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Environmental and human health risk indicators for agricultural pesticides in estuaries

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ABSTRACT

The present study aims to contribute to a better assessment of pesticide environmental and human health (here evaluated in the context of human exposure via food items) risks for the estuarine system by comprehensively studying the spatial and temporal occurrence of the pesticides atrazine, azoxystrobin, bentazon, λ-cyhalothrin, penoxsulam and terbuthylazine in the River Mondego estuary (Portugal). Pesticide quantification was performed in surface water, sediment, macroalgae (*Ulva* spp., *Gracilaria gracilis*, *Fucus vesiculosus*), aquatic plants (*Zostera noltii*, *Spartina maritime*, *Scirpus maritimus*) and bivalves (*Scrobicularia plana*). Since intense precipitation could promote the runoff of pesticides from the surrounding agricultural fields, a single long-duration flood event was also studied in this estuarine system. Under normal flow conditions, quantified concentrations were determined mostly during summer in agreement with the pesticide application period. Azoxystrobin presented the highest detection frequency and atrazine (an herbicide used globally but banned in the EU) presented the second highest frequency, thus highlighting the need to include legacy pesticides in monitoring programmes. Pesticide concentrations in surface water determined in the present study suggest low risk to estuarine organisms. However, all the pesticides were bioaccumulated by *S. plana*, leading us to consider that pesticides may not only cause adverse effects on the aquatic organism itself, but should also be an alert for human exposure, for this is an edible species and is considered of economic interest. Concern is also expressed about edible seaweeds, since s-triazine pesticides were found in *Ulva* spp. and *G. gracilis*. Acknowledging these concerns, developing and establishing allowable pesticide safety values for edible seaweeds and bivalves is recommended, as well as monitoring bivalve pesticide levels, using the whole animal, as a human health exposure indicator for estuarine systems. During the studied flood event, it appears that no serious pesticide contamination has occurred in the River Mondego estuary.

1. Introduction

Estuarine environments are considered especially rich and diverse ecosystems which provide feed, refuge and reproduction conditions to aquatic communities, as well as ecosystem services to humans. Even though estuaries are usually located downstream fertile agriculture areas used for intensive farming, comprehensive knowledge of concentration levels of agricultural pesticides in estuaries is lacking in the scientific literature. Moreover, pesticide residue concentrations in edible species may pose human health risks, and numerous estuarine species are edible and considered of economic interest. Finally, the remobilization of pesticides already present in the environment may be promoted during flood events with potential environmental and human health consequences, and a possible approach for minimizing risk is to identify these potential pesticide sources before extreme weather events.

Several review studies concluded that there is a lack of concentration levels of pesticides in biota to perform pesticide environmental and human health risk assessments (e.g., in China: Grung et al., 2015; in Portugal: Ribeiro et al., 2016). Nonetheless, some regular environmental monitoring programmes for pesticides using aquatic biota are currently under way, namely one carried out by the Nordic cooperation (TemaNord 514, 2007), and another taking place in Korea coastal areas (Choi et al., 2010), among others. Thus, an ample understanding of pesticide levels in aquatic systems is required to provide proper environmental and human health risk assessments.

The present study aims to contribute to a better assessment of pesticide environmental and human health risks for the estuarine

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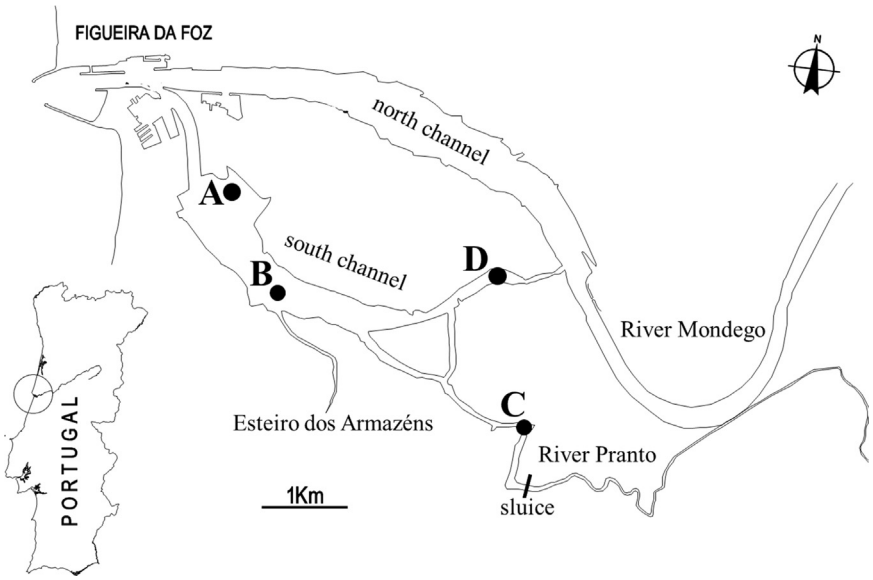

Fig. 1. Map of the Mondego estuary showing the study area. A, B, C and D represent the sampling stations.

system by comprehensively studying the spatial and temporal occurrence of the pesticide atrazine, excluded as an active substance in 2004 from *annex I* of the Directive 91/414/EEC (European Commission, 2004), and of the current-use pesticides azoxystrobin, bentazon, λ-cyhalothrin, penoxsulam and terbuthylazine in the River Mondego estuary (Portugal). The levels of pesticide residues were determined in surface water, sediment, macroalgae (*Ulva* spp., *Gracilaria gracilis* and *Fucus vesiculosus*), aquatic plants (*Zostera noltii*, *Spartina maritima* and *Scirpus maritimus*), and bivalves (*Scrobicularia plana*) before the beginning of (March 2014) and after (August 2014) the production season in the Lower Mondego (agricultural area located upstream of the estuary). Furthermore, taking advantage of a single long-duration river flood event caused by intense precipitation that triggered large-scale destruction and substantial damage in the Lower Mondego, destroying vegetable crops, covering house floors with a thick layer of mud and rubble, and blocking roads, the above-mentioned pesticide levels were also assessed in February 2016. According to the Portuguese Environment Agency, the magnitude of the flood-peak discharge was 1920 m^3 s^{-1}, and the previous comparable flood episode had taken place in January 2001, with a flood-peak discharge of 1942 m^3 s^{-1}.

Under EU, the potential hazard assessment of agricultural pesticides in the environment is achieved by determining Risk Quotients (RQ), which are the ratio between Predicted Environmental Concentration (PEC, supported by modelling practices) or Measured Environmental Concentration (MEC, real exposure concentrations) values, and Environmental Quality Standard (EQS) values (European Commission, 2011). If RQ > 1, a potential adverse effect due to environmental exposure to the pesticide of concern must be considered. The use of MEC values provides accuracy to the risk determination process, making them essential to validate and eventually calibrate the models used to compute PEC values (Pereira et al., 2014). Regarding pesticide risk to human health, it cannot be determined without detailed information on the occurrence of residues in food (Zhang et al., 2011), and health risk evaluation in the present study was performed through the comparison of quantified pesticide residues in food items with the respective established Acute Reference Dose (ARfD), which is the amount of the pesticide that can be consumed in a single intake. A comparison with Maximum Residue Levels (MRLs) was also performed, elucidating if pesticides were applied correctly (Good Agricultural Practice) in the Lower Mondego. Since the bivalve digestive gland is considered the main metabolic site and the target detoxification organ, where accumulation of organic toxic substances may occur, pesticide residues were determined separately in the digestive gland and remaining tissues of some of the animals.

The data gathered by the present study is fundamental to accurately make hazard and environmental risk assessments of estuarine systems, as well as to evaluate their vulnerability during extreme weather events. Since numerous estuarine species are edible and considered of economic interest, results of pesticide levels could be useful alerts for human exposure by food consumption, as they are important human health exposure indicators for estuarine systems. In a more comprehensive overview, results could also contribute to an informed decision-making process for the conservation and management of estuarine systems.

2. Materials and methods

2.1. Choice of pesticides and species

Atrazine (CAS 1912-24-9) was chosen as it is considered a persistent herbicide (Jablonowski et al., 2010) which had been extensively used in the region, and is currently included in the European 33 priority pollutant list (*annex II*, Directive, 2008/105/EC), as well as in the Endocrine Disruption Screening Program of the US Environmental Protection Agency (US-EPA, 2009). The choice of the current-use pesticides azoxystrobin (CAS 131860-33-8), bentazon (CAS 25057-89-0), λ-cyhalothrin (CAS 91465-08-6), penoxsulam (CAS 219714-96-2) and terbuthylazine (CAS 5915-41-3) was based on the technical information provided by the Regional Direction of Agriculture and Fisheries of the Centre of Portugal.

The studied species were chosen as they represent different trophic/functional groups, and the bivalve *S. plana* is considered a key species of the River Mondego estuary (Verdelhos et al., 2005). Moreover, *Ulva* spp. (sea lettuce), *G. gracilis* (slender wart weed) and *S. plana* (peppery furrow shell) are edible species.

2.2. Study area

The River Mondego estuary (6.4 Km^2) is located in southern Europe, in the central coast of Portugal, and was classified as a mesotidal well-mixed estuary with irregular river discharges by Bettencourt et al. (2004). The estuary drains a hydrological basin of 6659 km^2 (APA, 2015) and its most downstream part is divided into two channels (Fig. 1). The northern channel is deeper (4–8 m deep at high tide), with regularized banks for navigation and harbour facilities, while the southern channel is shallower (2–4 m deep at high tide) and