Chemosphere 74 (2009) 1275–1278

Contents lists available at ScienceDirect

Chemosphere

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

Short Communication

Ecotoxicity of the degradation products of triphenylborane pyridine (TPBP) antifouling agent

H. Okamura [a,*], S. Kitano [a], S. Toyota [b], H. Harino [c], K.V. Thomas [d]

[a] Graduate School of Maritime Sciences, Kobe University, Kobe 658-0014, Japan
[b] Department of Chemistry, Faculty of Science, Okayama University of Science, Okayama 700-0005, Japan
[c] Osaka City Institute of Public Health and Environmental Sciences, Osaka 543-0026, Japan
[d] Norwegian Institute for Water Research, Oslo N-0411, Norway

ARTICLE INFO

Article history:
Received 12 August 2008
Received in revised form 24 October 2008
Accepted 10 November 2008
Available online 17 December 2008

Keywords:
Artemia
Bioassay
Biocide
Biphenyl
Marina
Skeletonema

ABSTRACT

Triphenylborane pyridine (TPBP) is an alternative to organotin antifouling compounds. This work aimed to identify the unknown Peak #1, and to evaluate the ecotoxicity of TPBP and its degradation products. Peak #1 was produced from TPBP dissolved in acetonitrile under UV-A photolysis using a high-pressure mercury lamp. The Peak #1 fraction was purified using two-step column chromatography from a TPBP–acetonitrile solution. The major compound of the fraction was identified as being biphenyl from the ^{1}H NMR and ^{13}C NMR spectra. The ecotoxicity of four degradation products (diphenylborane hydroxide, phenylborane dihydroxide, phenol, and biphenyl) and TPBP towards two marine planktons were assessed. The 48 h LC_{50} values of the crustacean, *Artemia salina*, were 0.13 mg L^{-1} for TPBP, 14 mg L^{-1} for biphenyl, 17 mg L^{-1} for phenol, and >50 mg L^{-1} for the other degradation products. The 72 h EC_{50} values of the diatom, *Skeletonema costatum*, were 0.0022 mg L^{-1} for TPBP, 1.2 mg L^{-1} for biphenyl, and >2 mg L^{-1} for the other degradation products. Thus, the ecotoxicity of biphenyl and the other degradation products were not high compared to the parent compound, TPBP.

1. Introduction

Antifouling compounds are used to prevent biofouling on ship's hulls, with minimum risk to aquatic environments. Triphenylborane pyridine (TPBP) is an alternative to organotin antifouling compounds, whose use has been prohibited in Japan since the late 1980s. The usage of TPBP is increasing in popularity in some Asian countries due to the effectiveness of the Antifouling System Convention that banned organotin compounds on ship's hulls. A summary of TPBP as an antifouling biocide, including the environmental aspects, has been published by Amey and Waldron (2004). An analytical method using ion pair HPLC to determine TPBP residues was reported recently by Takahashi et al. (2005). However, analysis of TPBP residues in seawater, sediments, and biota has not been reported on to date. The environmental effect of TPBP on fish and fish cell lines (Okamura et al., 2002), sea urchin embryos (Kobayashi and Okamura, 2002), some plant species (Okamura et al., 2003), and marine planktons (Mieno et al., 2004) have been reported, based on nominal concentrations of TPBP. There is little information on the fate of TPBP in water, except for the hydrolysis and photolysis study carried out by Zhou et al. (2007). In that report, a persistent unknown compound, Peak #1, was found in both hydrolysis and photolysis products of TPBP in water. The aims of this work were (1) to identify Peak #1, and (2) to evaluate the ecotoxicity of TPBP and its degradation products to estimate the environmental effect of TPBP in aquatic environments.

2. Materials and methods

2.1. Chemicals

The triphenylborane pyridine (TPBP), diphenylborane hydroxide (DPB) and phenylborane dihydroxide (MPB) used were donated by the Hokko Chemical Industry Co. Ltd., Japan. The phenol, benzene, biphenyl (pesticide grade), pyridine (spectroscopy grade), acetonitrile (HPLC grade), dimethyl sulfoxide (DMSO, spectroscopy grade), methanol (HPLC grade), and dichloromethane (HPLC grade) used were purchased from Wako Pure Chemical Industries, Ltd., Japan. The tetrabutyl ammonium phosphate (TBAP, 0.5 M) was used as an ion pair reagent and was purchased from the Tokyo Kasei Kogyo Co. Ltd., Japan. The water used to prepare all the aqueous solutions was obtained using an Aquarius RFU554CA ultrapure water system (Advantec, Japan). In the toxicity tests, all the compounds tested were dissolved in DMSO at 5000 mg L^{-1} for TPBP and at 10,000 mg L^{-1} for DPB, MPB, benzene, phenol, and biphenyl.

* Corresponding author. Tel./fax: +81 78 431 6272.
E-mail address: okamurah@maritime.kobe-u.ac.jp (H. Okamura).

0045-6535/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.chemosphere.2008.11.014