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# Risk assessment of pesticides detected in surface water of the Alqueva reservoir (Guadiana basin, southern of Portugal)

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## HIGHLIGHTS

- Increasing amounts of bentazone, terbuthylazine and metolachlor
- The north part of the reservoir is the most contaminated
- All pesticides concentrations complied with the EQS
- Terbuthylazine, chlorfenvinphos and diazinon showed high risk for aquatic species
- Water resource management must integrate chemical and ecotoxicological evaluation.

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## ABSTRACT

The purpose of this study was to evaluate the potential impact of the pesticides detected in the Alqueva reservoir (Guadiana Basin, South Iberian Peninsula) on the aquatic organisms belonging to this ecosystem. For this purpose, the occurrence and risk assessment of 25 pesticides and of a number of their degradation products were determined in the Alqueva surface waters. The areas (sampling stations) most polluted by pesticides were Sra. Ajuda, Lucefecit and Álamos in the northern and in the middle portions of the reservoir, respectively. The aquatic risk assessment revealed that from the various compounds analysed terbuthylazine, chlorfenvinphos and diazinon presented non-acceptable risk when maximum concentrations were used as the measured environmental concentrations (MEC). The locations that had more samples with risk quotients higher than 1 (high risk) were Sra. Ajuda followed by Lucefécit. The use of risk assessment allowed us to conclude that, despite that the pesticides' concentrations in the water column fulfil the European environmental quality standards, a number of the compounds show a high ecotoxicological risk for the aquatic organisms in the Alqueva ecosystem. The results thereby demonstrate that to have an efficient risk management process, the regulatory authorities of each country must consider an integrative chemical and ecotoxicological approach.



## 1. Introduction

The use of pesticides plays an important role in harvest quality and food protection, providing benefits for increasing production, such as the reduction of pests, but also inducing damage to most of the agricultural soils and their ecosystems (Herrero-Hernández et al., 2013). As a result of massive global uses, pesticides and their degradation products spread through the environment and contaminate water, soil and atmosphere matrices, leading to a consequent potential risk to human populations and the environment. Surface waters located in intensive agriculture areas are more vulnerable to pesticides, which is a major concern if the water is intended for human consumption. A number of authors have reported the presence of pesticides in the rivers and groundwaters of Portugal, primarily in association with the wide range of agriculture practices taking place in the surrounding areas (Azevedo et al., 2000; Cerejeira et al., 2003; Melo et al., 2012; Silva et al., 2012). However, few researchers have investigated the impact of these classes of contaminants in reservoirs (heavily modified waters), which in the case of the Alentejo region (South Portugal) are the most

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important water sources for multiple uses, such as irrigation and public water supply. The analysis of pesticides in reservoirs and their risk assessment is now a topic of considerable environmental interest due to: (i) the ecosystems of these water bodies being especially endangered because of the risk of high pollutant loads from anthropogenic activities in shallow water with low dilution capacity; (ii) the increase in the types and amounts of the pesticides detected in the water from the intensification of agriculture practices; (iii) the high toxic potential of these compounds for the aquatic ecosystem and for human populations; and (iv) the establishment of strict directives by the European Commission to minimise the impact of these pollutants in heavily modified waters. The European Union Water Framework Directive (ECC, 2000) demands a "good ecological potential" and a "good chemical status" for all European heavily modified water bodies by 2015. The good chemical status will be reached when the concentrations of the priority compounds (such as, alachlor, atrazine, chlorfenvinphos, chlorpyrifos, diuron, isoprotorun and simazine) are below the environmental quality standards (EQS) established in the Directive 2013/39/EC (ECC, 2013) and the priority hazardous compounds (endosulfan, hexachlorobenzene) are withdrawn from the water body. The EQS are limit values derived for chemical substances that pose a significant acute and chronic risk to or via the aquatic environment (European Communities, 2011). A large number of substances with EQS values belong to the pesticide classes. The pesticides' ecological risk assessment (ERA) is expressed as a function of the environmental exposure and ecotoxicological effects. This parameter is usually expressed as the ratio of the predicted environmental concentration (PEC) and the predicted no-effect concentration (PNEC). The PNEC is derived by selecting the most sensitive biotest (representing the most sensitive trophic level) and applying an appropriate assessment factor (AF), which accounts for intra and interlaboratory variation of the data, biological variance, short-term to long-term extrapolation and laboratory to field extrapolation (European Chemical Agency, 2008). The PEC values are calculated using several models which take into consideration the application rates, persistence, leaching, runoff, drift, sorption and compound bioaccumulation (Verro et al., 2009) or directly monitored data (measured environmental concentrations, MEC). The PNEC values are usually calculated on the basis of critical ecotoxicological concentrations, e.g., the median effective concentration ($EC_{50}$), median lethal concentration ($LC_{50}$) or no observed effect concentration (NOEC) (Palma et al., 2004). The determination of the risk quotient (RQ) of samples (ratio between the exposure and the hazard of the mixture) is based on a set of single substance ecotoxicity data from different trophic levels (groups of species) and involves two extrapolation steps: (i) the extrapolation from the experimental toxicity data for the tested species after a certain exposure duration, a step that is implemented for single substances by calculating the PNEC using AF; and (ii) the extrapolation from single substances to chemical mixtures, which can be achieved by the application of concentration addition (CA) or independent action (IA) models (Backhaus and Faust, 2012).

The assessment of the dynamics and the ecological risk of the major pesticides existing in the water bodies is important to provide to the environmental management authorities of each state member, including information about the identification and prioritisation of the most relevant target compounds in each water body to allocate monitoring and management efforts towards the achievement of the objectives set forth the Water Framework Directive (Guillén et al., 2012; López-Doval et al., 2012).

The Alqueva reservoir is the largest man-made lake in the European Union, draining a 53,912 $km^2$ watershed into the Guadiana Basin, which is the fourth largest river in the Iberian Peninsula. The reservoir is located in a semi-arid region with high levels of water scarcity and where agriculture is one of the main economic activities. The construction of the Alqueva reservoir resulted in an increase in agricultural activities, changing the types of crops and the agricultural techniques used from extensive to intensive practices. In recent years, we observed an increase of intensive olive groves and vineyards in the cultivated fields around the reservoir resulting in intensified pesticide application and, consequently, an increase in the degradability of the soils and water resources. Furthermore, the north part of the Guadiana Basin, in the Portuguese territory, is extremely contaminated by pesticides from Spanish olive crops (Hermosin et al., 2013; Palma et al., 2009). Studies conducted in the Alqueva reservoir in 2006 and 2007 showed that, in certain areas and periods, some pesticides classified as hazardous substances according to the Directive 2008/105/EC (ECC, 2008), surpassed their environmental quality standard values (Palma et al., 2009).

Considering these facts, the primary objectives of this study were: (1) to assess the progress of the pesticides' dynamics in the reservoir; and (2) to analyse the ecological risk impact of the present pesticides to quantify their potential environmental effects.

The results of this study in combination with the outcomes obtained in previous studies are intended to help water resource managers and regulatory authorities establish priority actions aimed at achieving the chemical and ecological status objectives set forth in the Directive 2013/39/EC (ECC, 2013).

## 2. Materials and methods

### 2.1. Site description and sampling procedures

The Alqueva reservoir is located in southern Portugal, along 83 km of the main course of the Guadiana River Basin. The hydrologic regime of the Alqueva reservoir reflects the regional expression of the Mediterranean climate (Morales, 1993). During the study period, the climate was characterised by a mean atmospheric temperature of 16 °C, ranging from 3 °C in January to 33 °C in August (www.snirh.pt, 2010/2011; 2011/2012). The average monthly precipitation for the hydrologic year 2010/2011 was 46.5 mm (www.snirh.pt, 2010/2011) and 20.3 mm for the hydrologic year 2011/2012 (www.snirh.pt, 2011/2012). Thus, the precipitation values in the hydrologic year 2011/2012 were extremely low compared to the previous year. The land uses obtained from the Coordination of Information on the Environment (CORINE) land cover classes (2006) identify agricultural activities as being the most ubiquitous in the Alentejo region (68.8%), followed by semi-natural areas (28.1%) (ARHAlentejo, 2011).

Five sampling sites were established at the Alqueva reservoir: three upstreams at Ajuda (Aj; 38°46′28.56″N, 7°10′47.00″W), Alcarrache (Ac, 38°19′1.53″N, 7°19′51.10″W) and Álamos (Al; 38°20′30.00″N, 7°34′40.00″W); and two in the middle of the reservoir at Mourão (Mr; 38°23′60.00″N, 7°23′25.80″W) and Lucefécit (Lf; 38°33′′6.32″N, 7°17′52.86″W) (Fig. 1). Ajuda was the only location with lotic conditions, and was chosen to provide information about the input flux to the Guadiana River coming from Spain. The sampling locations were selected taking into account the Alqueva's monitoring programme, developed by the Portuguese enterprise responsible for the Alqueva reservoir exploitation (Empresa de Desenvolvimento e Infra-estruturas de Alqueva, EDIA), and the previous reservoir water quality assessment results (Morais et al., 2007; Palma et al., 2009, 2010a,b).

Pesticides were evaluated during 12 sampling campaigns, performed from February 2011 to November 2012 (in the months of February, April, June, July, September and November; for both years). The rainy season included the months of November, February and April, and the dry season included the months of June, July and September; these periods were defined by the Portuguese Environment Agency (APA) for the Alentejo region (ARHAlentejo, 2011). During the study period, a total of 60 water samples (1 L) were collected at a depth of 50 cm, transported to the laboratory at 4 °C, and stored in amber PET bottles in the dark at −18 °C until analysis. This sampling followed the same temporal and spatial scheme used in the previous studies in order to make the results as much comparable as possible, always taking into account the uncertainty introduced by varying conditions, such