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## COMPARATIVE TOXICITY EFFECTS OF CLEANING PRODUCTS ON FISH, ALGAE AND CRUSTACEA

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### Abstract

The hygiene process imposes a high usage of household cleaning products and personal care products, which after use reach the municipal and industrial wastewater of the sewerage networks and finally the surface waters. Depending on the physic, chemical and biological properties of the constituent substances, they could manifest various harmful effects on the aquatic organisms such as mortality, inhibition or stimulation of growth / development, and changes of the community structure linked to particular ecosystems and water quality degradation.

The study objective was to highlighted the aquatic toxicity effects of some cleaning products on freshwater fish, green microalgae and planktonic crustaceans in order to correspond to EU ecolabel criteria. Three products based on anionic, non-ionic and amphoteric surfactants were tested using OECD methodologies. The laboratory experiments showed non-toxic acute effects on tested organisms. The acute toxicity concentrations (EC50 / LC50) being more than 100 mg/l for each tested product. According to international norms for toxicity classification all the products were non harmful for aquatic live.

**Keywords:** *toxicity, aquatic, detergents*

### Introduction

The modern world standards generate a continuous market development of the cleaning products, especially for the ecological products. Unfortunately, the surfactants have polluted the fresh waters and affected aquatic organisms such as zooplankton, phytoplankton and fish (Tomislav 2010). Non-harmless effects of the products and their active substances on living organisms could be proved by ecotoxicological studies (Gheorghe 2012). The criteria for cleaning product EU ecolabel are set by Regulation (EC) No 66/2010 of the European Parliament. The products must to meeting high environmental standards throughout their life-cycle: from raw material extraction, to production, distribution and disposal. The norm limits the presence in to the product composition of the substances with harmful effects on aquatic environment, promote a high biodegradability and the small and eco-friendly packages. In 2018, the statistics showed a gradually increase of the number of EU Eco labelled products mainly indoor and outdoor paints and varnishes, converted paper, tissue paper and hard surface cleaning products (<http://ec.europa.eu>). The European Commission make available a User Manual for Ecolabel of detergents and cleaning product that include all the criteria.

Toxicity to aquatic organisms is one of most important criteria for eco labelling and is applied both for the ingredients and also for the final products. Their toxicity shall not be classified as hazardous for the aquatic environment according to REACH Regulation. This paper presents the toxicity responses of three freshwater species (fish - *Cyprinus carpio*, microalgae – *Pseudokirchneriella subcapitata* and the planktonic crustacean - *Daphnia magna*) under acute intoxication with commercial cleaning products based on anionic, non-ionic and amphoteric surfactants.

### Material and methods

Three commercial products based on anionic, non-ionic and amphoteric surfactants have been tested. The composition and CAS number are presented in table 1.

**Table 1** – Tested cleaning products (ingredients)

Product 1 – hard surface cleaning product	Product 2 – sanitary cleaning product	Product 3 – hand dish cleaning product (10% a.s.)
15-20% s.a		
Alcohols, C12-C14, ethoxylated, sulphate, sodium salt (SLES) – <i>anionic</i> CAS 68891-38-3	Alcohols, C12-C14, ethoxylated, sulphate, sodium salt (SLES) – <i>anionic</i> CAS 68891-38-3	Alcohols, C12-C14, ethoxylated, sulphate, sodium salt (SLES) – <i>anionic</i> CAS 68891-38-3
Alkane C6-C8 (even numbered), 1-sulphonic acid, sodium salt) – <i>anionic</i> CAS 5324-84-5	Alkane C6-C8 (even numbered), 1-sulphonic acid, sodium salt) – <i>anionic</i> CAS 5324-84-5	Coco Fatty Acid Diethanolamide - <i>amphoteric</i> CAS 8051-30-7
Alcooli, C8-18 etoxilați propoxilați – <i>non-ionic</i> CAS 69013-18-9	Alcooli, C8-18 etoxilați propoxilați - <i>non ionic</i> CAS 69013-18-9	Cocoamidopropil betaina (CAPB) - <i>amphoteric</i> CAS 61789-40-0
Other ingredients: Alcohol izipropilic, 1-methoxy-2-propanol	Citric Acid monohidratat; Acid fosforic	Potasiu cocoate Glicerina

\* a.s. – total active substance

The tested organisms belonged to three trophic levels: vertebrates (fish), invertebrates (crustaceans as *Daphnia*) and plants (algae). Indigenous species were used to evaluate the acute toxicity on aquatic ecosystem. The working methodology respect the OECD principles concerning the use of vertebrate and is aligned to Detergent Regulation no. 648/2004 and RECH Regulation and their amendments (Gheorghe 2011). Using the step-down approach, the LC50 biotests with fish were developed considering the EC50 values obtained for algae and crustacean.

At least five concentrations between 1 - 1000 mg product / l, were incubated, in static conditions, up to 96h, in the presence of the testing biological models (table 2).

**Table 2.** Toxicity methods (Gheorghe 2012)

Species	Test	Type of test	Endpoint effect	Test period / incubation
<i>Cyprinus carpio</i>	OECD 203	Static, acute	Mortality, LC50 Clinical signs	96h, 21-22°C
<i>Daphnia magna</i>	OECD 202	Static, acute	Mortality / immobilization LC50	24-48h, 20°C
<i>Pseudokirchneriella subcapita</i>	OECD 201	Static, acute	Algal growth rate inhibition EC50	72h, 21-25°C

## Results and discussion

### *Daphnia magna* test

The tested products revealed no toxicity on planktonic crustacean *Daphnia magna*. After 48h of exposure the *Product 1* based on anionic and non-ionic surfactants don't induced mortality effects for concentrations between 31.25 - 250 mg /l. The *Product 1* at 500 mg /l induced small toxic effects of around 5-10%.

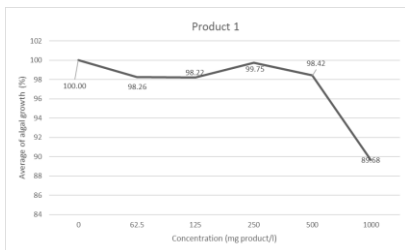
*Product 2* based on the same anionic and non-ionic surfactants (table 1) was non-toxic in concentrations between 31.25 – 62.5 mg / l. At 125 mg/l about 5% mortality was observed. In concentration more than 250 mg/l the effects increased to 45 - 100%. The toxicity differences could be influenced by the other chemical ingredients such as citric acid or phosphoric acid.

*Products 3* based on anionic and amphoteric surfactants revealed non toxicity of crustacean. About 5% mortality effects at 60 mg product/l, 30% at 125 mg product/l and 70 – 95% at 250 and 500 mg product/ l were obtained.

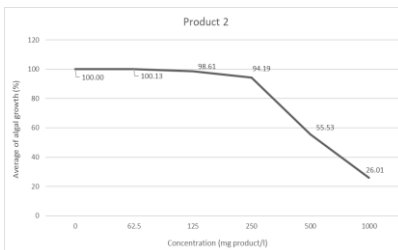
### *Algae* test

The two products (products 1 and 2) based on 10% active surfactants (anionic and non-ionic) don't induced toxic effects on algal growth, but they could enhance the water eutrophication if their concentrations exceed the 500 mg / l and the water temperature is growing more than 25 degrades. *Product 1* at 62.5 – 1000 mg /l showed a great algal growth about 90 - 95 % from the control (figure 1). *Products 2*, similar with *Product 1* showed the same increase of algal biomass at 62.5 – 125 mg / l. In this case inhibitions about 40% for 500 mg/l and 70% for 1000 mg/l were obtained. A decrease specific growth rate about 0.41 / day compared with the control 1.58 / day was observed (Figure 2).

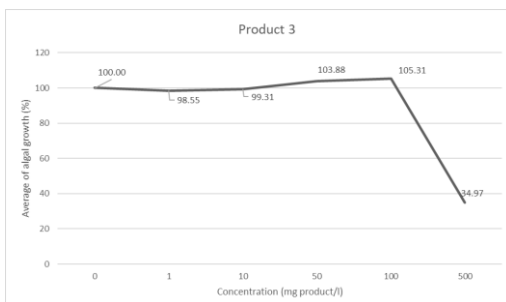
*Product 3* have demonstrated a different behaviour on algae growth. At small concentrations about 1 - 10 mg / l the results were in the control limits. At 50 – 100 mg / l showed a small stimulation of algal growth (3-6%) followed by a significant inhibition estimated at 65% (Figure 3).



**Figure 1.** Algal growth induced by product 1



**Figure 2.** Algal growth induced by product 2



**Figure 3.** Algal growth induced by product 3

### *Fish test*

All the products were tested in concentration of 100 – 1000 mg product/ l. The fish tests showed that the cleaning products don't induce any mortality effects even at the highest concentrations (500 mg/ l or 1000 mg/l). A stress factor for the fish was the foam occurred especially at the highest tested concentrations, especially in case of Product 3 based on amphoteric surfactant. An increased frequency of opercula ventilator movement was observed in all tested containers.

The foam intensity decreased to the end of test, this fact being correlated with the surfactant presence.

The concentration of total active substances was instable during fish tests, decreased more than 50% after 96h of exposure, due to a high volume of tested solutions, large surface of test containers and tank aeration.

Overall, the total active substances used for crustacean and alga tests were reduced less than 20% after 48h or 72h.

The order of toxicity level on tested aquatic organisms was: Product 3 > Product 2 > Product 1. The laboratory experiments showed non-toxic acute effects on tested organisms, the acute toxicity concentrations (EC50 / LC50) being >100 mg/l for each tested product (table 3).

**Table 3** Aquatic toxicity results

Product	<i>Daphnia magna</i>	<i>Pseudokirchneriella subcapitata</i>	<i>Cyprinus carpio</i>
	EC50 /LC50		
1	>1000 mg/l	>1000 mg/l	>1000 mg/l
2	382.55	596.53	>1000 mg/l
3	181.55	463.23	>1000 mg/l
Toxicity class	Non-toxic	Non toxic	Non – toxic

### Conclusion

According to Regulation (EC) no 1272/2008 on Classification, Labelling and Packaging (CLP) of substances and mixtures based on the United Nations' Globally Harmonized System (GHS) of REACH 1907/2006 modification, non toxic classification was established for all tested cleaning products. The results showed that the most sensitive was *Daphnia magna* and fish were the least sensitive (Lechuga 2016). Product 3 was more harmful comparing to Product 1 and 2 because of the presence of amphoteric surfactant. These results have been confirmed through previous studies on cocamidopropyl betaine (Gheorghe 2012).

Even if the commercial cleaning products can be classified as non-hazardous to the aquatic environment, a differentiated sensibility was observed according to the type of active substances or other ingoing ingredients or the solution acidification. Only in case of algae, it could be observed some eutrophication effects. No other effects were observed in case of recommended doses for use.

The tested products meet the EU Ecolabel criteria for the final products referring to the harmful to the aquatic environment.

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