Environ Sci Pollut Res (2018) 25:13283–13291
DOI 10.1007/s11356-016-7861-0

Toxic effect of commercial detergents on organisms from different trophic levels

A. Sobrino-Figueroa [1]

Received: 14 March 2016 / Accepted: 6 October 2016 / Published online: 18 October 2016

Abstract The toxic effects of four powder detergents: two laundry detergents (A and B), one household detergent (C), one dishwashing detergent (D), and the surfactant alkylbenzene sulfonate (LAS) were analyzed in this study on organisms from different trophic levels (microalgae, cladocerans, ostracods, amphipods, macrophytes, and fish). LC_{50} and EC_{50} values obtained in the toxicity bioassays varied between 0.019 and 116.9 mg L^{-1}. The sensitivity of the organisms to the detergents was (from most sensitive to least sensitive) Ostracods > microalgae > amphipods > cladocerans > fishes > macrophytes. The toxicity of the commercial products (from most toxic to least toxic) was LAS > D (dishwashing detergent) > A (laundry detergent) > B (laundry detergent) > C (household detergent). When comparing the sensitivity of organisms that inhabit temperate zones (T = 18 °C) to those that are found in tropical zones (T > 25 °C), it was clear that the species that inhabit the tropics are more sensitive to detergents.

Keywords Detergents' toxicity · Zebrafish · *Daphnia exilis* · *Chirostoma jordani* · *Lemna gibba*

Introduction

The accelerated industrialization and urbanization processes in our country, over the last six decades, have caused alterations in the aquatic ecosystems due to the input of xenobiotics (Albert 2012).

Domestic detergents are among the contaminants with the greatest impact, since it is estimated that 2 billion kg per year are used worldwide. In Mexico, around 470,000 t are produced (INEGI 2014), and the final destinations of these products are the aquatic systems (Cserhati et al. 2002; Rebello et al. 2013).

A detergent is a chemical compound of complex structure that is formed by a surfactant agent, which can be of three different types: anionic, such as alkylbenzene sulfonate (LAS), dodecyl benzene sulfonate, and alkyl lauryl sulfonate; cationic, such as cetyl trimethyl ammonium chloride, benzalkonium chloride, and ethoxylated alcohols; and nonpolar, such as alkyl polyglycosides, Triton X, and Tween 80. Additionally, detergents contain additives such as water softeners (polyphosphates and silicates), anti-redeposition agents (silicates and carbonates), bleaching agents (perborates), preservatives (sodium sulfate), corrosion inhibitors, brightening pigments, enzymes (proteases and amylases), foam stabilizers, dyes, perfumes, and minor components (Warne and Schifko 1999; Pettersson et al. 2000; Rebello et al. 2013).

LAS is one of the major anionic surfactants used in cleaning products. LAS is commonly used in all-purpose cleaning products at a typical concentration from 1 to 37 %. The powdered laundry detergents contain between 3 and 22 % and dishwashing detergents between 2 to 30 % (HERA 2012).

The additives contained in different powder detergents are poly-phosphate (20–25 %), silicate (0.2–15 %), sodium perborate (7–16 %), fluorescent pigment (0.1 %), sodium sulfate (10–20 %), and enzymes (0.007–0.1 %) (PROFEPA 2002; HERA 2012). The formulations of commercial detergents are confidential.

The detergents are found in the discharges that end up in aquatic systems in a continuous manner, causing plant and animal species to be chronically exposed to these compounds.

Responsible editor: Thomas Braunbeck

✉ A. Sobrino-Figueroa
coco@xanum.uam.mx

[1] Laboratorio Alejandro Villalobos, Departamento de Hidrobiología, Universidad Autónoma Metropolitana-Iztapalapa, Av. San Rafael Atlixco No. 186 Colonia Vicentina, C.P. 09340 Ciudad de México, México

The toxicity caused by detergents to aquatic organisms has been evaluated since the 1960s (Lemke and Mount 1963; Abel 1974; Cserhati et al. 2002; Warne and Schifko 1999; Rebello et al. 2013); however, only the effects of the surfactants have been determined. The harmful effects of anionic compounds are inhibition of the activity of important enzymes such as esterases and phosphatases; changes in the nerve receptors of fish that induce disorders in feeding and thermoregulation; alterations in the permeability of cell membranes caused by variations in phospholipid composition, as well as inhibition or modification of the transport functions of proteins in the membrane; and alterations in the epithelial tissue of the gills, causing respiration problems in fish and molluscs (Bardach et al. 1965; Alcaraz et al. 1993; Bao-Quey and Dar-Yi 1994; Hansen et al. 1997; Rebello et al. 2013). Elevated concentrations of these compounds produce cellular lysis and cause the death of sensitive organisms (Sandbacka et al. 2000).

Additionally, it has been observed that anionic surfactants induce inflammatory reactions and oxidative stress (Susmi et al. 2010). Furthermore, there is evidence that the surfactant alkylbenzenesulfonate is bioaccumulated in crustaceans (Renaud et al. 2014).

Moreover, anionic surfactants cause important alterations in aquatic systems by producing changes in water quality and eutrophication due to the input of phosphates (Hoffman and Bishop 1994; Stow et al. 2001).

Cationic surfactants are highly toxic to aquatic species. Alkylphenols, ethoxylates, and their metabolites can act as endocrine disruptors in fish (Sonnenschein and Soto 1998; Koerner et al. 1998).

Recent studies have demonstrated that the additives present in commercial detergents have harmful effects. Sodium citrate, sodium perborates, polycarboxylates, corrosion inhibitors, and perfumes with lemon fragrances have genotoxic effects (Tükoglu 2007; Pedrazzani et al. 2012). The enzymes present in the detergents contribute to the toxicity of commercial detergents, causing tissue damage due to their lytic activity (Davis 2004; HERA 2012).

The studies carried out on commercial detergents are scarce, and their toxic effects have only been evaluated on the following microalgae: *Euglena gracilis* (Azizullah and Häder 2011; Azizullah et al. 2013), *Plagioselmis prolonga* (Aizdaicher and Markina 2006), *Attheya ussurensis* (Markina and Aizdaicher 2007), *Dunaliella salina* and *Plagioselmis prolonga* (Markina and Aizdaicher 2010); Cladocerans: *Daphnia magna* (Pettersson et al. 2000; Pedrazzani et al. 2012) and *Ceriodaphnia dubia* (Warne and Schifko 1999); polychaetes: *Laeonereis culveri* (Uc-Peraza and Delgado-Blas 2012) and *Capitella* sp. (Uc-Peraza and Delgado-Blas 2015); the gastropod, *Physa acuta* (Sobrino-Figueroa 2015); and in the zebra fish, *Danio rerio* (Sobrino-Figueroa 2013).

Since the studies on commercial detergents are few and there are no previous studies for species native to our country, the objective of this work was to evaluate the toxicity of four commonly used detergents, two laundry detergents, one household detergent, one dishwashing detergent, and the surfactant LAS, on organisms from different trophic levels: the microalgae: *Pseudokirchneriella subcapitata* and *Monoraphidium* sp.; the cladocerans: *D. magna*, *Daphnia exilis*, *Moina macrocopa*, and *Simocephalus mixtus*; the ostracod *Cypris* sp.; the amphipod *Hyallela azteca*; the fish: *D. rerio* and *Chirostoma jordani*; and the macrophytes: *Lemna gibba* and *Egeria densa*, in order to determine their sensitivity to these products.

Methods

Detergents

Four common brands of detergents were selected, two used for washing clothes: Ariel Oxianillos (A) (P&G) and Foca (B) (La Corona), one dishwashing powder: Salvo (D) (P&G), and one general use detergent: Roma (C) (La Corona). The compounds found in each detergent are listed in Table 1, based on the information available on the packaging and the corresponding Material Safety Data Sheets. The tensoactive agent LAS (80 %) was obtained from Sigma-Aldrich (CAS 151-21-3).

From each detergent, a stock solution of 1000 mg L^{-1} (ppm) in deionized water was prepared. From this solution, the test solutions were prepared and used for the toxicity bioassays. The stock solution was prepared on the same day on which the bioassays were performed. The pH of the stock solution was between 7.2 and 8.2.

Toxicity bioassays

The organisms used in this study were obtained from laboratory cultures under controlled conditions.

Toxicity bioassays were carried out. The duration of the bioassays was 48 h for the testing on cladocerans, 72 h for the assays on ostracods, and 96 h for the assays on microalgae, amphipods, macrophytes, and fishes. The organisms were exposed to six concentrations of each of the detergents, in triplicate (0.1, 0.5, 1, 2, 4, and 8 ppm for microalgae and ostracods; 2, 4, 8, 16, 32, and 64 ppm for cladocerans and amphipods, and 10, 20, 30, 40, 80, and 160 ppm for macrophytes and fishes), and a control without detergent. The test organisms were not fed during the course of the experiment. Each assay was repeated at least three times.

Static bioassays were carried out with microalgae. The conditions during the tests were continuous illumination (4000 lx) and temperature 25 ± 1 °C. The test volume was 5 mL, with a number of cells in the initial inoculum of 10,000 cells mL^{-1}. Reconstituted water with a water hardness of 160 mg of $CaCO_3$ and supplemented with nutrients was used as dilution

Table 1 Surfactant agents and additives containing in the commercial detergents tested

Compounds	Ariel	Foca	Roma	Salvo
Surfactant agent	Alkyl larylsulfonate lauryl dimethyl hydroxyethylammonium	Dodecylbenzene sulfonate	Alkylbenzene sulfonate	Dodecylbenzene sulfonate
Water softeners	Sodium triphosphate, sodium silicate	Sodium phosphate, sodium silicate	Sodium silicate, sodium phosphate	Sodium phosphate
Anti-redeposition agents	Yes	Yes	Yes	No
Bleaching agents	Sodium carbonate, peroxides	Yes	No	No
Preservatives	Sodium sulfate	Sodium sulfate	Sodium sulfate	Sodium sulfate
Brightening pigments	Yes	?	No	No
Enzymes	Yes	Yes	No	Yes
Dyes	Yes	Yes	No	Yes
Perfumes	Yes	Yes	Yes	Lemon

Information obtained in the package detergents and their safety data sheets

water. The effect measured was population growth. At the end of the toxicity tests (96 h), an aliquot of 0.1 mL was taken and the number of cells present in each sample was counted by using a hemocytometer (American Optical). The percentage of inhibition of population growth was calculated with the formula proposed by USEPA 1992:

$$\% \text{ Inhibition} = 100 - [(\text{average cells per test}/\text{average cells in control group})] \times 100$$

Toxicity tests with cladocerans were made following the recommendations of the Mexican Standard NMX-AA-087-1995-SCFI. All experiments were made with third to fifth brood neonates (18 to 24 h old) derived from a healthy parent stock. The conditions during the bioassay were reconstituted water with a water hardness of 160 mg of $CaCO_3$, temperature 18 ± 1 °C (for tests on *D. magna*) and 25 ± 1 °C (for bioassays with *D. exilis*, *M. macrocopa*, and *S. mixtus*), Photoperiod 16:8 h light/dark, test volume 100 mL, number of organisms per test 10 neonates, and response measured: immobility at 24 and 48 h.

With juveniles (5 days old) of the *H. azteca* amphipod, static acute toxicity tests were performed. The tests were carried out with reconstituted water with a hardness of 160 mg of $CaCO_3$ with 10 organisms per concentration. During the bioassay, the amphipods were maintained under the following conditions: temperature 25 ± 1 °C, photoperiod of 16:8 light/dark, test volume 100 mL, and measured effect: death of the juveniles. The criterion used to establish the death of the juvenile was the absence of a response when stimulated mechanically (Cano et al. 1996).

For the tests with ostracods, juveniles 3 days old (150 ± 12 mm length) were used. The physical and chemical conditions of the acute toxicity tests were temperature 25 ± 1 °C, total water hardness of 160 mg of $CaCO_3$, volume of the test solution 50 mL, number of organisms per condition 20 juveniles, and measured effect immobility at 24, 48, and 72 h.

The assays with fishes were carried out following the protocol suggested by APHA (1994). Ten juveniles (0.52 ± 0.20 g) were placed in 10-L glass containers, in triplicate, and were exposed to six concentrations of each type of detergent during 4 days. Reconstituted water with hardness of 160 mg L^{-1} of $CaCO_3$ was used as dilution water in the tests. Bioassays were maintained at the following conditions: temperature 25 ± 1 °C, photoperiod 12:12 (light/dark), and dissolved oxygen >4 mg L^{-1}. Every 24 h, the water with the detergent solution was changed for each condition. The effect measured was the mortality of the fish.

The experiments with aquatic macrophytes were made with axenic cultures of *L. gibba* and *E. densa.* For each test, healthy young plants were used. Colonies of four to five leaves of *L. gibba* and stems (3 cm) of *E. densa* were placed in containers with 350 mL of test solution (modified Hoagland's culture medium) with different concentrations of the detergents. The conditions recorded during the bioassay were temperature 25 ± 1 °C, pH 7.6, continuous illumination (6500 lx), and measured effect: increase of biomass as wet weight (OECD 2002).

In the assays with cladocerans, amphipods, ostracods, and fish, the number of dead organisms was evaluated every 24 h and these were removed from each container to avoid the production of toxic metabolites.

With the mortality data, the lethal concentration 50 (LC_{50}) with its confidence intervals were determined, by using the Probit method (Probit-EPA, version 1.5).

In the tests on the microalgae and macrophytes, the EC_{50} was calculated, which corresponds to the detergent concentration which reduces the cell production number of the microalgae or the biomass (wet weight) of macrophytes by 50 %.

The calculation for comparison between the LC_{50} and the EC_{50} and the corresponding confidence intervals was carried out by using the statistical analysis described by APHA (1994) and then used to evaluate the statistical significance of the differences found between the different treatments with the detergents.

f_2 = Lower endpoint of the 95 % confidence interval
$f_{1,2} = 1.96\ \mathrm{SD}/\mathrm{LC}_{50\,f\,1,2}$

$$f_{1,2} = \mathrm{antilog}\sqrt{(\log\ f_1)^2 + (\log\ f_2)^2}$$

LC_{50} upper/LC_{50} lower > $f_{1,2}$ = There are significant differences.
where

SD	standard deviation
LC_{50}	lethal concentration 50
f	confidence limit factor
f_1	upper endpoint of the 95 % confidence interval

Results

Validity of the tests—abiotic variables

Three bioassays were carried out for each species; in total, there were 36 assays. The mortality in the control groups of all of the tests was below 10 %, a value considered to be acceptable in standardized protocols. The values for O_2 in the bioassays were above 70 % saturation; the pH values varied between 7.2 and 7.6; the temperature was maintained at 25 ± 1 °C, except for the tests on *D. magna* where it was 18 ± 1 °C.

The average LC_{50} and the confidence intervals ($p < 0.05$) are shown in Table 2. In all of the cases, we observed significant differences in the response of the organisms exposed to xenobiotics as compared to the control group.

In the tests performed by using detergent A, it was observed that the most sensitive organism to this product was the cladoceran *D. exilis* and the least sensitive was the macrophyte *E. densa*. Significant differences in sensitivity between the species were detected by using a Tukey test ($p < 0.05$), showing differences in the responses of the microalgae, cladocerans, ostracods, amphipods, and macrophytes.

The LC_{50} values obtained in the experiments by using detergent B varied between 0.67 and 90.6 ppm. The most susceptible species to this detergent was the ostracod, and the least susceptible was the macrophyte *E. densa*. There were significant differences between the responses of the microalgae, cladocerans, ostracods, fishes, and macrophytes.

The data obtained from the tests by using the detergent C showed that the most sensitive organism was the ostracod and the least sensitive was the macrophyte *E. densa*. No significant differences were observed between the responses shown by the macrophyte *L. gibba* and the cladoceran *D. magna*, and the fishes.

In the lethality tests by using the detergent D, the most sensitive species was the ostracod *Cypris* and the least sensitive was the macrophyte. There were significant differences in the response to the detergent between the microalgae, macrophytes, cladocerans, and fishes. There were no significant differences observed between *D. magna* and the macrophytes, and the fishes.

In the bioassays by using the tensioactive compound LAS (alkyl lauryl sulfonate), the LC_{50} varied between 0.263 and 79.7 ppm. LAS was most toxic to the cladoceran *D. exilis* and least toxic to the macrophyte *E. densa*. Significant differences in the responses were detected between the macrophytes and the other species.

When comparing the average values of LC_{50} obtained in the tests with the different brands of detergents, we observed that the most toxic product was the surfactant LAS and the least toxic was the commercial detergent C.

The toxicity of the detergents under study was

$$\mathrm{LAS} > \mathrm{D(Salvo)} > \mathrm{A(Ariel)} > \mathrm{B(Foca)} > \mathrm{C(Roma)}$$

Based on the average of the calculated LC_{50}, the sensitivity of the different species to the detergents used in this study was (from most sensitive lo least sensitive)

Cypris sp. > *P. subcapitata* > *M. macrocopa* > *H. azteca* > *Monoraphidium* sp. > *D. exilis* > *S. mixtus* > *C. jordani* > *D. rerio* > *D. magna* > *L. gibba* > *E. densa*.

Degree of toxicity of the detergents

Based on LC_{50} values obtained by the assays, the compounds were classified as established by the Globally Harmonized System of Classification and Labeling of Chemicals (GHS) (Fig. 1):

(i) Highly toxic: LC_{50}, $EC_{50} \leq 1\ \mathrm{mg\ L^{-1}}$
(ii) Toxic: LC_{50}, EC_{50}: $1 \leq 10\ \mathrm{mg\ L^{-1}}$
(iii) Harmful to aquatic organisms: LC_{50}, EC_{50}: $10 \leq 100\ \mathrm{mg\ L^{-1}}$
(iv) Nontoxic: LC_{50}, $EC_{50} > 100\ \mathrm{mg\ L^{-1}}$

The detergent A was highly toxic for the cladoceran *D. exilis* and the ostracods; toxic for the microalgae, the cladocerans: *D. magna* and *M. macrocopa*, and the amphipod;

Table 2 Lethal concentration 50 (LC_{50}) and effective concentration 50 (EC_{50}) values and confidence intervals, obtained in tests with aquatic organisms exposed to detergents

Organisms	LC_{50} or EC_{50} (mg L^{-1}) Confidence intervals (95 %)				
	Ariel	Foca	Roma	Salvo	LAS
Pseudokirchneriella subcapitata	2.1 ± 0.8^{a1}	3.9 ± 1.02^{a1}	6.6 ± 2.3^{a2}	1.4 ± 0.8^{a1}	2.1 ± 0.7^{a1}
Monoraphidium sp.	2.9 ± 1.3^{a1}	8.4 ± 2.6^{b2}	7.8 ± 2.4^{a2}	2.1 ± 0.75^{a1}	3.52 ± 2.02^{a1}
Daphnia magna	1.6 ± 0.9^{a1}	41.6 ± 12.5^{c2}	52.9 ± 20.5^{b2}	34.3 ± 18.4^{b2}	6.31 ± 1.21^{b1}
D. exilis	0.32 ± 0.11^{b1}	6.9 ± 3.1^{b2}	21.4 ± 10.1^{b3}	2.1 ± 0.9^{a2}	0.263 ± 0.14^{c1}
Moina macrocopa	3.5 ± 1.7^{a1}	2.3 ± 1.2^{a1}	5.24 ± 1.5^{a1}	1.24 ± 0.7^{a2}	5.89 ± 1.6^{b1}
Simocephalus mixtus	19.08 ± 7.4^{c1}	23.8 ± 6.1^{c1}	11.4 ± 3.4^{b1}	4.6 ± 1.1^{c2}	1.86 ± 1.04^{a3}
Cypris sp.	1.15 ± 0.88^{a1}	0.67 ± 0.3^{d2}	0.91 ± 0.3^{c2}	0.12 ± 0.096^{d3}	3.01 ± 1.11^{a4}
Hyallela azteca	8.07 ± 2.77^{d1}	6.4 ± 3.2^{b1}	7.07 ± 1.27^{a1}	1.15 ± 0.54^{a2}	0.918 ± 0.70^{c2}
Danio rerio	28.8 ± 17.1^{e1}	29.9 ± 11.1^{c1}	18.4 ± 5.1^{b1}	7.2 ± 2.1^{c2}	6.6 ± 1.56^{b2}
Chirostoma jordani	19.2 ± 3.4^{e1}	21.4 ± 4.5^{c1}	24.3 ± 2.4^{b1}	4.8 ± 3.1^{c2}	2.64 ± 0.8^{a2}
Lemna gibba	32.25 ± 11.4^{e1}	46.4 ± 19.2^{c1}	51.5 ± 10.1^{d1}	42.8 ± 21.8^{b1}	22.7 ± 12.2^{d1}
Egeria densa	116.9 ± 22.6^{f1}	90.6 ± 17.9^{d1}	87.9 ± 12.6^{e1}	53.7 ± 8.3^{b2}	79.7 ± 25.7^{e1}

Superscript letters (a, b, c) indicate statistical differences between specie at one detergent ($p < 0.05$). Different superscript numbers indicate significant differences between tests of different detergents ($p < 0.05$), where test results sharing the same letter and number did not differ significantly from each other

harmful to the cladoceran *S. mixtus*, the fishes, and the macrophyte *L. gibba*; and nontoxic to the macrophyte *E. densa*.

The degree of toxicity of detergent B was high for the ostracods; toxic to the microalgae, the cladocerans: *D. exilis* and *M. macrocopa*, and the amphipods; and harmful to the cladocerans: *D. magna* and *S. mixtus*, fishes, and macrophytes.

The product C was highly toxic to the ostracods; toxic to the microalgae, the cladoceran *M. macrocopa*, and the amphipods; and harmful to the cladocerans: *D. magna*, *D. exilis*, and *S. mixtus*, fishes, and macrophytes.

The toxicity of the detergent D was high for the microalgae and the ostracods; toxic for the cladocerans: *D. exilis*, *M. macrocopa*, and *S. mixtus*, the amphipods, and the fishes; and Harmful to the cladoceran *D. magna* and the macrophytes.

The surfactant LAS was highly toxic to the cladoceran *D. exilis* and the amphipods; toxic to the microalgae and the cladocerans: *D. magna*, *M. macrocopa*, and *S. mixtus*, the ostracods, and the fish; and harmful to the macrophytes (Fig. 2).

Discussion

As mentioned above, the toxicity of detergents to aquatic organisms has been studied since late 1960s (Rebello et al. 2013). However, the majority of the studies have only determined the toxic effects of the surfactants (Abel 1974; Lewis 1990; Lewis and Suprenant 1983; Cserhati et al. 2002; Liwarska et al. 2005) or of a few of the ingredients that are present in the detergents (Warne and Schifko 1999), and studies carried out on products of commercial use are very scarce (Pettersson et al. 2000; Azizullah and Häder 2011; Sobrino-Figueroa 2013).

The detergents used in this study have anionic surfactants, and only detergent A also contains cationic tensioactive compounds. Additionally, all of the detergents contain sodium silicate as a water softener and sodium sulfate as a preservative (to prevent clumping of the detergent). Three of the products tested (A, B, and D) contain enzymes, dyes, and perfumes. Only two detergents (A and B) contain bleaching compounds.

The difference in the degree of toxicity among the detergents used for this study is due to the composition of each product. The most toxic detergents were D and A.

Detergent D is a product used to wash dishes; it contains enzymes (proteases) as well an anionic surfactant compound, perfumes, dyes, and silicates. Detergent A is a detergent used to wash clothes. It contains anionic and cationic tensioactive compounds, whiteners, enzymes, perfumes, dyes, and silicates. A previous study by Warne and Schifko (1999) showed that the toxic components of detergents are the surfactants, silicates, whiteners, enzymes, and dyes.

In this study, it was found that the most toxic detergents were those used for washing clothes and dishes.

In other studies, it has been reported that concentrations of the surfactant LAS between 1.4 and 116 ppm are toxic to microalgae (EC_{50} at 96 h) (Lewis 1990). The EC_{50} values obtained in this study were of 2.1 ± 0.7 and 3.52 ± 2.02 ppm for tests carried out on *P. subcapitata* and *Monorraphidium*

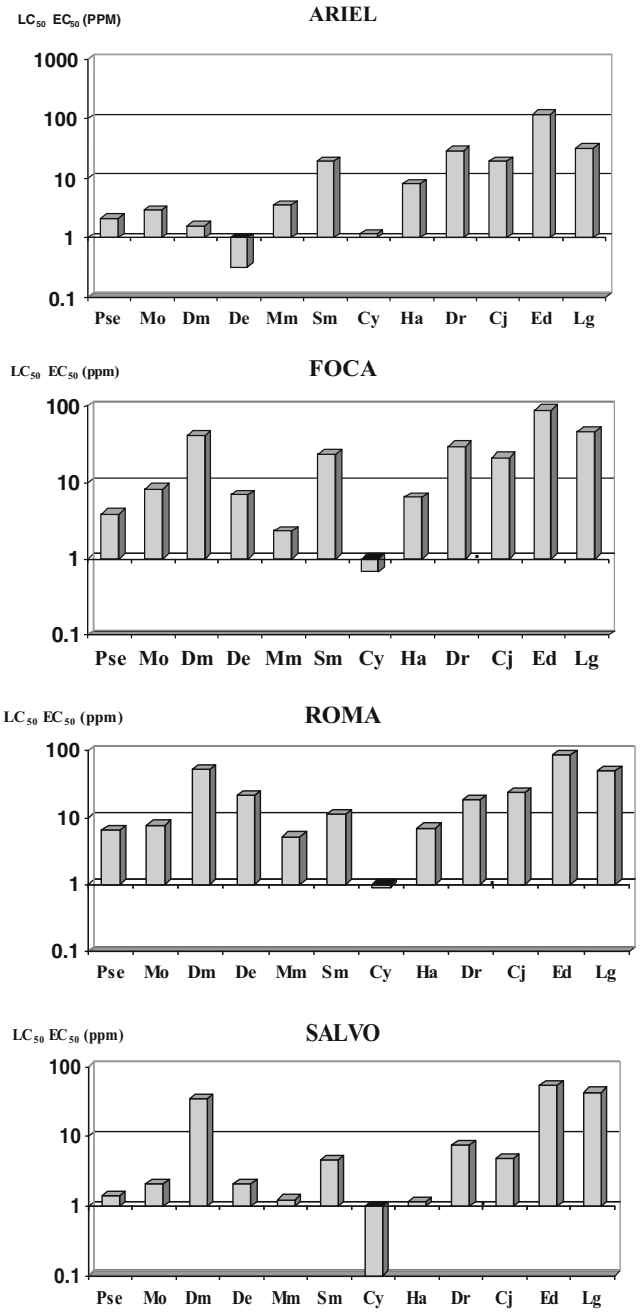

Fig. 1 Toxicity of commercial detergents on aquatic organisms. Highly toxic: LC_{50} or $EC_{50} \leq 1$ ppm. Toxic: LC_{50} or EC_{50}: $1 \leq 10$ ppm. Harmful: LC_{50} or EC_{50} $10 \leq 100$ ppm. Nontoxic: LC_{50} or $EC_{50} > 100$ ppm

sp., respectively. This indicates that these two species are more sensitive to the surfactant than diatoms, *Nitzschia fonticola* (EC_{50} = 50 ppm), cyanophyte *Microcystis aeruginosa* (20 ppm) (Yamane et al. 1984), and chlorophytes *Chorella vulgaris* (32 to 50 ppm) (Canton and Slooff 1982) and *Cladophera glomerata* (100 ppm) (Whitton 1967).

Azizullah and Häder (2011) evaluated the effects of detergent A on the microalgae *E. gracilis* and observed that concentrations of 917 ppm produced a reduction of 50 % in the motility of this organism. The data obtained in this study indicates

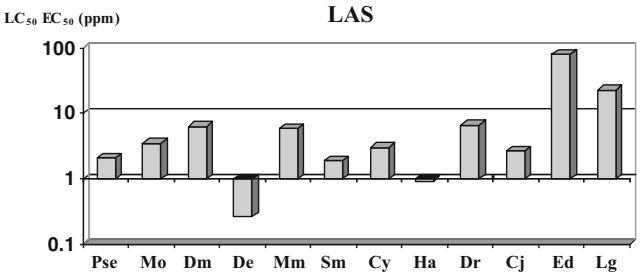

Fig. 2 Toxicity of alkylbenzene sulfonate surfactant in tests with aquatic organisms. Highly toxic: LC_{50} or $EC_{50} \leq 1$ ppm. Toxic: LC_{50} or EC_{50}: $1 \leq 10$ ppm. Harmful: LC_{50} or EC_{50} $10 \leq 100$ ppm. Nontoxic: LC_{50} or $EC_{50} > 100$ ppm. Microalgae: *Pseudokirchneriella subcapitata* (*Pse*), *Monoraphidium* sp. (*Mo*); cladocerans: *Daphnia magna* (*Dm*), *D. exilis* (*De*), *Moina macrocopa* (*Mo*), and *Simocephalus mixtus* (*Sm*); the ostracod *Cypris* sp. (*Cy*); the amphipod *Hyallela azteca* (*Ha*); the fishes: *Danio rerio* (*Dr*) and *Chirostoma jordani* (*Cj*); and the macrophytes *Egeria densa* (*Ed*) and *Lemna gibba* (*Lg*)

that *P. subcapitata* and *Monorraphidium* sp. (LC_{50} = 2.1 ± 0.95 and 2.9 ± 1.3 ppm, respectively) are more sensitive to the detergent A than *E. gracilis*, a species that is used for the tertiary treatment of residual waters (Rebello et al. 2013).

The invertebrates, especially in their juvenile phases, are extremely sensitive to surfactants, since concentrations below 1 ppm can cause alterations in their survival, conduct, and growth rate. The toxicity of the anionic surfactant LAS varies from 1 to 270 ppm in tests carried out on aquatic invertebrates (Lewis 1993; Lewis and Suprenant 1983; Cano et al. 1996; Iannacone and Alvariño 2002; Da Silva-Coelho and Rocha 2010).

The LC_{50} values obtained in this work, in the tests carried out on cladocerans, amphipods, and ostracods, vary from 0.91 ± 0.73 to 6.31 ± 1.21 ppm. These concentrations are found within the interval of toxic values for aquatic invertebrates, but it is evident that the organisms used in this study are more sensitive to the tensioactive LAS than the isopods (*Asellus* sp. LC_{50} = 270 ppm), nematodes (*Rhabditis* sp. LC_{50} = 16 ppm), the midge *Paratanytarsus parthenogenica* (LC_{50} = 23 ppm), and gastropods *Physa heterostropha* (LC_{50} = 34.2 ppm), *Physa integra* (LC_{50} = 9 ppm), *Campeloma decisum* (LC_{50} = 27 ppm), and *Goniobasis* sp. (LC_{50} = 92 ppm).

In another study, Pettersson et al. (2000) evaluated the toxicity of 25 commercial detergents on the cladoceran, *D. magna*, and found that the toxicity of these products varied between 4 and 85 ppm (LC_{50} to 48 h). Furthermore, Warne (1995) estimated the toxicity of 25 detergents on *C. dubia* obtaining LC_{50} values between 1.6 and 70.3 ppm. The LC_{50} values obtained in this study, from tests of commercial detergents on *D. magna*, varied between 1.6 ± 0.9 and 52.9 ± 20.5 ppm, values that are within the range on those reported by those authors.

Fishes are considered to be a bioindicator species since, due to their sensitivity to different xenobiotics, they play an important role in water quality monitoring studies (Sen and

Semiz 2007). The results obtained in this study by using the fishes *C. jordani* and *D. rerio* show that their sensitivity to the surfactant LAS is similar to that found for the fish *Rita rita* (Debasish 1988). Omotoso and Fagbenro (2005) evaluated the toxic effect of three brands of commercial detergents on *Oreochromis niloticus*, finding LC_{50} values that varied between 12.04 and 41.8 ppm. The average LC_{50} values from our bioassays on *C. jordani* and *D. rerio* were 17.42 ± 8.67 and 21.12 ± 10.5 ppm, respectively. These values are within those reported by the authors cited above.

Another factor that can influence the toxicity of detergents and pollutants is the temperature.

The effects of increasing temperatures on chemical toxicity are relatively documented on aquatic species.

Mayasich et al. (1986) assessed the effects of atrazine and temperature in *Nannochloris oculata* microalgae; these researchers detected a significant dependence between atrazine's toxicity and temperature, the toxicity increasing with increased temperature. Gaunt and Barker (2000) evaluated the toxic effect of atrazine herbicide on catfish (*Ictalurus punctatus*), and they observed that toxicity increased when the temperature rose and dissolved oxygen decreased. These authors mentioned that changes in these two parameters probably enhanced the toxicity of atrazine on some aquatic species. Ratushnyak et al. (2005) reported that the toxicity of three pesticides (fenvalerate, cypermethrin, and deltamethrin) in *D. magna* was enhanced as water temperature increased. Kim et al. (2010) observed that water temperature was one of important factors that influenced the toxicity of three drugs: Scetaminophen, Enrofloxacin, and Chlortetracycline on *D. magna*, as the temperature was increased from 15 to 25 °C; the toxicity of the drugs increased significantly from three to eight times.

The manner in which the temperature increases the toxic effect of pollutants is not completely explained, but some authors mention that when temperature rises, important changes occur in the homeostasis, the physiological and depuration rates, causing greater incorporation of compounds and higher production of toxic metabolites that affect the integrity of organisms (Noyes et al. 2009; Kim et al. 2010). Furthermore, it has been found that ectothermic organisms, such as microcrustaceans, ostracods, fishes, amphibians, and reptiles, may be most vulnerable to the temperature and contaminant interactions (Gordon 2003; Patra et al. 2007).

Additionally, the effects of temperature increase in the toxicity of detergents have been documented by many researchers: Pantani et al. (1997) observed changes in sensitivity to detergents with increasing temperature in tests performed with *Gamarus* sp.; in bioassays carried out at 8 °C, the LC_{50} for LAS is 20.5 ± 1.4 and in assays at 23 °C, the LC_{50} is 3.3 ± 0.5 ppm. Likewise Orathai et al. (1987) found that the toxicity of detergents in freshwater prawns *Macrobrachium rosenbergii* increases with increasing water temperature; these authors mention that the cause of death of prawns was probably extensive gill damage, because the solubility of detergents increases with increasing water temperature, and consequently, the rate of adsorption of the detergents by epithelial cells of the gills and the surface body of the prawns increases with increasing water temperature, thus rendering them more sensitive to detergents.

Moreover, Lewis and Horning (1991) observed an increase in sensitivity to sodium dodecyl sulfate (SDS) in assays with *D. magna* at a higher temperature (26 °C) (mean LC_{50} = 13.5 mg L^{-1} at 20 °C and 10.3 mg L^{-1} at 26 °C). These authors concluded that toxicity tests conducted at 20 and 26 °C may give significantly different results with *D. magna.* Likewise, Sobrino-Figueroa (2015) (unpublished data) observed that the values of LC_{50} for the anionic surfactant LAS ranged between 29.5 and 21.5 ppm in tests carried out at 18 °C; however, if the assays were carried out at a higher temperature (25 °C), the LC_{50} were 0.013 ± 0.012 ppm, almost 2300 times lower.

In Mexico, *D. magna* is used as a test organism to evaluate the toxicity of effluents that discharge into different aquatic systems. *D. magna* has a limited geographical distribution since it is found in temperate regions (Gutiérrez 2008). In our country, natural populations of this organism have not been found (Gutiérrez 2008).

The use of species from temperate climates to carry out ecotoxicological studies in subtropical and tropical environments has been questioned by various authors (Hong et al. 2004; Azad and Agard 2006; Freitas and Rocha 2011, 2012), since the majority of the test protocols are carried out at temperatures between 18 and 20 °C (OECD 1984; APHA 1994), conditions which are less than optimal in latitudes where the climates are subtropical or tropical.

In many cases, the native species that inhabit tropical and subtropical regions are more sensitive to xenobiotics than the test species (Hong et al. 2004; Freitas and Rocha 2011*). D. magna* has been reported to be one of the organisms that is most sensitive to chemical compounds (Lewis 1993; USEPA 1982; ISO 6341 1982); however, the species of cladocerans, amphipods, and ostracods used for this study were more sensitive to the commercial detergents, compared to the response observed for *D. magna.*

The average LC_{50} value obtained in our assays with *D. magna* exposed to the detergents was 32.65 ± 12.04 ppm, while the average LC_{50} values obtained from our bioassays on *D. exilis*, *M. macrocopa, S. mixtus*, *Cypris* sp., and *H. azteca* were 9.68 ± 5.5, 3.07 ± 1.71, 14.72 ± 8.46, 0.685 ± 0.49, and 5.67 ± 3.09 ppm, respectively, values between 55 and 98 % lower than those obtained in the tests on *D. magna*.

This data indicates that native species in our country are more sensitive to detergents as compared to the organism commonly used to assess toxicity in water (*D. magna*). This fact is important because native species are not being

protected if the indicator organism for water toxicity is more tolerant to the compounds.

From the previous argumentation, it is evident that commercial detergents have harmful effects on aquatic organisms, and the data from this study shows that the organisms belonging to different trophic levels have different sensitivities to these xenobiotics and that the temperature has an effect on its toxicity.

Conclusions

The four commercial detergents tested in this study had LC_{50} values that varied from 1.4 to 8.4 ppm in the tests on microalgae, from 0.1 to 52.9 ppm in the bioassays on invertebrates (cladocerans, amphipods, and ostracods), from 4.8 to 29.9 ppm in the assays on fishes, and finally from 32.25 to 116.9 ppm in the tests on macrophytes. The most sensitive organisms to these products were the ostracods, the amphipods, and the cladocerans, with the exception of *D. magna*.

The most toxic detergents were the products D and A, which are used for dishwashing and laundry, respectively. The toxicity of the products that contained surfactants, silicates, bleaching agents, enzymes, and dyes was greater compared to the detergents that lacked some of these compounds. Additionally, it was evidenced that the toxicity of the detergents increases when the temperature rises.

The presence of detergents in natural waters can cause a great impact on aquatic organisms. Since wastewater treatment is limited and often detergents are discharged directly into the environment, it is important to know the potential adverse effects of these compounds in order to propose appropriate measures to reduce the risk caused by their presence in aquatic environments.

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