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Predicting the aquatic risk of realistic pesticide mixtures to species assemblages in Portuguese river basins

*Emília Silva**, *Michiel A. Daam*, *Maria José Cerejeira*

Centro de Engenharia dos Biossistemas (CEER), Instituto Superior de Agronomia (ISA), University of Lisbon (UL), Tapada da Ajuda, 1349-017 Lisbon, Portugal

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ABSTRACT

Although pesticide regulatory tools are mainly based on individual substances, aquatic ecosystems are usually exposed to multiple pesticides from their use on the variety of crops within the catchment of a river. This study estimated the impact of measured pesticide mixtures in surface waters from 2002 and 2008 within three important Portuguese river basins ('Mondego', 'Sado' and 'Tejo') on primary producers, arthropods and fish by toxic pressure calculation. Species sensitivity distributions (SSDs), in combination with mixture toxicity models, were applied. Considering the differences in the responses of the taxonomic groups as well as in the pesticide exposures that these organisms experience, variable acute multi-substance potentially affected fractions (msPAFs) were obtained. The median msPAF for primary producers and arthropods in surface waters of all river basins exceeded 5%, the cut-off value used in the prospective SSD approach for deriving individual environmental quality standards. A ranking procedure identified various photosystem II inhibiting herbicides, with oxadiazon having the relatively largest toxic effects on primary producers, while the organophosphorus insecticides, chlorfenvinphos and chlorpyrifos, and the organochloride endosulfan had the largest effects on arthropods and fish, respectively. These results ensure compliance with European legislation with regard to ecological risk assessment and management of pesticides in surface waters.

Introduction

Ecosystems are usually exposed to a cocktail of chemicals rather than one individual substance. This is particularly apparent in surface waters, where a multitude of potentially toxic substances enter the watercourse as a result of human activities throughout the drainage basin (Verro et al., 2009). Different agricultural practices can cause the presence of mixtures of pesticides in the aquatic environment, which can vary in terms of their complexity (Altenburger et al., 2014). As cumulative stress of toxicants may be identified as a main pressure affecting ecological status, mixture risks have to be evaluated and reduced (Brock, 2013).

The component-based approach, an option for regulatory mixture ecotoxicity assessment, calculates the expectable joint toxicity from toxicity data for individual mixture components by applying corresponding models, in particular those based on the reference models of concentration addition (CA), response addition (RA), and so-called mixed-model (Altenburger et al., 2014). The summation of PEC/PNEC (predicted environmental concentration/predicted no effect concentration) ratios and the summation of toxic units are examples of CA-based approaches

* *Corresponding author*. E-mail: emiliasilva@isa.ulisboa.pt (Emília Silva).

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used in the authorization procedure for technical mixtures of several active substances and their co-formulants (EC, 2009a; EFSA, 2013) and in the derivation of environmental quality standards for well-defined mixtures, *i.e.*, those with a well-defined qualitative and quantitative composition (*e.g.*, PCBs, dioxins) (EC, 2011). However, the sum of these ratios has no toxicological meaning, *i.e.*, if two substances have the same ratio > 1, their environmental impacts may be quite different (Traas et al., 2002).

As an alternative, this study proposes to use species sensitivity distributions (SSDs) based on laboratory toxicity data to derive a measure of effects that can be used in ecological risk assessment. This method is an improvement over current quotient methods, since it encompasses the often non-observed nonlinearity of species sensitivity and, especially, it allows for comparisons of (aggregated) ecological risk over compounds in a mixture, between *taxa*, and with other stressors (in very specific conditions) (Traas et al., 2002). The combi-potentially affected fraction (PAF) concept was developed by Hamers et al. (1996) and assumes that only compounds exerting narcotic effects are addressed by CA, while all other compounds are handled by RA (mixed-model approach). When the mixture contains compounds with highly specific toxic modes of action (TMoA) that differ among species groups, such as pesticides, it is also possible to generate mixed-model (CA and RA) multi-substance potentially affected fraction (msPAF) values for the individual taxonomic groups (Traas et al., 2002; De Zwart and Posthuma, 2005).

To our knowledge, only few studies (Pérez, 2013; Silva et al., 2012b) have been conducted on the risk assessment of realistic pesticide mixtures in Portuguese freshwaters for individual species by applying whole mixture and component-based approaches. Given also the need for quantitative data on mixture toxicity risks for other relevant assessment endpoints, as species assemblages, *i.e.*, on a higher tier level, toxic pressures (quantified as msPAFs) were calculated (1) to estimate the overall impacts for primary producers, arthropods and fish of measured pesticide mixtures in surface waters of three important Portuguese river basins ('Mondego', 'Sado' and 'Tejo'); and (2) to rank the relative contribution of individual pesticide compounds (or groups of pesticides with the same TMoA) *per* taxonomic group and river basin. The findings from this study will allow the derivation of optimized programs of measures to reduce ecological risks of pesticides in surface waters and evaluation of the control measures for this aquatic compartment. These ensure compliance with the prospective and retrospective risk assessment and management procedures for pesticides in surface waters as laid down in European legislation (EC, 2000, 2009a,b).

1. Experimental

1.1. Study area

In terms of water resources, 'Tejo', 'Sado' and 'Mondego' belong to the largest hydrological basins of continental Portugal occupying 25,666, 12,149 and 6659 km^2, respectively (APA, 2014). Several studies related to surface and ground water contamination have been performed in these basins, since they are located in some of the main Portuguese agricultural areas and, therefore, are potentially at risk. In the 'Médio Tejo' and 'Lezíria do Tejo' regions, located in the 'Tejo' river basin, there are some important irrigated crops such as maize, tomato for industry, rice, sugar beet, open-air horticultural crops and potato, as well as wheat and vines (RGA, 2001a). Some of these crops are also found in the 'Baixo Mondego' area, particularly maize, rice and potato, which occupy an important part of the agricultural area of this region (RGA, 2001b). Concerning the 'Sado' river basin, the agricultural area is mainly occupied by paddy rice (RGA, 2001c).

1.2. Pesticide compounds selected for the study and their TMoA

Twenty one herbicides, five insecticides and three metabolites were selected in this study due to their inclusion in the list of priority substances in the field of water policy (EC, 2013), the amount sold in Portugal (DGAV, 2014) since 2002, their approval for use on the main crops of the studied agricultural areas (see Section 1.1), their detection in previous studies performed in Portugal (Batista, 2003; Batista et al., 2001, 2002; Cerejeira et al., 2000, 2003; Pereira, 2003; Silva et al., 2006, 2011, 2012a, 2012b), and/or their inclusion in the priority list defined in the European project 'Optimization and evaluation of multiresidue methods for priority pesticides in drinking and related waters' (Jaskulké et al., 1999).

Taking into account the TMoA of these pesticide compounds and the presence or absence of specific target sites of toxic action in three important taxonomic groups of the freshwater environment (primary producers, arthropods and fish), nine specific TMoAs were distinguished, *i.e.*, seven groups of herbicides (and their metabolites) with the same specific TMoA for primary producers, and two for arthropods and fish. The organisms that lack the target receptor are not sensitive to pesticide exposure and will experience narcotic baseline toxicity or a secondary level of toxicity (Table 1).

1.3. Risk analysis

1.3.1. Exposure data

The exposure data used in this study correspond to 281 surface water samples collected at 43 sampling sites chosen to give a general environmental status of the 'Mondego', 'Sado' and 'Tejo' river basins during the main period of agricultural practices from 2002 to 2008, both in terms of pesticide application and irrigation. The pesticides alachlor, atrazine, chlorfenvinphos, chlorpyrifos, cyanazine, dichlobenil, endosulfan, ethofumesate, lindane, metolachlor, metribuzin, molinate, oxadiazon, pendimethalin, pirimicarb, prometryn, propanil, propazine, simazine, terbuthylazine, terbutryn, trifluralin, and the metabolites 3,4-dichloroaniline (3,4-DCA), desethylatrazine (DEA) and desisopropylatrazine (DIA) were extracted by solid-phase microextraction (SPME) followed by qualitative and quantitative analysis by gas chromatography (Varian ChromPack CP-3800, Walnut Creek, CA, USA) with mass spectrometric detection (Varian ChromPack Saturn 2000 ion trap MS, Walnut Creek, CA, USA) (Silva et al., 2012a,b), while the pesticides cycloxydim, MCPA, profoxydim and triclopyr by solid-phase extraction (SPE) followed by liquid chromatography