and 8mg/g dw in sediment). TeCBZ, presenting a higher biodegradability, display lower equilibrium levels in biota and sediment, while the accumulation degree is practically negligible for the DCBz case.

In the POP case, repeated simulations of the pollutant distribution dynamics reveal very high differences among representatives, as indicated by the axial concentration profiles displayed in figure 3. The PCB pollutant load in biota and sediment is higher, and distributed closer to the source, as its molecular mass is higher, corresponding to higher chlorine and phenyl content, and higher $\lg K_{ow}$ and $\lg K_{oc}$ constants. Such a result can be explained by the very low volatility and biodegradability of all investigated PCBs, the differences in the pollutant fate being determined by the thermodynamic limitations of the transport between water-biota [i.e. $\lg(BCF)$ value] and water-sediment [i.e. $\lg(K_{uv})$ value] phases.

There are some similarities in the pollutant fate between different POP classes, in the sense that heavy compounds tend to reach quickly the saturation levels in biota and sediment near the release point, and then the pollution front is slowly moving downstream, eventually polluting the whole river on a long term. It is also to remark that the saturation levels in biota and sediments are very high, even if the POP concentration in water is fluctuating around the admissible level. For instance, in the benzopyrene case (fig. 3), for a concentration in water in the discharge section of ca. 200 ng/L, the saturation concentrations in the same section in biota (500 ng/g ww) and sediment (5500 ng/g dw) are very high due to the large values of the phase partition coefficients BCF and $K_{\mu\nu}$. The same observation is valid for the heavy HCBz and hexa-CB. Consequently, frequent accidental releases of such POPs, even if of low levels, not exceeding much the admissible limits, are very dangerous due to their high bioaccumulation potential and persistence in the environment.



Fig. 4. PAH concentrations along the river longitudinal axis in water, biota and sediment, downstream the source, after 250 days of continuous release, for a discharge below the regulations' limits (of 2400 ng/L for naphthalene, 63 ng/L for anthracene, and 50 ng/L for benzopyrene). The discharged pollutant flow rate is of 1.5×10⁻⁶ kg PAH/s (ca. 40 ng/L at source)

To confirm such a conclusion, one simulates release scenarios of PAHs of low levels, corresponding to ca. 40 ng/L concentration in water at source, that is lower than the admissible limit of 50 ng/L. The results, presented figure 4, reveal a very interesting situation. After 1000 days of quasi-continuous release, the content of naphthalene and anthracene in biota is still low, not reaching the phaseequilibrium, and negligible in sediment. In the benzopyrene case, the situation is completely different: its high bioaccumulation potential determines a high accumulation in biota (100 ng/g ww) and sediment (1100 ng/g dw), overstepping the admissible limits.

Conclusions

By using a 2D dispersion model, of medium complexity, combining the spatial dispersion with bioaccumulation

dynamics, it is possible to simulate the pollutant transport and its fate in a riverine pathway, downstream a smallsize contamination source. The model can be used to predict the negative effects of accidental discharges of POPs on a riverbed (water, sediment and biota) over long time intervals. The solution precision can be controlled by means of the chosen integration time-step used to solve the differential mass balance written for all aquatic phases in contact. The model is guite flexible, and can easily be extended to account for variations in flow rates and pollutant loads, in a riverbed of variate geometry, by dividing the analyzed riverbed in multiple sections. The model can be coupled with a statistical analysis associated to the accidental release of a pollutant, in order to derive the risk contours, predicted effects, and environmental impact downstream the river for various release scenarios [21].

For the analyzed POP representatives, it appears that small, but quasi-continuous discharges of low level, not exceeding much or close to the admissible levels in water, can become dangerous for the whole riverine pathway on a long term (years), due to the "moving pollution front" effect propagated downstream the river as soon as the aquatic inter-phase equilibrium tends to be reached in the critical discharge section. The danger is as high as the POP molecular mass and the inter-phase partition constants (BCF water-biota, and K_{ws} water-sediment) are higher, and its volatility and biodegradability are smaller. Simulations proved that after ca. 15 days of quasi-continuous release, the phase-equilibrium is reached in the discharge section for the heavy POPs, then leading to the pollution propagation downstream the river.

The study indicates that a holistic approach of the river pollution is necessary, by accounting transport among all phases in contact, but also considering all relevant pollutant properties such as volatility and biodegradability. Thus, in the case of POPs presenting a significant bioaccumulation potential [lg(BCF) > 2, lgK > 3], their high biodegradability and/or volatility can induce a lower bioaccumulation rate and a much longer time to reach the phase-equilibrium in the riverbed.

For the heavy, low biodegradable POPs, frequent releases of low level, close but lower than the admissible limits, are still very dangerous due to their high bioaccumulation potential and persistence in the environment. Simulations reveal that such a situation (e.g. the benzopyrene case) will inevitably lead to high and unacceptable levels of POP in the aquatic biota and sediment on a long term, and to the same "moving pollution front" effect in the riverbed.

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

References

1. POP - Persistent organic pollutant, Wikipedia - the free encyclopedia, Wikimedia Foundation, Inc., 2011. http://en.wikipedia.org/wiki/ Persistent_organic_pollutant

2. LANG, C., TAO, S., WANG, X., ZHANG, G., LI, J., FU, J., Atmospheric Environment, **41**, 2007, p. 8370

- 3. GREENFIELD, B.K., DAVIS, J.A., Chemosphere, 60, 2005, p. 515
- 4. FABBRI, D., BARAVELLI, V., GIANNOTTI, K., DONNINI, F., FABBRI,
- E., Chemosphere, 64, 2006, p. 1083

- 5. DE LUCA, G., FURESI, A., MICERA, G., PANZANELLI, A., PIU, P.C., PILO, M.I., SPANO, N., SANNA, G., Marine Pollution Bulletin, **50**, 2005, p. 1223
- 6. MARIA, C., MARIA, G., Rev. Chim. (Bucharest), **59**, no.10, 2008, p. 1122
- 7. MARIA, G., MARIA, C., Chem. & Biochem. Eng. Quarterly, **23**, 2009, p. 121
- 8. MARIA, C., MARIA, G., Rev. Chim. (Bucharest), **60**, no. 7, 2009, p. 699-705
- 9. MARIA, G., MARIA, C., Chem. & Biochem. Eng. Quarterly, **20**, 2006, p. 333
- 10. MACKAY, D., Environmental Science and Technology, **16**, 1982, p. 274
- 11. MACKAY, D., Multimedia environmental models The fugacity approach, Lewis Publ., Boca Raton, 2001.
- 12. MACKAY, D., FRASER, A., Environmental Pollution, **110**, 2000, p. 375
- 13. BARBER, M.C., Environmental Toxicology and Chemistry, **22**, 2003, p. 1963
- 14. TOLLS, J., SIJM, D.T.H.M., Eniron. Toxicology & Chemistry, 14, 1995, p. 1675
- 15. SUTER II, G.W., EFROYMSON, R.A., SAMPLE, B.E., JONES, D.S., Ecological risk assessment for contaminated sites, Lewis Publ., Boca Raton, 2000
- 16. LOPES, R.B., PARAIBA, L.C., CECCARELLI, P.S., TORNISIELO, V.L., Chemosphere, **64**, 2006, p. 56
- 17. LIU, H., YAO, X., ZHANG, R., LIU, M., HU, Z., FAN, B., Chemosphere, **63**, 2006, p. 722
- 18. PAH Polycyclic aromatic hydrocarbon, Wikipedia the free encyclopedia, Wikimedia Foundation, Inc., 2011. http://en.wikipedia.org/wiki/Polycyclic aromatic hydrocarbon
- 19. MANEA, I., MANEA, L.C., Rev. Chim. (Bucharest), **61**, no. 12, 2010, p. 1254

20.CARAFA, R., MARINOV, D., DUERI, S., WOLLGAST, J., VIAROLI, P., ZALDIVAR, J.M., Development of a bioaccumulation model for herbicides in Ulva and clams, EC Directorate General Joint Research Centre, Institute for Environment and Sustainability, EUR 22517EN Report, 2006

21. MARIA, G., Quantitative risk evaluation of chemical processes and modelling of accident consequences, Printech Publ., Bucharest, 2007 (in Romanian)

22.CARBERRY, J.J., Chemical and catalytic reaction engineering, McGraw-Hill, New York, 1976

23. FISCHER, H.B., In: Proc. of Conference on Dispersion and Transport of Pollutants in Waterways, Sept. 24, 1974, California State Univ., Riverside

24. ToxProbe, Benzo[a]pyrene and other polycyclic aromatic hydrocarbons, Research Report Prepared by ToxProbe Inc. for Toronto Public Health (Canada), B78-B95, 2002. http://www.toronto.ca/health/pdf/cr_appendix_b_pah.pdf

25. CHIAO, F.F., CURRIE, R.C., McKONE, T.E., Intermedia transfer factors for contaminants found at hazardous waste sites -Benzo(a)pyrene, Report prepared for The Department of Toxic Substances Control (DTSC) and the California Environmental Protection Agency, Department of Environmental Toxicology, University of California, Davis (CA), March 1995

26. JANIKOWSKA, G., WARDAS, W., Polish Journal of Environmental Studies, **11**, 2002, p. 345

27. AXELMAN, J., BROMAN, D., NÄF, C., PETTERSEN, H., Environ. Sci. & Pollut. Res., **2**, 1995, p. 33

- 28. BRION, D., PELLETIER, E., Chemosphere, 61, 2005, p. 867
- 29. van NOORT, P.C.M., Chemosphere, 74, 2009, p. 1018

30. DJOHAN, D., YU, Q., CONNELL, D.W., Water, Air, and Soil Pollution, **161**, 2005, 157

31. NEHC, Ex-ORISKANY Artificial Reef Project, Prospective Risk Assessment Model (PRAM 1.4c), Navy Environmental Health Center, SPAWAR Systems Center, San Diego, 2006

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