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Baseline

Pathways of priority pesticides in sediments of coastal lagoons: The case study of Óbidos Lagoon, Portugal

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ABSTRACT

This study reports the concentrations of the priority pesticides (PPs) in 14 surface sediments and 21 layers of a sediment core from Óbidos Lagoon, a shallow Portuguese coastal lagoon. Results show that the PPs are confined to the upper part of the lagoon that receives most of the inputs from surface runoff of the surrounding agricultural fields and from small tributaries. Past and recent applied PPs were registered in sediments, aluminum normalized concentrations varying between 0.05×10^{-7} and 6.85×10^{-7}. The PP risk assessment based on sediment quality guidelines like the "Probable Effect Level" (PEL) shows no biological effects in either sediments or aquatic organisms of Óbidos Lagoon, except for dieldrin, lindane, DDT, heptachlor epoxide and its parent compound heptachlor.

Plants, animals and humans are vulnerable to thousands of diseases caused by bacteria, viruses, fungi, algae, nematodes, insects, etc. (Ware, 1983). This implies a massive application of pesticides that have many benefits; however, depending on their toxicity and if not properly applied, they can pose many risks (Burton and Allen, 1992; Ware, 1983). In the European Union (EU) the pesticides are legislated through many directives depending on the sector they are applied. Directive 2000/60/EC (European Commission, 2000), also known as Water Framework Directive (WFD), is a good example concerning the good quality status of surface waters. It covers fresh, transitional and coastal waters. WFD requires the progressive reduction and/or phase-out of some toxic and persistent substances defined as priority substances (PSs) and priority hazard substances (PHSs) (European Commission, 2000). Organochloride pesticides like DDT and lindane among others are included in the list of the PSs published under Annex X of WFD (European Commission, 2000). Most of them are extremely toxic and are known by their persistency and high tendency to accumulate in sediments and biologic tissues (European Commission, 2000; Wu et al., 2013). Most of the priority pesticides (PPs) have been banned, although they are still a reality in Portuguese soils (Gonçalves and Alpendurada, 2005). PPs can easily enter into coastal lagoons, estuaries and coastal waters from human activities like agricultural, urban discharges and industries. Heavy rains and runoff facilitate the transport of these compounds. The Óbidos Lagoon, Portugal, is of considerable ecological and economic interests. Despite its importance, only few studies were performed concerning pesticide screening (Pinto et al., 2013; Carvalho et al. 2006). The aim of this study was thus to evaluate the concentrations of the PPs in sediments of the upper part of the lagoon where most fine particles from the watershed settle and to assess possible ecotoxicological risks.

Surface sediment samples (0–2 cm) were collected in November of 2013 at 14 stations located in the upper part of Óbidos Lagoon (Fig. 1). In addition, a 50-cm long sediment core was sampled at site 3. The core was sliced at 2-cm intervals. After collection, all samples were air dried for 48 h, sieved to remove stones and gravel (2 mm mesh sieve), homogenized and stored at room temperature for chemical analyses (ASTM, 2001; Covaci et al., 2005).

The PPs listed in Table 1 were extracted from sediment samples by ultrasonic assisted extraction (UAE) and determined by gas-chromatography mass spectrometry (GC–MS) following the analytical method developed and validated by Pinto et al. (2013). Sample clean-up carried out prior to GC–MS analysis was done by stir bar sorptive extraction (SBSE) (Pinto et al., 2013). More details about the experimental conditions of PP determination can be found at Pinto et al. (2013). Aluminum (Al) was quantified by flame atomic absorption spectrometry (AAS) after sediment samples have been mineralized with a mixture of acids (HF, HNO_3 and HCl) as described by Caetano et al. (2013). Total organic carbon (TOC) was determined by combustion with a CHN analyzer

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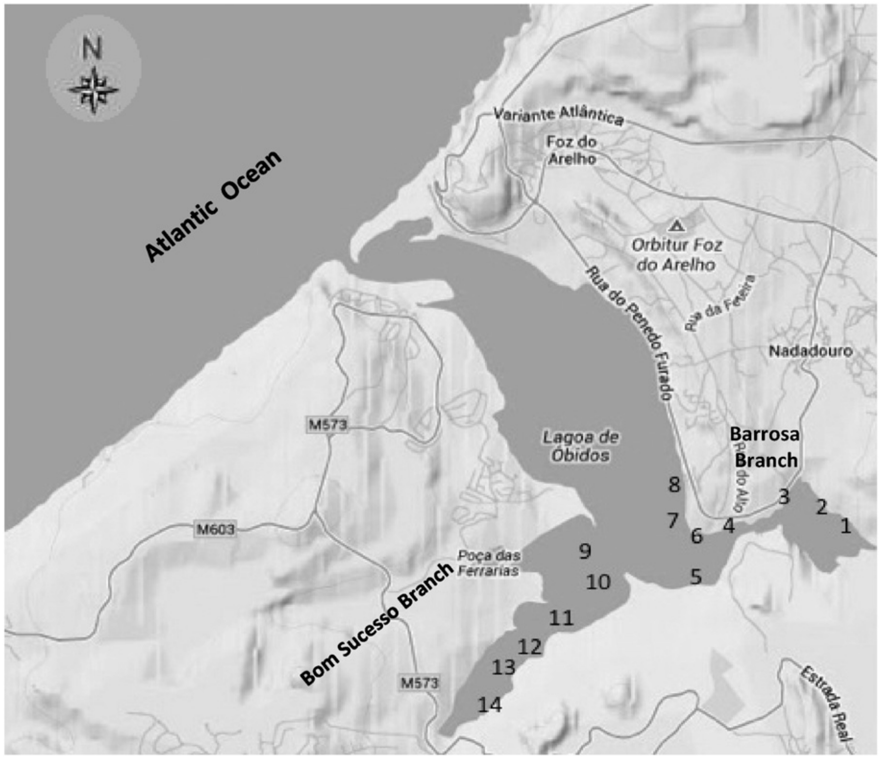

Fig. 1. Location of the sediment sampling sites in Óbidos Lagoon.

(CHN Fisons NA 1500 Analyzer, Fisons Instruments, Italy) (Caetano et al., 2013). The quality control of the results was made by running blanks, spiked samples, samples in duplicate, and certified reference materials (CRMs) as described by Pinto et al. (2013) and Caetano et al. (2013). Three CRMs were used: CRM 1646a (estuarine sediment) and 1941b (organics in marine sediments) purchased from

Table 1
Aluminum (%, dry weight), total organic carbon (%, dry weight) and aluminum normalized concentration of priority pesticides (PPs) (PPs/Al × 10^{-7} in dry weight) in surface sediments of Óbidos Lagoon.

	Sites and respective normalized PP concentration (PPs/Al × 10^{-7})													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Al (%)	5.96	6.01	6.31	1.34	2.35	3.99	1.02	0.51	3.77	5.71	5.67	5.91	5.77	6.28
TOC (%)	3.04	4.58	2.13	0.03	0.58	1.34	0.04	0.06	2.91	1.96	1.96	1.63	2.34	1.75
Priority pesticide (CAS)[a]	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Chlorpyrifos (2921-88-2)	1.91	1.93	2.27	1.67	1.22	0.82	[b]	[b]	0.43	0.35	0.49	0.60	0.47	0.35
Chlorfenvinphos (470-90-6)	5.73	6.85	5.64	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
PCNB (82-68-8)	0.89	0.96	1.19	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
Trifluralin (1582-09-8)	0.58	0.68	0.72	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
Hexachlorobutadiene (87-68-3)	0.92	1.42	1.76	[b]	[b]	[b]	[b]	[b]	[b]	0.05	0.08	0.14	0.09	0.10
Hexachlorobenzene (118-74-1)	1.75	1.80	2.27	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
γ-HCH–Lindane (58-89-9)	2.25	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
α-HCH (319-84-6)	0.93	1.04	1.55	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
δ-HCH (319-86-8)	[b]	1.34	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
α-Endosulfan (959-98-8)	0.98	1.59	1.84	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
β-Endosulfan (33213-65-9)	0.68	1.13	1.39	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
Endosulfan sulfate (1031-07-8)	[b]	[b]	1.23	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
Heptachlor (76-44-8)	1.15	1.73	1.81	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
Heptachlor epoxide (1024-57-3)	0.54	0.65	0.83	0.31	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
Aldrin (309-00-2)	0.89	0.70	1.13	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
Dieldrin (60-57-1)	0.37	0.48	0.68	[b]	[b]	0.07	0.34	[b]	[b]	[b]	[b]	[b]	[b]	[b]
Isodrin (602-050-00-4)	1.53	1.83	2.52	[b]	[b]	[b]	1.21	2.55	[b]	[b]	[b]	[b]	[b]	[b]
Endrin (72-20-8)	1.88	2.38	2.63	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
Chlordane (57-74-9)	0.62	0.72	0.72	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
Mirex (2385-85-5)	1.02	0.90	1.02	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
p,p′-Methoxychlor (72-43-5)	1.34	1.15	1.93	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
p,p′-DDT (50-29-3)	0.81	0.89	1.18	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]
p,p′-DDE (72-55-9)	1.07	1.14	1.62	0.30	0.37	0.21	0.77	1.20	0.43	0.29	0.30	0.34	0.33	0.21
p,p′-DDD (72-54-8)	0.64	0.72	1.15	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]	[b]

HCH — hexachlorocyclohexane; PCNB — pentachloronitrobenzene.
[a] CAS — Chemical Abstract Service.
[b] Not detected.