

A PROPOSED ECOTOXICITY WATER QUALITY STANDARD FOR HEXACHLOROBENZENE (HCB)

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Introduction

A common procedure for calculating water quality standards is to apply a safety/uncertainty factor to data generated from laboratory-generated, single species toxicology studies. The resulting Predicted No Effect Concentration (PNEC) becomes the basis for setting a water quality standard. A criticism of this approach is that the PNEC is usually calculated by applying an arbitrary safety factor to the most sensitive acute LC₅₀ or chronic NOEC value, thereby producing a single criteria concentration that is assumed to be highly conservative but that does not include any expression of uncertainty. The PNEC also excludes pertinent data from other organisms. As a result of these limitations, species sensitivity distributions (SSDs) are increasingly recommended to either complement or replace the use of assessment factors in the risk assessment of chemicals in the U.S. and in Europe. Overall, the use of the 5% species affected level (i.e., the HC₅) is becoming widespread in ecological risk assessment applications. For example, the SSD concept is now being formally incorporated into ecological risk assessment frameworks at the U.S. EPA¹ (<http://www.epa.gov/oppefed1/ecorisk/>) and is under consideration for use within the Organization for Economic Co-Operation and Development or OECD².

The SSD methodology offers a clear advantage over the traditional calculation of a predicted no-effect concentration as it incorporates available toxicity data for a range of species and permits assemblage-level uncertainties to be estimated and expressed quantitatively. It thereby allows a risk assessor to estimate a level of protection based on the proportion of species impacted, to identify those taxa most at risk, and to estimate the costs and benefits to the environment of particular environmental criteria and levels of protection. The U.S. EPA has observed on deriving water quality criteria for chemicals³ that "protection of all species at all times and places is not deemed necessary.... a reasonable level of protection will probably be provided if all except a small fraction of the taxa are protected".

In the SSD approach, the concentration protective of most single species is calculated from a distribution plot that is typically log-transformed. A number of assumptions are inherent in this approach: (1) the SSD is well modeled by the selected distribution; (2) the sensitivity of the species in the laboratory approximates the sensitivity of species in the field; (3) the sample of species is random, or at least representative of an ecosystem; and (4) protection of the prescribed percent of species confers an appropriate level of protection on both ecosystem structure and function. It is this final point that has garnered the majority of criticisms concerning the SSD approach and extrapolation to protection at the ecosystem level.

In examination of this latter assumption, Versteeg et al.⁴ examined the application of single-species chronic toxicity data from the open literature (via the SSD approach) with published, high quality chronic model ecosystem (e.g., microcosms, model ecosystems, and field situations) data on the same chemical. These authors compared the SSD output to ecosystem NOEC values for a

variety of substances (n = 11), including organic compounds, metals, pesticides, and surfactants. The authors noted that observed field ecosystem NOEC values corresponded to concentrations expected to exceed the SSD NOEC of 10 to 52% of species centile values, i.e., the researchers found that the 5% centile value in an SSD (i.e., the HC₅) was quite conservative and a good predictor of the lower 95% confidence interval on the mean ecosystem NOEC value.

Recently, the Fraunhofer Institute was contracted to calculate draft environmental quality standards (EQS) for 33 substances under the European Union's Water Framework Directive (<http://www.europa.eu.int/scadplus/leg/en/lvb/l28002b.htm>). The technical guidance employed in setting the draft EQS values used a simple deterministic approach. Using the published literature data for hexachlorobenzene (HCB), we will compare and contrast the proposed draft EQS water quality standard to that determined using an SSD approach.

Materials and Methods

The methodology for deriving the EQS for HCB is based on the revised Technical Guidance Document, with additional guidance from the Fraunhofer Institute (www.ime.fraunhofer.de/oeko/abt/riscon/riscon_p9_content.htm). The ecotoxicity data set for HCB meets the necessary threshold for evaluation with an SSD analysis (n = 15 chronic values, etc.) and consists of chronic laboratory studies conducted on aquatic species encompassing a spectrum of taxa.

Results and Discussion

The EU's draft freshwater EQS value for HCB was determined to be 0.013 µg/L. This concentration was based on the most sensitive reported chronic NOEC value of 0.13 µg/L, derived from a 21-day reproduction study with *Daphnia magna*⁵; applying an assessment factor of 10 to the daphnid NOEC gives the proposed EQS value. A major difficulty in using these data³ is that no detailed reference or information is provided, i.e., the original paper by Scheubel (1984)⁵ could not be obtained to validate the quality of the data. However the IUCLID data set on hexachlorobenzene citing the same reference indicates the NOEC value was calculated, not experimentally determined. The study of Scheubel (1984)⁵, based on the quality assessment criteria recommended by the EU Commission Regulation 1488/94/EEC (<http://europa.eu.int/scadplus/leg/en/lvb/l21274.htm>), is considered to have a Reliability Level of 4, (i.e., "information to give an adequate opinion is not available").

In addition to questions about the potential inappropriate referencing and the calculated NOEC value, the NOEC of 0.13 µg/L used to derive the proposed EQS value for HCB differs markedly from other well documented studies examining the chronic toxicity of HCB in crustaceans; these data were included in the EQS analysis on HCB. For example, in a study with a detailed experimental description (Reliability Level 1), Caspers et al.⁶ reported the chronic NOEC for reproduction with *Daphnia magna* (21-day HCB exposure) at 17 µg/L. It is noteworthy that the results reported by Caspers et al. are in reasonable agreement with Calamari et al.⁷, who reported a 14-day LOEC for *Daphnia magna* of 23 µg/L. Based on these data, it is proposed that the NOEC of 17 µg/L from Caspers et al.⁶ likely provides the most reliable valid chronic NOEC for HCB with *Daphnia magna*. There is also a NOEC for reproduction in *Ceriodaphnia dubia* with HCB at 7 µg/L (Reliability Level of 2), cited by the U.S. EPA⁸. The data collectively suggest that cladocerans are not as intolerant as predicted by the extrapolated NOEC value presented by

Scheubel (1984)⁵. Additionally, in a 30-day HCB exposure study with the benthic invertebrate *Hyalella azteca* (Reliability Level 1), the NOEC for growth, survival, and reproduction was 4.7 $\mu\text{g/L}$ ⁹. The lowest NOEC for HCB providing acceptable reliability was reported by Nebeker et al.⁹ for the freshwater amphipod *Gammarus lacustris* (Reliability Level 2), with a chronic NOEC of 1.8 $\mu\text{g/L}$.

These chronic laboratory data on HCB from the EU's draft Substance Data Sheet on HCB were modified with additional data from other open literature studies examining the chronic toxicity of HCB with other aquatic species. An additional HCB study on the crayfish (*Procambarus clarkii*) by Laska et al.¹⁰ reported a 10-day NOEC of 2.7 $\mu\text{g/L}$ (Reliability Level 2). A chronic *Ceriodaphnia dubia* survival and reproduction study with a Reliability score of 2 produced a NOEC value of 7 $\mu\text{g/L}$ ⁸, while a long-term (70-84 day) mesocosm study by examining growth, survival, and fecundity of the marsh snail (*Lymnaea palustris*) produced a NOEC value with HCB of 5 $\mu\text{g/L}$ (Reliability level 3)¹¹.

If all the chronic NOEC data from studies noted in the EU's draft Substance Data Sheet on HCB are included and the NOEC values from the noted chronic studies on *Procambarus clarkii*, *Ceriodaphnia dubia*, and *Lymnaea palustris* are added, the SSD plot appears as shown in Figure 1 (n = 15 and correlation coefficient of 0.8191). As seen in Figure 1, the questionable *Daphnia magna* NOEC value from Scheubel (1984)⁵ of 0.13 $\mu\text{g/L}$ appears to deviate significantly from the log-normal distribution of the other chronic effect data. If the datum of Scheubel (1984)⁵ is removed due to its Reliability Level of 4, a revised chronic SSD plot for HCB appears as shown in Figure 2 (n = 14 and correlation coefficient of 0.9262). The NOEC values of Figure 2 appear to fit the log-normal distribution quite well, with a resulting 5th centile NOEC value for HCB of 1.2 $\mu\text{g/L}$. Therefore, the proposed freshwater HCB criteria value is 1.2 $\mu\text{g/L}$, based on the 5th centile SSD protection level. The HCB SSD analysis in Figure 2 (EQS_{freshwater} = 1.2 $\mu\text{g/L}$) uses 14 chronic values and none of the experimental data fell below the 5th percentile of the SSD value of 1.2 $\mu\text{g/L}$. This proposed water criteria value is comparable to the draft ambient water criteria value of 3.7 $\mu\text{g/L}$ developed by the U.S. EPA on HCB⁸.

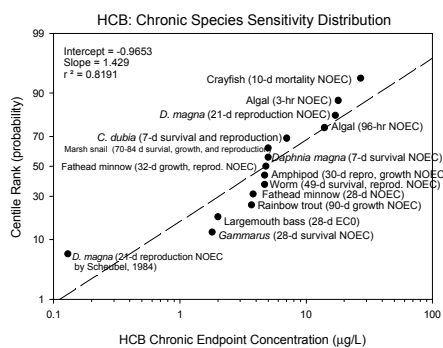


Figure 1. Chronic toxicity species sensitivity distribution (SSD) plot for HCB.

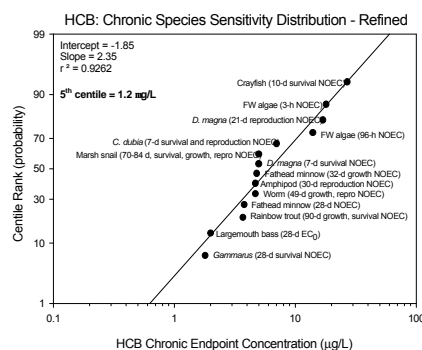


Figure 2. Refined chronic toxicity species sensitivity distribution (SSD) plot for HCB.

References

- ¹ ECOFRAM. 1999. Ecological Committee on FIFRA risk assessment methods: Report of the Aquatic Workgroup. U.S. EPA, Office of Pesticide Programs, Washington D.C.
- ² OECD. 1992. Report of the OECD workshop on the extrapolation of laboratory aquatic toxicity data to the real environment. OECD Monograph 59, OECD/GD (92)169, Paris, France.
- ³ U.S. Environmental Protection Agency. 1985. Guidelines for deriving numerical national water quality criteria for the protection of aquatic organisms and their uses. PB85-227049.
- ⁴ Versteeg, DJ et al. (1999) Understanding single-species and model ecosystem sensitivity: Data-based comparison. *Environ. Toxicol. Chem.* 18: 1329-1346.
- ⁵ Scheubel, JB. 2001. Überprüfung der Durchführbarkeit von Prüfvorschriften und der Aussagekraft der Stufe I und II des Chemikaliengesetzes. Chem. Werke Huls A.G., Abt. Umweltschutz, kUBA Bericht 106 04 011/5 CHW.
- ⁶ Caspers N, Hartmann P, Kanne R, Knoop G. 1993. UWSF-Z. Umweltchem. Oekotox 5: 265-270.
- ⁷ Calamari, D, Galassi, S, Sett, F, Vighi, M. 1983. Toxicity of selected chlorobenzenes to aquatic organisms. *Chemosphere* 12: 253-262.
- ⁸ U.S. Environmental Protection Agency. 1988. Draft: Ambient aquatic life water quality criteria for hexachlorobenzene. Office of Research and Development, Environmental Research Laboratory, Duluth, MN. EPA Number: 440588092.
- ⁹ Nebecker AV, Griffis WL, Wise CM, Hopkins E, Barbitta JA. 1989. Survival, reproduction and bioconcentration in invertebrates and fish exposed to hexachlorobenzene. *Environ. Toxicol. Chem.* 8:601-611.
- ¹⁰ Laska A, Bartell C, Condie D, Brown J, Evans R, Laseter J. 1978. Acute and chronic effects of hexachlorobenzene and hexachlorobutadiene in red swamp crayfish (*Procambarus clarki*) and selected fish species. *Toxicol. and Appl. Pharmacol.* 43:1-12.
- ¹¹ Barturo, W, Lagadic, L. 1996: Benzo[a]pyrene hydroxylase and glutathione s-transferase activities as biomarkers in *Lymnaea palustris* (Mollusca, Gastropoda) exposed to atrazine and hexachlorobenzene in freshwater mesocosms. *Environ. Toxicol. Chem.* 15: 771-781.