Can We Possibly Derive Sediment Quality Guidelines for Chemical Mixtures ?

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1. Introduction

- Sediment quality guidelines (SQGs) are primarily developed based on ecotoxicity data obtained from laboratory-based bioassays, in which a target chemical is spiked into the test sediment as an imperfect proxy of the field exposure.
- In reality, many chemical pollutants are indeed coexisting in the sediment.
- For example, many antifouling biocide residues (e.g., copper, butyltins, phenyltins, Irgarol 1051, diuron etc.) are often detected as a cocktail in water and sediment samples collected from coastal environments.
- Based on literature review of documented studies on the combined ecotoxicity of antifouling biocides, we found that both additive and synergistic effects together account for 78% of all cases in which about 35% cases are synergistic [Fig. 1].
- More strikingly, Silva et al. (2002) tested the combined effect of eight estrogenic compounds and concluded that the estrogenic compounds can act together to produce significant estrogenic effects when combined at concentrations below their no observed effect concentrations [1].
- Therefore, the ecological risk of chemical mixtures should not be overlooked. To allow more accurate risk assessment of concurrently occurring chemicals, there is a need to develop SQGs for their mixtures which are commonly coexisting in the aquatic environment.
- This poster will introduce four possible methods for deriving water quality guidelines (WQGs) and/or SQGs with consideration of the effect of chemical mixtures.

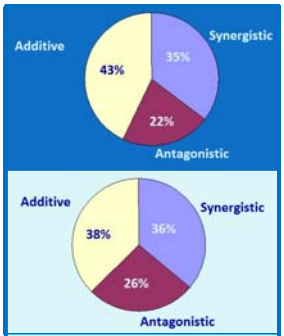

Fig. 1. The combined toxic effects of various mixtures of antifouling biocides (Upper figure) and mixtures of copper and an antifouling booster biocides (Lower figure) to marine organisms.

Overall, 78% of cases show additive or synergistic effects. For mixtures containing copper, 74% of cases exhibit additive or synergistic effects.

2. Materials and Methods

- **Toxic equivalency quotient (TEQ) based approach**: If all components in a chemical mixture are known to share a similar toxic mode of action, we can assume that the combined toxicity of the mixture would follow a simple concentration addition model, and the concept of TEQ could be applied to derive the SQG based on lethal and/or effect concentrations expressed in terms of TEQ and/or TEQ concentration. This "standard" method has been widely applied to various chemical groups such as polychlorinated biphenyls (PCBs), dioxins, dioxin-like compounds and environmental estrogens.
- **Multidimensional species sensitivity distribution (m-SSD) approach:** If the mixture contains chemicals with different toxic modes of action, it is possible to explore the use of the m-SSD approach. Here, binary mixtures of copper (Cu) and zinc pyrithione (ZnPT) are used as an example to illustrate the method. Standard acute toxicity tests have been conducted with an array of marine organisms for each chemical alone, and for their mixtures [2]. The mixtures show a strong synergistic toxic effect to all nine test organisms. By utilizing the toxicity data, a two-dimensional SSD in form of a response surface is constructed for deriving any specific hazardous concentration for the two compounds. This novel method can be potentially applicable to a more complex mixture.
- **Field-based SSD approach:** This method is integrated with the quantile regression method, can be used to derive SQGs for any target chemical with consideration of the presence of chemical mixtures and biological interaction. The method is described in Leung et al. (2005) & Kwok et al. (2008) [3,4].
- **Field-based community sensitivity distribution (f-CSD) approach:** This is a novel nonparametric approach (i.e., Empirical Bayesian Method) to model the toxicity effect of chemicals on species density of benthic infauna. Each point along the CSD represents the hazardous concentration for a drop in species density by a proportion (γ) and thus the percentage (100 – γ)% of species density being protected under this concentration can be adopted as a SQG [7].

3. Results and Discussion

3.1. The TEQ-based approach

- In this method, the concentration of PCB congeners and mixtures are converted to TCDD-TEQ using the toxic equivalent factors [5]. All toxicity data are converted to TCDD-TEQ values and thus, the WQG or SQG would be expressed as µg TCDD-TEQ/L [Fig. 2].
- However, the assumption of all PCBs to follow "concentration addition" model could be questionable and uncertainty exists. Usually, toxic equivalency factors (TEFs) are only derived for a proportion of congeners, and thus surrogate TEFs would be applied to untested compounds with a similar structure.
- Although this method has been successfully applied for polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and PCBs, it is not universally applicable to other groups of compounds. Peters and Gonzalez (2011) [6] discovered that this method cannot be used for perfluoroalkyl compounds, because they can activate and/or interfere with other receptors, and different chemical species can trigger different receptors leading to different toxicities.

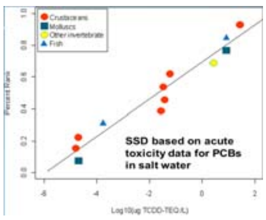

Figure 2. Distributions of acute toxicity data for PCBs in seawater. To fit the SSD with a log-normal model, an acute EQB can be derived at hazardous concentration of 5% (i.e., HC5; 95% protection level).

3.2. The m-SSD approach

- The results show that ZnPT-Cu mixtures have strong synergistic effects to test organisms even at Cu as low as 2 µg/L. An example is shown in **Fig. 3 [2]**. Predicted effect concentrations of ZnPT decrease with increasing Cu concentrations at environmentally realistic levels (0-20 µg/L).
- At any given Cu concentration, EQBs of ZnPT can be readily derived from the 2D-SSD (with adjusted r^2 of 0.90; i.e., 90% of variance being explained by the model) [Fig. 4].
- Our team has also developed non-parametric surface response models for describing the 2D-SSD of more complex mixtures that cannot be fitted with conventional parametric models.
- This Cu-ZnPT example demonstrates the need to develop WQGs and SQGs for ZnPT with consideration of ambient Cu levels, and established an empirical based framework.
- But this m-SSD approach is data-intensive and requires a large number of toxicity tests (e.g., N = 9 species x 6 [Cu] x 3 replicates = 162 tests for the current study; i.e., one 4-yr PhD work).
- This is only applicable to known mixtures that commonly exist in the environment.
- Multiple stressors like temperature and salinity can affect both 1D- and 2D-SSDs, and thus influence the resultant WQG or SQG.

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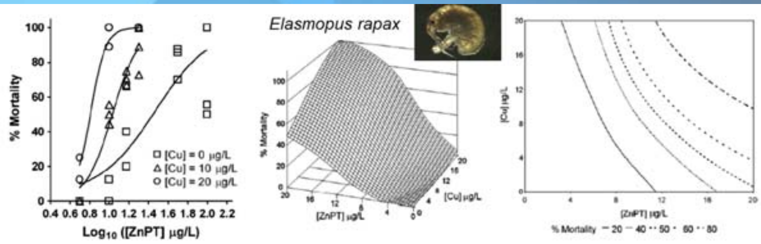


Figure 3. An example of combined toxicity of Cu and ZnPT to the amphipod *Elasmopus rapax*: concentration-response relationships (Left); non-parametric response surface is constructed to model the mixture toxicity (Middle); and isobols bowing downward indicate synergistic effect (Right) [2].

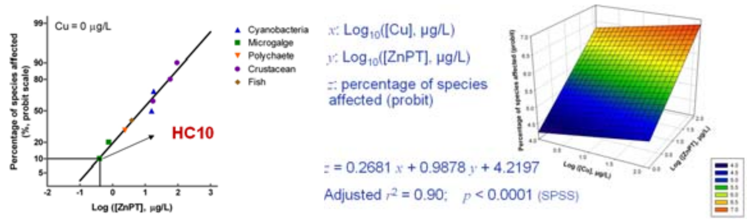
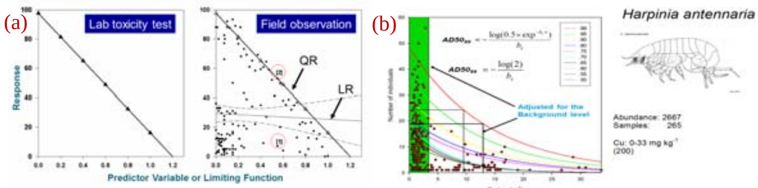


Figure 4. A SSD for ZnPT without Cu addition (Left; as an example) and a 2D-SSD constructed from all SSDs of ZnPT at various Cu concentrations.

3.3. The f-SSD approach

- The application of quantile regression in the f-SSD can account for the effects of chemical mixtures with some empirical examples [Fig. 5a].
- The results of the f-SSD approach can serve as a check-and-balance of the laboratory driven SQGs while it can enhance ecological realism in the SQG values.
- Nonetheless, this method can only deal with existing chemical pollutants, and requires a massive dataset of concurrently obtained biodiversity and chemical concentration data.



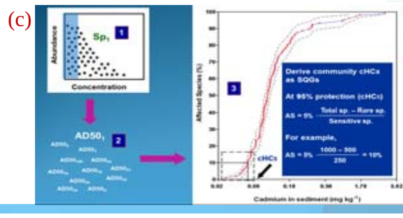


Figure 5. The f-SSD approach: (a) quantile regression (QR) vs. linear regression; (b) an application of QR to determine the concentration for abundance drop by 50% (AD50) of a sensitive species; and (c) an overall summary of the f-SSD approach [4].

3.4. The f-CSD approach

- Like the f-SSD approach, the f-CSD method also requires a large dataset of concurrently obtained biodiversity and chemical concentration data, and sophisticated computation [Fig. 6].
- The SQGs values derived by this approach can be directly linked to species loss (or species protection) in relation to sediment quality, and thus provide additional invaluable information for ecological risk assessment and environmental remediation [7].

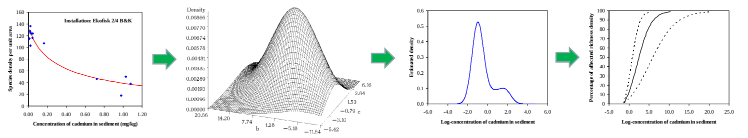


Figure 6. An example of deriving SQGs for cadmium (Cd) using the Norwegian Oil Industrial Association database: Step 1 - determining the relationship of species density and Cd concentration in sediment samples collected from each region; Step 2 - estimating joint densities of parameters *b* and *c* for all regions using Empirical Bayesian Method; Step 3 – estimating species densities along various Cd concentrations by the Kernel method; Step 4 – estimating the CSD based on the median Cd concentration from which hazardous concentrations (HCx) can be determined and used as SQGs.

4. Concluding Remarks:

- Chemical mixtures do matter as reflected by the fact that 78% cases for mixtures of antifouling biocides would result in additive or synergistic effects to marine organisms.
- It is possible to use TEQ-based approach to derive SQGs for mixtures consisting chemicals with a similar mode of toxic action.
- For mixtures containing chemicals with different modes of toxic action, the multidimensional SSD approach maybe adopted. But this method is time-consuming and not cost-effective.
- Field based approaches such as f-SSD and f-CSD potentially serve as an alternative way to derive SQGs and account for interacting effects of chemicals and biological interaction.
- **There is no perfect solution but we can always find a better one.**

5. Cited References:

[1] Silva E, et al. (2002) Environmental Science & Technology 36:1751-1756; **[2]** Bao VWW, Leung KMY, et al. (2008) Marine Pollution Bulletin 57: 616-623; **[3]** Leung KMY, et al. (2005) Environmental Science & Technology 39: 5148-5156; **[4]** Kwok KWH, et al. (2008) Environmental Toxicology and Chemistry 27:226-234; **[5]** Takasuga T, et al. (2006) Chemosphere 62:469-484; **[6]** Peters JM, Gonzalez FJ (2011) Chemical Research in Toxicology 24: 2601-1609; **[7]** Lui CSG, et al. (in press) Environmental Science and Pollution Research.