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Ecotoxicological assessment of the micelle encapsulator F-500

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ABSTRACT

Surfactants are synthetic chemicals utilized as detergents and cleaning products or as dispersants and emulsifiers to face water pollution. In spite of this, due to their wide diffusion, surfactants can induce water and soil pollution, notably in developed countries, and can be toxic to organisms. Taking into account that the assessment of new compounds is mandatory in the European Union, in this research the ecotoxicity of fire-fighting micelle encapsulator F-500, newly utilized as dispersant in seawaters polluted with oil dumping, was evaluated. The assessment was carried out on a battery of test-organisms (freshwater algae, crustaceans, and larval fish; seawater algae, crustaceans, and bivalves; soil earthworms, and seeds) as well as on cultured cells (L-929 mouse fibroblasts), which were exposed to F-500 concentrations. According to the toxicity thresholds provided by GESAMP, F-500 resulted to be slightly or moderately toxic to all test-organisms, excluding the freshwater alga *Pseudokirchneriella subcapitata* that suffered highly toxic effects with IC_{50} values ranging from 0.21 to 0.49 mg/L. The IC_{50} for mouse fibroblasts was 5.41 μg/L after 24 h treatment.

1. Introduction

Surfactants, surface-active agents, are synthetic organic chemicals having a polar (hydrophilic) and a non-polar (hydrophobic) portion. They are currently classified as anionic, cationic, amphoteric, and non-ionic (Ivanković and Hrenović, 2010). Surfactants are used in the formulation of synthetic detergents, household and personal care cleaning products, as dispersants and emulsifiers, as well as for different industrial employments, such as in food as potential multipurpose ingredients or additives (Kralova and Sjoblom, 2009), mining, oil and textile (Nyberg, 1988; Sandbacka et al., 2000). Some non-ionic surfactants, such as alcohol ethoxylates and alkylamine ethoxylates, are employed as pesticide adjuvants (Krogh et al., 2003).

The increasing utilization of these compounds results in the increase of spreading in the environment. For this reason, they are viewed as a source of pollution to be carefully controlled (Seki and Tokita, 2009), whose environmental impact is a matter of concern, mainly in industrially developed countries (Yamane et al., 1984). Notably, the occurrence of surfactants in untreated effluents can induce toxicity to aquatic organisms and microorganisms, causing a lot of problems to fisheries as well (Ankley and Burkhard, 1992; Mori et al., 2002). Surfactants are supposed to have a remarkable impact also on soil ecosystem, even though the acute and chronic toxicity on soil fauna and plants is greatly unknown (Liwarska-Bizukojc, 2009). As a matter of fact, the environmental risk they may cause should be taken carefully into consideration. Therefore, the improvement of knowledge about surfactant toxicity and the evaluation of the ecotoxicological risk are research priorities.

The micelle encapsulator agent F-500 (Hazard Control Technologies Inc., Fayetteville, GA, USA), according to the recent Material Safety Data Sheet (MSDS) (HCT, 2013) belongs to the surfactant chemical family. It is an aqueous (35–55%) complex mixture whose quantitative composition is unavailable and kept secret, containing nitrilotrisethanol aliphatic soap (1–4.5%), alkyl ether amine reaction with aliphatic acids (25–55%) and linear aliphatic alcohols (3–10%). F-500 is an effective fire suppressor (at the concentration of 0.5% in water), having good cooling properties. It is also able to reduce the likelihood of re-ignition (Lennard, 2001). In addition, it is specifically employed as dispersant to fight hydrocarbon dumping in marine and freshwaters (NICNAS, 2004; HCT, 2010; HCT, 2012a, 2012b).

F-500 falls into the Surface Washing Agent (SWA) category (US EPA, 2002) and, per se, it is reported into the NCP (National Oil and Hazardous Substances Pollution Contingency Plan) list. A list of approvals of F-500 is available (http://www.fctservices.co.uk/F-500-approvals/).

F-500 allows the solvation of non-polar organic compounds and is able to elute actively fuels adsorbed into the soil (Clemson University, 1997).

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Taking into account that a single species able to describe the ecotoxic effects of chemicals does not exist, the overall evaluation of a compound needs the utilization of representative and properly chosen test-species belonging to different trophic levels. On this basis, considering also the key role of planktonic organisms in the aquatic environments (Sánchez-Bayo, 2006), the aim of this research was to assess the toxicity of F-500 to some representative organisms. The hypersaline phyllopod *Artemia salina*, littoral copepods *Tigriopus fulvus*, seawater algae *Chlorella minutissima*, marine mussels *Mytilus galloprovincialis*, freshwater algae *Pseudokirchneriella subcapitata*, daphnids *Daphnia magna*, larval fish *Oncorhynchus mykiss*, soil plants (seeds of *Lepidium sativum*, *Cucumis sativus*, *Sorghum* sp.), earthworms *Eisenia fetida*, as well as cultured mammalian cells have been utilized to evaluate the suitability of F-500 to be used as dispersant in polluted waters. The rating scheme from the Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection (GESAMP, 2002) and the rules of the Italian Law about the protection of waters against pollution, which sets out the execution of short- and long-term tests on selected species (Ministero dell'Ambiente e della Tutela del Territorio e del Mare, 2011), have been taken into account. The effect of F-500 to mussels was considered as a preliminary assessment of bioaccumulation, according to the American Society of Testing and Materials Standards (ASTM, 1998) guidelines.

2. Materials and methods

The tests have been carried out employing standardized methods or internal methods (Table 1 and 2).

2.1. Algal tests

Cultures of marine algae *C. minutissima* (Chlorophyta: Trebouxiophyceae), originating from axenic stocks, were maintained in filtered seawater (Millipore 0.2 μm) supplemented with Walne medium and B_1–B_{12} vitamin solution (Walne, 1966). All chemicals were of analytical grade (Sigma, Milano, Italy). Algae were incubated at 20 ± 0.5 °C in a refrigerated incubator (BK6160 Heraeus), at 16:8 h light:dark (L:D). Algal growth was evaluated at intervals by cell counting (Thoma hemocytometer). Growth inhibition induced by F-500 concentrations chosen after a preliminary test (0.125, 0.25, 0.5, 1, 2, and 4 mg/L) was evaluated through cell counting (Thoma hemocytometer) in triplicate after 24, 48, and 72 h on 2×10^6 cells/mL. The 50% inhibition concentration (IC_{50}) was calculated for each time-exposition.

Cultures of the motionless green alga *P. subcapitata*, formerly *Selenastrum capricornutum*, (Chlorophyta: Chlorococcales) were prepared from axenic stocks and maintained in culture medium (IRSA-CNR, 2005) at 22 ± 0.5 °C in a refrigerated incubator (BK6160 Heraeus) and 16:8 h L:D. 5×10^4 cells/mL in triplicate

Table 1
Growth inhibition of algae and acute (a) and chronic (c) toxicity to crustaceans, mollusks, fish and earthworms after exposition to F-500. Data are expressed as mortality (§), growth (♂) or reproduction (♀) inhibition. End-points are expressed as IC_{50} for algae and as LC_{50} (acute toxicity) and NOEC (chronic toxicity) for other organisms. End-points and confidence limits are calculated according to Hamilton et al. (1977). n.c.=not calculable. (*) applied to *Acartia tonsa* (Crustacea: Copepoda). (**) applied to *Mysidopsis bahia* (Crustacea: Mysidacea).

Organisms	Test-species	Method	Exposition (time)	End-point mean ± SD (mg/L)	Confidence limits	
					95% Lower (mg/L)	95% Upper (mg/L)
Algae	*Chlorella minutissima*	UNI EN ISO 10253 (2000)	24 h (a) (♂)	2.20 ± 0.52	1.53 ± 0.11	3.95 ± 2.09
			72 h (a) (♂)	2.51 ± 0.52	1.93 ± 0.64	3.65 ± 0.02
	Pseudokirchneriella subcapitata	IRSA-CNR (2005)	24 h (a) (♂)	0.21 ± 0.01	0.10 ± 0.05	0.35 ± 0.05
			72 h (a) (♂)	0.49 ± 0.09	0.40 ± 0.09	0.60 ± 0.09
Crustaceans	*Artemia salina*	IRSA-CNR (1997)	24 h (a) (§)	15.73 ± 3.91	12.94 ± 3.61	19.13 ± 4.18
			48 h (a) (§)	8.29 ± 1.56	6.99 ± 1.52	9.83 ± 1.56
			72 h (a) (§)	5.19 ± 0.07	4.60 ± 0.53	5.87 ± 0.16
			96 h (a) (§)	4.79 ± 0.47	4.16 ± 0.53	5.53 ± 0.39
	Tigriopus fulvus (nauplii I–II)	ISO 14669 (1999)(*)	24 h (a) (§)	3.17 ± 0.31	2.34 ± 0.19	4.31 ± 0.50
			48 h (a) (§)	1.48 ± 0.13	0.98 ± 0.18	2.24 ± 0.03
	Tigriopus fulvus (adult females)	Internal method; ISO 14669 (1999)(*)	24 h (a) (§)	14.05 ± 1.73	7.90 ± 1.83	22.47 ± 6.98
			48 h (a) (§)	12.69 ± 2.89	6.54 ± 3.12	20.56 ± 8.11
			72 h (a) (§)	6.94 ± 2.02	3.74 ± 1.35	12.93 ± 2.85
			96 h (a) (§)	5.61 ± 0.98	2.89 ± 0.56	10.91 ± 1.81
		IRSA-CNR (1998a) (**)	7 days (c) (§)	2	–	–
	Daphnia magna	OECD 202 (1984a)	24 h (a) (§)	5.17 ± 0.43	3.84 ± 0.00	6.31 ± 0.00
			48 h (a) (§)	3.81 ± 0.96	2.69 ± 1.00	5.43 ± 0.78
Mollusks	*Mytilus galloprovincialis*	Internal method	24 h (a) (§)	> 13	n.c.	n.c.
			48 h (a) (§)	4.53 ± 0.80	2.58 ± 0.43	7.97 ± 1.60
			72 h (a) (§)	2.98 ± 0.87	2.00 ± 0.11	4.39 ± 0.48
Fish	*Oncorhynchus mykiss* (alevins)	IRSA-CNR (1998b)	24 h (a) (§)	1.62 ± 0.10	1.36 ± 0.20	1.94 ± 0.20
			48 h (a) (§)	1.41 ± 0.05	1.25 ± 0.11	1.58 ± 0.02
			72 h (a) (§)	1.30 ± 0.12	1.03 ± 0.11	1.56 ± 0.19
			96 h (a) (§)	1.26 ± 0.19	0.95 ± 0.23	1.53 ± 0.23
		Internal method	7 days (c) (§)	0.5	–	–
Earthworms	*Eisenia fetida*	OECD 207 (1984b); ISO 11268-1 (1993)	24 h (a) (§)	n.c.	n.c.	n.c.
			48 h (a) (§)	4.72 ± 1.64	n.c.	n.c.
			72 h (a) (§)	1.65 ± 1.08	n.c.	n.c.
		ISO 11268-2 (1998)	28 days (c) (♂)	> 1.4	–	–
		ISO 11268-2 (1998); OECD (2004)	60 days (c) (♀)	< 0.6	–	–