Journal of Materials and Environmental Sciences
ISSN : 2028-2508

JMES, 2017 Volume 8, Issue 10, Page 3496-3501

http://www.jmaterenvironsci.com/

Organochlorine pesticides level evaluation in a Morocco Southernwetland: Massa estuary

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Received 16 Dec 2016,
Revised 04 Mar 2017,
Accepted 08Mar 2017

Keywords

- ✓ Massa Estuary
- ✓ Sediment
- ✓ Organochlorine
- ✓ Pesticide

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Abstract

Extensive pesticide usage in modern agriculture in Souss Massa region (south of Morocco) represents a considerable anthropogenic stressor to the coastal ecosystems and particularly estuarine ecosystems at risk from the effects of these contaminants. In order to assess the organochlorine pesticides (OCPs) contamination in Oued Massa estuary, surface sediment sample are collected seasonally between winter 2009 and autumn 2010. The concentrations of organochlorine pesticides (OCPs) in sediment, were analyzed by gas chromatography using electron capture detector (GC/ECD). Five OCPs residues are detected in the ecosystem: Endosulfan, bifentrin, deltamethrin, aldrin and lindane. The total OCPs concentrations ranged from 57.39 to 281 ng g1 dw. Endosulfan and lindane were abundant in the estuarine sediment. The concentrations of OCPs in sediment collected in winter 2009 (281 ng g−1dw) were higher than those in other seasons. The results obtained in this study show a presence of the pesticides residues during all sampling season. This contamination could be related to the most intense use of this product in Souss Massa region. Therefore, continued monitoring of pesticides in this area is needed to determine the potential risks and ensure the health of the aquatic organisms within the Oued Massa estuary throughout the year.

1. Introduction

The Massa estuary situated at 45 km to the south of the Agadir city (Morocco). It constitutes an indispensable and natural shelter for a number of biological species, particularly migratory birds and is included in the list of wetlands protected under the Ramsar Convention at January 2005. It is also a part of the Souss Massa National Reserve and contents a lot of endemic flora and fauna.This area is also the last refuge for the last wild population of endangeredspecies in the world *Geronticuseremita* [1]. Otherwise, Massa river crosses one of the more modern and productive agriculture areas in the Morocco, whose products are destined to a large market[2-3]. Considering that this activity use a lot of organochlorine pesticides (OCPs), Massa river drains probably a part of these chemicals to the estuary and marine ecosystems. Theorganochlorine pesticides (OCPs) are one of the most important persistent organic pollutants (POPs) that are characterized by being lipophilic and hydrophobic (low solubility in water)[4]. Consequently, OCPs may be associated either organic components of soils, sediments and biological tissues or dissolved organic carbon in aquatic systems rather than being in solution in water [5-6]. In this fact, the marine sediment is one of the most important reservoirs of these contaminants[7-8]. Once disturbed, the sediment can be resuspended and the contaminants can reenter the marine aquatic environment and circulate in ecosystems, resulting in a second contamination[9]. Thus, it is important to monitor and analyze pesticide residues in sediments that serve as the primary sink for a majority of pesticides used in agriculture, also can provide important information on anthropogenic impact in the environments. The first time we assessed the OCPs contamination in Souss river estuary, the results reveals the link between the agricultural use of pesticides in Souss Massa region and the contamination of coastal ecosystems[10].

The aim of the present study is to determine organochlorine pesticides residues levels in sediment, who is monitored for the first time in this important ecological and socio-economical region and to provide information on the levels of pesticide residues in this costal ecosystem, that will assist in a scientific assessment of the impact of pesticides on public health, agriculture and the environment in Morocco.

2. Materials and Methods

2.1. Study area and sampling

Surface sediment samples were collected from the Oued Massa estuary between January 2009 (winter) and October 2010 (autumn). The location site (30°04.162 N ; 9°39.865 W), situated at 45 kilometres to the south of the Agadir city, is shown in the Figure 1. Collected samples were stored in a cooler box with ice and immediately transported to the laboratory, where they were frozen at -20 C° until extraction.

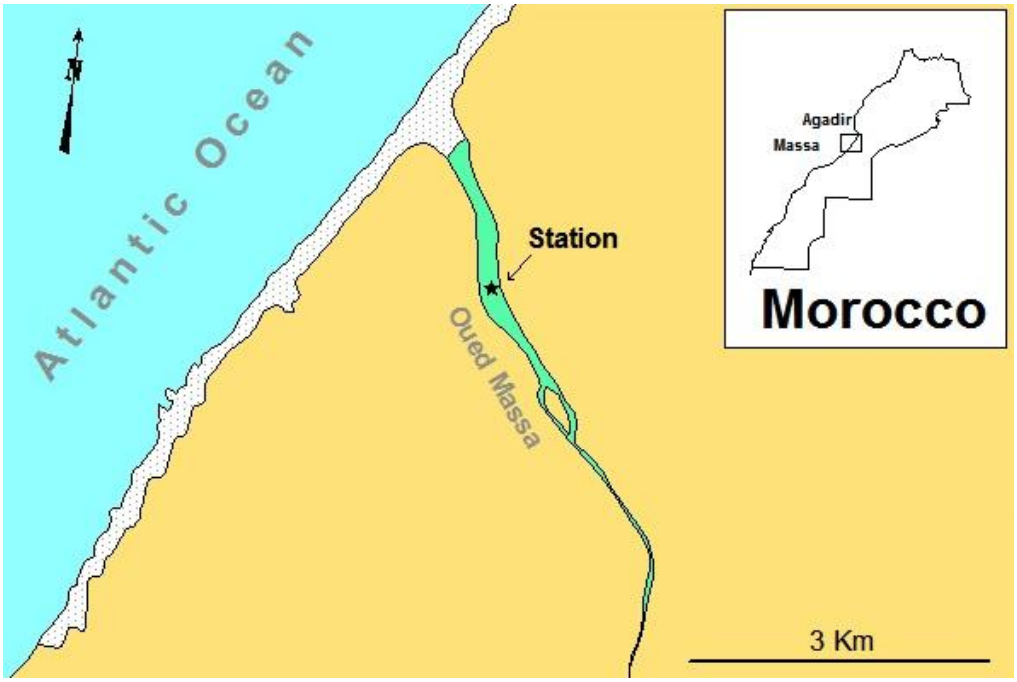

Fig. 1: Location of Massa River in Morocco and the sampling site.

2.2. Extraction and cleanup

Sediment samples were homogenized and freeze-dried. Approximately 20 g of dried and homogenized sediment samples were extracted for 8 hours in a Soxhlet apparatus with 250 ml of n-hexane. The extract was concentrated up to a volume of about 2–3 ml on a rotary evaporator at 40 °C, the mercury were added to the collection flask to remove elemental sulfur. A florisil column was used to clean up and fractionate the extract, and the OCPs were eluted with 70 ml of n-hexane, the second fraction with 50 ml of hexane/ dichloromethane (2:1). All fractions were further concentrated to about 1-2 ml with a rotary vacuum evaporator and at 1ml under a gentle gas stream of purified nitrogen and analyzed by gas chromatography (GC-ECD). 10g of dried sediments were heated at 500°C for about 6 h to determine organic matter. Concentrations of the residues are expressed in dry weight basis (ng/g), and in % for organic matter content in sediment.

2.3. Compounds Identification

An HP7890 gas chromatograph equipped with two Ni electrons captures detectors (GC-ECD) was used for detecting the Organochlorine levels in sediment samples. 1µL ofeach samples and a blank extract were injected, separately, into the GC. For every five injections made, the GC programmed conditions were calibrated by injecting 1µL of hexane. Quantification was achieved by comparing the peak areas of sample injections with those of the 17 standards analyzed under the same conditions.

3. Results and discussion

3.1. Total of OCPS in sediments and distribution of different compounds

The total concentration of Organochlorine pesticides (OCPs) in sediments has a wide range of fluctuations, from 57.39 ng/g dry weight (dw) in summer 2010 to 281 ng/g dry weight in winter 2009 (fig1). Among the OCPS detected in Oued Massa estuary sediment, endosulfan was mainly the dominant compound with a percentage varying between 30.08% in spring 2010 and 100% in autumn 2010 during the study period (fig2), followed by bifenthrin has a percentage of 63.84% in spring 2010. Lindane was detected in tree samples of sediment, representing 65.02% in winter 2010. The percentage proportion of aldrin varied between 0% and 32.51% in spring 2009. Finally the deltamethrin was the minor compound among the five pesticides detected in samples sediment.

The levels of sediment contamination by POC presented a temporal variation (Fig. 2), during all study period the highest concentrations of OCPs were obtained in winter 2009 (281.03 ng g^{-1}dw), and summer 2010 (277.33 ng g^{-1}dw), compared to other seasons.

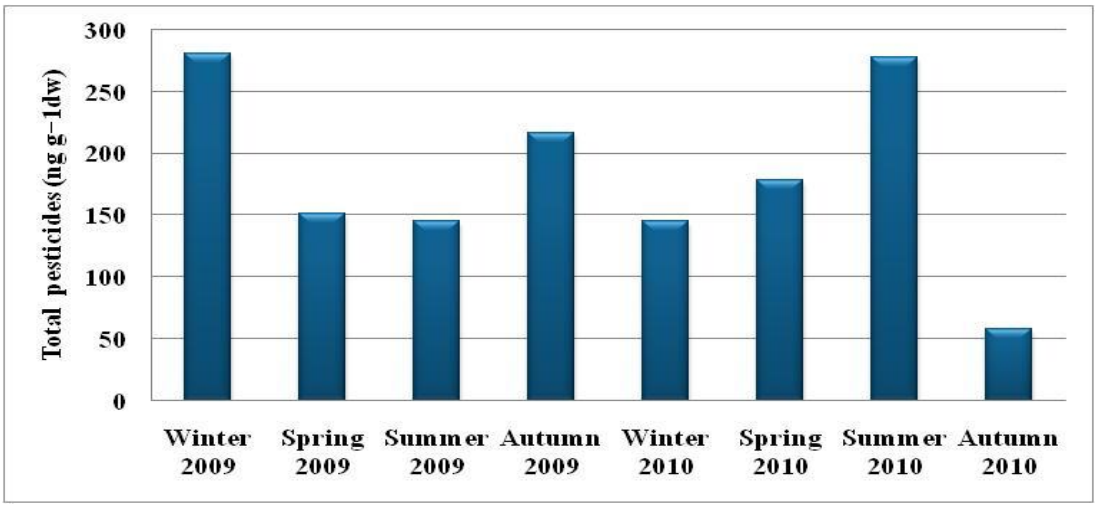

Fig. 2: Total of pesticides (ng g^{-1}dw) in sediment

The results may suggest that the high concentrations of OCPs in the surface sediments are caused by inputs from the intense agricultural activity in Massa region. Endosulfans were detected in 100% at autumn 2010 (Figure 2) of sediment samples analyzed with the highest concentration of 211.09 ng g^{-1} at summer 2010. This result my be explained by the important use of the prosulfan (commercial product) as insecticide and acaricide in Massa region [11], and their environmental persistence, the half-life for degradation of endosulfan (A) is about one to three months whereas that of endosulfan B and endosulfan sulfate can be from two to six years depending on environmental conditions [12], which explains the higher concentration of endosulfan detected in the Oued Massa estuary. Befinthrin was detected in 63.84% of sediment samples in spring 2010, is another pesticide used in agriculture[11], Higher concentration of aldrin (67.27 ng g^{-1}dw) observed in the autumn 2009 and Deltametrin (19.17 ng g^{-1}dw) in summer 2010, reflect a more recent contamination due to increased application of Decis (commercial product) for pest control purposes[13]. The presence of the lindane during all sampling season could be related to the recent use of this product in Massa region. Compared to other regions of the world, The lindane concentrations in Oued Massa estuary sediment is higher (94.39 ng g^{-1}dw) than those from Wu-shi estuary (3.78 ng g^{-1}dw) [14], Quanzhou Bay (1.63 ng g^{-1}dw) [15], Ulsan Bay (0.64 ng g^{-1}dw) [16] and Qiantang River (44.10 ng g^{-1}dw) [17], also the concentration ranges of endosulfans (50.77 - 211.90 ng g^{-1}dw) and aldrin (ND - 67.27 ng g^{-1}dw) were more higher than those reported in sediment from Lake Bosomtwi in Ghana endosulfans 3.75-14.40 ng g^{-1}dw and 0.30-0.46 ng g^{-1}dw for aldrin[18].It should be noted that these pesticides are the cause of several disturbances in the estuarine ecosystem. It effect in the case of the OuedSouss estuary, which was the subject of an initial study[10]. According to AitAlla and collaborators, the estuary has continued to record the inhibition of acetylcholinesterase activity in the molluscs living there despite discontinuation of the releases. These authors explain the inhibition of AchE activity by presence of pesticides. However, Nadir et al., [19] observed the inhibition of AChE activity in a bivalve living on a neighboring ecosystem (PlageM'zar) located two kilometers south of the OuedSouss estuary. These last authors explained their results by the excessive agricultural use of pesticides in Souss Massa regionand arrived toM'zar beach as endpoint according to the marine currents direction (from North to South).

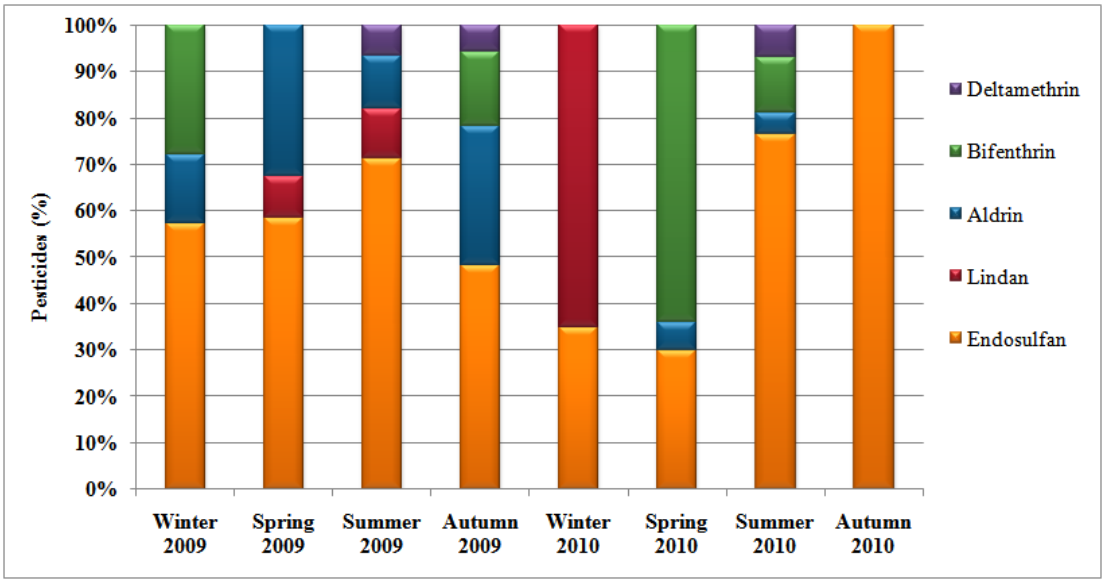

Fig. 3. Organochlorine pesticides composition in the surface sediment from Oued Massa estuary.

3.2.*Iindividual variability Seasonalof OCPs in sediment*

Surface sediments can reflect the current sediment contaminant status. The range for individual contaminant in Oued Massa estuary sediment samples studied are presented in table 1. The level of contamination of sediment by organochlorine pesticides presented a seasonal variation, the endosulfan is the most abundant residue in sediment samples, and the highest concentrations are obtained in summer 2010 and the lowest in the winter and spring 2010. followed by bifenthrin with concentrations varying between nd - 107.77 ng / g dw, aldrin the highest value (67.27 ng/g dw) is observed in winter 2009, while the lowest value (10.24 ng/g dw) are found in spring 2010 , Whereas, the level of lindane showed a temporal variation (0.33 – 16.41 ng/ g dw) and deltamethrin between (nd – 19.17 ng / g dw).

The seasonal variations in OCPs composition observed between sampling seasons can be explained by the seasonal use of pesticides in agriculture in addition to seasonal and regional variations in rainfall and flood runoff [20] (Hong Et al., 1999). Also the physicochemical properties of sediments or hydrological characteristics may be influenced the distribution of OCPs [21] (Glynn et al., 1995). The dilution effect during the flood season is one of the possible reasons for the low concentration of OCPs recorded during the winter and autumn of 2010. During the flood period sediments can be resuspended in the river and pollutants Adsorbed on the sediment particles can be diluted by flow during the flood season.

Table 1: Concentrations of OCPs in surface sediments of Oued Massa estuary

Pesticides ($ng\ g^{-1}dw$)	**Winter 2009**	**Spring 2009**	**summer 2009**	**Autumn 2009**	**Winter 2010**	**Spring 2010**	**summer 2010**	**Autumn 2010**
Endosulfans	157.99	88.43	110.06	108.00	50.77	50.77	211.90	57.39
Lindane	5.33	13.43	16.41	4.50	94.39	0.62	0.33	ND
Aldrin	41.12	49.08	17.76	67.27	ND	10.24	13.04	ND
Bifentrin	76.56	ND	ND	35.76	ND	107.77	32.89	ND
Deltamethrin	ND	0.68	1.00	1.25	ND	9.05	19.17	ND

Nd : not detected

3.3.Relationship between OCPs concentrations and Organic matter content in sediment

The organic matter content in Oued Massa estuary sediments showed a variation along the sampling period thy are ranged from 1% to 5.58%, the highest value are observed at spring 2009 (5.58%), while the lowest value are found at winter 2009 (1%) (figure4). The accumulation of OCPs in sediments is a complex process influenced by chemical properties of the matrix, the partition coefficients of individual compounds, and the organic content of sediment particles[22], due to the fact that sediments, with high organic carbon, are more likely to absorb lipophilic organochlorine than those with lower organic carbon levels [23- 24]. In this study the total organic matter content having no good correlation with the concentration of OCPs ($r = 0.26$; $p < 0.05\%$). The total organic matter content and the contamination levels of OCPs inOuedSouss estuary sediment[10] were higher than those in the Oued Massa estuary sediments. This phenomenon is mainly largely related to sediment granulometry. Sediments that have a large quantity of clay minerals can keep large amounts of organic matter as well as pesticide residues than sandy clay or sandy silt Sediments[25].

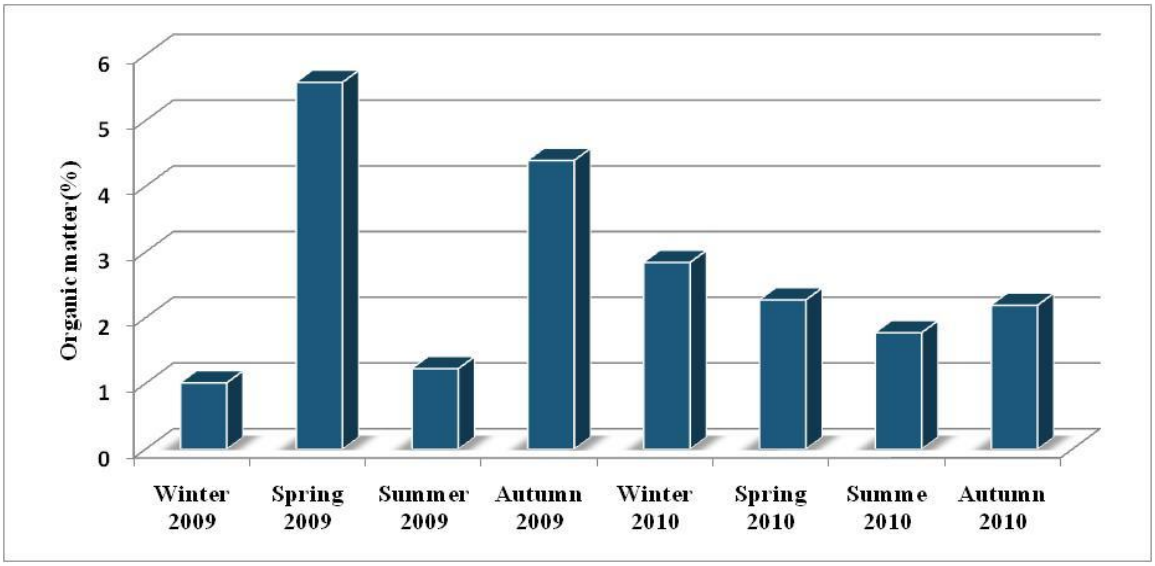

Fig. 4: The percentage of organic matter content in sediment

Conclusions

It should be notedthat the levels of Organochlorine pesticidesin the estuary oftheOuedMassaranged from 57.39 ng g^{-1} and281 ngg^{-1} dry matter, so that the sedimentcan beconsidered astoxic toorganisms livingin that ecosystem, the Oued Massa estuary is a wetland constitute a depository of pollutants originating from sources located in the greater catchment river basin. The pollution sources in the drainage basin of Massa river may include domestic effluents, as well as runoff from the agricultural areas, the transported pollutants include organic matter and pesticides. The pollution by organochlorine pesticides may create serious problems to this wetland ecosystem because of their toxic effects and their bioaccumulation in the organism tissues. The data presented in this work shows the extent of pollution by pesticides used in agriculture, to coastal ecosystems and incites the taking into consideration of this impact in monitoring and management of the environment to ensure sustainable development in Souss Massa region.

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(2017) ; http://www.jmaterenvironsci.com