Environmental Pollution 204 (2015) 233–240

Contents lists available at ScienceDirect

Environmental Pollution

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

Spatial analysis of 4,5-dichloro-2-*n*-octyl-4-isothiazolin-3-one (Sea-Nine 211) concentrations and probabilistic risk to marine organisms in Hiroshima Bay, Japan

Kazuhiko Mochida*, Takeshi Hano, Toshimitsu Onduka, Hideki Ichihashi, Haruna Amano [1], Mana Ito, Katsutoshi Ito, Hiroyuki Tanaka, Kazunori Fujii

National Research Institute of Fisheries and Environment of Inland Sea, Fisheries Research Agency, 2-17-5 Maruishi, Hatsukaichi, Hiroshima 739-0452, Japan

ARTICLE INFO

Article history:
Received 6 January 2015
Received in revised form
13 April 2015
Accepted 5 May 2015
Available online 14 May 2015

Keywords:
Antifouling biocide
Bayesian inference
Expected potentially affected fraction
Inverse distance weighted interpolation
Species sensitivity distribution

ABSTRACT

We analyzed the spatial distribution of an antifouling biocide, 4,5-dichloro-2-*n*-octyl-4-isothiazolin-3-one (Sea-Nine 211) in the surface water and sediments of Hiroshima Bay, Japan to determine the extent of contamination by this biocide. A quantitative estimate of the environmental concentration distribution (ECD) and species sensitivity distributions (SSDs) for marine organisms were derived by using a Bayesian statistical model to carry out a probabilistic ecological risk analysis, such as calculation of the expected potentially affected fraction (EPAF). The spatial distribution analysis supported the notion that Sea-Nine 211 is used mainly for treatment of ship hulls in Japan. The calculated EPAF suggests that approximately up to a maximum of 0.45% of marine species are influenced by the toxicity of Sea-Nine 211 in Hiroshima Bay. In addition, estimation of the ecological risk with a conventional risk quotient method indicated that the risk was a cause for concern in Hiroshima Bay.

1. Introduction

Since the regulation of the use of organotin compounds in antifouling paints, many organotin-free antifouling biocides have been developed and used in commercial antifouling paints (Voulvoulis et al., 1999). In Japan, at least 16 biocides, such as cuprous oxide, 3-(3,4-Dichlorophenyl)-1,1-dimethyl urea (Diuron), 2-methylthio-4-tert-butylamino-6-cyclopropylamino-*s*-triazine (Irgarol 1051), triphenylborane-pyridine, and zinc-2-pyridinethiol-1-oxide (zinc pyrithione), are on the registered list of compounds approved by the Japan Paint Manufacturer's Association (Okamura and Mieno, 2006). The Seto Inland Sea of Japan is a confined body of waters with relatively weak tides, and it is bordered by many fishing ports, marinas, and harbors. It should come as no surprise that many reports have documented the occurrence of these biocides, including their degradation products, in the Seto Inland Sea (Okamura et al., 2003; Harino et al., 2009; Balakrishnan et al., 2012; Mochida et al., 2012a,b). Many communities surrounding the Seto Inland Sea rely economically on, inter alia, local fisheries, aquaculture, cargo-ship transportation, and marine leisure activities. Management of the ecological risks associated with the use of antifouling biocides on ship hulls and fishing nets has therefore been an important issue.

Taking steps to effectively reduce ecological risks first requires quantitative assessment of the relative risk of each biocide, followed by a determination of the use of which substances should be given priority for reduction. Probabilistic risk analysis is one of the ways to quantify ecological risks (Posthuma et al., 2002). In the real world, factors such as toxicity are variable, and factors affecting risk are uncertain rather than known precisely. Probabilistic approaches are not simply methods to quantify risk, but can also be used to quantify variability and uncertainty in risk assessment (EURFAM, 2006; Hayashi and Kashiwagi, 2011). Methodologies that rely on species sensitivity distributions (SSDs) are widely used in probabilistic ecological risk assessment (Posthuma et al., 2002; European Commission, 2003). A SSD is a statistical distribution describing both the degree and variability of the toxicity of a certain compound to all relevant trophic levels, such as algae, crustaceans, and fish, in a particular ecosystem, and is derived by assuming that

* Corresponding author.
E-mail address: kmochida@fra.affrc.go.jp (K. Mochida).
[1] Present address: Kitasato University School of Marine Biosciences, Kitasato 1-15-1, Minami-ku, Sagamihara, Kanagawa 252-0329, Japan.

http://dx.doi.org/10.1016/j.envpol.2015.05.012
0269-7491/

toxicity values are log-normally distributed (Aldenberg et al., 2002). In a probabilistic risk assessment based on a SSD, risk is quantified by calculating the probability that a randomly sampled concentration from an environmental concentration distribution (ECD) will exceed a randomly sampled species sensitivity from a SSD. This probability is a function of the areas under the curves of the probability density function of the ECD and the cumulative SSD distribution function; it is referred to as the ecological risk/probability of failure (Aldenberg et al., 2002) or expected potentially affected fraction (EPAF) (Hayashi and Kashiwagi, 2011). The fraction is a quantitative measure of the risk, because it considers the entire distributions of both the species sensitivity and environmental concentrations.

The primary aim of this study was to quantify the ecological risk by calculating the EPAF for 4,5-dichloro-2-*n*-octyl-isothiazoline-3-one (Sea-Nine 211; Rohm and Haas, Philadelphia, PA, USA) as a model chemical in Hiroshima Bay, Japan. Sea-Nine 211 has been used in many paint products, especially in three-biocide mixtures that also contain cupric oxide and Diuron (Okamura and Mieno, 2006). Sea-Nine 211 has been detected in seawater and sediment samples from several European countries (Martinez et al., 2001; Steen et al., 2004) as well as from Japan (Tsunemasa et al., 2006; Harino et al., 2007, 2009). In addition, toxicity data for marine organisms associated with several trophic levels (e.g., algae, crustaceans, and fish) are available (Shade et al., 1993; Mochida et al., 2010; Onduka et al., 2013). Quantification of the ecological risk in the coastal areas of Japan associated with the use of the model antifouling biocide Sea-Nine 211 is therefore feasible.

We first determined the occurrence of Sea-Nine 211 in 58 surface water samples and 50 sediment samples from Hiroshima Bay, Japan, including regions in the vicinity of fish farms, fishing ports, marinas, and river mouths (see Supplementary Data 1). Although Tsunemasa et al. (2006) have studied the occurrence of Sea-Nine 211 in Hiroshima Bay, their sampling points were limited to several fishing ports and marinas. We therefore conducted a survey of Sea-Nine 211 contamination throughout almost all of Hiroshima Bay and derived an ECD based on that survey. In addition, we carried out a spatial analysis of the concentrations of Sea-Nine 211 to visualize the distribution of the concentrations in both the surface water and sediments of Hiroshima Bay. In this way we were able to consider the state of contamination at the time of sampling, as well as the source and fate of the Sea-Nine 211.

Second, we used published toxicity data for 29 marine organisms to drive the parameters that characterize the SSD. We then carried out a risk assessment for Sea-Nine 211 in Hiroshima Bay in two ways: (1) a quantitative probabilistic methodology, in which we calculated the EPAF by using the parameters from both the SSD and ECD, and (2) a conventional way, in which we used the hazard ratio method to compare predicted no-effect concentrations (PNECs) to environmental concentrations. The use of SSDs facilitates estimation of hazardous concentrations (HC_p), which may then be used to determine the PNECs that would protect ecosystems from the adverse effects of hazardous chemicals. The HC_p is the *p*th percentile of the SSD distribution, and a statistical cutoff value of 5% for *p* is often used to obtain the PNEC (Kooijman, 1987; van Straalen and van Leeuwen, 2002). In the present study, we also estimated the HC_5 and HC_1 of the SSD (i.e., 5th and 1st percentile of the SSD) and compared those values to environmental concentrations.

A practical difficulty in calculating the EPAF is proper handling of the uncertainties and variabilities involved in the derivation of both the ECD and SSD. In many instances, environmental concentration data include values below the detection limit [i.e., "not detected" (ND)]. In the case of the SSD, only a limited number of toxicity data are available in some cases, especially for marine organisms, and there is often concerned that the list of species is a biased selection, but the extent of bias is very difficult to assess. Under such conditions it is necessary to assess the uncertainties of both the ECD and SSD, and in numbers derived from them (Posthuma et al., 2002). In the present study we estimated the ECD and SSD by using HCs derived with Bayesian inference. We then computed medians and confidence intervals of the EPAF values by using Markov chain, Monte Carlo (MCMC) samples of the posterior distributions of the ECD and the SSD parameters as input values. Ellison (1996) has described the advantages of using Bayesian statistics in environmental decision-making. These advantages include the ability to treat uncertainty in an explicit and consistent way, and to update inferences with new data. Indeed, Bayesian statistical inference has been used to calculate the confidence limits of a typical SSD and to quantify the confidence limits of the mean values (Aldenberg and Jaworska, 2000; Hayashi and Kashiwagi, 2011).

2. Materials and methods

2.1. Environmental and toxicity data collection

2.1.1. Environmental data

Environmental samples were gathered from 58 stations in the region bounded by 132.2–132.6°E and 34.15–34.40°N in Hiroshima Bay (Hiroshima Prefecture, Japan) from July to December 2010 (Supplementary Data 1). Fifty-eight seawater samples were taken from the top of the water column (surface water) with a stainless steel bucket, and 50 sediment samples were collected using, in most cases, an acrylic pipe core sampler.

Analyses of Sea-Nine 211 concentrations in the samples were carried out with the method previously described by Harino et al. (2007). Briefly, 1 L of a seawater sample was mixed with 50 mL of hexane. After dehydration with sodium sulfate, the extracts were removed impurity with Sep-Pak® Vac Silica Cartridges (Nihon Waters K.K., Tokyo, Japan) and then concentrated to 1 mL under nitrogen gas and subjected to further analysis. In the case of sediment samples, an aliquot of 10 g of wet sample was mixed with 25 mL of acetonitrile, and the mixture was extracted for 10 min in a mechanical shaker and then centrifuged at 1000 g for 5 min. After removal of the supernatant, the residue was re-extracted with acetonitrile for 10 min and again centrifuged at 1000 g for 5 min. The combined supernatants were concentrated with a rotary evaporator to 5 mL, and 45 mL of distilled water was added. The 50-mL aqueous solution was extracted twice with 20 mL of dichloromethane. After dehydration with sodium sulfate and cleaned up with the Sep-Pak® Vac Silica Cartridges (Nihon Waters K.K.), the extracts were concentrated to 1 mL under nitrogen gas and subjected to further analysis.

The concentration of Sea-Nine 211 was analyzed by using a capillary gas chromatography – negative ion chemical ionization – mass spectrometer (GC–NCI–MS). Gas chromatographic separation was performed using an Agilent 7890N (Agilent Technologies, Tokyo, Japan) with 5%-phenyl methyl siloxane (HP-5MS, 30 m × 0.25 mm, Agilent). The mass spectrometer was operated by using an Agilent 5975C under the selected-ion monitoring mode. The ion monitored for Sea-Nine 211 was 245 (*m*/*z*). The detection limits of the surface water and the sediment sample for Sea-Nine 211 were <0.1 ng/L and <1 μg/kg-dry weight, respectively.

2.1.2. Toxicity data

We collected acute toxicity data from previously published reports (Shade et al., 1993; Bellas, 2006; Myers et al., 2006; Mochida et al., 2010; Tsunemasa and Okamura, 2011; Onduka et al., 2013). As mentioned in the Introduction, species sensitivities, such as LC_{50},