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To cite this version:

Takoua Mhadhbi, Olivier Pringault, Habiba Nouri, Sylvie Spinelli, Hamouda Beyrem, et al.. Evaluating polar pesticide pollution with a combined approach : a survey of agricultural practices and POCIS passive samplers in a Tunisian lagoon watershed. Environmental Science and Pollution Research, 2019, 26 (1, SI), pp.342-361. 10.1007/s11356-018-3552-3 . hal-01993770

HAL Id: hal-01993770

https://hal.umontpellier.fr/hal-01993770

Submitted on 31 Jan 2020

Evaluating polar pesticide pollution with a combined approach: a survey of agricultural practices and POCIS passive samplers in a Tunisian lagoon watershed

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Abstract

A study of pesticides in the Bizerte lagoon watershed on the Mediterranean coast of Tunisia showed that herbicides and fungicides are the most commonly used compounds. A survey was made of selected farmers. Pesticide contamination was monitored in the water column and sediments at four selected sampling sites (lagoon (A) and in three oueds: Chegui (B), Garaa (C) and Tinja (D)). Polar organic chemical integrative samplers (POCIS) were used to assess pesticide contamination. Thirty-two pesticides were investigated; the total concentration of active ingredients ranged from 35.9 ng L^{-1} in Tinja oued to 1,246 ng L^{-1} in Chegui oued. In the lagoon, the total concentration of pesticides was 67.7 ng L^{-1}. In the sediments, the highest concentration was measured in Chegui oued in the spring (31 ng g^{-1}

d.w). The main compounds found in the analyzed sediments were Prosulfocarb and Tebuconazole molecules.

Keywords: Agriculture. Tunisian lagoon. Pesticides. POCIS. Sediments.

1. Introduction

The impact of agricultural activities on the environments has strongly increased in the last decade. The use of pesticides improves crop productivity by reducing the adverse effects of pathogens (Ben Salem 2017), but their exces can be a major source of ecosystem pollution (Arellano-Aguilar et al. 2017). Monitoring of the contamination of water and sediments by pesticides is thus needed to evaluate the impact of human activities on ecosystems (ESF-Marine Board 2011).

Pesticides can reach aquatic ecosystems via direct applications, spray drift, aerial spraying, atmospheric fallout, soil erosion and runoff from agricultural land, discharge of industrial and domestic sewage, leaching, careless disposal of empty containers and equipment washing (Kaushik et al. 2010). Many of these compounds have been detected in different matrices, including surface water (De Gerónimo et al. 2014; Palma et al. 2014), sediments (Guo et al. 2014; Li et al. 2014), fish pulp (Zhang et al. 2012; Yohannes et al. 2014) and bivalves (Boonyatumanond et al. 2002; Khaled et al. 2004; Carro et al. 2014; Herceg-Romanić et al. 2014). Guidelines for concentrations of pesticides in waters are published by the International Union of Pure and Applied Chemistry (IUPAC) (Hamilton et al. 2003) and permissible limits are laid down in the European reports: 2008/105/EC (EU 2008) and 2013/39/EU (EU 2013).

In Tunisia, the use of pesticides has increased in recent years due to the expansion of agricultural activities. Although national legislation on their uses is scarce, their concentrations are regulated by the Stockholm convention (2004), with serious restrictions on the use of several compounds, including aldrin, chlordane, dieldrin, endrin, heptachlor, hexachlorobenzene (HCB), mirex and toxaphene molecules (Ben Salem et al. 2016). In 2016, 668 commercial pesticides were approved for use by Tunisian legislation (Mezghani et al. 2016); these products have to be homologated before being sold to ensure that they do not pose a risk to human health and the environment. Pesticides comprise 31% insecticides, 39% fungicides, 20% herbicides and 8% other products (rodenticides, nematicides, etc.) (Mezghani et al. 2016).

The Bizerte lagoon is one of the most important economic areas in Tunisia with farming, fishing, ceramics, metallurgy, oil refineries and tire production (Barhoumi et al. 2014). Agriculture represents a major activity in the zone with cereal crops accounting for 7,800 ha, vegetables for 3,400 ha and tree crops for 500 ha (Barhoumi 2014). Large quantitites of fertilizers and pesticides are used to increase productivity (Necibi et al. 2015), and as a consequence, the quality of the lagoon water might be affected by the discharge of effluents (Macdonald et al. 2005; Botta et al. 2009). This environmental pollution is not only a concern in Tunisia, but it has been the subject of studies worldwide in recent years (Comoretto and Chiron 2005; Vryzas et al. 2009; Momplaisir et al. 2010; Palma et al. 2014). The protection of coastal wetlands, including lagoons, in the Mediterranean region has become a priority in resource conservation policies. Like other countries around the world, Tunisia reacted to increasing anthropogenic pressures by developing several national regulations and participating in several internationnal Conventions; e.g., Ramsar Convention (FAO 2015) and Stockholm Convention (UNEP 2001). In previous studies on the Bizerte lagoon, Barhoumi et al. (2013) and Ben Salem et al. (2016) detected organochlorine pesticides (OCPs) in sediments with total concentrations of 11.5 ng g^{-1} dw and 574 ng g^{-1} dw, respectively. Several other authors also reported the presence of pollutants in the Bizerte lagoon, including inorganic mercury, methyl-mercury (Mzoughi et al. 2002), organotin (Mzoughi et al. 2005) and polycyclic aromatic hydrocarbons (Mzoughi et al. 2002; Barhoumi et al. 2016). Necibi et al (2015) found OCPs and polychlorinated-biphenyl (PCBs) in water samples collected from the lagoon.

However, there is no published literature on the pollution of the lagoon ecosystem by polar pesticides, mainly herbicides and fungicides. Water quality is usely monitored by spot (grab) sampling, but due to the low concentrations of micro-pollutants (trace level), a large volume has to be collected to enable detection of these molecules (Poulier et al. 2014). and this sampling has to be repeated frequently to obtain a diagnosis of contamination over time (Greenwood et al. 2007). Thanks to its ability to accumulate pollutants through time-weighted average concentration (TWAC), in recent decades passive sampling has been widely used to increase the representativeness of the contamination of different water bodies (surface water, lakes, marine water, etc.) (Ahrens et al. 2015). Polar organic chemical integrative samplers (POCIS) are widely used to investigate hydrophilic contaminants such as pesticides (Ibrahim et al. 2013a; Lissalde et al. 2014; Poulier et al. 2014; Desgranges 2015). Due to its effective exposed surface area, POCIS is particularly useful tool to determine the concentrations of trace compounds (Liess et al. 1999; Miège et al. 2013; Martínez Bueno et al. 2014; Poulier et al. 2015; Terzopoulou and Voutsa 2016).

The main goal of this work was to identify and quantify the common pesticides present in the water and sediments of Bizerte lagoon by combining a survey of farmers in the region and monitoring of water pollution using passive samplers. Both spot and POCIS sampling techniques were used. This is the first time these techniques have been used in Tunisia to identify contamination by polar pesticides.

2. Material and methods

2.1 Study area

The Bizerte lagoon is located in the southwestern Mediterranean Sea, on the northern coast of Tunisia (37°8’−37°14’ N. 9°46−9°56’ E; Fig. 1). Its surface area is 128 km^2 and its average depth is 7 m (Béjaoui et al. 2008). A 7 km long channel (300 m wide and 12 m deep) connects the lagoon to the Mediterranean Sea. The lagoon is supplied with fresh water from the surrounding 384 km^2 watershed through seven oueds (M'razig, Garaa, Guenine, Ben Hassine, Chegui, Gharek and Tinja) (Fig. 1). By definition, an oued is a stream whose size depends on the quantity of rainfall. It can be a big river or a small stream (Ben Salem 2017). The watershed receives waste from several anthropogenic activities (aquaculture waste, industrial sewage, fertilizers and pesticides) (Ben Said et al. 2010). The Bizerte lagoon watershed is surrounded by agricultural zones (Tinja, Menzel Bourguiba, and South of Bizerte) (Fig.1).

The smallest agricultural areas are located in the Tinja region, particularly around Tinja oued (D). The area represents 39% of the total area. The majority of crops planted there are cereals and fodder crops. One oued was selected in each of the three areas for sampling; Chegui oued (B) (Menzel Bourguiba), Garaa oued (C) (South of Bizerte) and Tinja oued (D) (Tinja) (Fig. 1). The Chegui oued (B) is located in the downstream part of the Bizerte lagoon watershed, with a high percentage of arable land. The two other oueds are situated in the upstream part of the catchment with a smaller percentage of arable land. These surrounding oueds discharge their effluents into the lagoon, and for this reason, a lagoon sampling site (A) was chosen to study the impact of agricultural pesticides on this aquatic ecosystem. To combat fungal diseases and weeds, farmers apply different pesticides depending on the season. Hence, samples were collected in three sampling campaigns in October 2015 (autumn), March 2016 (spring) and June 2016 (summer).

2.2 Survey of pesticides used: methodology

Three zones (South of Bizerte, Tinja and Menzel Bourguiba) were chosen to investigate the pesticides used. Data was first collected from the Regional Commissioner for Agricultural Development (RCAD) and their representatives in delegations called Extension Territorial Cells (ETC), to better understand the characteristics of the watershed. Representative samples of the general population of farmers were interviewed (50 people), all of whom cultivate land around the Bizerte lagoon (Fig.1). The farmers who were selected for the survey were those whose land was located closest to the lagoon and to the oueds that feed the watershed. The interview was semi-directive.

The interviews were structured in two parts: the first part collected general information (age, gender, level of education), while the second part focused on farming (extent of arable land, type of crops cultivated, disease frequency, pesticides used, period and frequency of treatments). The field survey was carried out in February and March 2015.

A list of commercial pesticides with numerous active ingredients was drawn up based on the data and on the information collected in the survey. For each commercial pesticide, the suppliers provided the dose per gram and per hectare, and the dose of active ingredients per hectare was determined according to the pesticide formula. The concentration of active ingredients used by farmers was calculated based on the dilution and the volume of water sprayed per hectare (applied dose g ha^{-1}). A list of active ingredients was selected and ranked according to this dose (g ha^{-1}).

2.3 Water sampling procedures

Both passive and grab sampling was performed at the four sites (the lagoon ((A); 37°10.957′N 9°51.355′E), Chegui oued ((B); 37°9'20" N and 9°54'13" E)), Garaa oued ((C); 37°13'34" N and 9°44'29" E) and Tinja oued ((D); 37°11'18" N and 9°46'54"E) (Fig. 1). Three sampling campaigns were conducted in October 2015 (autumn), March 2016 (spring) and June 2016 (summer). At each site, POCIS were deployed in triplicate (n=3) for a mean period of 21 days (Ibrahim et al. 2013b). They were placed in cages and submerged vertically in the water column. As quality control, a field blank was transported to the site and exposed to the air each time the immersed samplers were retrieved from the water (Ibrahim et al. 2013b). On the days of the deployment and retrieval of the POCIS samplers, grab water samples were collected in clean amber glass bottles at the spot where each cage was immersed. The retrieved POCIS were rinsed with ultrapure water, wrapped in aluminum foil and placed in a plastic bag. Both grab and POCIS samples were stored in cool conditions during transport to the laboratory and until extraction. During each sampling campaign, the physical parameters (water column temperature, pH, dissolved oxygen, and salinity) were determined using field multi-parameter sensors.

2.4 Sediment sampling procedure

Sediment samples were collected at the four selected sites in the Bizerte lagoon watershed (the lagoon (A), Chegui oued (B), Garaa oued (C) and Tinja oued (D)) (Fig. 1), at three sampling campaigns (autumn, spring, summer). Sediments were sampled using plexiglass cylindrical cores (30 cm long, 3.6 cm diameter). Only the superficial sediment layer (less than 10 cm) was sampled. Three replicates were collected per sampling site then transferred to an icebox in the dark. In the laboratory, the samples were kept in the freezer until extraction. Before extraction, frozen samples were freeze-dried then passed through a stainless steel sieve (200-µm mesh) and stored at 4 °C until analysis (Barhoumi et al. 2013).

2.5 Analytical procedures

2.5.1 Chemicals and materials

Thirty-two targeted compounds, mainly herbicides and fungicides, were analyzed (Table1). The compounds included 25 pesticides (Acetochlor, Alachlor, Atrazine, Azoxystrobin, Carbendazim, Chlortoluron, Dimethomorph, Diuron, Epoxiconazole, Flazasulfuron, Imidachloprid, Isoproturon, Linuron, Metalaxyl, Metholachlor, Oxadixyl, Penconazole, Prochloraz, Propyzamide, Prosulfocarb, Pyrimethanil, Simazine, Tebuconazole, Terbuthylazine, Tetraconazole) and seven degradation products (DCPMU, DCPU, DEA, DET, DIA, Simazine hydroxy, Terbuthylazine hydroxy).

Analytical standards (purity > 99%) were purchased from Cluzeau Info Labo (Sainte Foy la Grande, France). Deuterated-labeled compounds were atrazine-d5 (CAS: 163165-75-1) as recovery control and simazine-d5 (CAS: 220621-41-0) as internal standard. High performance liquid chromatography (HPLC) grade solvents used were acetonitrile from Biosolve (Dieuze, France) and formic acid from Carlo Erba Reagents (Peypin, France). Ultrapure water was generated with a MilliPore Synergy UV water purification system from Merck Millipore (Billerica, US). Glass-fiber filters (GF/F) (0.7 µm pore size) purchased from Whatman (Maidstone, UK) were used to filter the water samples. Oasis HLB® cartridges (60 µm, 6 cm^3, 500 mg) were obtained from Waters Corporation (Milford, USA) and a Visiprep Solid Phase Extraction (SPE) vacuum manifold from Supelco (Bellefonte, USA) was used for SPE. POCIS were purchased from Expos Meter AB Company (Tavelsjö, Sweden) with the pharmaceutical receiving phase comprised of approximately 230 mg of the solid adsorbent *N*-vinylpyrrolidone-divinylbenzene (Oasis HLB®). The sampling area of the POCIS device was 41 cm^2. The 3 mL polypropylene cartridges used to recover the POCIS receiving phases were from Supelco (Bellefonte, USA).

2.5.2 POCIS and water sample extraction

Grab samples (500 mL) were filtered through GF/F filters to eliminate suspended matter, spiked with 50 µL of atrazine d5 (1 ng μL^{-1} acetone) and extracted by solid phase extraction (SPE) using Oasis HLB® cartridges. Prior to extraction, the Oasis HLB® cartridges were activated with 5 mL of acetonitrile under vacuum, followed by 5 mL of methanol (MeOH) and 5 mL of ultrapure water (Ibrahim et al. 2013b). Before elution, they were dried under vacuum for 1 hour. Analytes were recovered by eluting the cartridges with 8 mL of acetonitrile at a flow rate of 1 mL min^{-1}.

After they were retrieved, the receiving phases of the POCIS were transferred into an empty solid-phase extraction tube packed with polyethylene (SPE) frit, 20 µm porosity. The sorbents were spiked with 50 µL of atrazine d5 (1 ng μL^{-1} acetone) then eluted with 8 mL of acetonitrile.

Both for Oasis HLB® cartridges and POCIS receiving phase elution, the extracts were concentrated under a gentle stream of nitrogen to obtain a final extract of 1.5 mL. This final extract were then spiked with 150 µL of the internal standard simazine d5 (1 ng μL^{-1} acetonitrile) and analyzed by HPLC-MS/MS (Ibrahim et al. 2013).

2.5.3 Sediment extraction

The extraction was carried out using an Accelerated Solvent Extraction (ASE) system (Dionex®, France) with a hexane/acetone mixture of solvents (50/50, v/v). The parameters used during the extraction procedure were as follows: temperature 120 °C, static time 5 min, pressure 1500 psi, heating time 6 min, flush volume 60%, and purge time 100 s. Atrazine d5 recovery control (1 ng μL^{-1} acetonitrile) was added to the sediment prior to the ASE step and the resulting extracts (hexane/acetone) were cleaned on a Strata SAX® (8B-S008-JCH). To recover analytes, elution was carried out with 3 mL of MeOH and 3 mL of dichloromethane (CH_2Cl_2), respectively. Purified extracts were completely evaporated under a gentle stream of nitrogen and then dissolved in 1.5 mL of acetonitrile (Barhoumi et al. 2013). Before analysis, all sample extracts were spiked with 120 µL of the deuterated internal standard simazine d5 (1 ng μL^{-1} acetonitrile) and then analyzed by HPLC-MS/MS.

The percentage of finer grain size fractions (< 63 µm) of each sediment sample was determined gravimetrically after wet sieving (Savinov 2000). Total organic carbon (TOC) content was measured using the coulometry method in a 702 Coulomat, after decarbonization of sediments with 2N HCl at 60 °C overnight (Ouertani et al. 2006).

2.5.4 Liquid chromatography–mass spectrometry (HPLC-MS/MS) analysis

The pesticide analysis was performed by HPLC-MS/MS using an Alliance HPLC system (Waters Series 2695). The HPLC is equipped with a quaternary pump, a vacuum degasser and an autosampler. Analytic separation was achieved with a Kinetex C18 analytical column (100 mm ∗ 4.6 I.D ∗ 260 Å, Phenomenex). The volume injected was 25 µL. Acetonitrile (A) and ultrapure water (B), both with 0.05% formic acid, were used as mobile phases at a constant flow rate of 0.4 mL min^{-1}. The linear gradient was started at 40% for 0.2 min, ramped to 80% for 8 min, then to 100% for 1 min and finally back to the initial conditions for 2 min. A triple quadrupole mass spectrometer (Micromass Quatromicro TM, Waters) equipped with an electrospray ionization source (ESI) was used as the detector device. The spectrometer operated in positive ESI mode under the following conditions: capillary voltage (3.5 kV), source temperature (120 °C), desolvation temperature (300 °C), drying (600 L h^{-1}), and nebulization gas (N_2) flow (30 L h^{-1}). Argon was used as the collision gas. For each compound, acquisition was performed in the multiple reaction-monitoring modes (MRM). Two transitions were retained: one was used for quantification and the other for confirmation (Table S1: Supplementary materials).

2.5.5 Concentrations of pesticides in the water during POCIS deployment

The accumulation of contaminants by passive samplers typically follows first-order kinetics, which includes an initial integrative phase, followed by curvilinear and equilibrium-partitioning phases. In the linear region of the POCIS uptake, the amount of a chemical accumulated in the sampler (*M*) is described by equation (1):

$$M = C_w . R_s . t \qquad (1)$$

where R_s is the sampling rate (L day^{-1}), C_w is the time-weighted concentration of the compound in water (ng L^{-1}) and *t* the exposure time (days).

For each pesticide, the sampling rate was determined by dividing the slope of the linear regression curve by the mean aqueous concentration of the selected compounds over the 15 days of exposure time (Ibrahim et al. 2013b). POCIS sampling rates (Table 1) were determined in laboratory conditions for each compound (Ibrahim et al. 2013b). Given that they depend on environmental conditions such as flow, temperature, pH, organic matter and biofouling (Charlestra et al. 2012; Yabuki et al. 2016), they allow the calculation of semi-quantitative concentrations of pesticides in water and the comparison of the relative levels of contamination between sites (Ibrahim et al. 2013b). Time-weighted averaged concentrations (TWAC) in water were calculated with the equation proposed by Miège et al. 2013 (2):

$$C_{water} = C_{pocis} . M_{pocis} / Rs. t \ (2)$$

where C_{water} is the mean concentration of the contaminant (over the sampling period) in the ambient water (µg L^{-1}); C_{pocis} is the concentration in the POCIS (µg g^{-1}); M_{pocis} is the mass of adsorbent phase in the POCIS (g); Rs is the sampling rate (L day^{-1}), which corresponds to the volume of water purified per unit of time; and t is the total exposure time (days).

Among the 40 compounds inventoried in the survey, 15 were selected (Table 2) as being the most representative, according to (i) the use rate per hectare; (ii) the type of crops grown in the zone; (iii) the concentration of active ingredient in the commercial pesticide. For analytical reasons, not all the selected active ingredients could be analyzed by the HPLC-MS/MS method developed in our laboratory. In particular, glyphosate and 2,4 D were not included in the final list of targeted pesticides. The final list of active ingredients comprised 32 compounds analyzed by liquid chromatography mass spectrometry (Table 1).

2.5.6 Quality assurance/control

The linearity, limits of detection (LODs) and limits of quantification (LOQs), precision and accuracy of the analytical methods were carefully checked. The LODs were calculated as 3Sy/x/b and the LOQs as 10Sy/x/b, where Sy/x is the residual standard deviation and b is the slope of the matrix calibration curves. The LODs and LOQs obtained by HPLC-MS/MS (analytical LOD and LOQ expressed in µg L^{-1}) are listed in Table 1. The LODs and LOQs of all the selected pesticides were detemined from the calibration curves for each analytical campaign in which $R^2 > 0.98$. The analytical limits of detection ranged from 0.10 µg L^{-1} to 2.20 µg L^{-1} and the limits of quantification from 0.40 µg L^{-1} to 7.50 µg L^{-1}. The LOQs of the POCIS (which were calculated from the equation of (Poulier et al. 2014)), water and sediment samples are also listed in Table 1.

Mean recovery from the synthetic water solution spiked with the 32 compounds was 63%, the highest recovery being for simazine (101%) and the lowest for DCPU (8%). Flazasulfuron, hydroxy-terbuthylazine and hydroxy-simazine were not recovered (Table 1).

A certificated reference material (WaRTM Pollution Nitrogen Pesticides, Lot No, P246-674) purchased from the ERA Waters Company (Golden, USA) was used to determine pesticide recoveries in water samples. The reference material was a water solution composed of 24 pesticides including six of the pesticides selected for our study (Alachlor, Atrazine, DEA, DIA, Metolachlor and Simazine). The concentrations of pesticide in the reference material ranged between 16.80 µg L^{-1} and 3.37 µg L^{-1}. The global recovery yields were for atrazine (108±4%), for alachlor (78±4%), for DEA (61±3%), for DIA (58±3%), for metolachlor (110±2%), for simazine (79±2%) after solid phase extraction (Oasis HLB) and HPLC-MS/MS analysis (n=9) with our laboratory method. The mean extraction recoveries with atrazine-d5 were 98±11% and 92±12% for the passive and grab samples, respectively (n=36 samples). The relative standard deviation (RSD) obtained for the analysis of the internal standard simazine-d5 was 17±6% for all the HPLC-MS/MS injections (n=108 injections).

2.6 Statistical analyses

Triplicate analytical measurements were made for all the analyses and the data are reported as mean ± standard deviation. Pearson’s correlation coefficient was calculated to investigate possible relationships between parameters. Statistical significance was set as $p < 0.05$. The statistical treatment of the data was performed using the STATISTICA 6.0 Analysis System version 5.

3. Results and discussion

3.1 Survey results

According to the farmers and engineers of Regional Commissioner for Agricultural Development (RCAD), field crops (wheat, legumes and oats) occupy the largest percentage of cultivated fields. Wheat accounts for 58% (i.e., 3.153 ha) of the total cultivable area, and legumes and oats for 13% and 10%, respectively. The dominance of this type of crop could be related to economic factors. Indeed, since the 1970s, Tunisia and other North African countries have benefited from the support of ICARDA (International Center for Agricultural Research in Arid Zones) to develop their cultivar production programs, with the objective of intensifying the amount of cereal crops and legumes (Nefzaoui et al. 2012). This result is consistent with those obtained in an investigation commissioned by the Tunisian Ministry of Agriculture (DGEDA, 2006), which reported that the areas treated in Tunisia correspond to low crops, which represent 73% of all cereals grown.

Our survey results showed that farmers use 47 commercial pesticides, mainly fungicides (42.5%), herbicides (42.5%), and insecticides (15.0%). The prospected regions are wetlands, where fungal diseases (Septoria, rust and mildew) develop easily, hence, intensive use of fungicides by farmers was observed. Fungicides are used twice a year (at the end of March and May) as preventive treatments. They are also used as a curative treatment for "rust" whenever there is an outbreak of the disease. The survey also revealed high use of herbicides to control the weeds that compete with crops for access to water, light and soil nutrients. Herbicides are usually applied twice a year, in autumn (October) and spring (March).

Table 2 lists the most frequently used active ingredients based on our inventory of commercial pesticides in the regions around the Bizerte lagoon surveyed. The active ingredients are classified first according to the type of pesticide (herbicides, fungicides and insectides) then by the dose of the active ingredients applied per hectare (calculated according to the dilution and the water volume sprayed per hectare) and by target crop, mainly field crops (wheat, legumes, oats). The list contains 40 active ingredients (Table 2). Among these compounds, 87.5% are approved for use in Tunisia (Mezghani et al. 2016). Our list of active ingredients is in agreement with the results of a study by Ben Salem et al. (2016), who used another approach to calculate the total quantities of active ingredients, i.e., the percentage use of active ingredients was calculated by dividing the number of farmers who used the active ingredient concerned by the total number of farmers surveyed (∗100). Finally, the amount of each active ingredient (Qsubstance) is the product of the cultivated area (ha) divided by the percentage of pesticide used by the assay of the active ingredient in the pesticide. Despite the different methods of calculation used in the two studies, some of the ingredients we found were also found by Ben Salem et al. (2016) including herbicides (e.g, Iodosulfuron, Mesosulfuron, 2,4-dichlorophenoxyacetic acid (2,4 D), Glyphosate, and Fenoxaprops) and fungicides (e.g, Tebuconazole, Epoxiconazole, Azoxystrobin). The study by Ben Salem et al. (2016) revealed that insecticides are the least used, and only two pyrethroids were inventoried (Deltamethrin and Bifenthrin).

For our study, based on the calculations of the dispersed dose (g ha^{-1}), the inventoried active ingredients were ranked to obtain a list of 40 targeted compounds (Table 2). The survey revealed that most of the pesticides were used on wheat, legumes and oats, which are the main crops grown in the regions surveyed. A restricted list is thus proposed containing 15 active ingredients of fungicides (Azoxytrobin, Chlorothalonil, Prochloraz, Tebuconazole, Fluzilazole, Flutriafol, Propiconazole, Carbendazim, Prothioconazole, and Epoxiconazole) and herbicides (Glyphosate, Simazine, Bentazone, Prosulfocarb, 2,4D). The estimated concentrations of these compounds ranged from 200 g ha^{-1} for Azoxystrobin to 0.47 g h^{-1} for

Epoxiconazole. Despite their high dose per hectar, some pesticides were not included in this list because they are not used to treat the field crops grown in the survey area, mainly wheat. This is the case of Difenoconazole, Mancozeb, Maneb, Zineb, and Boscalid, which are used to protect vines.

3.2 Surface water quality

3.2.1 Occurence of pesticide in water

To study the occurrence of target pesticides, detection and quantification frequencies were calculated, based on the results obtained by the two sampling techniques (grab and passive sampler). By definition, the frequency of detection and quantification campaigns correspond to the ratio of the number of times in which one compound was detected and quantified divided by the total number of sites analyzed in the campaigns, respectively.

Of the 32 pesticides studied (Table 1), 23 were detected using passive sampling technique (Fig. 2A), which represents 72% of the total studied pesticides. Whereas, 11 compounds were quantified (34 %) with the same sampling technique (POCIS): Simazine, Chlortoluron, DIA, Acetochlor, Alachlor, DCPU, Isoproturon, DET, Epoxiconazole, Tebuconazole, Azoxystrobine (Fig. 2A). Among the detected compounds using POCIS, two fungicides (Epoxiconazole and Tebuconazole) and one herbicide (Simazine) were detected at a frequency of 100%. The accumulation of these compounds in the POCIS receiving phase (OASIS HLB) is favored by their $log\ K_{ow}$ values (3.30 for Epoxiconazole; 2.18 for Simazine; 3.70 for Tebuconazole) (Hijosa-Valsero et al. 2016; Zhang et al. 2016). Grab sampling allowed the detection of 44% of all target pesticides and the quantification of 31% (Fig.2B).

Acetochlor and Alachlor were only quantified by POCIS. Conversely, Prosulfocarb was not quantified by POCIS, which can be attributed to the low sampling rate (R_s= 0.071 L d^{-1}) (Fig.2A). Retention of Prosulfocarb by POCIS is not favored and the concentration obtained was lower than the analytical LOQ. It should be noted that DET, by-products of terbuthylazine, was quantified only by the POCIS (5.00 ng L^{-1}, Table 3).Thus, passive samplers could lead to a more representative level of contamination than that provided by grab sampling and allowed us to measure low concentrations of pesticides (Lissalde et al. 2011; Poulier et al. 2015; Van Metre et al. 2017).

The most frequently detected and quantified compounds at all the study sites, were two herbicides (Simazine, Chlortoluron), and two fungicides (Epoxiconazole, Tebuconazole) regardless of the sampling technique (Fig.2 A and B). The high level of detection and quantification of these compounds at the different sites by passive sampling (Fig.3) can be explained by their intensive use in the treatment of crops in the Bizerte lagoon watershed. Indeed, Simazine is the active ingredient of "Agzozine", which is a pesticide sold in Tunisia to treat weeds and field crops, particularly legumes, one of the main crops cultivated in our survey areas. Epoxiconazole and Tebuconazole are the active ingredients most widely used by farmers to treat crops. Both are applied to wheat, barley and oats. They are used to control powdery mildew, helminthosporiasis, septoria and brown rust. Even if Chlortoluron is not inventoried in the list of active ingredients used for crops in the watershed, this substance was one of the major compounds detected during the sampling campaigns (up to 60%). This compound is one of the active ingredients of two commercial products, "Dicuran 500" and "Tolurex 50" that are used to treat weeds and wild oats in wheat and barley fields; problably, it was used by farmers who were not interviewed in our survey.

3.2.2 Space and time variations in concentrations of pesticides in water

The total amount of pesticides (∑pesticides), obtained by passive sampling and present at each sampling site, was used to assess the impact of the agricultural activity. The sum of pesticides (∑pesticides) measured for all the seasons vary according to sites (Table 3). The highest concentration of ∑pesticides was measured in Chegui oued (B): 1,246 ng L^{-1}, and the lowest in Tinja oued (D): 35.9 ng L^{-1} (Table 3). The total concentrations of pollutants in Garaa oued (C) were close to 202.6 ng L^{-1}. Among the oued sites, the least impacted sites were Tinja (D) and Garaa (C) oueds. This may be due to the fact they are located in the downstream part of the Bizerte lagoon watershed, and to the lesser presence of large agricultural areas around them. Total pesticide concentrations in the lagoon itself were only 68 ng L^{-1}; this low concentration compared to the concentration in Chegui oued can be explained by the dilution of the oued water in the lagoon (Carafa et al. 2007).

The intensity of agricultural activities is another argument to justify the high concentration of target compounds in Chegui oued. According to the survey, wheat accounts for 60% of crops grown at this site and legumes for 65%. These crops are treated with herbicides and fungicides, mainly Simazine and Tebuconazole. Our results are in agreement with the results of previous studies showing that the highest concentrations of pesticides are generally measured at sampling sites located in areas with a high proportion of arable land (Zhang et al. 2016).

Variations over time showed that the concentrations of ∑pesticides vary with the season (Fig. 4). The high concentrations measured in the Chegui oued (B) compared to concentrations at the other sites can be explained by its geographical and hydrological properties. Chegui oued is located on the upstream side of the Bizerte lagoon catchment, the highest concentrations were found in Chegui oued in summer (B) (832.5 ng L^{-1}); this could be due to the transport of pollutants from agricultural lands into the oued beacause of the rains, which drain the pesticides from crops to the sampling sites. Whereas, value of 413.8 ng L^{-1} was found in the spring season (Fig. 4). Concerning Garaa oued (C), the highest concentration was observed in spring (194.1 ng L^{-1}). For site (A) and (D), the ∑pesticides was very low regardless the season (e.g.concentrations were 20.8 ng L^{-1} in the spring in sites (A) and (D)). These results can be explained by the environmental conditions in these areas (solar radiation and water temperatures) (Bondarenko et al. 2004; Navarro et al. 2004; Carafa et al. 2007; Carvalho et al.

2009). Temperature can affect the sorption rate of pollutants onto suspended matter and organic matter (Wu and Gschwend 1986). When temperatures increase, the solubility of the compounds increases, and biodegradation and photodegradation are favored (Eriksson et al. 2003).

In the Mediterranean basin, the annual average global solar radiation reaching the surface is 168 W/m^2 (Chelbi et al. 2015). In Bizerte city (located in the study area), the annual average global solar radiation is 208 W/m^2 (Ben Othman et al. 2018).

The most frequently measured compounds with high concentrations were Simazine and Tebuconazole in the spring and summer in Chegui oued (B) (Table 3). This result is not surprising as these pesticides are mostly used to treat the wheat and legumes grown around this study site. The concentrations of Simazine found in spring and summer by passive sampling were 168 ng L^{-1} and 431.6 ng L^{-1}, respectively (Table 3). The concentrations of Tebuconazole were 142 ng L^{-1} and 190.5 ng L^{-1} in spring and summer (Table 3). Moreover, the significant concentrations of fungicides (Tebuconazole, Epoxiconazole) in the spring can be explained by their application in April and May to protect wheat against fungal diseases such as septoria and rust.

The results suggest significant variations in concentrations as a function of the agricultural seasons. For example, herbicides are widely applied to field crops, particularly legumes and wheat, in spring and autumn. This explains the abundance of herbicides at the study sites during these periods and a few months after they were sprayed in the fields (Zhang et al. 2016).

Pesticide concentrations (obtained by grab sampling) (Table 4) are in agreement with those obtained by POCIS (Table 3). Indeed, the highest concentration of DIA, Simazine, Tebuconazole, and Epoxiconzole were observed in spring even for Chegui oued (B), Garaa oued (C).

Simazine was mainly found in spring in Chegui oued (B), Garaa oued (C) and Tinja oued (D) with concentrations of 730.9 ng L^{-1}, 56.9 ng L^{-1} and 32.5 ng L^{-1}, respectively (Table 4). These values are below than those of the existing Quality Standards in Directive 2013/39 / EU of the European Parliament and the Council of 12 August 2013 (1 µg L^{-1}) (EU 2013). The concentrations of Tebuconazole in the same season and at the same sites were 500.3 ng L^{-1}, 178.4 ng L^{-1} and 56.5 ng L^{-1}, respectively (Table 4). According to previous studies, for a representative diagnosis of pesticide occurrence, POCIS and spot sampling should be used as a complement to grab sampling (Poulier et al. 2014; Miège et al. 2015, Branchet et al. 2018). Passive sampling is recommended by water policy in the European Commission Guidance Document (EC Guidance document n°19) and in Directive 2013/39/EU (EU 2013).

Additionally, the results of monitoring of the water column by passive and grab sampling confirmed those of the survey (Table 3, Table 4). Indeed, screening revealed some pesticides identified during the survey, including Simazine, Tebuconazole, Prosulfocarb, and Epoxiconazole. These are among the compounds most widely used by farmers to treat wheat.

3.3 Occurrence and variations in pesticide concentrations in sediments in space and over time

3.3.1 Occurrence of pesticides in sediments

Studying the composition of coastal sediments is one of the main ways used to identify the level and source of contamination of marine ecosystems (Zaghden et al. 2017). Indeed, sediments are known to trap hydrophobic contaminants, particularly non-polar pesticides like chlorinated compounds (Meakins et al. 1995). Consequently, sediments were also investigated to complete the diagnosis of the contamination of the Bizerte lagoon watershed by agricultural pesticides. The detection and quantification frequencies of the targeted compounds during the three campaigns and at the four study sites are summarized in Fig. 5. No compounds were quantified in Tinja oued (D). The most impacted sediments were those of Chegui oued (B) and Garaa oued (C). The majority of the targeted compounds, e.g.

Alachlor, Acetochlor, Metolachlor, were detected at a frequency of 34%. Prosulfocarb, Epoxiconazole and Tebuconazole were detected at a frequency of 100% in the Chegui and Garaa oueds. These compounds were also quantified at these two sites (B and C). Indeed, Prosulfocarb was quantified at frequencies of 100% and 34% in Garaa oued (C) and Chegui oued (B), respectively. However, Tebuconazole and Epoxionazole were quantified at frequencies of 100% and 68% in Chegui oued (B) and Garaa oued (C), respectively.

3.3.2 Space and time variations in the concentration of pesticide in sediments

The sum of pesticides (∑pesticides) in the sediments of the watershed of the Bizerte lagoon ranged from 9.8 ng g^{-1} dw in the lagoon (A) to 53 ng g^{-1} dw in the Chegui oued (C) (Table 5). Particle size is an important parameter to consider when analyzing sediment samples (Ackermann 2008). In the present study, the percentage of fine particles (< 63 µm) in the sediments differed at each site, varying from 12% to 69% in the lagoon (A), from 62% to 77% in Chegui oued (B), from 94% to 100% in Garaa oued, and from 11% to 57% in Tinja oued (D) (Table 5). In spring saison, the higher total concentration of pesticides in Chegui oued sediments (31.1 ng g^{-1}), can be explained by the higher content of fine particles; the large surface area available (per unit of mass) of the small particles increases the adsorption of pollutants onto the grains (Gao et al. 1998). Additionally, fine sediment particles may accumulate pesticides due to their mineral compounds (e.g, silicate, goethite and hematite, montmorillonite, iron oxides, manganese oxides, illite, etc). No apparent relationship was found between TOC and grain size (< 63 µm) at the sites analyzed ($p > 0.05$, $n=12$). In addition, no significant correlations were found between TOC content, grain size (< 63 µm) and the majority of compounds analyzed. This implies that the distributions and concentrations of pesticides are not only determined by sedimentary characteristics such as TOC and grain size (Mai et al. 2005), but probably by other factors such as sources, transport, mixing, and deposition that were not analyzed in this study.

Table 5 reports the individual concentration of pesticides, the highest concentration of Tebuconazole was found in Chegui oued (B) in spring (31.1 ng g^{-1}, dw) (Table 5). The highest concentration of Prosulfocarb (6.3 ng g^{-1} dw) was measured in Garaa oued (C) in autumn. A relatively high *log* K_{ow} (octanol/water coefficient) means that polluants can be strongly adsorbed onto sediments particules and organic matter (PAPP 2010). For Tebuconazole and Prosulfocarb, *log* K_{ow} values were 3.70 and 4.48, respectively (INERIS 2011, 2013), these values indicate that Tebuconazole and Prosulfocarb are sorbed to sediments (Chamberlain et al. 1996; Čadková et al. 2013).

3.4 Space time variations in pesticide concentrations in the Bizerte lagoon watershed

These results reveal a space-time variation in pesticide concentrations in the water column and in the sediments in the Bizerte lagoon watershed. These results show that among the pesticides found in the sediments and water, 60% are approved for use in Tunisia (20% herbicides, 36% fungicides, 4% insecticides).

These results are in agreement with those of Jiménez et al. (1999), who showed that pesticide concentrations in water and sediments were subject to seasonal variations in 27 Mediterranean lakes. Moreover, the presence and distribution of pesticides in the water and/or in the sediments depends on the physical-chemical properties of the compounds (*log* K_{ow} and water solubility). Some of the pesticides (e.g, Atrazine, Diuron) found in the water at the sites we investigated are not yet approved for use in Tunisia. These herbicides (Atrazine, Diuron) pose a serious risk for aquatic ecosystems as well as for the environment (Moncada 2004; Ralston-Hooper et al. 2009).

Literature on levels of polar pesticides in samples of water is scarce (in particular on fungicides and herbicides), making it difficult to compare our results with those obtained elsewhere in the world. In sediments, the studied pesticides are mainly the organochlorines (Barhoumi 2014; Ben Salem et al. 2016). The concentrations of total pesticides in water and sediments in the lagoon and oueds were lower than those measured in Mondego River Estuary in Portugal (Cruzeiro et al. 2016), Ria Formosa lagoon in Portugal (Cruzeiro et al. 2015), Tagus River basin in Greece (Papadakis et al. 2015), in a river basin in Costa Rica (Carazo-Rojas et al. 2018) and in Méfou watershed in Cameroon (Branchet et al. 2018). However, the concentrations we measured were higher than those measured in the Arade River estuary in Portugal (Gonzalez-Rey et al. 2015), in the River Ugie in Scotland (Zhang et al. 2016) and in the Marque River in France (Criquet et al. 2017).

The concentrations of total pesticides in the lagoon and oued sediments studied here are lower than those reported in Mediterranean coastal lagoons in SE Spain (Moreno-González and León 2017).

4. Conclusion

This study highlights a worrying issue that affects the majority of Mediterranean lagoons: human pressure, especially agricultural pollution. The Bizerte lagoon is one of the most affected by this anthropization in particular by agriculture activities, justifying our investigation of the occurrence of herbicides and fungicides. This study confirmed contamination by polar pesticides (herbicides and fungicides) in the watershed and in the lagoon ecosystem. Analyses of samples from the four sampling sites revealed the highest contaminations in the water and sediments of Chegui oued. The results of our analyses are in agreement with survey data: several molecules (including Simazine, Tebuconazole and Prosulfocarb) were found at the target sites. Simazine and Tebuconazole molecules, the most significant species present in the water samples, were identified by passive sampling at a maximum concentration of 431.6 ng L^{-1} and 190.5 ng L^{-1} in the Chegui oued, respectively. The molecule found at the highest concentrations in the sediments was Tebuconazole (31.1 ng g^{-1}, dw) and although Prosulfocarb was detected in trace amounts in the water samples, a concentration of 6.3 ng g^{-1} dw was found in the sediments of the Garaa oued. The POCIS technique was used for the first time in Tunisia and was shown to improve the analysis of the trace concentrations of polar pollutants. The results of this work support the hypothesis that the ability of passive samplers (POCIS) to integrate the contaminant concentrations over a period of exposure enables better quantification of contamination at low concentrations.

Acknowledgements

This study was financed by LMI Cosy-MED (IRD), *Institut Mines Télécom Mines Alès* and the Tunisian Ministry of Higher Education and Scientific Research (Carthage University), The authors would like to thank the Tunisian farmers and fishermen of Bizerte for their kind assistance in the monitoring studies.

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Figure

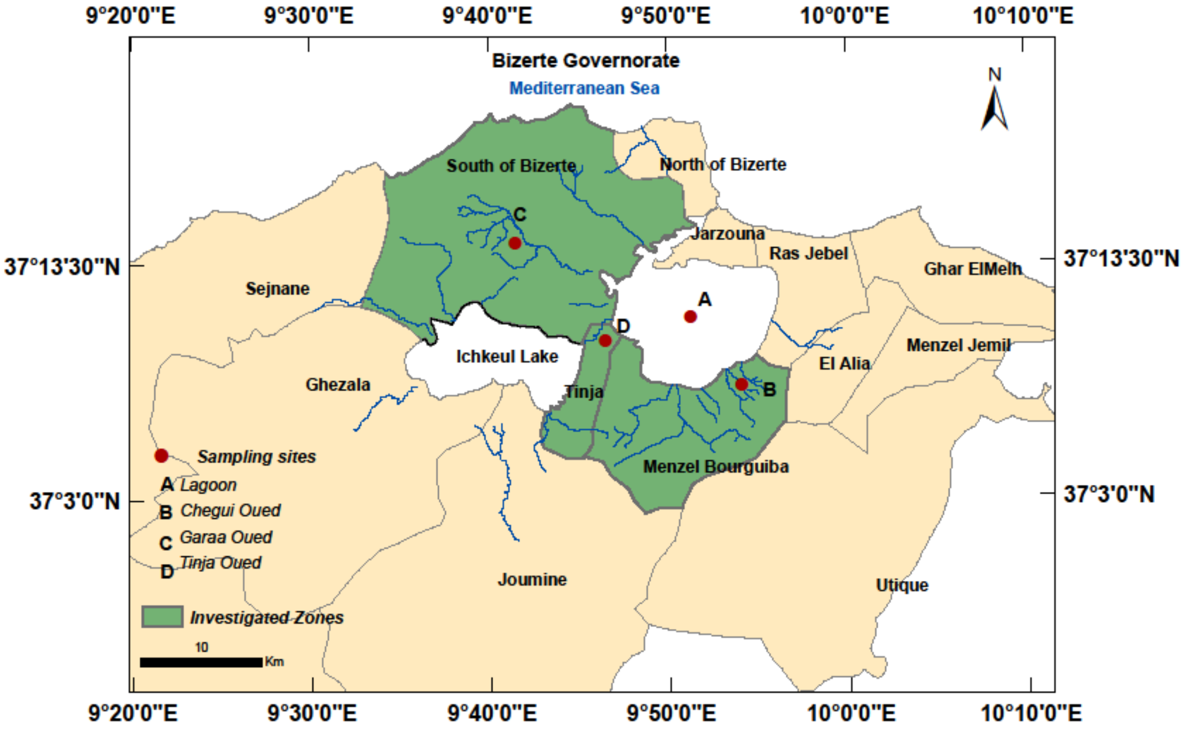

Fig. 1 Study zones and sampling sites (A: lagoon, B: Chegui oued, C: Garaa oued and D: Tinja oued) in the Bizerte lagoon watershed

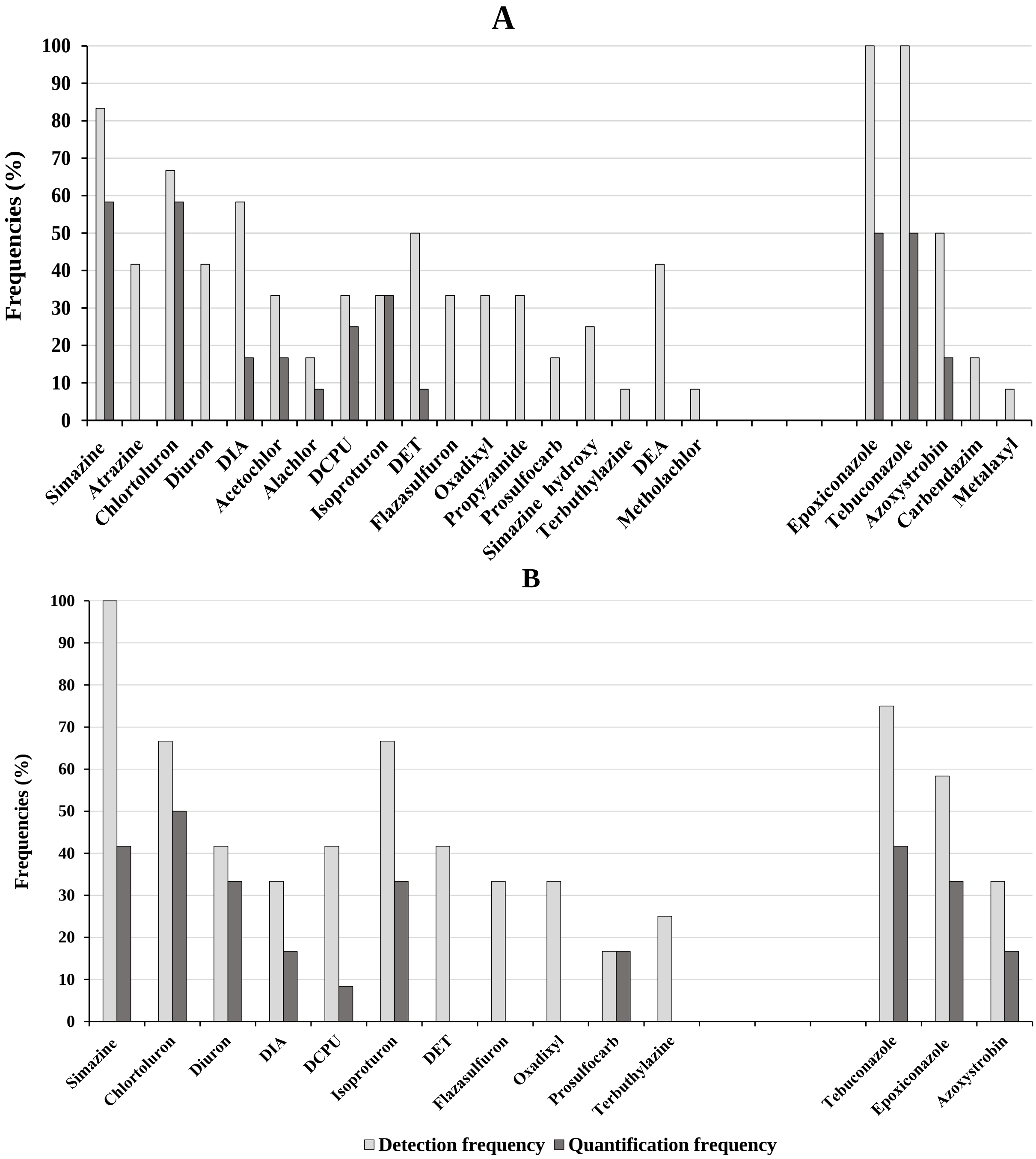

Fig.2 Global detection and quantification frequencies obtained by passive sampling (A) and grab sampling (B) at the four study sites during the three sampling campaigns

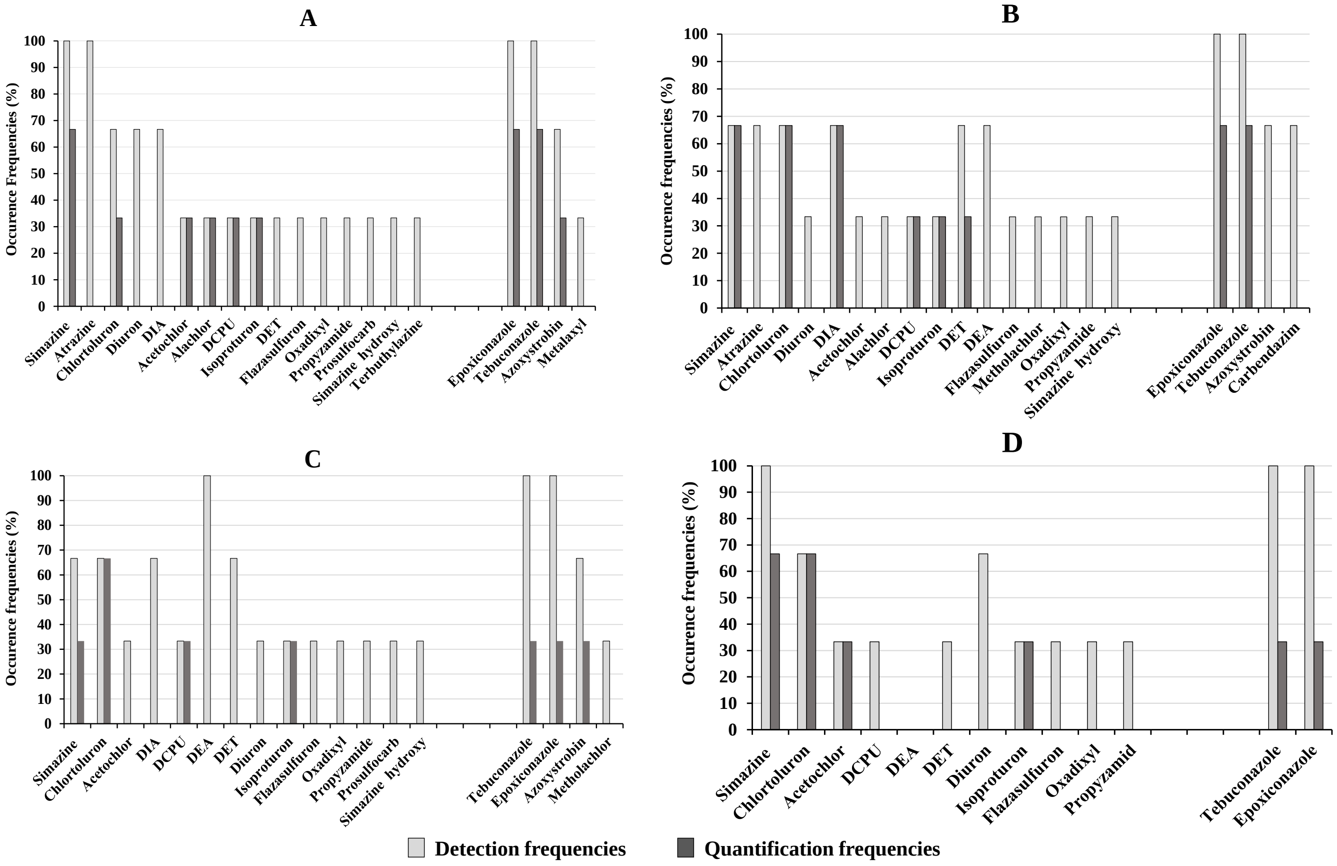

Fig. 3 Detection and quantification frequencies of targeted herbicides and fungicides in the lagoon (A), Chegui oued (B), Garaa oued (C) and Tinja oued (D), the sites sampled by passive sampling during the three sampling campaigns in 2015 and 2016

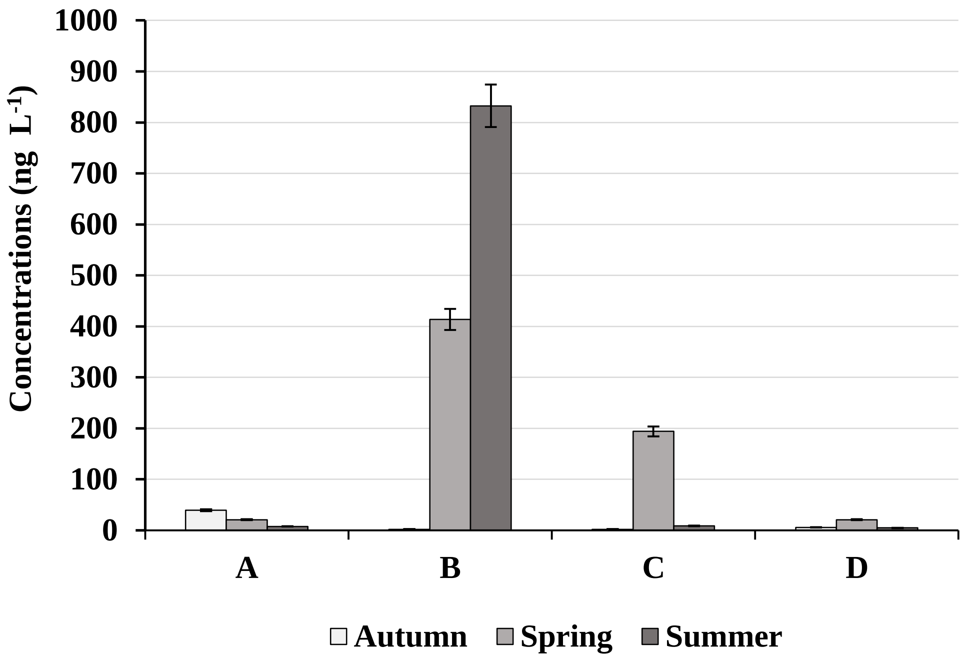

Fig. 4 Total pesticide concentrations (ng L^{-1}) in the water obtained by passive sampling as a function of the sampling site (lagoon (A), Chegui oued (B), Garaa oued (C) and Tinja oued (D)) and season

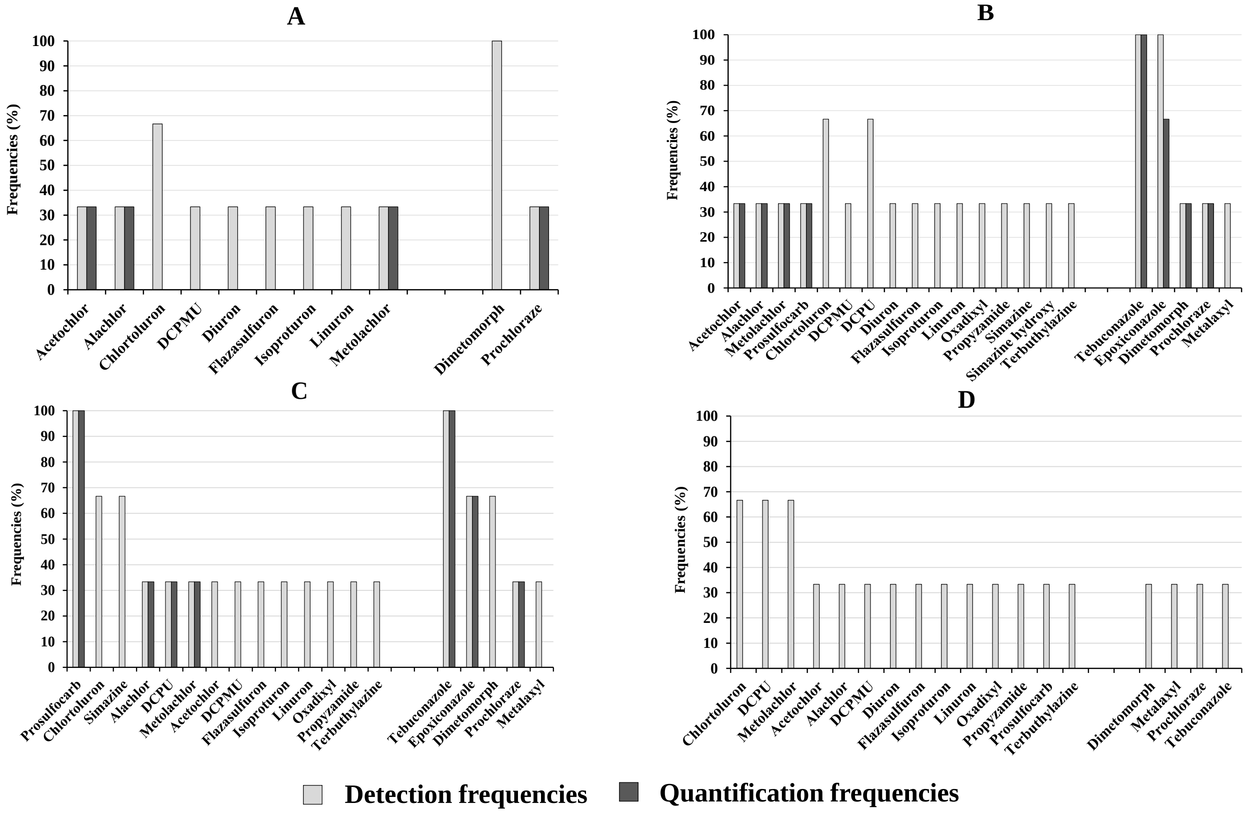

Fig. 5 Detection and quantification frequencies of targeted herbicides and fungicides in the sediments at sampling sites in the lagoon (A), Chegui oued (B), Garaa oued (C) and Tinja oued (D) during the three sampling campaigns in 2015 and 2016

Table

Table 1 Limits of detection (LOD) and quantification (LOQ) obtained by HPLC-MS/MS, and LOQ calculated for POCIS (Poulier et al., 2014), water, sediment and laboratory sampling rates of the 32 targeted compounds

Pesticide active substance	Chemical class	Analytical LOD (µg L^{-1})	Analytical LOQ (µg L^{-1})	LOQ POCIS (ng L^{-1})	LOQ water (ng L^{-1}	LQ sediment ng g^{-1}	Water recovery rate (%)	Sampling rates (L d^{-1})	Rs references (L d^{-1})
Herbicides									
Acetochlor	Chloracetanilide	2.2	7.5	1.6	22.5	2.2	83	0.223	(Ibrahim et al. 2013a)
Alachlor	Chloroacetamide	1.1	3.8	0.7	11.4	1.1	76	0.256	(Ibrahim et al. 2013a)
Atrazine	Triazine	0.4	1.5	0.3	4.4	0.4	88	0.254	(Ibrahim et al. 2013a)
Chlortoluron	Urea	0.7	2.3	0.4	6.8	0.7	43	0.252	(Ibrahim et al. 2013a)
DCPMU**	Urea	1.0	3.5	0.6	10.4	1.0	19	0.285	(Ibrahim et al. 2013a)
DCPU**	Urea	1.2	4.0	0.6	12.0	1.2	8	0.333	(Ibrahim et al. 2013b)
DEA**	Triazine	1.1	3.7	1.3	11.0	1.1	92	0.133	(Ibrahim et al. 2013b)
DET**	Triazine	0.5	1.7	0.3	5.0	0.5	69	0.254	(Ibrahim et al. 2013b)
DIA**	Triazine	1.0	3.4	2.4	10.1	1.0	69	0.068	(Ibrahim et al. 2013b)
Diuron	Phenylurea	0.7	2.3	0.4	6.9	0.7	68	0.257	(Ibrahim et al. 2013a)
Flazasulfuron	Sulfonylurea	0.7	2.2	-	6.6	0.7	0	Unavalaible	-
Isoproturon	Urea	0.9	2.9	0.6	8.7	0.9	48	0.237	(Ibrahim et al. 2013a)
Linuron	Urea	0.9	2.8	1.0	8.5	0.9	90	0.141	(Ibrahim et al. 2013a)
Metolachlor	Chloracetanilide	0.4	1.3	0.2	4.0	0.4	69	0.268	(Ibrahim et al. 2013b)
Oxadixyl	Phenylamide	1.1	3.6	0.7	10.8	1.1	55	0.263	(Ibrahim et al. 2013a)
Propyzamide	Benzamide	0.8	2.6	0.6	7.8	0.8	90	0.195	(Ibrahim et al. 2013a)

Prosulfocarb*	Thiocarbamate	0.5	1.6	1.0	4.7	0.5	67	0.071	(Ibrahim et al. 2013a)
Simazine*	Triazine	0.1	0.4	0.1	1.2	0.1	101	0.218	(Ibrahim et al. 2013a)
Simazine Hydroxy	Triazine	0.7	2.3	-	6.9	0.7	0	Unavalaible	-
Terbuthylazine	Triazine	0.3	1.1	0.3	3.3	0.3	87	0.163	(Ibrahim et al. 2013a)
Terbuthylazine Hydroxy	Triazine	0.7	2.5	-	7.4	0.7	0	Unavalaible	-
				Fungicides					
Azoxystrobin*	Strobilurin	1.0	3.2	1.0	9.5	1.0	66	0.154	(Ibrahim et al. 2013a)
Carbendazim*	Bendimidazole	0.5	1.6	0.3	4.8	0.5	21	0.304	(Poulier et al. 2015)
Dimetomorph	Morpholine	0.6	1.9	0.2	5.8	0.6	66	0.395	(Poulier et al. 2015)
Epoxiconazole*	Triazole	0.7	2.3	0.4	6.9	0.7	73	0.280	(Ahrens et al. 2015)
Metalaxyl	Phenylamide	0.8	2.7	0.5	8.0	0.8	55	0.264	(Ibrahim et al. 2013a)
Penconazole	Triazole	1.0	3.4	0.6	10.2	1.0	99	0.279	(Ibrahim et al. 2013a)
Prochloraz*	Azole	0.200	0.7	0.4	2.0	0.2	60	0.080	(Desgranges 2015)
Pyrimethanil	Anilinopyrimidine	1.1	3.6	0.7	10.9	1.1	89	0.231	(Ibrahim et al. 2013a)
Tebuconazole*	Triazole	0.7	2.2	0.4	6.5	0.7	71	0.240	(Greenwood et al. 2007)
Tetraconazole	Triazole	0.7	2.2	-	6.6	0.7	92	Unavalaible	-
				Insecticides					
Imidacloprid	Neonicotinoide	1.7	5.6	0.9	16.7	1.7	0.8	0.290	(Poulier et al. 2015)

**Pesticides inventoried in the survey*

*** Degradation products: DCPMU: 1-(3,4-dichlorophenyl)-3-methylurea / DCPU: 3,4-dichlorophenyl urea / DEA: desethylatrazine / DET: desethyl terbuthylazine / DIA : deisopropylatrazine*

Table 2 Inventoried active ingredients in the agricultural regions of the Bizerte lagoon watershed surveyed (south of Bizerte, Tinja, and Menzel Bourguiba)

Active ingredients	Chemical classes	Pesticides	Estimated doses(g ha^{-1})	Crops
Fungicides				
Azoxystrobin**	Strobilurins	Fungicide	200	Wheat. pulses
Difenoconazole	Triazoles	Fungicide	125	Vine
Mancozeb	Carbamates	Fungicide	40	Vine
Maneb	Carbamates	Fungicide	10	Vine
Zineb*	Carbamates	Fungicide	10	Vine
Boscalid	Carboxamides	Fungicide	7.50	Vine
Chlorothalonil**	Organochlorines (chloronitriles)	Fungicide	5.50	Pulses
Prochloraz**	Imidazoles	Fungicide	2.25	Wheat . barley
Tebuconazole**	Triazoles	Fungicide	1.25	wheat. barley. oat. pulses
Spiroxamine	Spirocetalamines	Fungicide	1.12	Vine
Flusilazole**	Triazoles	Fungicide	1	Barley
Thiophanate-methyl	Benzimidazoles	Fungicide	0.78	Vine
Flutriafol**	Triazoles	Fungicide	0.6	Barley
Propiconazole**	Triazoles	Fungicide	0.63	Barley
Carbendazim**	Benzimidazoles	Fungicide	0.50	Cereals. wheat
Prothioconazole**	Triazolinthiones	Fungicide	0.50	Cereals
Epoxiconazole**	Triazoles	Fungicide	0.47	Wheat . barley
Kresoxim-methyl	Strobilurins	Fungicide	0.44	Vine
Cyproconazole	Triazoles	Fungicide	0.20	Oat
Metconazol*	Triazoles	Fungicide	0.01	Wheat . barley
Insecticides				
Bifenthrin	Pyrethroides	Insecticide	80	Vine . fruit trees
Deltamethrin	Pyrethroides	Insecticide	62.5	Vine. fruit trees. cereals
Herbicides				
Glyphosate**	Amino- phosphonates	Herbicide	21.60	All crops
Simazine**	Triazines	Herbicide	3.75	Pulses
Bentazone**	Diazines	Herbicide	3	Cereals . pulses
Prosulfocarb**	Thiocarabamates	Herbicide	1	Wheat
2.4D**	Esters	Herbicide	0.90	Wheat. barley . oat
Clethodim	Cyclohexanes diones	Herbicide	0.60	Pulses
Fenoxaprop-p-ethyl*	Aryloxyphe-noxy-propionates (FOPS)	Herbicide	0.28	Cereals
Mefenpyr-diethyl	Pyrazoles	Herbicide	0.23	Cereals

Clodinafop-propagyl	Aryloxy-phenoxy-propionates (FOPS)	Herbicide	0.14	Wheat
Pinoxaden*	Phenylpyrazolines	Herbicide	0.14	Wheat
Pyroxulam*	Triazolopyrimidines	Herbicide	0.12	Cereals
Mesosulfuron-methyl	Sulfonylurea	Herbicide	0.08	Cereals
Tribenuron-Méthyl	Sulfonylurea	Herbicide	0.05	Cereals
Aminopyralid	Triazolopyrimidines	Herbicide	0.05	Wheat. oat!
Cloquintocet-mexyl	Phenylpyrazolines	Herbicide	0.03	Barley
Florasulam	Thiocarabamates	Herbicide	0.02	Cereals
Iodosulfuron	Sulfonylurea	Herbicide	0.02	Cereals
Trifluralin	Dinitroanilines	Herbicide	0.01	Pulses

** Active ingredients not approved in Tunisia (Mezghani et al. 2016)*

***Active ingredients from the list of 15 selected pesticides*

Table 3 Pesticides quantified by POCIS as a function of the site and the season (mean concentrations ng L $^{-1}$; n=3 injections)

Pesticides	Survey	Lagoon (A)						Chegui oued (B)						Garaa oued (C)						Tinja oued (D)					
		Autumn 2015		Spring 2016		Summer 2016		Autumn 2015		Spring 2016		Summer 2016		Autumn 2015		Spring 2016		Summer 2016		Autumn 2015		Spring 2016		Summer 2016	
		Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Herbicides																									
Acetochlor	nd	13.5	1.2	<LOD		<LOD		<LOQ		<LOD		<LOD		<LOD		<LOQ		<LOD		<LOD		5.0	1.3	<LOD	
Alachlor	nd	2.7	0.3	<LOD		<LOD		<LOQ		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
Atrazine	nd	<LOQ		<LOQ		<LOQ		<LOQ		<LOQ		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
Chlortoluron**	nd	<LOQ		<LOD		3.6	0.1	<LOD		2.3	1.6	3.1	0.1	<LOD		17.0	5.3	4.1	0.3	<LOD		3.0	1.2	2.3	0.2
DCPMU*	nd	<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
DCPU*	nd	1.8	0.1	<LOD		<LOD		<LOD		1.0	0.9	<LOD		<LOD		0.9	0.3	<LOD		<LOQ		<LOD		<LOD	
DEA*	nd	<LOD		<LOD		<LOD		<LOQ		<LOD		<LOQ		<LOQ		<LOQ		<LOQ		<LOD		<LOD		<LOD	
DET*	nd	<LOD		<LOD		<LOQ		<LOD		<LOQ		5.0	0.9	<LOQ		<LOD		<LOQ		<LOD		<LOD		<LOQ	
DIA*	nd	<LOQ		<LOD		<LOQ		<LOD		93.3	6.1	192.0	4.6	<LOD		<LOQ		<LOQ		<LOD		<LOD		<LOD	
Diuron	nd	<LOQ		<LOD		<LOD		<LOD		<LOD		<LOQ		<LOD		<LOD		<LOQ		<LOQ		<LOD		<LOQ	
Flazasulfuron	nd	<LOQ		<LOD		<LOD		<LOD		<LOQ		<LOD		<LOD		<LOQ		<LOD		<LOD		<LOQ		<LOD	
Isoproturon	nd	<LOD		<LOD		4.0	1.1	<LOD		<LOD		1.8	0.2	<LOD		<LOD		4.4	0.2	<LOD		<LOD		2.4	0.1
Linuron**	nd	<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
Metolachlor	nd	<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOQ		<LOD		<LOD		<LOD		<LOD	
Oxadixyl	nd	<LOD		<LOQ		<LOD		<LOD		<LOQ		<LOD		<LOD		<LOQ		<LOD		<LOD		<LOQ		<LOD	
Propyzamide	nd	<LOD		<LOD		<LOQ		<LOD		<LOQ		<LOD		<LOD		<LOQ		<LOD		<LOD		<LOQ		<LOD	
Prosulfocarb**	d	<LOD		<LOQ		<LOD		<LOD		<LOD		<LOD		<LOD		<LOQ		<LOD		<LOD		<LOD		<LOD	
Simazine**	d	9.0	0.8	4.5	2.1	<LOQ		<LOD		168.0	11.1	431.6	7.2	<LOD		20.0	1.3	<LOQ		5.7	1.2	10.0	0.2	<LOQ	
Simazine hydroxy*	nd	<LOD		<LOD		<LOQ		<LOD		<LOD		<LOQ		<LOD		<LOD		<LOQ		<LOD		<LOD		<LOD	
Terbuthylazine**	nd	<LOD		<LOD		<LOQ		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
Terbuthylazine hydroxy*	nd	<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
Fungicides																									
Azoxystrobine**	d	<LOD		6.5	1.3	<LOQ		<LOD		<LOQ		<LOQ		<LOD		8.0	0.1	<LOQ		<LOD		<LOD		<LOD	
Carbendazim**	d	<LOD		<LOD		<LOD		<LOD		<LOQ		<LOQ		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
Dimetomorph**	nd	<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
Epoxiconazole**	nd	8.4	0.9	5.8	3.0	<LOQ		<LOQ		7.2	1.8	8.5	0.9	<LOQ		46.0	2.0	<LOQ		<LOQ		2.0	0.9	<LOQ	
Metalaxyl**	nd	<LOD		<LOD		<LOQ		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
Penconazole**	nd	<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
Prochloraze**	d	<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
Pyrimethanil**	nd	<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
Tebuconazole**	d	3.9	0.9	4.0	0.3	<LOQ		<LOQ		142.0	9.0	190.5	11.4	<LOQ		102.2	3.2	<LOQ		<LOQ		0.8	0.2	<LOQ	
Tetraconazole	nd	<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
Insecticides																									
Imidacloprid**	d	<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
Total concentrations		39.3		20.8		7.6		<LOD		413.8		832.5		<LOD		194.1		8.5		5.7		20.8		9.4	

*d: determined in the survey; nd: not determined in the survey; < LOD: concentration below the analytical detection limit; < LOQ: concentration below the analytical quantification; *: Degradation products; **: pesticides approved in Tunisia*

Table 4 Pesticides quantified by grab sampling as a function of the site and the season (mean concentrations ng L^{-1}; n=3 injections)

Pesticides	Survey	Lagoon (A)						Chegui oued (B)						Garaa oued (C)						Tinja oued (D)					
		Autumn 2015		Spring 2016		Summer 2016		Autumn 2015		Spring 2016		Summer 2016		Autumn 2015		Spring 2016		Summer 2016		Autumn 2015		Spring 2016		Summer 2016	
		Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Herbicides																									
Acetochlor	nd	<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
Alachlor	nd	<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
Atrazine	nd	<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
Chlortoluron**	nd	<LOD		<LOD		15.1	0.5	<LOQ		<LOQ		16.4	1.1	<LOD		40.0	12.3	24.4	0.6	<LOD		15.0	11.7	15.4	0.5
DCPMU*	nd	<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
DCPU*	nd	<LOQ		6.1	3.5	<LOD		<LOD		<LOQ		<LOD		<LOQ		<LOD		<LOD		<LOQ		<LOD		<LOD	
DEA*	nd	<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
DET*	nd	<LOD		<LOD		<LOQ		<LOD		<LOQ		<LOQ		<LOD		<LOD		<LOQ		<LOD		<LOD		<LOQ	
DIA*	nd	<LOD		<LOD		<LOQ		<LOD		286.2	22.8	182.0	94.2	<LOD		<LOD		<LOQ		<LOD		<LOD		<LOD	
Diuron	nd	<LOQ		<LOD		15.0	0.6	<LOD		<LOD		14.8	0.9	<LOD		<LOD		15.9	1.1	<LOD		<LOD		15.5	0.7
Flazasulfuron	nd	<LOD		<LOD		<LOQ		<LOD		<LOD		<LOQ		<LOD		<LOD		<LOQ		<LOD		<LOD		<LOQ	
Isoproturon	nd	<LOD		<LOQ		10.2	0.4	<LOD		<LOQ		10.4	0.5	<LOQ		<LOD		11.2	0.3	<LOQ		<LOD		105.0	0.2
Linuron**	nd	<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
Metolachlor	nd	<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
Oxadixyl	nd	<LOD		<LOD		<LOQ		<LOD		<LOD		<LOQ		<LOD		<LOD		<LOQ		<LOD		<LOD		<LOQ	
Propyzamide	nd	<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
Prosulfocarb**	d	<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		25.4	4.0	10.6	0.4	<LOD		<LOD	
Simazine**	d	<LOQ		<LOQ		<LOQ		<LOQ		730.9	27.9	<LOQ		<LOQ		56.9	6.3	11.6	0.3	12.9	0.3	32.5	7.3	<LOQ	
Simazine hydroxy*	nd	<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
Terbuthylazine**	nd	<LOQ		<LOD		<LOD		<LOD		<LOD		<LOQ		<LOD		<LOD		<LOD		<LOQ		<LOD		<LOD	
Terbuthylazine hydroxy*	nd	<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
Fungicides																									
Azoxystrobin**	d	<LOD		<LOD		<LOD		<LOD		11.6	1.8	<LOQ		<LOD		17.5	2.6	<LOD		<LOD		<LOD		<LOQ	
Carbendazim**	d	<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
Dimetomorph**	nd	<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
Epoxiconazole**	nd	<LOQ		<LOQ		<LOD		106.6	2.8	43.4	2.5	<LOQ		<LOD		99.5	5.5	12.6	0.2	<LOD		<LOD		<LOD	
Metalaxyl**	nd	<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
Penconazole**	nd	<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
Prochloraze**	d	<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
Pyrimethanil**	nd	<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
Tebuconazole**	d	<LOQ		<LOQ		<LOD		<LOQ		500.3	21.8	84.9	42.7	<LOD		178.4	67.5	60.4	3.9	<LOQ		56.5	16.0	<LOD	
Tetraconazole	nd	<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
Insecticides																									
Imidacloprid**	d	<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
Total concentrations		< LOD		6.1		40.3		106.6		1572.4		308.5		<LOD		392.3		161.5		23.5		104.0		135.9	

*d: determined in the survey; nd: not determined in the survey; < LOD: concentration below the analytical detection limit; < LOQ: concentration below the analytical quantification; *: Degradation products; **: pesticides approved in Tunisia*

Table 5 Pesticides quantified in sediments as a function of the site and the season (mean concentrations ng g $^{-1}$ d.w; n=3 injections) and physical-chemical parameters of sediment samples

Pesticides	Survey	Lagoon (A)						Chegui oued (B)						Garaa oued (C)						Tinja oued (D)					
		Autumn 2015		Spring 2016		Summer 2016		Autumn 2015		Spring 2016		Summer 2016		Autumn 2015		Spring 2016		Summer 2016		Autumn 2015		Spring 2016		Summer 2016	
		Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Herbicides																									
Acetochlor	nd	<LOD		<LOD		4.8	0.7	<LOD		<LOD		2.8	0.3	<LOD		<LOQ		<LOD		<LOQ		<LOD		<LOD	
Alachlor	nd	<LOD		<LOD		2.3	0.9	<LOD		<LOD		2.5	0.1	<LOD		<LOD		1.8	0.3	<LOQ		<LOD		<LOD	
Atrazine	nd	<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
Chlortoluron	nd	<LOQ		<LOD		<LOQ		<LOQ		<LOQ		<LOD		<LOQ		<LOD		<LOQ		<LOQ		<LOQ		<LOD	
DCPMU*	nd	<LOQ		<LOD		<LOD		<LOQ		<LOD		<LOD		<LOQ		<LOD		<LOD		<LOD		<LOQ		<LOD	
DCPU*	nd	<LOD		<LOD		<LOD		<LOQ		<LOQ		<LOD		0.5	0.1	<LOD		<LOD		<LOQ		<LOQ		<LOD	
DEA*	nd	<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
DET*	nd	<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
DIA*	nd	<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
Diuron	nd	<LOD		<LOQ		<LOD		<LOD		<LOD		<LOQ		<LOD		<LOD		<LOD		<LOQ		<LOD		<LOD	
Flazasulfuron	nd	<LOD		<LOD		<LOQ		<LOD		<LOQ		<LOD		<LOD		<LOQ		<LOD		<LOD		<LOQ		<LOD	
Isoproturon	nd	<LOQ		<LOD		<LOD		<LOQ		<LOD		<LOD		<LOD		<LOD		<LOQ		<LOD		<LOD		<LOQ	
Linuron**	nd	<LOD		<LOQ		<LOD		<LOD		<LOQ		<LOD		<LOD		<LOD		<LOQ		<LOD		<LOD		<LOQ	
Metolachlor	nd	<LOD		<LOD		1.5	0.1	<LOD		<LOD		0.8	0.2	<LOD		<LOD		0.7	0.1	<LOD		<LOQ		<LOQ	
Oxadixyl	nd	<LOD		<LOD		<LOD		<LOQ		<LOD		<LOD		<LOQ		<LOD		<LOD		<LOD		<LOD		<LOQ	
Propyzamide	nd	<LOD		<LOD		<LOD		<LOD		<LOD		<LOQ		<LOQ		<LOD		<LOD		<LOD		<LOQ		<LOD	
Prosulfocarb**	d	<LOD		<LOD		<LOD		<LOD		<LOD		5.0	0.1	6.3	0.3	4.1	0.6	5.2	0.3	<LOD		<LOD		<LOQ	
Simazine**	d	<LOD		<LOD		<LOD		<LOQ		<LOD		<LOD		<LOQ		<LOD		<LOQ		<LOD		<LOD		<LOD	
Simazine hydroxy*	nd	<LOD		<LOD		<LOD		<LOD		<LOQ		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
Terbuthylazine**	nd	<LOD		<LOD		<LOD		<LOQ		<LOD		<LOD		<LOD		<LOQ		<LOD		<LOD		<LOQ		<LOD	
Terbuthylazine hydroxy*	nd	<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
Fungicides																									
Azoxystrobine**	d	<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
Carbendazim**	d	<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
Dimetomorph**	nd	<LOQ		<LOQ		<LOQ		<LOD		<LOD		0.7	0.1	<LOQ		<LOQ		<LOD		<LOD		<LOQ		<LOD	
Epoxiconazole**	nd	<LOD		<LOD		<LOD		1.0	0.1	<LOQ		0.8	0.2	4.2	0.5	3.3	1.7	<LOD		<LOD		<LOD		<LOD	
Metalaxyl**	nd	<LOD		<LOD		<LOD		<LOD		<LOQ		<LOD		<LOD		<LOQ		<LOD		<LOD		<LOD		<LOQ	
Penconazole**	nd	<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
Prochloraze**	d	<LOD		<LOD		1.2	0.7	<LOD		<LOD		1.8	0.1	<LOD		<LOD		1.2	0.5	<LOD		<LOD		<LOQ	
Pyrimethanil**	nd	<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
Tebuconazole**	d	<LOD		<LOD		<LOD		1.4	0.1	31.1	2.3	5.1	1.1	8.9	0.3	6.2	1.1	5.7	0.8	<LOD		<LOD		<LOQ	
Tetraconazole	nd	<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
Insecticides																									
Imidacloprid**	d	<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD		<LOD	
Total concentration		<LOD		<LOD		9.8		2.4		31.1		19.5		19.9		13.6		14.6		<LOD		<LOD		<LOD	
Physico-chemical parameters																									
%<63 µm		69		66		12		63		77		62		100		94		100		57		11		16	
TOC (%)		1		1		1		1		1		1		2		2		2		1		2		1	

*d: determined in the survey; nd: not determined in the survey; < LOD: concentration below the analytical detection limit; < LOQ: concentration below the analytical quantification; *: Degradation products; **: pesticides approved in Tunisia; TOC (%) : percentage of total organic carbon; %<63 µm : percentage of finer grain size fractions.*

Supplementary Material