Environmental Pollution 224 (2017) 384–391

Contents lists available at ScienceDirect

Environmental Pollution

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

Acute water quality criteria for polycyclic aromatic hydrocarbons, pesticides, plastic additives, and 4-Nonylphenol in seawater☆

I. Durán, R. Beiras*

ECIMAT, Universidade de Vigo, Illa de Toralla, E-36331, Galicia, Spain

ARTICLE INFO

Article history:
Received 9 September 2016
Received in revised form
20 January 2017
Accepted 9 February 2017
Available online 20 February 2017

Keywords:
Acute water quality criteria
Species sensitivity distribution
Early life stages
Marine species
Aromatic chemicals
Plastic additives

ABSTRACT

Probabilistic environmental quality criteria for Naphthalene (Nap), Phenanthrene (Phe), Fluoranthene (Flu), Pyrene (Pyr), Triclosan (TCS), Tributyltin (TBT), Chlorpyrifos (CPY), Diuron (DUR), γ-Hexaclorocyclohexane (γ-HCH), Bisphenol A (BPA) and 4-Nonylphenol (4-NP) were derived from acute toxicity data using saltwater species representative of marine ecosystems, including algae, mollusks, crustaceans, echinoderms and chordates. Preferably, data concerns sublethal endpoints and early life stages from bioassays conducted in our laboratory, but the data set was completed with a broad literature survey. The Water Quality Criteria (WQC) obtained for TBT ($7.1 \cdot 10^{-3}$ μg L^{-1}) and CPY ($6.6 \cdot 10^{-3}$ μg L^{-1}) were orders of magnitude lower than those obtained for PAHs (ranging from 3.75 to 45.2 μg L^{-1}), BPA (27.7 μg L^{-1}), TCS (8.66 μg L^{-1}) and 4-NP (1.52 μg L^{-1}). Critical values for DUR and HCH were 0.1 and 0.057 μg L^{-1} respectively. Within this context, non-selective toxicants could be quantitatively defined as those showing a maximum variability in toxicity thresholds (TT) of 3 orders of magnitude across the whole range of marine diversity, and a cumulative distribution of the TT fitting to a single log-logistic curve, while for selective toxicants variability was consistently found to span 5 orders of magnitude and the TT distribution showed a bimodal pattern. For the latter, protective WQC must be derived taking into account the SSD of the sensitive taxa only.

1. Introduction

Probabilistic environmental quality criteria obtained from species sensitivity distributions (SSD) allow in theory the protection of a given percentage of the species occurring in an ecosystem (e.g. 95%) with a known confidence level (Aldenberg and Slob, 1993). This approach was frequently used in order to derive scientifically sound water quality criteria (WQC) (US-EPA, 1985; OECD, 1995; ANZECC, 2000; CCME, 2007; EC, 2011; Durán and Beiras, 2013). The derivation of probabilistic WQC demands the use of toxicity data for a variety of taxa representative of the communities of interest, covering a wide range of phylogenetic and physiological variability (Van Straalen and Denneman, 1989), and including at least one species from each major taxon, although the minimum requirements differ among procedures (see US-EPA, 1985; EC, 2011). In addition to the implementation of general values of universal application, based on standard test species, the posterior derivation of site-specific WQC based on toxicity data sets better matching in taxonomic composition the biological assemblages that reside at the sites to be protected is commonly advised (CCME, 2007; US-EPA, 2013).

Most standard biological models used in experimental aquatic toxicology are freshwater organisms such as *Rhaphidocellis* (formerly known as *Selenastrum* and *Pseudokirchneriella*), daphnia or zebra fish. For marine species, toxicity data are scarcer, and therefore, they are frequently extrapolated from freshwater species (EC, 2011). This approach has been questioned because freshwater species may not represent the sensitivity of saltwater organisms (Leung et al., 2001, but see also Robinson, 1999), increasing in any case the uncertainty of the actual degree of protection for marine ecosystems. In a recent study, Durán and Beiras (2013) demonstrated that for several trace metals the maximum admissible concentrations reflected in the applicable legislation were above the toxicity thresholds for early life stages of saltwater species with high commercial value, evidencing the need to improve the regulations by taking into account toxicity data from marine species. In the case of organic pollutants the need of additional toxicological information is even more evident. For example, in the European

☆ This paper has been recommended for acceptance by Maria Cristina Fossi.

* Corresponding author.
E-mail address: rbeiras@uvigo.es (R. Beiras).

http://dx.doi.org/10.1016/j.envpol.2017.02.018
0269-7491/

Directive 2013/39/EU common aquatic pollutants such as phenanthrene or pyrene, or emerging substances such as pharmaceuticals and plastics components that are becoming ubiquitous in the aquatic environments (Richardson, 2008), lack water quality standards, and in North America environmental criteria for most of these pollutants are not available or derived for continental waters only (see CCME, 2016; US-EPA, 2016). In order to choose substances which may pose a risk to water-column organisms, in this study we have selected organic pollutants with molecular weight lower than 360, water solubility above 0.1 mg/L and log K_{ow} (octanol-water partition coefficient) within the range from 3 to 6.

The objective of the present work was to derive preliminary acute saltwater quality criteria for selected organic pollutants, including PAHs Naphthalene (Nap, CAS 91-20-3), Phenanthrene (Phe, CAS 85-01-8), Fluoranthene (Flu, CAS 206-44-0) and Pyrene (Pyr, CAS 129-00-0), biocides Triclosan (TCS, CAS 3380-34-5), Tributyltin (TBT, CAS 36643-28-4), Chlorpyrifos (CPY, CAS 2921-88-2), Diuron (DUR, CAS 330-54-1) and γ-Hexaclorocyclohexane (γ-HCH, CAS 58-89-9), and plastics components Bisphenol A (BPA, CAS 80-05-7) and 4-Nonylphenol (4-NP, CAS 104-40-5), on the basis of marine ecotoxicological data. With that aim, the data set used consisted of acute toxicity threshold values obtained from tests conducted with marine species only. In order to maximize sensitivity and thus protective value of the resulting criteria, preference was given to sublethal endpoints and early life stages. The currently applicable national and international criteria and standards will be assessed at the light of the obtained WQC, and the degree of protection offered to marine ecosystems will be discussed.

2. Material and methods

2.1. Toxicity data set

For obvious reasons, the universal sensitivity of all species of an ecosystem to a given chemical must be estimated from the experimental data obtained with a small number of representative species. On the basis of computer simulations, Kooijman (1987) found that a sample size between 5 and 30 provides a good compromise between statistically acceptable estimations and excessive experimental effort. US-EPA (1985) required the use of 8 different families for the derivation of saltwater criteria, while EC (2011) demands at least 10 species covering a minimum of 8 taxonomic groups.

The current study used for each chemical between 12 and 20 endpoints obtained from between 6 and 17 species including at least one representative of each of the main taxonomic groups of marine organisms: algae, mollusks, crustaceans, echinoderms and chordates. For crustaceans, data were searched for at least one representative of non-decapods (copepods, mysids, etc.) and one decapod. For most chemicals, data on toxicity to macroalgae and marine annelids were not available.

In order to maximize sensitivity, and thus protective value of the WQC, sublethal endpoints (algal population growth, reproduction, embryogenesis and larval development) and early life stages (embryos, larvae, neonates) were chosen, and adult mortality was included only when more sensitive endpoints for the species were not available. When possible, data were obtained from toxicity tests conducted in our laboratory according to standard, internationally accepted protocols under strict quality assurance procedures (see below). However, when data on relevant marine taxa were lacking or they were not sufficient to obtain significant SSD models, the data set was completed with values from a broad literature survey for comparable taxa, endpoints and life stages. Since environmental factors such as light or salinity affect the toxicity of organic chemicals, estimates of toxicity obtained for the same endpoint under different conditions were included in the data set as long as values vary within environmentally relevant conditions.

Definition of acute toxicity varies among protocols and testing organisms. Therefore, a pragmatic approach was taken and tests up to a maximum of 5 days were selected (Giddings et al., 2014). When toxicity values were reported for different periods of exposure, only data for the longest period were considered (Giddings et al., 2014).

2.2. Toxicity tests methods

Toxicity tests using microalgae and early life stages of bivalves, crustaceans, echinoderms and chordates were carried out under strict quality assurance/quality control following internationally adopted standard methods. A detailed description of the procedures is available on the Supplementary material. Nap, Phe, Flu, Pyr, TCS, BPA and 4-NP were purchased from Sigma–Aldrich, TBT and DUR from Aldrich Steinheim, CPY from Chem Service, and γ-HCH from Merck Schucdart.

2.3. Statistical methods

The SSD curves were obtained by fitting for each chemical the cumulative distribution of the toxicity thresholds (TT) obtained for the different species and life stages to a log-logistic model (Van Straalen and Denneman, 1989) described by the equation:

$$C_p = 1 - \frac{1}{1 + e^{\frac{\log TT - \log a}{b}}}$$

where *Cp* is the cumulative probability of the TT, and *a* and *b* are fitting parameters. The value of *a* equals the TT value for a cumulative probability of 0.5, and the value of *b* is inversely related to the slope of the curve. Non-linear fitting was performed using SigmaPlot (version 10.0) statistical software. In those cases where the shape of the curve reflected two different statistical populations, the WQC were derived using the distribution of the most sensitive organisms (CCME, 2007; EC, 2011). Only significant parameters ($p < 0.05$) are reported.

According to standard procedures (ANZECC, 2000; CCME, 2007; EC, 2011), the TT were estimated using the cumulative SSD of the EC_{10} and NOEC/LOEC data. Due to the well-known weaknesses of the NOEC/LOEC approach, such as dependence on experimental design and statistical power (OECD, 1998b; Reiley et al., 2003; Vighi et al., 2003), EC_{10} were preferred. In the cases where EC_{10} data were not available, the TT was estimated using $EC_{50}/3$, or LOEC, based on the mean ratios between EC_{10} and the remaining toxicity parameters obtained from the toxicity data base generated in our laboratory for >60 compounds tested with marine species ($EC_{50}/EC_{10} = 3.3$, n = 202; EC_{10}/LOEC = 1.1, n = 137).

Following previous consensus (US-EPA, 1985; Van Straalen and Denneman, 1989; EC, 2011), the criteria were derived from the 5th percentile (HC_5) of the TT distribution, i.e. it is intended to protect 95% of the species in the ecosystem. Since the fitting parameters in the logistic equation above, *a* and *b*, are estimates obtained from a limited number of TT values measured in a small number of species, the HC_5 is thus an estimate of the percentile from the actual sensitivity distribution of all ecosystem species. We need thus to take into account the probability that the actual value was lower than the estimate, which would cause under-protection, and fix that probability to an acceptable low value, customarily 5%. The WQC will thus be defined as the lower end of the 95% confidence intervals for the HC_5 (Aldenberg and Slob, 1993; Smith and Cairns, 1993; EC, 2011; Durán and Beiras, 2013). Therefore, these WQC should protect 95% of the species with a 95% certainty.