MATHEMATICAL MODEL FOR ASSESSING/PRIORISING THE EMISSIONS OF POPs/PBTs CHEMICALS FROM CONSUMER PRODUCTS

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Introduction

Cities concentrate population in small areas with a high material demand regarding production and human consumption. The situation entails several environmental problems. Among them, chemical contamination associated to waste disposal and effluent discharges is one of the main causes of concern[1].

Although Sewage Treatment Plants (STPs) across the world have improved their technologies for reducing this contamination, the majority of them are not designed to remove polar persistent organic pollutants[2]. In addition, the retention of bound non-polar chemicals is extensive but not complete. As a consequence, this kind of chemicals (of particular attention, those that fulfil the required criteria for Persistent Organic Pollutants-POPs-/Persistent Bioaccumulable and Toxic-PBTs- substances) are entering to the environment through STPs effluent and due to sludge application. The release of these compounds from urban centres to sewer systems could be from multiples pathways which are not fully understood. For example, emerging POPs such as Brominated Flame Retardants (BFR) or Fluorinated compounds are present in many domestic/office articles and their leachate from in-service articles has been reported[3,4]. In general, many chemicals including POPs/PBTs are present in a wide variety of consumer products and are discharged into the urban sewer systems[5]. Actually, there is a lack of information about the amount of these compounds in the technosphere (including consumer products and therir potential release) and hence, their discharge pattern from STPs. Due to the myriad of potentially occurring compounds, prioritization tools are required for a proper and cost/benefit assessment. In this work, a mathematical model involving the potential release of chemicals from private household uses to the environment was implemented. As a preliminary approach, the model estimations were checking by a sensitivity analysis and an assortment of simulations taking into consideration the physico-chemical characteristics of POPs/PBTs.

Material and Methods

Model framework. The model implemented in this study was base on the exposure scenario employed in the Environmental Risk Assessment (ERA) protocols of industrial chemicals[6]. Briefly, in this scenario, the release of a chemical from STP to the environment and their subsequent distribution among abiotic compartments (soil, water, sediment, groundwater and atmosphere) is described considering process such as sedimentation, atmospheric deposition and sludge application on soil.

Table 1. Industrial Categories (ICs) and their associated Use Categories (UCs) included into the model.

IC Code	Industrial Category (IC)	UC Code*
5	Personal / Domestic	2; 3; 5; 7; 8; 9; 10; 11; 15; 19; 26; 35; 36; 38; 41; 47; 48; 50; 0.
9	Mineral Oil and Fuel Industry	All UC
10	Photographic Industry	42
13	Textile Processing Industry	10 (10.1; 10.2; 10.3)
14.1	Paints, Lacquers And Varnishes Industry. (In Water)	10, 14; 20; 47; 48; 50; 52; 0
14.2	Paints, Lacquers And Varnishes Industry. (In Solvent)	3; 10, 14; 20; 47; 48; 52; 0

*UC Code: 2. Adhesive, binding agents; 3. Aerosol propellants; 5. Anti-freezing agents; 7.Anti-static agents; 8.Bleaching agents; 9.Cleaning/washing agents and additives; 10.Colouring agents; 11.Complexing agents; 14.Corrosion inhibitors; 15.Cosmetics; 19.Fertilizers; 20.Fillers; 26.Food/feedstuff additives; 35.Lubricants and additives; 36.Odour agents; 38.Plant protection products, agricultural; 41..Pharmaceuticals; 42.Photochemicals; 47.Softeners; 48.Solvents; 50.Surface-active agents; 52.Viscosity adjustors; 0.Other.

The release at each life-cycle stage of the chemical (Production, Formulation, Industrial/Private Use and Waste Disposal) is detailed in this scenario depending on its use patterns. To consider this pattern, 18 Industrial Categories (ICs) and 55 Use Categories (UCs) are contemplated. In this study, an adaptation of such scenario

was performed for covering entirely the *personal or domestic use* of chemicals. For such proposal, among the 18 ICs described in the original model, just those including *private or domestic use* as life-cycle stage was chosen. The rest of life-cycle stages and ICs were removed for developing the final model. As a result, 6 ICs with 24 associated UCs were integrated (Table 1).

After adaptation, the model for private use was mathematically implemented into Excell® sheets. The model was parameterised using i) physico-chemical characteristics of chemicals and ii) their use pattern (Table 2 details all *inputs* of the model). As a result, the model allowed estimating, among other parameters, the PECs (Predicted Environmental Concentration) in different abiotic compartments (Table 2 details some *outputs*).
The model was probabilistically implemented by Cristall Ball® software. That allowed including the *inputs* as probability distribution instead of one unique value. As a result, the model estimations were obtained also as probability distributions. The simulations were carried out by Monte Carlo analysis (n = 10000).

Table 2. Parameters that feed the model (*inputs*) and any of their estimations (*outputs*)

Inputs [Units]	**Outputs**	**[Units]**
Biodegradability [-]	PEC $_{water, atmosphere, soil, sediment, groundwater}$	[mg/Kg]
log H [-]	Fstp $_{water, sludge, air}$. Emission fraction directed to compartments from STP*	[%]
log Kow [-]	Release $_{water, air, soil}$ use. Emission factors to compartments by use	[-]
log Koc [-]	F main,source. Release fraction at the main source during use	[-]
Solubility [mg/l]	T emission. Time during the emission takes place	[days]
Vapour Pressure [Pa]		
Industrial Category (IC)		
Use Category (UC)		
Tonnage, use [Tn/year]		

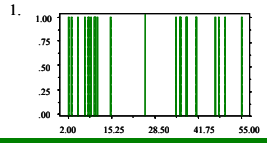
*F_{stp} for chemicals with log Kow ≥ 6 were obtained from Alonso et al., 2007[7]

Results and Discussion

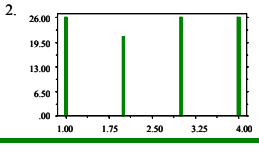
Model checking. ***Comparison among groups of chemicals.*** The model was run using the physico-chemical characteristics of five hypothetical groups of chemicals. Four of them were established for covering the total range of potential POPs/PBTs characteristics (Group I, II, III and IV respectively). The fifth group (Group V) symbolizes values for other substances estimated from the EU ESIS database. Physico-chemical characteristics of the POP/PBT groups were chosen after examination of values corresponding to the 12 POPs included into the Stockholm Convention. The fifth group represents the 50th percentile of over 100 large production volume substances. The Industrial Category nº5 (Personal/Domestic) was chosen for comparing the model estimations related to POPs/PBTs characteristics. All *inputs* were included as deterministic parameters excepting the Use Category (for the five groups) and the Biodegradability for Group V, which were included as probabilistic *inputs* (custom distribution). Four increasing degree of biodegradability (1, 2, 3 and 4) were considered in Group V for covering all potential range. One tonnage of use was assumed in these simulations. The rest of parameters included in the model as *inputs* are detailed in Table 3. A group of *outputs* were selected for being showed in this work (Figure 1).

Table 3. Inputs included into the model for comparing their estimations for POPs/PBT characteristics.

	Group I	Group II	Group III	Group VI	Group V
log K_{ow}	4	8	8	4	1.20
log H (Pa·m^3/mol)	-1.2	1.5	-1.2	1.5	-0.45
Sol (mg/l)	0.2	0.2	0.2	0.2	11902
VaP (Pa)	-0.24	0.3	-0.24	0.3	-5355.9
Biodegradability	1	1	1	1	Custom distr.[2]
IC/UC	IC =5 / UC = custom distribution [1]				

1. 

UCs detailed in Table 1

2. 

1. No biodegradability
2. Inherent biodegradability
3. Ready biodegradability (<10d)
4. Ready biodegradability (>10d)

Figure 1 shows some of the potential results obtained after running the model for the five hypothetical groups of chemicals. These results illustrate the wide range of possibilities that the model offers as a tool for addressing the discharge of chemicals from consumer products including those substances with POPs/PBT characteristics.

Model checking. ***Sensitivity analysis.*** The goal of the sensitivity analysis was to check the weight of different *inputs* into the model estimations. In this work, the relative weight of industrial categories (ICs) on model estimations was exemplified. For that purpose, one simulation per each IC was performed considering the five groups of chemicals previously explained (Table 3). The estimations of PEC_{water} was the *output* chosen (Figure 2) for comparing the results. The *inputs* of the simulations are detailed in Table 3.
The analysis of sensitivity (Figure 2) showed how the most relevant ICs were nº 5, 10 and to a minor extent nº13. This information will be useful for setting priorities in the data collection and testing strategies in future studies.

Knowledge about the use pattern of substances is critical for modelling chemical release to the environment. Until now, this sort of information was limited but the requirements of the EU REACH Regulation will produce very relevant information. The regulation requires use specific authorization processes for PBT chemicals. Manufacturers or importers must provide information about the uses and use processes of the substances (on its own or in a preparation) that they want to register[8]. Hence, this information could be included in this model for addressing potential emissions of chemicals to the environment and setting priorities. Consequently, this model may be applicable for developing exposure scenario for the substances that the REACH regulation requires, in particular for those that fulfil the PBT criteria.

Figure 2. Summary of estimations generated by the model for PEC_{water} (50^{th} percentile) in the sensitivity analysis study considering Industrial Categories (ICs) and group of substances.

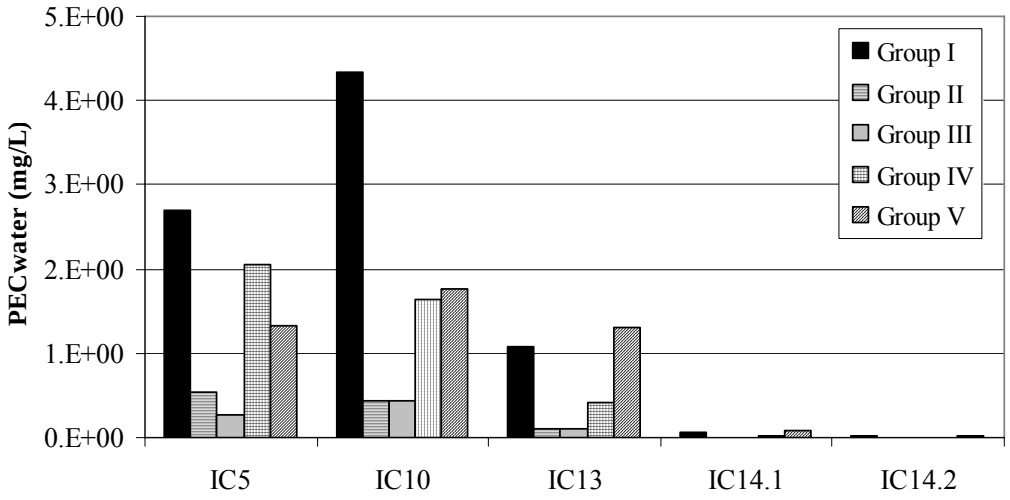


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Figure 1. Concentrations in different compartments and Predicted Environmental Concentrations (PECs) estimated by the model. Results from simulations carried out with *inputs* of Table 3. Estimations base on 1 Tn/ year of substance used.