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Deriving predicted no-effect concentrations (PNECs) for emerging contaminants in the river Po, Italy, using three approaches: Assessment factor, species sensitivity distribution and AQUATOX ecosystem modelling

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A B S T R A C T

Over the past decades, per- and polyfluoroalkyl substances (PFASs) found in environmental matrices worldwide have raised concerns due to their toxicity, ubiquity and persistence. A widespread pollution of groundwater and surface waters caused by PFASs in Northern Italy has been recently discovered, becoming a major environmental issue, also because the exact risk for humans and nature posed by this contamination is unclear. Here, the Po River in Northern Italy was selected as a study area to assess the ecological risk posed by perfluoroalkyl acids (PFAAs), a class of PFASs, considering the noticeable concentration of various PFAAs detected in the Po waters over the past years. Moreover, the Po has a large environmental and socio-economic importance: it is the largest Italian river and drains a densely inhabited, intensely cultivated and heavily industrialized watershed. Predicted no-effect concentrations (PNECs) were derived using two regulated methodologies, assessment factors (AFs) and species sensitivity distribution (SSD), which rely on published ecotoxicological laboratory tests. Results were compared to those of a novel methodology using the mechanistic ecosystem model AQUATOX to compute PNECs in an ecologically-sound manner, i.e. considering physical, chemical, biological and ecological processes in the river. The model was used to quantify how the biomasses of the modelled taxa in the river food web deviated from natural conditions due to varying inputs of the chemicals. PNEC for each chemical was defined as the lowest chemical concentration causing a non-negligible yearly biomass loss for a simulated taxon with respect to a control simulation. The investigated PFAAs were Perfluorooctanoic acid (PFOA) and Perfluorooctanesulfonic acid (PFOS) as long-chained compounds, and Perfluorobutanoic acid (PFBA) and Perfluorobutanesulfonic acid (PFBS) as short-chained homologues. Two emerging contaminants, Linear Alkylbenzene Sulfonate (LAS) and triclosan, were also studied to assess the performance of the three methodologies for chemicals whose ecotoxicology and environmental fate are well-studied. The most precautionary approach was the use of AFs generally followed by SSD and then AQUATOX, except for PFOS, for which AQUATOX yielded a much lower PNEC compared to the other approaches since, unlike the other two methodologies, it explicitly simulates sublethal toxicity and indirect ecological effects. Our findings highlight that neglecting the role of ecological processes when extrapolating from laboratory tests to ecosystems can result in under-protective threshold concentrations for chemicals. Ecosystem models can complement existing laboratory-based methodologies, and the use of multiple methods for deriving PNECs can help to clarify uncertainty in ecological risk estimates.

1. Introduction

Pollution is a major threat to aquatic ecosystems worldwide, impacting water quality and biodiversity and reducing the provision of ecosystem services which valuably contribute to human wellbeing (Millennium Ecosystem Assessment, 2005). Ecological risk assessment (ERA), the estimation of the risk posed by the presence of human-released chemicals to living organisms in ecosystems, is a fundamental step to guide management and inform policy towards sustainable solutions for mitigation of this threat. The basic steps of ERA include hazard identification, effects assessment, exposure assessment and risk characterization, where the main goal of the effects assessment is setting a safe threshold for the concentration of chemicals (Predicted No-effect Concentration, or PNEC), below which no adverse effects on ecosystem structure and functions are expected (De Laender et al., 2013; European Chemicals Bureau, 2003).

The foundation for ERA in the European Union is represented by several standardized procedures adopted for protecting ecosystems. The

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guidance for the implementation of the REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) regulation (REACH, EC, 2006), adopted to improve the protection of human health and environment from the risk posed by chemicals, and the Technical Guidance For Deriving Environmental Quality Standards as part of Common Implementation Strategy for implementation of the Water Framework Directive 2000/60/EC (European Community, 2000), provide a consistent approach to estimate ecologically-safe thresholds in aquatic ecosystems (ECHA, 2008; European Commission, 2011). Based on the abovementioned European regulations, PNECs can be derived in three manners: a deterministic approach based on the use of coefficients called assessment factors (AFs), a statistical approach based on the so-called species sensitivity distribution (SSD), and results from model ecosystems and field studies (European Commission, 2011). The most common approach is the use of assessment factors, where threshold exposure concentrations measured in the laboratory for individual species are extrapolated to populations in real-world ecosystems by dividing them by AFs, whose value depends on the amount and quality of available toxicity data (European Commission, 2011; Lei et al., 2010; Meli et al., 2014). When there is a sufficient amount of ecotoxicological data available for different taxa, the species sensitivity distribution (SSD) method is used instead (European Commission, 2011; Valsecchi et al., 2017). SSD is a cumulative probability distribution fitted to a set of toxicity thresholds for individual species of the ecosystem under the assumption that acceptable effects levels follow a certain distribution as a function of the concentration of the chemical (e.g. normal, logistic, triangle) and that the limited number of tested species is a random sample of the whole ecosystem (De Laender et al., 2013; Gao et al., 2014).

The AF and SSD methods rely on the assumption that ecosystem sensitivity to a given chemical can be related to the status of the most sensitive species, and that protecting ecosystem structure is enough to protect ecosystem functions too (Wright-Walters et al., 2011). However, population dynamics in polluted environments are not only driven by the direct toxicity effects of chemicals on single species, but also by ecological interactions between them and by the influence of abiotic factors (De Laender et al., 2007), therefore community- and ecosystem-level assessments could provide better indications of species' responses to chemicals than individual-level ones (Zhang et al., 2013). To assess ecological interactions, experimental ecosystems (microcosm, mesocosm and field enclosure studies), which can account for both direct and indirect effects of chemicals, have been used (De Laender et al., 2007, 2008a). Nevertheless, these methods are laborious, expensive and time-consuming, and the extrapolability of results to much more complex natural ecosystems, characterized by myriads of ecological interactions, remains uncertain (Lei et al., 2010; Naito et al., 2003; Zhang et al., 2013; Zhang and Liu, 2014). Considering that these methods cannot be used in the routine practice in lower tiers, there is a strong need for alternative approaches to extrapolate single-species effects information to ecosystem-level responses (De Laender et al., 2008b). Ecological models are cost-effective alternatives for ERA of toxic chemicals, providing rapid forecasting analyses, particularly under circumstances where field experiments cannot be conducted or experimental data are lacking (which is generally the case for the contaminants of emerging concern investigated here) (Grechi et al., 2016; Lombardo et al., 2015; Naito et al., 2003; Zhang and Liu, 2014).

Although several ecological models have been developed and reviewed for use in ERA for chemicals (Galic et al., 2010; Lei et al., 2008; Naito et al., 2003), mechanistic effects modelling has not been extensively used for regulatory purposes yet because of the lack of official guidance for models choice, development and use (Galic et al., 2010; Meli et al., 2014). Among the models used in ERA (De Laender et al., 2008b; Galic et al., 2010; Lei et al., 2008; Naito et al., 2003; Pereira et al., 2017; Zhang et al., 2013), the U.S. Environmental Protection Agency's AQUATOX, an aquatic ecosystem model, is one of the relatively few comprehensive and well documented models that have been designed specifically for environmental fate and ecological impact assessment of pollutants. AQUATOX simulates both abiotic and biotic (including trophic) processes as well as lethal and sub-lethal toxicant effects, and so it can depict the propagation of these effects through food webs and ecosystems (Lei et al., 2008; Park and Clough, 2014; Zhang and Liu, 2014).

Over the past decade, serious concerns have been raised regarding the presence of per- and polyfluoroalkyl substances (PFASs) in different environmental media, particularly water, in Northern Italy (Castiglioni et al., 2015; Loos et al., 2008; McLachlan et al., 2007; Squadrone et al., 2015; Valsecchi et al., 2017, 2015). Especially high PFAS concentrations were detected in the river Po when compared to other European rivers (McLachlan et al., 2007), confirming that the Po and its tributaries are highly polluted by different perfluoroalkyl acids (PFAAs) (Castiglioni et al., 2015; Loos et al., 2008; Valsecchi et al., 2015). Water quality management in the Po is a complex issue and matter for research, since this river crosses a densely inhabited, intensely cultivated and heavily industrialized watershed of about 71.000 km^2, representing one of the wealthiest areas of Europe whose human activities exert multiple large pressures on its high biodiversity (Grechi et al., 2016).

This work aims to assess the ecological risk posed by a few selected unregulated and emerging contaminants in the river Po by applying three methods for deriving PNECs: AF, SSD, and a novel method based on AQUATOX modelling. ERA is carried out for four PFAAs, two long-chained (perfluorooctanesulfonic acid PFOS, perfluorooctanoic acid PFOA) and two short-chained ones (perfluorobutanesulfonic acid PFBS, perfluorobutanoic acid PFBA). The AQUATOX model used here quantitatively simulates ecosystem functioning in the final lowland section of the Po River based on the extensive use of well-documented local data, and was previously calibrated against observations (Grechi et al., 2016). The goals of this work are to compute ecologically-safe thresholds (PNECs) for emerging contaminants in the Po River applying the two classical methods and the AQUATOX-based method proposed here, and then to compare the three methods highlighting their advantages and drawbacks for deriving PNECs for emerging contaminants in rivers. To better contribute to the discussion on the tools to use for the future regulation of contaminants of emerging concern, the three ERA methods were also applied to two well-studied personal care products, linear alkylbenzene sulfonate and triclosan, which had already been investigated by Grechi et al. (2016) using the AQUATOX Po model.

2. Materials and methods

2.1. Study area: the River Po and its biota

The Po is the longest river (652 km) in Italy, with the greatest average discharge (1470 $m^3 s^{-1}$). It flows through the entire northern Italy, and its drainage area covers about one fourth of Italy's surface, including the main industrial and most populated areas where nearly one third of all Italian population lives (Valsecchi et al., 2015). In this study the most representative species and taxa present in the lower stretch of the Po River were considered following the selection by Grechi et al. (2016) (Table 1).

The anthropogenic substances discharged to the river from its watershed exert high pressures not only on its water quality and ecological status, but also on downstream ecosystems: the Po freshwater discharge, which summed to those of other smaller Northern Italian river is about 20% of the river runoff into the whole Mediterranean Sea, carries large nutrient loads which caused severe eutrophication in the Adriatic Sea coastal zone some decades ago (Barausse et al., 2011; Vollenweider et al., 1992). The biomonitoring and ecosystem modelling efforts made for this river in the past (Grechi et al., 2016) make it an ideal study case to assess the ecological risk due to emerging contaminants such as PFAAs and to understand how the outcomes of ERA depend on the methodology chosen to quantify ecologically-safe chemicals thresholds.