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The European water-based environmental quality standard for pentachlorophenol is NOT protective of benthic organisms

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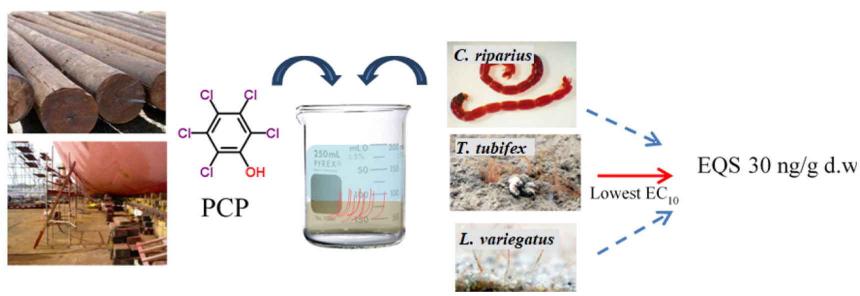
HIGHLIGHTS

- The ecotoxicity of pentachlorophenol (PCP) to benthic organisms was assessed.
- Sensitivity to PCP varies across organisms and end-points.
- A PCP quality standard (QS) for sediments is proposed: 30 ng/g dry weight.
- The European Union water-based QS may be under protective for benthic organisms.

GRAPHICAL ABSTRACT



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ABSTRACT

Risk management of toxic substances is often based on Environmental Quality Standards (EQS) set for the water compartment, assuming they will also protect benthic organisms. In the absence of experimental data, EQS for sediments can be estimated by the equilibrium partitioning approach. The present study investigates whether this approach is protective of benthic organisms against pentachlorophenol (PCP), a legacy contaminant and EU priority substance still used in some parts of the world. Three freshwater species of invertebrates with different life cycles and feeding behaviors (the oligochaetes *Lumbriculus variegatus*, *Tubifex tubifex* and the dipteran insect *Chironomus riparius*) were exposed to PCP spiked sediments (2.10–46.03 mg PCP/kg d.w. plus controls) in laboratory standard tests. Exposure duration was 28 days for *T. tubifex* and *L. variegatus* and 10 and 28 days for *C. riparius*; according to the corresponding OECD guidelines. For each investigated end-point, dose-response data were normalized to the mean control and fitted to a four-parameter log-logistic model for calculating the corresponding EC_{50} and EC_{10}. The ranges for EC_{50} and EC_{10} estimates were 4.39 (*Chironomus riparius-emergence*)–27.50 (*Tubifex tubifex–cocoon*) and 0.30 (*T. tubifex–young worms*) –16.70 (*T. tubifex–cocoon*) mg/kg d.w., respectively. The EC_{50} and the EC_{10} values of *L. variegatus* were within these ranges. Following the EU Technical Guidance for deriving EQS, the lowest EC_{10} value of 0.30 mg/kg (*T. tubifex–young worms*) resulted in a PCP quality standard (QS) for sediments of 30 ng/g, about one fourth of the tentative QS of 119 ng/g estimated by the equilibrium partitioning (EqP) approach. The response of benthic biota to PCP varied across organisms and across end-points for the same organism, so that the use of sediment PCP-QS calculated using the EqP-approach may be under-protective of the most sensitive organisms. Information on the possible effects of PCP on resident organisms must therefore be collected for appropriately managing aquatic systems.

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1. Introduction

1.1. Environmental Risk Assessment at the European level

Environmental Risk Assessment (ERA) is a fundamental tool for supporting decision making in the regulatory context. At the European level, ERA is guided by two important regulations: the Water Framework Directive (WFD), adopted in 2000, and the Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) regulation which came into force in 2007. Within the WFD, European Union Member States (MS) committed themselves to achieve good ecological and chemical status for all water bodies by 2015; however the objective has not fully met and further updates are due until 2021 and 2027 (EEA, 2015). At the same time, compliance with REACH regulation is required for all chemicals manufactured or imported into the EU, unless specifically exempted. During the REACH process, different companies generate a dossier containing data on physico-chemical characteristics, as well as toxicological and ecotoxicological properties for each substance. The dual processes of dossier and substance evaluation lead to the identification of chemicals that may pose unacceptable hazards to human health and/or the environment; also in connection with the WFD implementation (article 11 of Directive 2013/39/EU).

For risk assessment purposes in aquatic environments, REACH considers the water column and the sediments, which differ in chemical-physical characteristics and resident biota. For substances potentially capable of binding to sediments to a significant extent (Log K_{ow} or Log $K_{oc} \geq 3$), the European Chemicals Agency (ECHA) supports REACH registrants to use specific standard guidelines to assess the risk of chemicals in sediments and recommends the use of sediment-dwelling organisms for bioassays (ECHA, 2015). Similarly, the WFD and the Daughter Directive (DD) 2013/39/EU (European Commission, 2000; European Commission, 2013) establish Environmental Quality Standards (EQS) only for the water and biota matrices, but acknowledge the usefulness of sediment-based EQS for some priority substances. MS are allowed to develop and enforce EQS for sediments at the national level provided that such EQS are established through a transparent procedure and ensure a level of protection equivalent to the EQS for water (or biota) set up at the European Community level.

1.2. Pentachlorophenol

Pentachlorophenol (PCP) is a broad-spectrum pesticide which inhibits the synthesis of ATP (Mäenpää et al., 2008) and free amino acids, disrupting the organisms' energy metabolism, influencing the fecundity of certain invertebrates such as amphipods (Graney and Giesy, 1986). PCP is considered as a priority pollutant under the DD 2013/39/EU (European Commission, 2013). Even though its use has been restricted after the 1980s, it is still widely present in the environment, and it is considered as a chemical pollutant of concern (ATSDR, 2001). It has been used throughout the world for purposes as varied as antimicrobial agent, detergent and wood preservative (Gulcan et al., 2008). In 1996, imports of PCP to the EU amounted to 30 t, out of which 28 were synthesized to 46 t of pentachlorophenyl laurate (PCPL). In 1999, the only producer of PCPL in Europe purchased no >20 t of PCP for conversion into PCPL and its production of PCPL for 2000 was <30 t. With the Directive 91/173/EEC (European Commission, 1991), the marketing and use of PCP in substances or preparations in a concentration equal to or >0.1% by mass throughout the European Union has been prohibited, with some exceptions for the use of PCP for the treatment of wood, the impregnation of fibers and textiles, as a synthesizing agent in industrial processes and for the treatment of historical buildings. In other regions of the world (notably in China), PCP production still reached 3000 t in the early 2000s, mainly for use as a molluscicide (Chen et al., 2016). PCP concentrations in water displayed a downward trend in Northern Europe and any risk posed by PCP to the freshwater environment can largely be attributed to sediments contaminated from historic use (Muir and Eduljee, 1999). Due to its relatively high lipophilicity, PCP sorbs strongly to sediments (Sanchez et al., 2005) However in more recent years, PCP levels show increasing trends in some environmental media and regions (Zheng et al., 2011). PCP levels in sediments samples collected (mainly in China) after the year 1998 range from 0.56 to 200 ng/g, with peaks up to 48,300 ng/g at heavily impacted sites (Table S1). The limited available data (Table S1) on levels of PCP in freshwater sediments indicate a half-life of 2.7 yrs. (Zheng et al., 2011), meaning that PCP can persist in the environment for 1 to 2 decades. According to the estimation of Gabbert et al. (2014) after emissions ceased PCP maintains a "stock pollution effect" posing risks to aquatic ecosystems (Muir and Eduljee, 1999; Xing et al., 2012). PCP appears also in the endocrine disruptor list (Li et al., 2010; Zheng et al., 2012) with yet unpredictable effects on organisms.

Both chronic and acute PCP exposure are medical concerns. Acute inhalation exposures in humans have resulted in neurological, blood, and liver effects, and eye irritation (ATSDR, 2001; US EPA, 1999). Chronic exposure to PCP by inhalation has resulted in effects on the respiratory tract, blood, kidney, liver, immune system, eyes, nose, and skin (ATSDR, 2001; US EPA, 1999). Adverse effects of PCP have been recently reported on fetal growth and birth outcomes (Guo et al., 2016). Oral animal studies have reported increases in liver tumors and two uncommon tumor types. EPA has classified pentachlorophenol as a Group B2, probable human carcinogen (ATSDR, 2001; US EPA, 1999).

With the aim of environmental protection, the WFD has set water-based EQS of 0.4 μg/L and 1 μg/L of PCP as the annual average and the maximum admissible concentration in inland and other surface waters, but nothing is specified for biota and sediments where its concentrations are a matter of ongoing concern (Zheng et al., 2011). As the Kp_{susp} of PCP is 1.85–3.72, the trigger criterion to calculate a sediment quality standard is met (European Commission, 2011). The data sheet providing background information on the setting of the EQS for PCP (European Commission, 2005) reports a tentative EQS for sediments of 119 ng PCP/g d.w., calculated using the equilibrium partitioning (EqP) method.

1.3. Ecotoxicity of PCP in sediments

Even if not promptly evident, sediment contamination directly and indirectly affects the water environment reaching in the end human beings. Field observations suggest, and laboratory ecotoxicity assays confirm, that contaminated sediments can negatively affect benthic organisms such as oligochaetes and insect larvae, which occupy crucial positions in the food chain. Therefore selected species of benthic organism in controlled standard conditions can be used to assess the risk of specific substances through exposures in laboratory. Characterization of PCP ecotoxicological potential is available for several organisms and taxonomic groups, including benthic species (Zhao and Zhang, 2017). However, most studies rely on aqueous exposure and deal with acute ecotoxicity and, to the best of our knowledge, only a handful of studies examined PCP effects via exposure of *Lumbriculus variegatus* (Egeler et al., 2005, Mäenpää et al., 2008, Nikkilä et al., 2003) or *Chironomus prasinus* (Sanchez et al., 2005) to contaminated sediments. Furthermore, these previous studies used different methodologies and approaches, which complicates the comparison among different organisms. In order to verify whether sediment-based EQS for PCP derived using the EqP approach actually provide an appropriate degree of protection to benthic organisms, the present study intends to characterize PCP ecotoxicity to sediment-dwelling biota, as a model case study. We carried out long-term toxicity tests using three different benthic organisms, representing major taxonomic groups of freshwater benthic invertebrates with different life cycles and feeding behaviors: two species of oligochaetes (*Lumbriculus variegatus* and *Tubifex tubifex*) and an insect (*Chironomus riparius*). The chironomid non-biting midge *C. riparius* (OECD, 2004) is an epibenthic species, the most commonly tested organism among insects. Among the endobenthic aquatic