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# Aquatic risk assessment of priority and other river basin specific pesticides in surface waters of Mediterranean river basins

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## HIGHLIGHTS

- 29 pesticide compounds analysed in Mediterranean river basins.
- Derivation of EQSs for 20 pesticide compounds.
- 13 pesticide compounds pose risk in Portuguese surface waters.
- Improved classification of ecological status of surface water bodies.

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## ABSTRACT

To meet good chemical and ecological status, Member States are required to monitor priority substances and chemicals identified as substances of concern at European Union and local/river-basin/national level, respectively, in surface water bodies, and to report exceedances of the environmental quality standards (EQSs). Therefore, standards have to be set at national level for river basin specific pollutants. Pesticides used in dominant crops of several agricultural areas within the catchment of Mediterranean river basins ('Mondego', 'Sado' and 'Tejo', Portugal) were selected for monitoring, in addition to the pesticides included in priority lists defined in Europe. From the 29 pesticides and metabolites selected for the study, 20 were detected in surface waters of the river basins, seven of which were priority substances: alachlor, atrazine, chlorfenvinphos, chlorpyrifos, endosulfan, simazine and terbutryn, all of which exceeded their respective EQS values. QSs for other specific pollutants were calculated using different extrapolation techniques (i.e. deterministic or probabilistic) largely based on the method described in view of the Water Framework Directive. Non-acceptable aquatic risks were revealed for molinate, oxadiazon, pendimethalin, propanil, terbuthylazine, and the metabolite desethylatrazine. Implications of these findings for the classification of the ecological status of surface water bodies in Portugal and at the European level are discussed.



## 1. Introduction

Chemical pollution of surface water may present a threat to the aquatic environment with effects such as acute and chronic toxicity to aquatic organisms, accumulation in the ecosystem and losses of habitats and biodiversity, as well as a potential threat to human health (Schwarzenbach et al., 2006; Malaj et al., 2014). European Union (EU) legislation provides for measures against chemical pollution of surface waters. There are two components – the selection and regulation of substances of EU-wide concern (the priority substances) and the selection by Member States (MS) of substances of national or local concern (river basin specific pollutants, RBSPs) for control at the relevant level (EC, 2014a). The first component constitutes the major part of the Union's strategy against the chemical pollution of surface waters. It is set out in Article 16 of the Water Framework Directive (WFD) (EC, 2000), and outlines the steps to be taken. The first step was to establish by way of Decision 2455/2001/EC (EC, 2001) a first list of priority substances to become Annex X of the WFD. These substances were selected from amongst those presenting a significant risk to or via the aquatic environment, using the approaches specified in Article 16 of the WFD.

This first list was replaced by Annex II of the Directive on environmental quality standards (EQSD) (EC, 2008), also known as the priority substances directive, which set environmental quality standards (EQSs) for the substances in surface waters (river, lake, transitional and coastal) and confirmed their designation as

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priority or priority hazardous substances, the latter being a subset of particular concern. As required by the WFD and EQSD, the Commission subsequently reviewed the list and in 2013 it put forward a directive amending the WFD and the EQSD as regards to priority substances (EC, 2013) in the field of water policy. According to Annex V, point 1.4.3 of the WFD and Article 1 of the EQSD, good chemical status is reached for a water body when it complies with the EQSs for all the priority substances and other pollutants listed in Annex I of the EQSD (EC, 2014b).

In addition, the WFD (Annex V, Section 1.2.6) establishes the principles to be applied to the MS to develop EQSs for specific pollutants that are 'discharged in significant quantities'. These are also known as Annex VIII substances of the WFD. Compliance with EQSs for specific pollutants forms part of the assessment of ecological status. EQSs are therefore key tools in assessing and classifying chemical status and can thus affect the overall classification of a water body under the WFD. In addition, EQSs will be used to set discharge permits to waterbodies, so that chemical emissions do not lead to EQS exceedances within the receiving water (EC, 2011).

EQSs in view of the WFD should be derived according to the technical guidance document (TGD) on risk assessment (EC, 2003). A more detailed guidance was subsequently provided by Lepper (2005). At present, the new and existing substances regulation has been replaced by REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals), but the TGD is still into force for biocides. With respect to the aquatic ecosystem, the risk assessment methodology under REACH (ECHA, 2008) is basically the same as outlined in the TGD. The guidance of Lepper (2005) was revised recently, and an updated TGD for derivation of EQSs under the WFD was published in 2011 (EC, 2011).

In Portugal the substances adopted as RBSPs and the quality standard (QS) values applied were derived for previous legislation which may have been enacted before the WFD methodology was developed. A report on the comparison of specific pollutants and EQSs at the European level (Johnson, 2012) provided contradictory results, i.e., it concluded that Portugal has not identified any RBSPs at the time of collection (i.e. up to August 2012). Therefore, the presence in water bodies of substances 'discharged in significant quantities' and not identified as RBSPs may not be detected in the assessment of ecological status if no EQS values are applied (Johnson, 2012).

A prioritisation methodology to select RBSPs, needed for evaluation of ecological status, was introduced by Von der Ohe et al. (2011) and the prioritisation expert group of the NORMAN network (2014). The study by Slobodnik et al. (2012) utilised parts of the hazard/exposure prioritisation approach developed by the NORMAN Association and was applied to Slovak Republic (Slobodnik et al., 2012).

In this context, and in an attempt to improve the classification of ecological status of surface water bodies, the objectives of the present study were (i) to select priority (hazardous) substances and others of concern in relation to pesticide compounds to be analysed in surface waters of three Mediterranean river basins ('Mondego', 'Sado' and 'Tejo', Portugal); (ii) to calculate their QSs to protect aquatic organisms against long- and short-term exposure based on a simplified decision tree of the methods described in the TGD-EQS (EC, 2011); (iii) to assess the individual risk of priority and other pesticides of concern by comparing the measured concentrations with their respective QSs values as set in this study or established under Community legislation for priority substances (EC, 2013); and (iv) to discuss the implications derived from the aquatic risk assessment findings for the classification of ecological status of surface water bodies in Portugal and at the European level.

## 2. Materials and methods

### *2.1. Agricultural area of study and pesticide selection criteria for monitoring*

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 like maize, tomato for industry, rice, sugar beet, open-air horticultural crops and potato, as well as wheat and vine (RGA, 2001a) (Fig. 1). 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) (Fig. 1). Concerning the 'Sado' river basin, the agricultural area is mainly occupied by paddy rice (RGA, 2001c) (Fig. 1). Pesticides approved for use in the main crops within the catchment of those rivers and representing the most sold in Portugal (DGAV, 2014) were selected, being considered, also, other pesticides included in priority lists, defined in Europe (Jaskulké et al., 1999; EC, 2013), and relevant metabolites from them.

### *2.2. Exposure assessment*

#### *2.2.1. Surface water monitoring network*

A total of 103 grab water samples were collected in five rivers ('Arunca', 'Ega', 'Foja', 'Mondego' and 'Pranto' rivers) in the 'Mondego' river basin (Fig. 1) from April to October (2002–2004), during the main period of agricultural practices, both in terms of pesticide application and irrigation. The following pesticide compounds were monitored: alachlor, atrazine, chlorfenvinphos, endosulfan, metolachlor, molinate, oxadiazon, propanil, simazine, and the metabolite 3,4-dichloroaniline (3,4-DCA).

In the Sado river basin, a total of 56 grab water samples were collected in the 'Sado' river and the 'Santa Catarina de Sítimos' stream (Fig. 1) in 2002 and 2003 (April–November), during the main period of agricultural practices, and analysed for chlorfenvinphos, cycloxydim, endosulfan, MCPA, molinate, oxadiazon, profoxydim, propanil, triclopyr, and the metabolite 3,4-DCA.

Regarding the Tejo river basin, a total of 122 grab water samples were collected in four rivers ('Almonda', 'Alviela', 'Tejo' and 'Zézere' rivers), at the 'Alverca do Campo' embankment, a body of inland water, and drainage channels (Fig. 1) from 2004 to 2006 and 2008 (March–October), during the main period of agricultural practices. These samples were analysed for the following pesticide compounds: alachlor, atrazine, chlorfenvinphos, chlorpyrifos, cyanazine, dichlobenil, endosulfan, ethofumesate, lindane, metolachlor, metribuzin, pendimethalin, pirimicarb, prometryn, propanil, propazine, simazine, terbuthylazine, terbutryn, trifluralin, and the metabolites 3,4-DCA, desethylatrazine (DEA) and desisopropylatrazine (DIA).

#### *2.2.2. Exposure prediction using a screening model*

On the basis of a set of physicochemical and partition coefficient properties selected from different databases (McBean, 2012; FOOTPRINT, 2014), the environmental exposure was evaluated *a priori* through the Level I fugacity model (Mackay, 2001). The Level I calculation evaluates the equilibrium distribution of a fixed quantity of chemical (i.e., 100,000 kg) between the compartments in a closed evaluative or 'unit world' environment (Mackay et al., 1996). It is a steady state calculation with no inflow, outflow,