Chemosphere 139 (2015) 73–80

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Lightsticks content toxicity: Effects of the water soluble fraction on the oyster embryonic development

Milena Maria Sampaio de Araujo [c,d], Adalberto Menezes Filho [a,e], Iracema Andrade Nascimento [b,c], Pedro Afonso P. Pereira [a,c,f,*]

[a] Instituto de Química, Universidade Federal da Bahia, 40170-115 Salvador, Bahia, Brazil
[b] Instituto de Biologia, Universidade Federal da Bahia, 40170-115 Salvador, Bahia, Brazil
[c] CIEnAm – Centro Interdisciplinar de Energia e Ambiente, Universidade Federal da Bahia, 40170-290 Salvador, BA, Brazil
[d] Departamento de Ciências da Vida, Universidade do Estado da Bahia, 41150-000 Salvador, Bahia, Brazil
[e] Instituto Federal de Educação, Ciência e Tecnologia de Sergipe, 49055-260 Aracaju-Sergipe, Brazil
[f] INCT E&A, Universidade Federal da Bahia, 40170-115 Salvador, BA, Brazil

HIGHLIGHTS

- Chemical composition and toxicity of the WSF of lightsticks were investigated.
- Toxicity tests were based on the *Crassostrea rhizophorae* embryonic development.
- 19 substances were identified in the WSF by GC–MS, amongst them several phthalates.
- Low EC_{50} values were determined, both for new and one year activated devices.
- Results point out for high toxicities of components in both lightstick's compartments.

ARTICLE INFO

Article history:
Received 26 January 2015
Received in revised form 13 May 2015
Accepted 18 May 2015
Available online 9 June 2015

Keywords:
Lightsticks
Chemical content
Toxicity tests
Crassostrea rhizophorae embryos

ABSTRACT

Lightsticks are artifacts used as attractors in a type of commercial fishery, known as surface longline gear. Despite the excessive use, the contamination risks of these devices have not yet been properly investigated. This research aimed to fill up this gap by determining the chemical composition and the toxicity of lightsticks recently activated, compared to those one year after activation and to the ones collected on the beaches. The analyzes were carried out by Gas Chromatography coupled with Mass Spectrometry (GC–MS). Additionally, the variations in composition and the toxicity of their sea Water Soluble Fractions (WSF) were evaluated based on the WSF-effects of *Crassostrea rhizophorae* embryonic development. The GC–MS analysis made possible the identification of nineteen substances in the water soluble fraction of the lightsticks, such as dibutyl phthalate (DBP) and dimethyl phthalate (DMP). The value of the WSF-effective concentration (EC_{50}) was in an average of 0.35%. After one year of the lightsticks activation, the toxicity was even higher (0.65%). Furthermore, other substances, also present in the lightsticks-WSF caused persistent toxicity even more dangerous to the environment than DBP and DMP. This essay discusses their toxicity effects and possible environment damages.

1. Introduction

Lightsticks (LS) are devices used in commercial fishery to attract, specially, swordfish (*Xiphias gladius*) and some species of tuna (*Thunnus albacares*, *Thunnus atlanticus*). They are attached to each hook (800–1200) pending from metal clamps along the main line, which can be up to 80 km long (Hazin et al., 2005). This style of fishing usually occurs at night, with the line placed in the late afternoon or early evening, to be recovered the next morning. After being used, these chemical light devices are often lost or discarded into the sea, and represent a source of solid and chemical contamination, with risks that are not yet globally evaluated. There are several websites commercializing these attractors (light sticks, glow light sticks and glow sticks).

The economical activity of fishery may vary in importance and intensity for each country, depending on a series of conditions,

* Corresponding author at: Instituto de Química, Universidade Federal da Bahia, 40170-115 Salvador, Bahia, Brazil.
E-mail address: pedroapp@ufba.br (P.A.P. Pereira).

http://dx.doi.org/10.1016/j.chemosphere.2015.05.058
0045-6535/

linked not only to the activity itself but also to their political, social, cultural and economical situation (Domingo et al., 2014). Despite the available information from fishering reports to the competent authorities, a broad quantitative projection of the LS dumped from the lines does not exist as yet. However, one can get a rough picture of the problem, from several works done by nongovernmental institutions and researchers.

The international non-governmental organization (NGO) Global Garbage has reported about 69,300 LS, discarded by two Japanese ships, authorized for fishering in Brazilian waters, in just five fishing trips (Talento, 2005). In 2001, 1647 LS were found at 31 km of beaches at the Costa dos Coqueiros, in the Northern coast of Bahia (http://globalgarbage.org). Beach debris surveys identified, on average, 2 LS per 100 m of shoreline, although these quantities may be much higher after storms (Ivar do Sul, 2005). According to Ribeiro (2005), 5517 LS were collected in 2004, in 172 miles of beaches between Arembepe and Mangue Seco (Costa dos Coqueiros in Bahia). In 2007, more than 2500 LS were collected at about 200 km of the same Northern coast (Ribeiro and Hans, 2010). Members of the Global Garbage collected circa 7000 LS in a monitoring campaign performed 90 km off the Northern coast of Bahia State (Talento, 2005; Bechara et al., 2009; de Oliveira et al., 2014).

The risk of LS discard is greater in regions where there is no considerable dilution of their content, thus retaining the contaminants for a large time period and affecting the aquatic environment. Besides, there are reports about LS content being wrongly used as lubricants, suntan lotion, solvent for tar removing, medicine for body aches, insect repellent, or even as massage oil (Bechara et al., 2009) to combat fungal infections and scabies; more recently they have been used for lighting effects in night parties. Despite these evidences and the mutagenic risks (de Oliveira et al., 2014) that may result from overuse and misuse of these devices, risk analyzes and management guidelines are still lacking.

Each lightstick consists of two compartments, containing different substances, which are mixed when breaking the internal glass capillary tube (ampoule), triggering the chemiluminescence reaction. The chemical illumination of these attractors is produced by a reaction from an ester of oxalic acid and hydrogen peroxide in the presence of an activator (typically polycondensates of aromatic compounds with lower oxidation potentials and high fluorescence quantum yields), which varies according to the color of light to be emitted (Stevani and Baader, 1999). Diverse polycyclic aromatic compounds are used in the commercialized LS, such as 9,10-bis (phenylethynyl) anthracene (BPEA), 9,10-diphenylanthracene (DPA), 1-chloro-9,10-bis (phenylethynyl) anthracene and rubrene (5,6,11,12-tetraphenylnaphthacene) in order to produce green, blue, yellow and orange lights, respectively (Coleman, 2009; Fardy and Yang, 2008; Hanhela and Paul, 1981a, 1981b,1981c). The ester of oxalic acid normally used is the bis (2-carbopentyloxy-3,5,6-trichlorophenyl) oxalate (CPPO) or the bis (2,4,6-trichlorophenyl) oxalate (TCPO) (Thompson and Mcbee, 1988).

The scheme of the reaction between TCPO and hydrogen peroxide (H_2O_2), with BPEA as the activator, is illustrated in Fig. 1. The chemiluminescence reaction makes use of catalysts, such as sodium salicylate, and typically involves the formation of metastable intermediates or products in the electronically excited state (Hofmann et al., 2005), resulting in the emission of light, by converting the chemical energy of the substances into luminous energy (Maybodi et al., 2010; Nery and Baader, 2001; García-Campaña et al., 2000; Stevani and Baader, 1999). This mechanism of cold light was described by Rauhut (American Cyanamid Co. USA), who named it "peroxy-oxalate system", with chemical LS as the first practical application (Stevani and Baader, 1999; Rauhut, 1969).

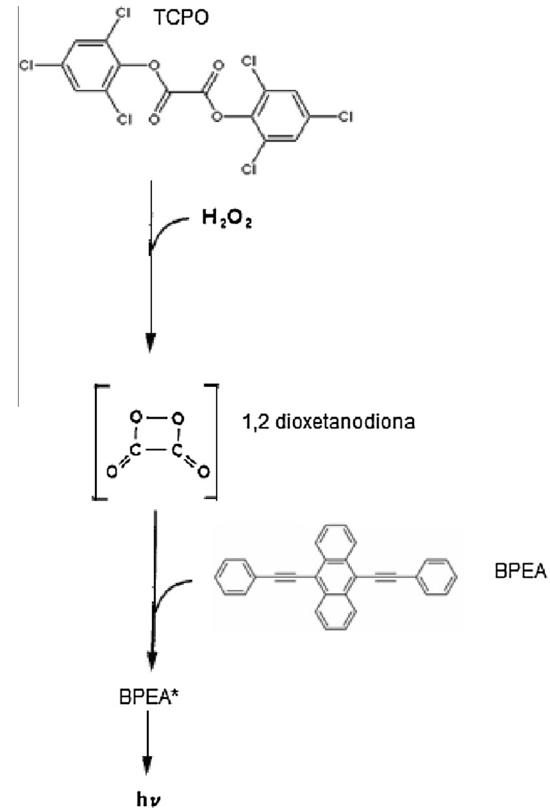

Fig. 1. Sequence proposed for the reaction of peroxy-oxalate used in the chemical lightsticks (adapted from Thompson and Mcbee, 1988).

The commercial packages containing the LS provide information regarding their non-toxicity. However, previous studies using *Artemia* sp. (Pinho et al., 2009) as test organism, had shown, on the contrary, a toxicity for them.

Changes on biological tissues through histopathological analysis were reported by Ivar do Sul et al. (2009) who detected alteration on the skin of mice Wistar, after prolonged contact with the chemical contents of LS collected on Costa dos Coqueiros beaches (Bahia Brazil), indicating that they can lead to skin cancer. According to de Oliveira et al. (2014), the LS contents were found to be highly cyto and genotoxic. Many kinds of LS are being marketed, with different composition from those already known. Besides, most LS sold in fishing stores in Salvador, Brazil, have no commercial packaging, and thus bringing no information concerning its composition.

Although there is evidence of the overuse and misuse of these devices, the risks of contamination to the coastal environment have not yet been adequately investigated. This study aims the evaluation of the chemical composition and toxicity of the content of chemical LS, sold in fishing stores of Salvador-Brazil, as well as those usually found on beaches of the "Costa dos Coqueiros".

2. Materials and methods

2.1. Experimental methodology

2.1.1. Samples

The new-non-reacted yellow sticks (15 mm I.D. × 150 mm length; imported by Mustad), also the most sold in Salvador, were acquired in the fishing and sport stores in Salvador-BA. Fifty new yellow LS were used along the experiments. Fig. 2 shows the LS one year after their activation (a) and when they are new, before the activation (b).