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Risk Evaluation of Seven Personal Care Detergents Based on Chemical and Ecotoxicological Characterization in Synthetic Aqueous Media

Oguz Kizek[1], Deniz İzlen Çifçi[1], Füsun Ekmekyapar[1,*], Antonietta Siciliano[2], Sureyya Meriç[1]

[1]Department of Environmental Engineering, Faculty of Corlu Engineering, Namik Kemal University, Turkey
[2]Department of Biology, Ecotoxicology Research Laboratory, Naples University, Italy

Abstract Personal care products (PCPs), composed of various chemicals as complex mixture nature, are evaluated among those MPs found often in treated sewage and greywater. Among PCPs, detergents (PCDs) are forming specific complex mixtures containing various endocrine disruptor chemicals, to be handled accurately. In this study, acute toxicity of seven PCDs including shampoos (4) and shower gels (3) collected from different Hotels located in different countries was investigated. Chemical characterization (Chemical oxygen demand, COD; Total organic carbon, TOC) was performed according to Standard Methods. Besides, absorbance spectrum of each PCD was screened using UV-vis instrument. Acute toxicity of synthetic solutions prepared by dissolving PCDs in distilled water was assessed on two freshwater crustaceans *Daphnia magna (D. magna)* and *Ceriodaphnia dubia (C. dubia)* according to ISO 6341 Method. Acute toxicity was assessed for 24 and 48 h of exposure time by dividing the number of immobile organisms by total tested organisms (20) to score immobilization percentiles of each sample tested. By this way it was possible to calculate the concentration of EC_{50} indicating a 50% population immobilization, using PROBIT program. The results of chemical characterization showed that the biodegradability by means of TOC/COD ratio of PCDs was very low. *C. dubia* was observed to be more sensitive than *D. magna* regarding lower values of EC_{50}. All tested chemicals were found to be harmful according to EC_{50} toxic chemical's evaluation scoring system.

Keywords Acute Toxicity, *Ceriodaphnia dubia, Daphnia magna,* Personal Care Detergents (PCDs), Risk Evaluation

1. Introduction

PCDs are widely used in everyday for personal care and as household products as well as in a variety of industrial applications. As a result, large amounts of products are commonly discharged in large quantities to sewage treatment plants or directly to the aquatic environment areas where there are no sewage treatments [1-2]. PCDs are a diverse group of compounds used in soaps, lotions, toothpaste, fragrances, and sunscreens. The primary classes of PCDs include disinfectants (e.g. triclosan), fragrances (e.g. masks), insect repellants (e.g. DEET), preservatives (e.g. parabens) and UV filters (e.g. methylbenzylidene camphor). PCDs are products intended for external use on the human body and thus are not subjected to metabolic alterations; therefore, large quantities of PCDs enter the environment unaltered through regular usage. Many of these compounds are used in large quantities, and recent studies have indicated many are environmentally persistent, bioactive, and have the potential for bioaccumulation [3]. Environmental fate and effect datasets of many ingredients used in personal care detergents (PCDs) are still limited. There is emerging focus on the use of a number of substances classified under this category, including the nitro- and polycyclic musk, UV blockers such as methylbenzylidene camphor, and preservatives such as the parabens, therefore, methods for prioritizing the environmental risk assessment for chemicals used in PCDs are needed [4]. PCDs which contain surfactants, can seriously damage the environment. The surfactant toxicity is primarily a function of the ability of the surfactant to adsorb and penetrate the cell membrane of aquatic organisms [5]. Lewis [6] summarized the chronic and sub-lethal toxicities of surfactants to aquatic animals and found that chronic toxicity of anionic and nonionic surfactants occurs at concentrations usually greater than 0.1 mg/L. Deleterious effects caused by surfactants have been reported in studies with *D. magna* and *Vibrio fischeri* [4], micro-crustaceans [7, 8], algae-crustaceans-fish [9]. Table 1 shows a set of acute toxicity test results of several compounds present in personal care products while Table 2

displays chronic toxicity of those compounds to several aquatic organisms [3].

There is a European Commission Decision (L186/36) for establishing ecological criteria for the award of the Community Eco-label to soaps, shampoos and hair conditioners [22]. The text makes reference to the Detergent Ingredient Database (DID list), which contains many of the most widely used ingredients in soap and shampoo formulations. Part A of DID list is used for deriving the data for the calculations of the CDV that is calculated for each ingredient (i) and for the whole product using the equations 1 and 2:

$$\text{CDV(ingredient i)} = \text{weight (i)} \text{ (i)} \times \text{DF(i)} \times 1\,000/\text{TF chronic (i)} \quad (1)$$

$$\text{CDV} = \Sigma\ \text{CDV(ingredient i)} \quad (2)$$

where weight (i) is the weight of the ingredient (in grams) per functional unit. DF (i) is the degradation factor and TF chronic (i) is the toxicity factor of the ingredient (in $mg.L^{-1}$). The values of DF and TF chronic should be as given in the DID list-part A. The CDV(tox) is summed for each ingredient, making the CDV for the product. For ingredients not included in the DID-list, test results and test methods for ecotoxicity (long-term effects (NOEC data) on fish, *D. magna*, and algae), biodegradation and bioaccumulation should be submitted. If the lowest toxicity is ≤ 10 $mg.L^{-1}$, then test results for potential bioaccumulation (Bio-concentration factor (BCF) or logKow) must also be given.

Table 1. Acute toxicity data for personal care products [Adopted from 3]

Compound	Category	Species	Trophic group	Endpoint/duration	LC_{50} ($mg.L^{-1}$)	Additional tox. values	Ref.
Triclosan	Antimicrobial	*D.magna*	Invert	48 h	0.39		Orvos et al. [10]
		Oryzias latipes	Fish	96 h	0.602 (larvae), 0.399 (embryos)		Ishibashi et al. [11]
Triclocarban	Antimicrobial	*P.subcapitata*	Algae	72 h Growth	>Sol		Yang et al. [12]
Musk ketone	Nitro musk	*V.fischeri*	Bacteria	Microtox	>1.0		Schramm et al. [13]
		Nitocra spinipes	Invert	96 h	1.32	LC_{10}=0.40	Breitholtz et al. [14]
		P.subcapitata	Algae	72 h			Schramm et al. [13]
Propylparaben	Preservative	*T.thermophila*	Protozoa	24 h, 28h	9.7, 12.5	LOEC=2.6	Bazin et al. [15]
		V.fischeri	Bacteria	15 min, 30 min Luminescence	2.5, 2.6	LOEC=0.9	Bazin et al. [15]
		P.leognathi	Bacteria	15 min, 30 min Luminescence	21, 25	LOEC=4.5	Bazin et al. [15]
		D.magna	Invert	48 h	12.3		Dobbins et al. [16]
		D.magna	Invert	24 h, 48 h Mobility	13.7	LOEC=6	Breitholtz et al. [14]
		Pimephales promelas	Fish	48 h	9.7		Bazin et al. [15]

Table 2. Chronic toxicity data for personal care products [Adopted from 3]

Compound	Category	Species	Trophic level	Endpoint/duration	LOEC ($\mu g.L^{-1}$)	NOEC ($\mu g.L^{-1}$)	Reference
Triclosan	Antimicrobial	*D.magna*	Invert	21 d Survival, Reproduction	Reproduction= 200	Survival= 200	Orvos et al. [10]
		C. dubia	Invert	7 d Survival, Reproduction		50, 6	Orvos et al. [10]
		Chironomus tentans	Invert	10 d Survival, Growth	LC25=100		Dussault et al. [17]
		Hyalella azteca	Invert	10 d Survival, Growth	LC25=60		Dussault et al. [17]
		Natural algal	Algae	96 h Biomass	0.12		Wilson et al. [18]
		D. tertiolecta	Algae	96 h Growth		1.6	De Lorenzo et al. [19]
Musk ketone	Nitro musk	*A. tonsa*	Invert	5 d Developmental Rate	EC50=66	EC_{10}=10	Wollenberger et al. [20]
		D. rerio	Fish	ELS 24-48 h Tail Extension, Coagulated Egss, Edema	1000	330	An et al. [21]
Propylparaben	Preservative	*D.magna*	Invert	7 d Growth, Reproduction	400, 6000		Dobbins et al. [16]
		Pimephales promelas	Fish	7 d Growth	2500		Dobbins et al. [16]

Nordic Cooperation on Green Public Procurement published the The First Set of Criteria Examples [23]. One of the groups included in the guideline covers hair shampoo, cream soaps/body shampoo and solid and liquid soap for professional use. Disinfectant soaps are not covered. One of the criteria is bioaccumulation or food chain exposure and hazardous effects on aquatic organisms.

In conclusion, safety evaluations for most surfactants in fresh water, and even more so in saltwater environments should be considered limited and preliminary in nature. There is therefore an obvious need of more toxicity data for different surfactants [24]. Thus, this paper aimed to characterize chemical characteristics and acute aquatic toxicity to *D. magna* and *C. dubia* of seven commercial PCDs collected from the hotels located in different countries. Based on ecotoxicological data obtained in synthetic aquatic media prepared based on the dilution factor in real wastewater samples, hazard score of each PCD was defined according to EC Directive on Safety of Chemicals (93/67/EC).

2. Material and Methods

2.1. Sample Collection and Solutions

The PCD samples were collected from different Hotels classified with 3-5 stars located in different countries. Four samples were shampoos while three samples were shower gels. No indication about their hazard class of ecotoxicity to aquatic organisms was present on the samples. All samples were first dissolved in 500-1000 mL distilled water and then diluted for having geometrical varying concentrations for EC_{50} determinations. Diluted samples were stored at +4 cooled during chemical and ecotoxicological characterization.

2.2. Analytical Methods

Because the ingredients of some samples tested were not clarified or their chemicals abstract numbers were lacking to compare with the data sets from the literature, organic content of the samples were defined with the standard cumulative parameter to be COD or TOC in this study.

TOC was measured using a Schimadzu TOC analyzer (6KVA model) at Central Laboratory of Namık Kemal University (NABILTEM). COD experiments were performed according to Standard Methods [25]. pH was measured using a WTW 3110 model pH-meter.

Absorbance spectra of PCD_s were determined using a Schimadzu Spectrophotometer (LAMDA 1800 model). As related to aroma city of the organics supposed to be present in the sample solutions absorbance values at 254 and 280 nm wavelengths were reported.

2.3. Ecotoxicity Tests

Acute toxicity of seven commercial PCDs was assessed on two freshwater crustaceans *D. magna* and *C. dubia* which are two primary consumers in the aquatic chain. *D. magna* were inoculated in a temperature constant vivarium at NKU Environmental Engineering Department's Laboratory according to ISO method 6341 [26]. The pH of the feeding solutions was kept at 8.0 and the total hardness was 250 $mg.L^{-1}$ (as $CaCO_3$). Tests were performed in the dark at 20 ^oC. For aqueous solution, 5 concentrations in a geometrical series were tested in the concentration range. New born daphnids (<24 h) were exposed to freshly prepared PCD solutions for 24 and 48 h. Experiments were performed as quadruplicate and 5 daphnids were tested in each replicate.

C. dubia cists were kindly provided from another laboratory and incubated at constant temperature room for 48 h in standard solutions for having nauplii. They, than, were inoculated in the constant room temperature to perform acute toxicity tests with new born daphnids (<24 h aged). All vivarium and experimental procedures were the same with *D. magna* [26].

Acute toxicity was assessed by means of immobilization percentage determined by dividing the number of immobilized organisms in four replicate to total 20 number of test organisms.

3. Results

3.1. Chemical Characterization

Results of pH, COD and TOC measurements of PCDs are given in Table 3. The ratio between TOC and COD indicated low biodegradability of all PCDs [27]. Absorbance curves of PCD_s are shown in Figure 1. According to this figure Shower gel 2 only showed the peak value. Absorbance values of all other detergent except Shampoo 1 are low. No peaks observed at 254 and 280 nm wavelengths indicated the presence of long chain chemicals instead of aromatic structures in the sample solutions.

Table 3. Chemical analysis of the PCDs studied.

PCDs (Dilution Rate, mL PCD/mL distilled water)	pH	COD ($mg\ L^{-1}$)	TOC ($mg\ L^{-1}$)	TOC/COD
Shampoo 1 (1/1000)	6.13	335	81	0.242
Shampoo 2 (1/1000)	6.15	270	53	0.196
Shampoo 3 (1/1000)	6.32	155	39	0.251
Shampoo 4 (1/1000)	6.30	260	59	0.226
Shower Gel 1 (1/1000)	6.26	270	53	0.196
Shower Gel 2 (1/500)	5.75	230	47.5	0.206
Shower Gel 3 (1/1000)	--	190	38	0.200

3.2. Toxicity Results of PCDs

Immobilization percentiles of *D. magna* exposed to PCDs are shown in Figure 2 while Figure 3 illustrates the immobilization percentiles of *C. dubia*. EC_{50} values of *D. magna* and *C. dubia* calculated by the PROBIT program are shown in Table 4 and Table 5 respectively. The results of PROBIT analysis remain within 95% confidence intervals (CI) and they displayed high regression coefficients. EC_{50} values ranged from 10.49 to 50.59 $mg.L^{-1}$ for *D. magna* and from 7.768 to 44.82 $mg.L^{-1}$ for *C. dubia*. These data confirm the findings on some detergents [3, 28].

EC_{50} values of *C. dubia* were found to be lower compared to the values calculated for the data sets of *D. magna*. These results indicated that *C. dubia* exhibited more sensitivity to the tested products than *D. magna*.

The results of acute toxicity tests performed with *D. magna* can be ranked in the following order:

- Shampoo 3>Shower Gel 1>Shampoo 4> Shampoo 1> Shower Gel 3> Shampoo 2> Shower Gel 2,

while this ranking changed in the case of *C. dubia* acute toxicity test results as:

- Shampoo 4>Shampoo 3>Shampoo 1>Shampoo 2>Shower Gel 1>Shower Gel 2>Shower Gel 3

Toxicity units ($TU=100/EC_{50}$) were also determined for the studied PCDs as shown in Figure 4.

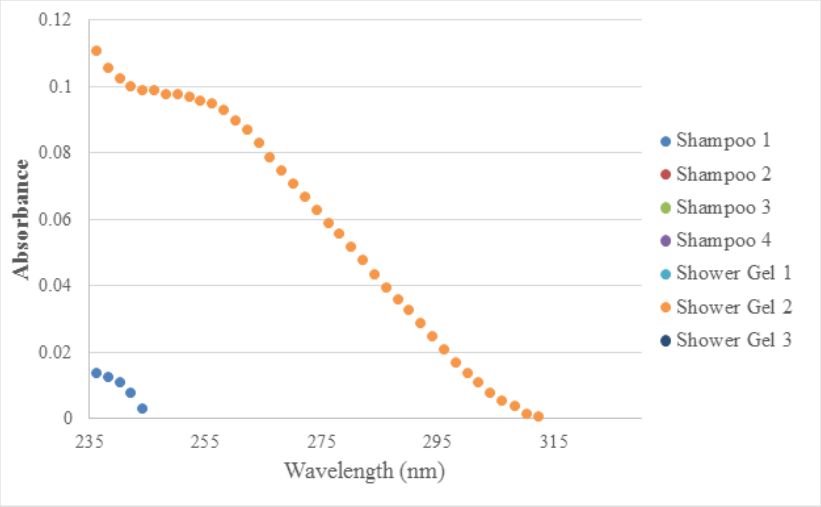
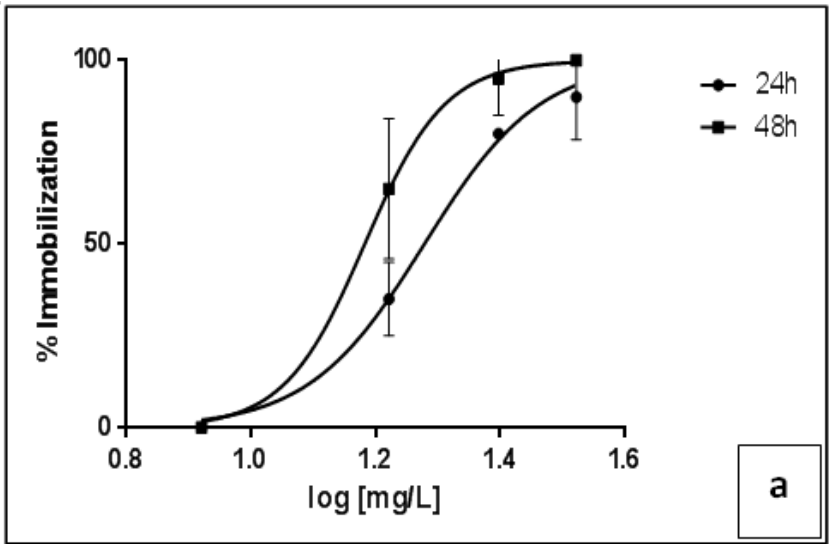
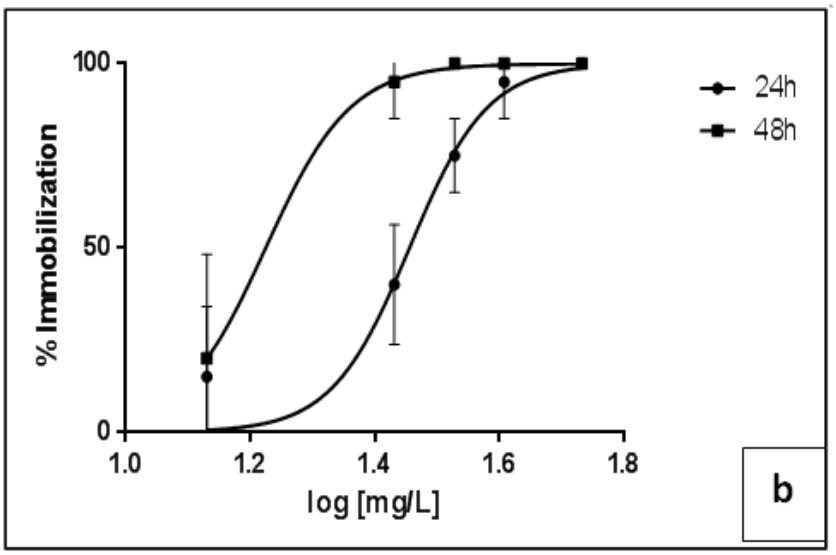


Figure 1. Absorbance curves of personal care detergents studied

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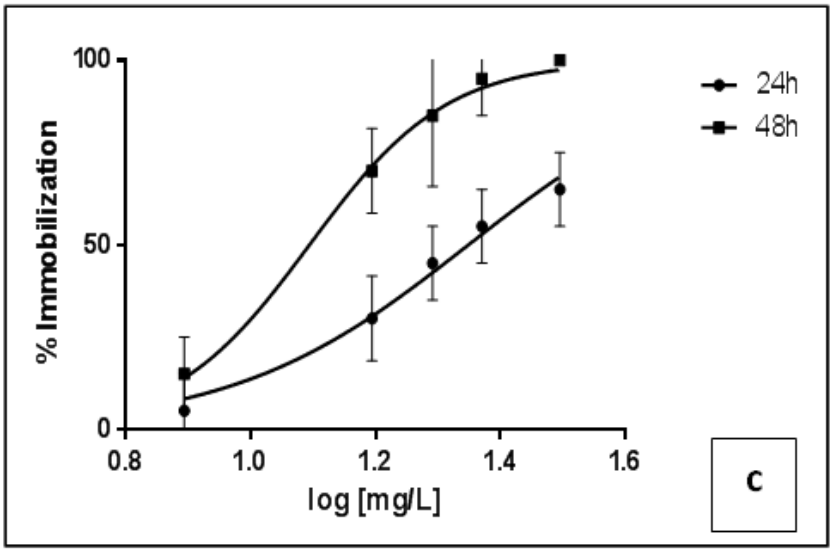
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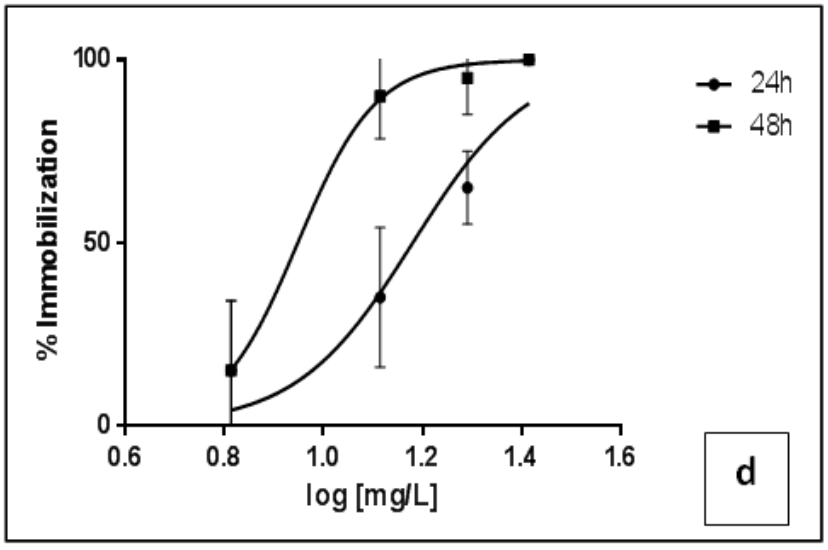
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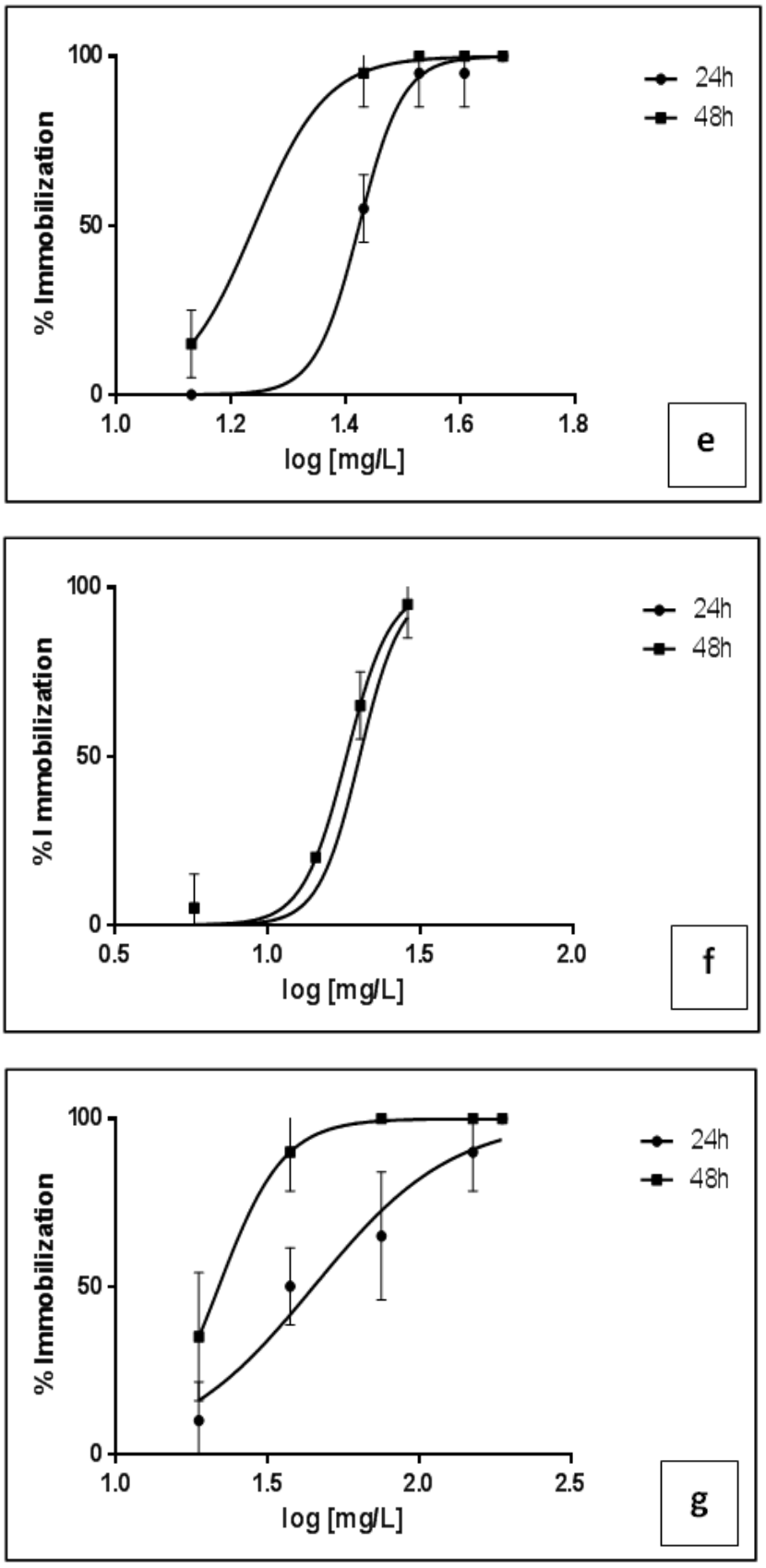
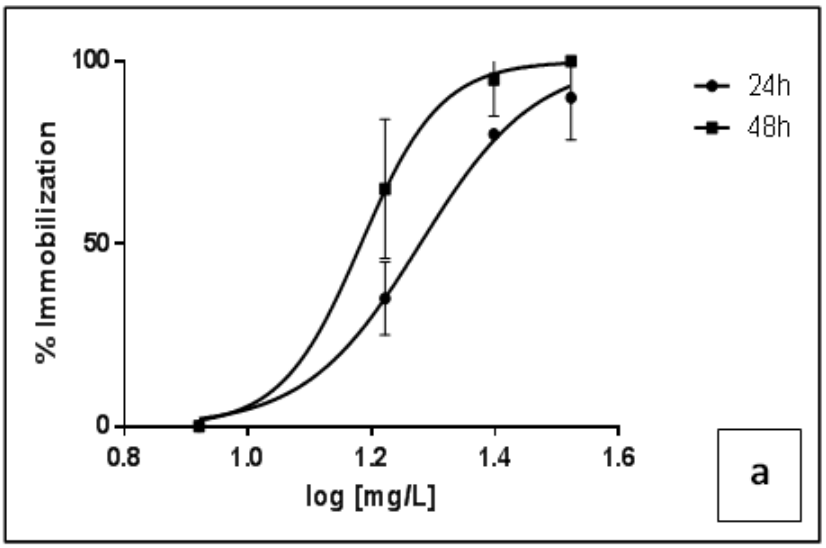


Figure 2. Immobilization percentiles profiles determined using the PROBIT for the data sets of *D. magna* (Shampoo 1(a), 2(b), 3(c), 4(d) and Shower gel 1(e), 2(f), 3(g))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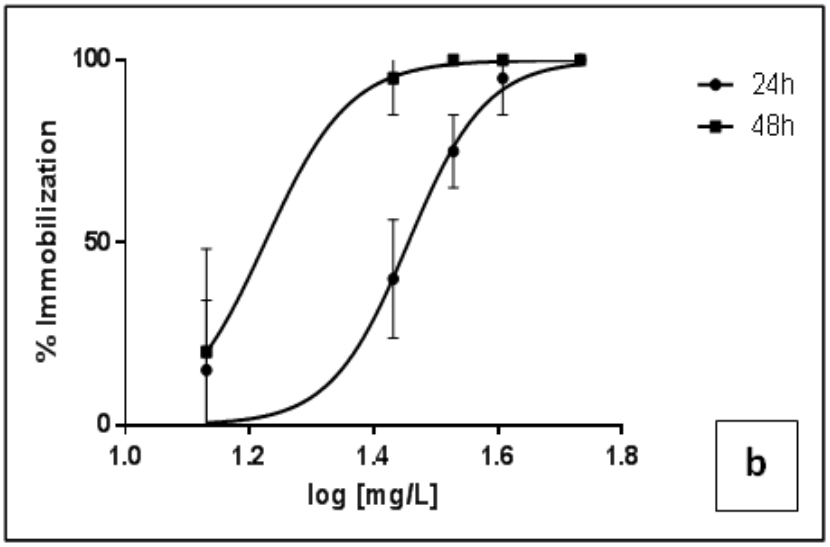
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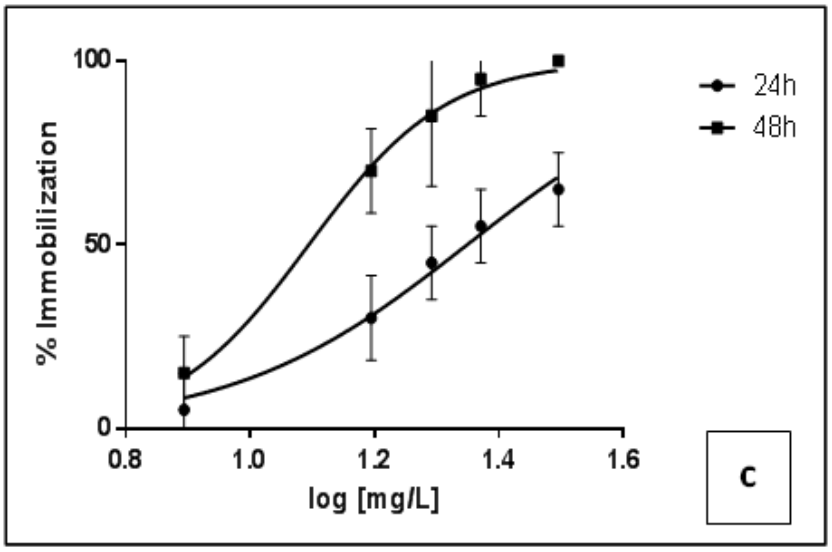
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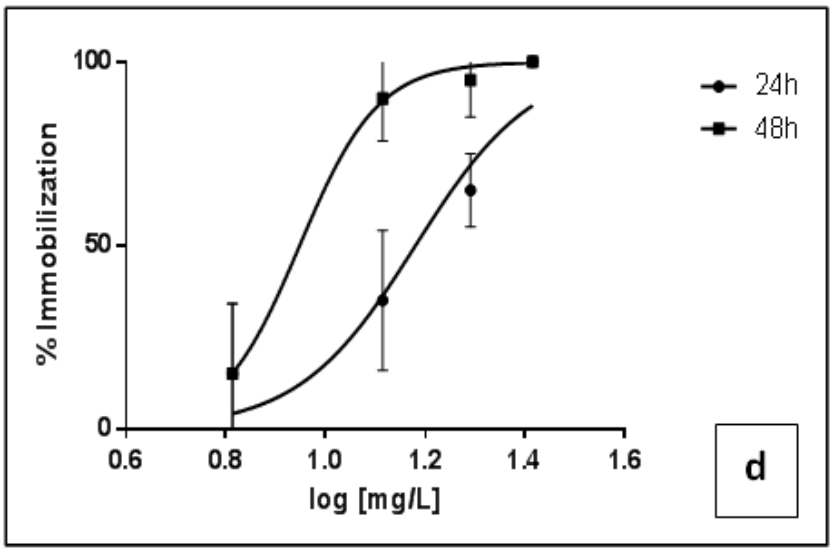
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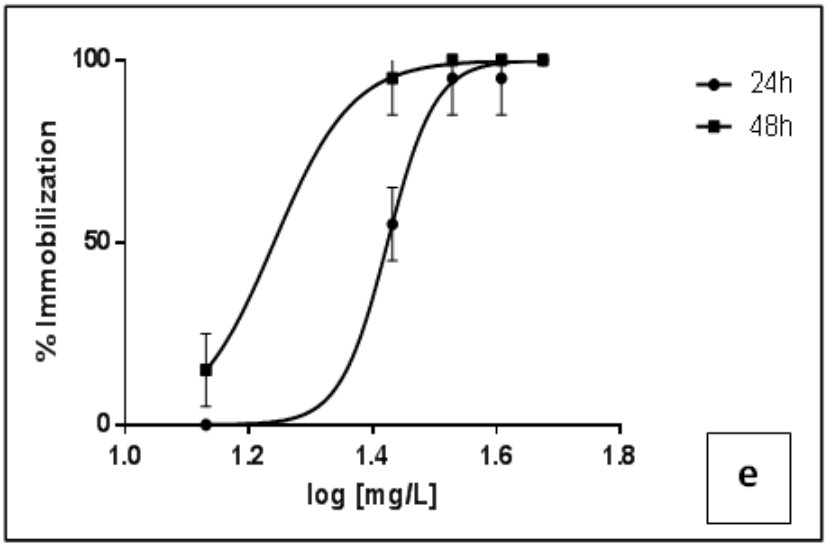
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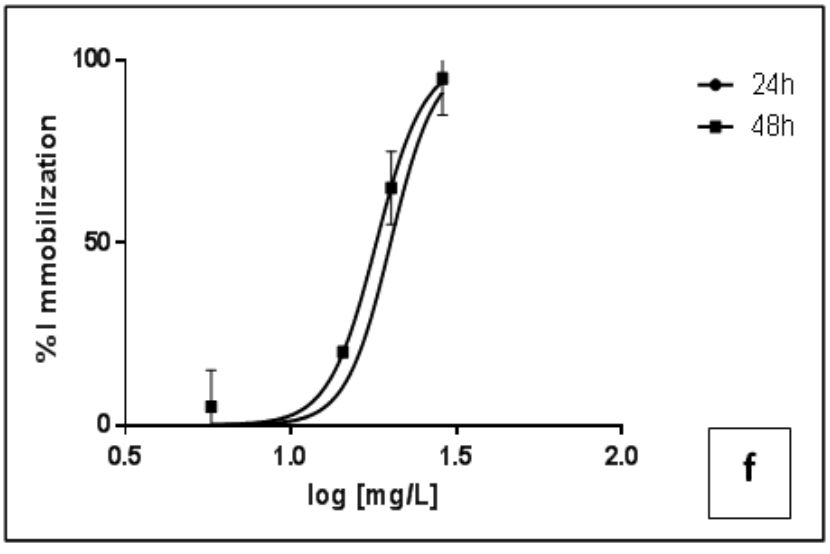
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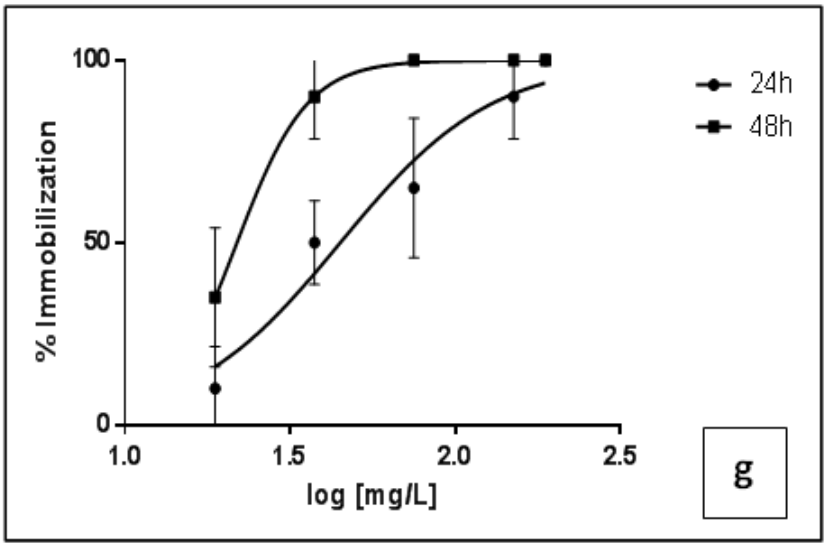

Figure 3. Immobilization percentiles profiles determined using the PROBIT for the data sets of *C. dubia.* (Shampoo 1(a), 2(b), 3(c), 4(d) and Shower gel 1(e), 2(f), 3(g))

Table 4. The values of EC_{50} and 95% confidence intervals for *D. magna* [R^2: Regression values]; (Confidence intervals)

D. magna	**EC_{50} ($mg.L^{-1}$)**			
Sample	24 h	95% CI	48 h	95% CI
Shampoo 1	35.14 [0.99]	(27.74-44.51)	25.3 [0.98]	(21.08-30.29)
Shampoo 2	45.65 [0.985]	(38.81-53.69)	31.93 [0.916]	(21.56-47.27)
Shampoo 3	30.99 [0.992]	(24.68-38.91)	10.49 [0.999]	(9.228-11.92)
Shampoo 4	30.4 [0.998]	(29.65-31.16)	22.14 [1.00]	(21.87-22.42)
Shower Gel 1	31.7 [0.99]	(28.95-34.72)	19.1 [1.00]	(14.78-24.69)
Shower Gel 2	50.59 [0.994]	(47.50-53.88)	43.38 [0.9839]	(39.12-48.12)
Shower Gel 3	33.13 [0.996]	(32.35-33.93)	26.97 [0.992]	(25.87-28.12)

Table 5. The values of EC50 and 95% confidence intervals for *C. dubia* [R^2: Regression values]

C. magna	**EC_{50} ($mg.L^{-1}$)**			
Sample	24 h	95% CI	48 h	95% CI
Shampoo 1	18.99 [0.997]	(17.26- 20.88)	15.23 [0.999]	(14.15-16.39)
Shampoo 2	28.56 [0.959]	(24.98-32.64)	16.78 [1.00]	(16.30-17.28)
Shampoo 3	22.32 [0.985]	(20.17-24.70)	12.42 [0.997]	(11.50-13.41)
Shampoo 4	15.14 [0.93]	(9.631- 23.80)	8.868 [1.00]	(7.768-10.12)
Shower Gel 1	26.52 [0.997]	(25.68-27.38)	17.39 [1.00]	(16.90-17.89)
Shower Gel 2	19.99 [0.9828]	(17.08- 23.38)	18.1 [0.9952]	(16.55-19.78)
Shower Gel 3	44.82 [0.9597]	(30.33-66.24)	21.82 [1.00]	(21.55- 22.09)

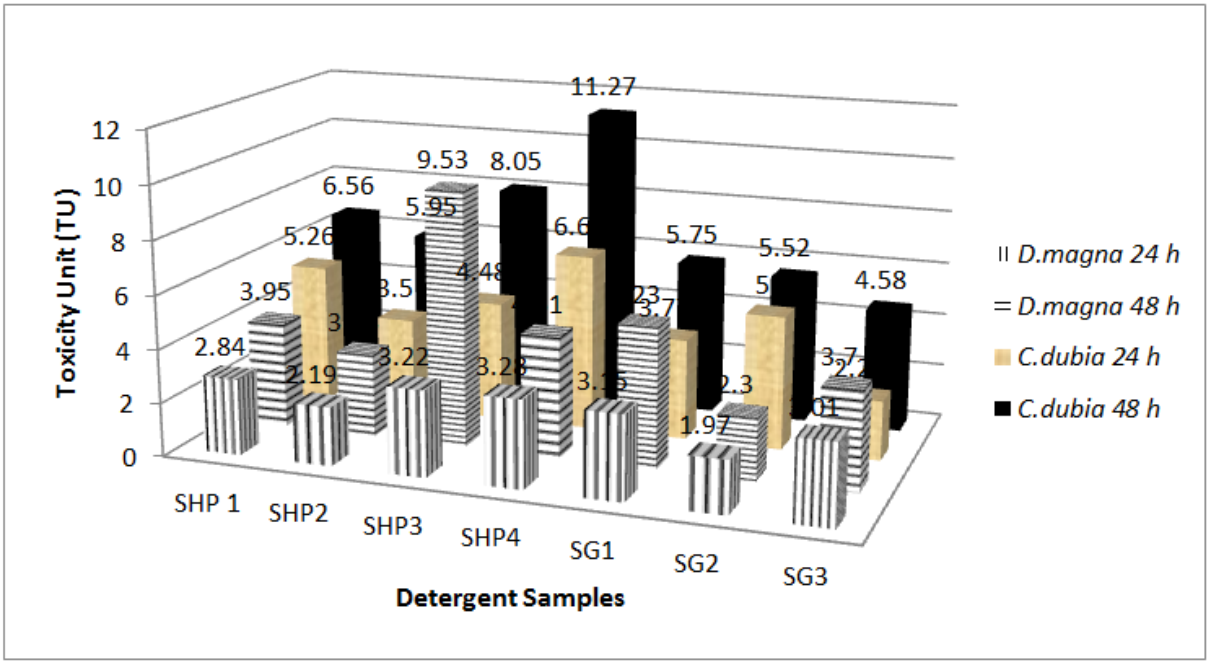

Figure 4. Toxicity unit values as determined using the PROBIT analysis (SHP: Shampoo products; SG: Shower gel)

3.3. Hazard Score Definition

Hazard scores of the studied PCDs are evaluated according to EC Directive (93/67/EEC) [29] are given in Table 6. This hazard classification is based on EC_{50} values and namely chemicals are classified in four classes. When EC_{50} values calculated using the PROBIT analysis for PCD_s (Tables 4-5) were compared with hazard classes shown in Table 6, all PCDs were classified as *harmful to aquatic organisms* (Hazard score was found to be 3) for both 24 and 48 h exposure times except that hazard scores were found to be 2 (Toxic for aquatic organisms) for *C. dubia* exposed to Shampoo 4 for 48 h.

Table 6. Classification of hazardous substances according to 93/67/EC Directive [15]

EC_{50} (mg L^{-1})	Risk Classification	Hazard Score
EC_{50}<1	Very toxic for aquatic organisms	1
1<EC_{50}<10	Toxic for aquatic organisms	2
11<EC_{50}<100	Harmful to aquatic organisms	3
EC_{50} >100	Not classifiable	4

4. Discussion

Our results of acute toxicity tests can be evaluated in the range of chemicals shown in Table 4. Although the PCDs tested at the estimated dilutions in synthetic solutions resulted in *harmful to aquatic organisms* in this study one can estimate that there can be adsorption, sedimentation, biodegradation factors in the sewage systems and WWTPs to decrease the concentration of PCDs before discharge [3, 30]. Anyway, The PCDs have become spread in sewage, in the effluents of $WWTP_s$, rivers, sludges and soils via sludges amended on [31].

From the point of Eco-labeling, as all EC_{50} values of acute toxicity tests shown in Tables 4 and 5 were calculated over 10 $mg.L^{-1}$, except Shampoo 4 (after 48 h of exposure), none of the products are assessed to be pretty acceptable either by the EU [22] or by the Nordic classification [23] because of lacking information of ingredients that requires to perform chronic tests. Our results can be accepted as the base to perform further evaluations and tests in this manner.

5. Conclusions

PCDs collected from different hotels located in different countries were characterized for biodegradability and acute toxicity to *D. magna* and *C. dubia*.

- Ratio between TOC and COD was found to be very low (approx.. 0.2) indicating low biodegradability of the tested chemicals. This fact emerges the need of advanced treatment processes.
- The results of acute toxicity tests showed that both species displayed different behaviour when exposed to the PCDs. *C. dubia* was found to be more sensitive than *D. magna*.
- According to EC_{50} values evaluated for hazard classification almost all PCDs tested were assessed to be *Harmful to aquatic organisms (Hazard score was found to be 3)* except shampoo 4 and shampoo 3 which were found to be *toxic for aquatic organisms*

(Hazard score 2) for *C. dubia* and *D. magna* exposed to the PCDs for 48 h.

- PCD_s are the chemicals of concern that their consumption has been increasing with the improving life quality standards. Although their fate and transformation in sewage and treatment systems have been documented they widely occur in the environmental compartments. Thus, the results obtained in this study show that this group of pollutants should be handled carefully before entering the aquatic environment.

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