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Factors responsible for rapid dissipation of acidic herbicides in the coastal lagoons of the Camargue (Rhône River Delta, France)

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ABSTRACT

This study was aimed at investigating which processes cause acidic herbicides (e.g., bentazone, MCPA and dichlorprop) to rapidly disappear in the lagoons of the Rhône delta, which are peculiar brackish and shallow aquatic environments. The use of the model MASAS (Modeling of Anthropogenic Substances in Aquatic Systems) revealed that sorption, sedimentation, volatilization, flushing and abiotic hydrolysis had a minor role in the attenuation of the investigated herbicides. Laboratory scale biodegradation and photodegradation studies were conducted to better assess the significance of these two processes in the natural attenuation of herbicides in brackish (lagoons) waters with respect to fresh waters (canals draining paddy fields). Herbicide biodegradation rates were significantly lower in lagoon water than in canal water. Consequently, photodegradation was the main dissipation route of all investigated herbicides. The contribution of indirect photolysis was relevant for MCPA and dichlorprop while direct photolysis dominated for bentazone removal. There is a need to further investigate the identity of phototransformation products of herbicides in lagoons.

1. Introduction

Estuarine waters are characterized by high salinity and dissolved organic matter (DOM) content. The chemical behavior and fate of anthropogenic pollutants are strongly influenced by these latter parameters (Hemond and Fechner-L, 2000). However, there is relatively little information about the environmental fate of pesticides in estuarine waters. Most studies have focused on photodegradation rather than on microbially-mediated degradation processes (Miller and Chin, 2002, 2005). The occurrence of chloride ions has been associated with an increase in the photodegradation rates of carbamazepine and fipronil with the formation of potentially toxic chlorinated derivatives (Walse et al., 2004; Chiron et al., 2006). Due to the nature of DOM, the generation rates of reactive photo-induced species such as hydroxyl radical (HO•), singlet oxygen ($^1O_2$) and chromophoric DOM triplet state (CDOM*) were found to be slightly higher in estuarine than in river water samples. Consequently, a higher contribution of the indirect photolysis processes to the pesticides removal might be expected (Al Housari et al., 2010). In contrast, salinity inhibited the growth of some bacteria resulting in a switch of the microbial community in subsurface flow constructed wetland leading to exponential inhibition of atrazine attenuation (Tao et al., 2008). Also, Tam et al. (2002) reported that high salinity (35 g L^{-1}) inhibited the growth of a bacterial culture isolated from mangrove sediments and the biodegradation of phenanthrene, a model PAH compound. Consequently, there is a need to better understand the behavior and fate of pesticides in brackish lagoon waters. For this purpose, field studies have been undertaken in the lagoons of the Rhône delta (France). Recent monitoring studies in these lagoons reported the rapid dissipation of bentazone, MCPA, and dichlorprop (Comoretto et al., 2007, 2008). Those herbicides were detected in the lagoons, with peak concentrations of 0.25, 0.35 and 0.2 μg L^{-1}, respectively in June (Comoretto, 2009) corresponding to their post-emergence usage. However, the concentrations in the lagoons decreased rapidly after these peaks, with half-life times on the order of 1–2 weeks. The primary objective of this work was to investigate the reasons for the rapid dissipation of acidic herbicides in the lagoons. For this purpose, a combined modeling and experimental approach was adopted. Removal rates and kinetics by direct, indirect photochemical and biological degradation as well as by hydrolysis processes were measured under natural in situ conditions. In addition, the elimination rates by sedimentation, volatilization and flushing were assessed by a reactive transfer model, using meteorological and hydrological data from the studied area.

2. Experimental section

2.1. Study area

The area from which the two different waters were sampled for this study is the Île de Camargue, the central part of the Rhône delta in the south of France (Chauvelon et al., 2003). A map of this area is published in Höhener et al. (2010). The Camargue regional nature

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park lies in the center of the Île de Camargue and covers 85,000 ha of lagoons, marshes and other lands separated from the Mediterranean Sea by a dike. Agricultural land borders the park to the North and South-East, and most of it is devoted to intensive flooded rice cultivation (Comoretto et al., 2007). Runoff from the rice parcels is collected from mid-April to September in canals. One of these canals, the Canal de Fumemorte, discharges into the Vaccarès lagoon which lies in the protected area. Both, the water of Fumemorte canal and Vaccarès lagoon, were studied here. The water samples represented fresh water (Canal) and brackish water (Vaccarès lagoon). They differ mainly in the type and quantity of organic matter, and in the salinity, which is below 1 g L^{-1} in the canal water and about 25 g L^{-1} in the Vaccarès lagoon. The selection of two different types of water samples was to elucidate if there is any or possible impact of water type on biodegradation and photodegradation. Ultraviolet–visible (UV) spectra and the chemical characterization of the water samples were reported previously (Al Housari et al., 2010).

2.2. Sampling and sample preparation

For the photochemistry experiments, water samples were taken from about 15 cm below the surface (lagoon and canal), filtered through 0.45 μm pore-size membranes, and stored at 4 °C in the dark till analysis. Storage and all measurements were performed at the pH of the natural water. Chloride ion content were $1.18 \pm 0.03 \times 10^{-3}$ M and $1.90 \pm 0.05 \times 10^{-1}$ M in canal water and lagoon water samples, respectively. Non Purgeable Organic Carbon (NPOC) values were 19.8 ± 0.3 and 32.1 ± 0.6 mg C L^{-1} in canal water and lagoon water samples, respectively. Water samples for the biodegradation test were filtered through coarse paper filter in order to remove coarse particles and were used on the day of collection.

2.3. Chemicals

Bentazone (3-isopropyl-1H-2,1,3-benzothiadiazin-4(3H)-one-2,2-dioxide), of 99.7% purity, and dichlorprop ((RS)-2-(2,4-dichlorophenoxy)propionic acid, 95%) were obtained from Riedel-de-Haën. MCPA (4-chloro-o-tolyloxyacetic acid, 95%) was from Aldrich. 2-hydroxybenzoic acid (2-HBA, 99%) was from Acros. $FeSO_4 \cdot 7H_2O$ from VWR, NaN_3 (99%) and acetonitrile (ACN) from Sigma-Aldrich, 30% w/w hydrogen peroxide solution was from Fischer. The ultra purity water (UHQ) for all experiments and all analyses by HPLC was obtained by a Milli-Q water system.

2.4. Analytical procedures

The quantification of herbicides in the photodegradation experiments was done directly by a Hitachi HPLC chromatograph equipped with a L-2400 UV detector and using a C-18 LiChrospher column (Merck, length 250 mm, diameter 4.6 mm, particle size 5 μM) and an UV detector run at the appropriate wavelength (see Table 1). Herbicides in biodegradation experiments were pre-concentrated by solid phase extraction (SPE). Samples (50 mL) of each flask were first adjusted to a pH value of 1.5. Then, samples were passed through 6 mL C-18 SPE cartridges (Supelco) under vacuum adjusted to a flow rate of 5 mL min^{-1} (10 mm Hg). SPE cartridges were preconditioned by eluting 5 mL methanol followed by 5 mL ethyl acetate, and finally by ultra pure water (pH = 2.5). The SPE cartridges were then completely dried by increasing vacuum to 25 mm Hg for 10 min. Herbicides were then eluted from the SPE cartridges with 3 mL of methanol and 3 mL of ethyl acetate. The eluate was evaporated to dryness under a gentle stream of nitrogen and then re-dissolved with 2 mL of a mixture of methanol and ultra pure water (50/50). Before HPLC analysis, the extracts were filtered through a 0.45 μm filter. Samples were then eluted with a mixture of acetonitrile and water acidified with formic acid (0.1%) at a flow rate of 0.8 mL min^{-1}. Details of HPLC conditions are given in Table 1. The limit of detection was 25 ± 3 μg L^{-1}. Three blank samples were obtained by spiking ultra pure water with the studied herbicides to give final concentrations of 10 μg L^{-1}. Blanks were analyzed as a control for memory effect in the instrument and for laboratory contamination. The average recoveries ranged from 83 to 90% for bentazone, MCPA and, dichlorprop, with relative standard deviations of 3–4%. All results were corrected with the corresponding recovery rates to provide accurate amounts.

Table 1
Details of HPLC methods for herbicide detection in biodegradation test.

Chemicals	Mobile phase	Wavelength (nm)	Flow rate (mL min^{-1})	Retention time (min)
Bentazone	Water 0.1% formic acid/ACN (50/50)	215	0.8	7.1 ± 0.5
MCPA	Water 0.1% formic acid/ACN (40/60)	206	0.8	6.5 ± 0.5
Dichlorprop	Water 0.1% formic acid)/ACN (40/60)	206	0.8	7.8 ± 0.5
Sodium benzoate	Ammonium acetate buffer/ACN (90/10)	225	0.8	11.8 ± 0.5

2.5. Photodegradation experiments under natural sunlight

The experiments were conducted using solutions of herbicides containing bentazone, dichlorprop and MCPA. The final concentration of the herbicides was 50 μM in filtered lagoon and canal water samples. The same concentrations in ultra pure water were used for the estimation of the direct photolysis of those herbicides. All experiments were conducted in triplicate. The samples were exposed to natural sunlight in summer conditions in Marseille (France), to determine the half-life of the herbicides. The samples were enclosed in 5 mL pyrex tubes (o.d. 1.3 cm, i.d. 1.1 cm). To simulate the environmental conditions, the tubes sealed with parafilm were placed in a basin filled with ultra pure water which was wrapped with aluminum foil. The basin (diameter 30 cm, depth 15 cm) with the tubes was then placed on a roof at our laboratory in central Marseille. Starting on 9th of July 2008, the experiments were run for eight days. Aliquots of samples (200 μL) were withdrawn at various time intervals and were analyzed by HPLC. Aqueous solutions of those herbicides at 50 μM in ultra pure water in tubes wrapped in aluminum foil and kept in the dark were used for the hydrolysis experiments.

2.6. Measurement of the second-order kinetic rate constant with OH radical

The second-order reaction rate constants $k_{(^{\bullet}OH)}$ of bentazone and dichlorprop with OH radicals was determined using competition kinetics with a dark Fenton's system (Haag and Yao, 1992). For this experiment, the typical procedure involved adding 0.02 mM of $FeSO_4 \cdot 7H_2O$ (freshly prepared) to equimolar concentrations (0.02 mM) of an herbicide and 2-HBA in ultra pure water. 2-HBA is a reference compound whose rate constant with OH radicals is known ($k_{(^{\bullet}OH)} = 1.7 \times 10^{10}$ M^{-1} s^{-1}, Amphlett et al., 1968). The whole solution was acidified to pH 3.3 with 0.1 M HCl. After that, H_2O_2 in final concentration of 10 mM was added to generate the OH radicals. To eliminate the interference of by-products, the measurements were done within 5 min. Then, 20 μL of a KI solution (0.1 M) was added to the samples. This quenching solution enabled the decomposition of residual H_2O_2 and the precipitation of Fe(II) and Fe(III) ions (Giroto et al., 2008). Samples were then analyzed by HPLC. Experiments were run in duplicate. The $k_{(^{\bullet}OH)}$ for each herbicide was calculated according the following equation:

$$\ln(P_t/P_0) = \ln(R_t/R_0) \times (k_P/k_R) \quad (1)$$