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Review

Priority pesticides in sediments of European coastal lagoons: A review

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ABSTRACT

This review summarizes the legislation applied to pesticides and highlights the physicochemical properties of the past and recently listed PPs under Water Framework Directive (WFD). It reports important information regarding the analysis, occurrence and long-term screening of PPs in sediments of European coastal lagoons. Among the entire list of PPs, those analyzed have been the organochloride insecticides, such as lindane, hexachlorobenzene and DDT. Although flood events pointed to the possible redistribution of pesticides, which may increase under climate change conditions, few studies are available concerning PPs screening in sediments of European coastal lagoons. Data is scarce not only in terms of the number of listed PPs that have been analyzed but also in terms of their long-term screening. This lack of data on PP concentrations is probably a consequence of the fact that less importance is given to the sediments contamination/quality.

Contents

1. Introduction

Pesticides constitute a vast class of compounds that have been used globally for many decades. Despite the advantages and benefits, their continuous application and release to the aquatic ecosystems has become a matter of concern. Under the context of the Water Framework Directive (WFD) (EC, 2000) a specific group of pesticides, classified as toxic, persistent and liable to bioaccumulate is a priority in surveillance programs. These types of compounds, herein designated as priority pesticides (PPs), tend to be sorbed by suspended particulate matter and are retained in the bottom of aquatic systems by sedimentation. Release of such contaminants can happen at any time via re-suspension by natural or human actions and therefore, their absence in water may not reflect their real bioavailability.

Coastal lagoons fall under the context of WFD, and the monitoring of PPs is a demand (EC, 2000). Coastal lagoons are shallow water bodies separated from the ocean by a barrier, connected at least intermittently, to the ocean by one or more restricted inlets (Anthony et al., 2009). Lagoons range in area from <0.01 km^2 to $>10{,}000$ km^2, and are typically <5 m deep (Anthony et al., 2009). They constitute 13% of coastal regions globally and 5.3% of the European coastlines (Anthony et al., 2009; Gaertner-Mazouni and De Wit, 2012). Lagoons are formed and maintained through sediment transport. These ecosystems are highly

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productive and support a variety of habitats, including salt marshes, sea grasses and mangroves (Anthony et al., 2009). The continental inputs in the coastal lagoons are mainly characterized by river waters and sometimes, by groundwater or rainwater that drains the surrounding soils. Drainage waters carry large amounts of fine particles and organic detritus, as well as nutrients and other substances arising from human activity in the lagoon region (Castel et al., 1996). Because of the restricted exchange with the ocean, coastal lagoons trap inorganic sediments and organic matter coming from distinct sources, serving as a repository of many and different types of organic contaminants such as pesticides (Carvalho et al., 2009; Parolini et al., 2010; Pinto et al., 2013; Ritson et al., 2014).

Coastal lagoons are the interface between terrestrial and marine environments and will probably be highly affected by global climate changes (Anthony et al., 2009; Gaertner-Mazouni and De Wit, 2012). About 70% of the coastlines worldwide are projected to experience sea level change (IPCC, 2013). A rise of the sea level will affect the salinity of lagoons through inundation, and in extreme cases some coastal lagoons will probably disappear (Anthony et al., 2009; Brito et al., 2012; Newton et al., 2014). An increase of the flushing rates might have a dilution effect on the levels of pesticides. Contrary, an increase of salinity may favor pesticide accumulation in sediments. Alterations of the rainfall patterns and an increase in extreme weather events will have a direct impact on coastal lagoons and on the fate of the pesticides. (Anthony et al., 2009). This surface runoff may lead to a rise in the concentration of pesticides and other substances (Bloomfield et al., 2006; León et al., 2015; Ritson et al., 2014; Zonta et al., 2005). Storms and floods will favor sediment redistribution and consequently leads to relocation of the most sorbed hydrophobic substances (Anthony et al., 2009).

An increase of pesticides concentration in sediments of coastal lagoons can be a threat to the aquatic organisms, whatever the causes. Exposure to contaminated sediments can result in a decrease of survival, reduced growth and impaired reproduction of many aquatic organisms (MacDonald et al., 2003). Benthic organisms can absorb the pesticides accumulated in the sediments and transform them to higher trophic levels through bioaccumulation and bio-magnification (Dueri et al., 2008). Moreover, contamination has a negative impact on sediment management. Handling of contaminated material, e.g. in the cases of dredging, is much more expensive than handling clean material (Salomons and Brils, 2004). Contaminated sediments are defined as those "that contain chemical substances at concentration that pose a known or suspected environmental or human health threat" (Burton, 1992). Traditionally, contaminated marine sediments were evaluated as part of navigational dredging and disposal assignments (Burton, 1992). Nowadays, sediments contamination is widespread and has emerged as matter of concern at an international level. Screening of pesticides or any other type of pollutant in such a type of matrix is, therefore, extremely important not only for the evaluation of the level of contamination for dredging proposals but also for the assessment of possible ecotoxicological risks (Burton, 1992; Barakat et al., 2013). Alterations on sediment dynamics in coastal lagoons and of pesticide pathways under climate change conditions may also lead to profound impacts on lagoon ecology. Due to their extensive application in the past more information is available for organochlorines PPs regarding their analysis and environmental fate in aquatic systems (Dueri et al., 2008; Köck-Schulmeyer et al., 2013; Ribeiro et al., 2016; Pinto et al., 2016). For the new added PPs less information is available concerning their quantification, behavior and persistence especially in sediments (EC, 2012a,2012b,2013). In this sense, the aims of this review are: (a) to summarize the legislation applied to pesticides lifecycle mainly at an European level; (b) to highlight the most important physiochemical properties of the PPs, including those recently added to the list of priority substances under Annex X of the WFD, that can be useful to predict their dispersion in coastal environments; (c) to assess the main drawbacks of PPs sediment analysis; (d) and to evaluate the extension of PPs screening and occurrence in sediments of European Coastal lagoons.

2. The priority pesticides (PPs)

2.1. Legislation framework

Over the last 20 years regulation of pesticides has become more complex and stringent. In the European Union (EU), the pesticides industry is regarded as one of the most regulated of all, with a large number of directives, codes and protocols administered and advised by a vast number of committees and other bodies (Carlile, 2006). Pesticide legislation covers not only the conditions concerning the placing of pesticides on the market but also the levels of pesticide residues allowed in water and food, pesticide statistics, as well as the action to be taken to promote sustainable use of pesticides and to minimize the negative impacts on human health and on environment (EC, 1991,1998,2000,2001, 2005,2008a,2008c,2008d,2009a,2009b,2009c,2012c,2012d,2012e). Until 1991, the Member States of the EU operated individually regarding registration and use of pesticides (Carlile, 2006). The introduction of Directive 91/414/EEC (EC, 1991) aimed to coordinate the regulation of pesticides thought the EU. Directive 91/414/EEC (EC, 1991) states that a plant protection product, where pesticides are included, must be tested and officially authorized. Pesticides cannot be introduced into the market unless the active substance or substances are listed in Annex I of Council Directive 91/414/EEC (EC, 1991). In food, the concentration of pesticide residues is controlled by Regulation (EC) n°396/2005 (EC, 2005). In water, Directive 2000/60/EC (EC, 2000) establishes a framework for Community action in the field of water policy. This Directive also known as Water Framework Directive (WFD), aims to protect the aquatic environment from pollution by preserving and improving the quality of inland surface waters, transitional waters, coastal waters and groundwater. Under WFD, Member States must adopt specific measures against pollution of surface water and groundwater to attain both good surface water status and good groundwater status 'Good surface water chemical status' is defined by the WFD as the chemical status achieved by a body of surface water in which concentrations of certain compounds do not exceed the environmental quality standards (EQSs) established for a list of substances, defined as priority substances (PS) and listed under Annex X of the WFD (EC, 2000,2001). With this control, WFD aims at enhancement, protection and improvement of the aquatic environment through specific measures for the progressive reduction of discharges, emissions and losses of PS and the cessation or phasing-out of discharges, emissions and losses of the priority hazardous substances (PHS), with the ultimate aim of achieving concentrations in the marine environment approaching background values for naturally occurring substances and close to zero for man-made substances (EC, 2000). The list of priority substances to be under control was initially integrated in the WFD by Decision n° 2455/2001/EC (EC, 2001). From the total of 33 priority substances of the list, 11 were classified as "priority hazardous substances" (EC, 2001). The list also includes 8 other substances that were already regulated at Union level (EC, 2008c). The EQSs for those substances were established by Directive 2008/105/EC (EC, 2008c). In 2013, Directive 2013/39/EU (EC, 2013) amended the WFD and Directive 2008/105/EC (EC, 2008c) as regards priority substances in the field of water policy. New substances were included in the list of priority substances making a total of 45 substances or group of substances that will be under strictly surveillance in the next decades. Among these substances or groups of substances, 27 have been used as pesticides.

2.2. Physicochemical properties

The pesticides listed under Annex X of the WFD were classified as PS and PHS due to their toxicity, persistence and bioaccumulation liability (EC, 2000,2001). The list of those pesticides, herein defined as "priority pesticides" (PPs), is presented in Table 1, together with some of their relevant physicochemical properties like the molecular weight, acute oral LD_{50}, logarithm of octanol-water partition coefficient ($logK_{ow}$),

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