UNIVERSITÉ DE PROVENCE
AIX- MARSEILLE I

ÉCOLE DOCTORALE
« Sciences de l'Environnement »

PhD THESIS
Chimie de l'Environnement

Fadi ALHOUSARI

Fate and Behaviour of Acidic Rice Herbicides in Lagoon Waters of Camargue (Rhône River Delta, France)

PhD thesis defended on 04 February 2011

Accepted on the recommendation of

Dr. David Werner	University of Newcastle upon Tyne, UK	reporter
Prof. Claude CASELLAS	University of Montpellier I, Montpellier	reporter
Prof. Julio GONÇALVÈS	University of Paul Cézanne	examiner
Dr. Serge CHIRON	University of Provence, Marseille	supervisor
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Where do pesticides fit into the picture of environmental disease?

They have the power to make our streams fishless
And our gardens and woodlands silent and birdless!

Rachel Carson
(Silent Spring)

SUMMARY

The Ile de Camargue basin is the central part of the Rhône Delta in the south of France included between the two branches of the river. The higher parts of this area are agricultural lands, mainly rice fields, whereas the lower parts are lagoons and natural wetlands of international importance for biodiversity preservation.

Bentazone, dichlorprop, and MCPA are post-emerging herbicides applied in rice fields from mid April to mid June. Rice fields grown under flooded conditions represent an environment with the potential for pesticides to transport in runoff from rice fields to surface waters in response to controlled water management procedures.

The persistence of those agrochemicals in a given environmental system depends on transport and degradation processes. To predict their fate in the surface waters of the Camargue and to assess their risk, it is necessary to understand their chemical reaction under environmental conditions.

Reactive photoinduced species (RPS, hydroxyl radical $HO^{\cdot}$, singlet oxygen $^1O_2$ and dissolved organic matter triplet state) in estuarine waters (Vaccarès lagoon) were characterized experimentally to estimate the role of photochemistry in rice paddies. Steady-state concentrations and initial production rates of RPS were determined for $HO^{\cdot}$ and for $^1O_2$. The steady-state measured concentration of $HO^{\cdot}$ was $(1.72 \pm 0.01) \times 10^{-16}$M and $(2.06 \pm 0.22) \times 10^{-13}$ M, respectively. These values were compared with those of fresh water (Canal). The respective concentrations were $(9.41 \pm 0.12) \times 10^{-17}$ M, and $(5.44 \pm 0.04) \times 10^{-14}$ M. We then developed a kinetic model describing the solar photo-transformation of xenobiotic organic compounds induced by the three different photooxidants RPS.

Sunlight photodegradation of bentazone, dichlorprop (DCPP), MCPA and alachlor (used as a surrogate for the similar Pretilachlor, pre-emergence herbicide) and microbial transformation were conducted experimentally to estimate near-surface half-lives in surface water. Parallel to the experimental study, an assessment of the elimination rates of those herbicides by sorption and sedimentation, and volatilization was obtained by the model MASAS (Modelling of Anthropogenic Substances in Aquatic Systems). The half-lives of the herbicides obtained experimentally were then compared with those obtained from field data from a previous Ph D study. This allowed assessing the main processes involved in the attenuation of herbicide concentrations.

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Paper II:

Fadi Al Housari, Patrick Höhener, Serge Chiron. 2010. Factors responsible for rapid dissipation of acidic herbicides in the coastal lagoons of the Camargue (Rhône River Delta, France)? Science of the Total Environment, doi:10.1016/j.scitotenv.2010.10.036

Paper III:

Patrick Höhener, Laetitia Comoretto, Fadi Al Housari, Philippe Chauvelon, Marc Pichaud, Yves Chérain, Serge Chiron. 2010. Modeling anthropogenic substances in coastal wetlands: application to herbicides in the Camargue (France). Environmental Modelling & Software (25) 1837-1844.

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Introduction

Pesticides have been intensively used world-wide in agriculture to protect crops from pests and diseases, and to maintain adequate productivity in order to make food more affordable to populations. Pesticides have become an integral part of commercial agriculture. Because of cost-effectiveness, herbicide use is likely to remain an important agronomic strategy for the foreseeable future.

Rice is an economically important cereal crop and the most widely consumed food grain. According to the International Rice Research Institute (IRRI), almost half of the world population depends on rice and the number of people feeding on rice will double by 2025. However, constraints for increasing productivity range from diminishing cultivable land, due to soil erosion and urbanization, to decreasing water resources and at the same time deterioration of water quality by micro pollutants. Rice fields represent a unique environment where rice is grown under flooded conditions. These conditions increase the potential for pesticides to transport in runoff from rice fields to surface waters in response to controlled water management procedures of flooding and draining during the growing season (Boesten and van der Linden 1991). There have been several cases where rice pesticides move out of their intended area and contaminate the surrounding environments like lagoons in Camargue. Comorotto and co-workers (2008) reported runoff accounted for as much as 18- 42% of mass loss for MCPA, and in rivers in Japan the rice pesticide runoff rates ranged from 0.3% for fenthion to 42% for benfuresate (Numabe and Nagahora, 2006). Moreover, the flooded conditions can also alter the physico-chemical and microbial composition of the soil leading to differences in both pathway and rate of degradation of rice pesticides (Cervelli and Jackson, 2008).

Pesticides are defined in the EC Drinking Water Directive (98/83/EEC) as being ‘organic insecticides, herbicides, fungicides, nematocides, acaricides, algicides, rodenticides, slimicides, related products such as growth regulators, and their relevant metabolites, degradation and reaction products’. Pesticides are of concern to water quality managers and environmental risk regulators who have to maintain and achieve a good water quality status. The regulations for the control of the water quality for human use in the European Union clearly established the maximum permissible values of different pesticides.

Individual pesticides applied in significant amounts in catchments and that are most likely to reach water supplies are required to be monitored under the European Water Framework Directive (Directive 2000/60/EC), each with a limit value of 0.1 µg l^{-1}, except for the banned organochlorine pesticides that are still found in water supplies, for which a lower limit value of 0.03 $\mu g\ l^{-1}$ has been set. Total pesticides means the sum of all individual pesticides detected and quantified in the monitoring procedure excluding the organochlorine pesticides, and is set at 0.5 $\mu g\ l^{-1}$ (Council Directive 98/83/EC, EU1998).

Due to the development of the agrochemical industry, the quantities of agrochemicals present in environmental compartments dramatically increased. However, public and scientific concerns have arisen about the potential adverse effects on the environment, wildlife and human health. Among the possible chronic effects of these compounds are carcinogenesis, neurotoxicity, effects on reproduction and cell development effects. Much of this concern has prompted research into the environmental behaviour and fate of pesticides and their potential for contamination the hydrologic system, including surface waters.

Research underlying the fate and transport of chemicals in the environment allows the more efficient selection and application of pesticides. An understanding of the fate of pesticides also is essential for rational decision-taking regarding their authorization. Moreover, information about the possible degradation pathways in aquatic natural systems is important in order to know how long these compounds persist in the environment.

There are two groups of processes controlling the fate of pesticides: transformation and phase transfer. Important transformation processes, which remove the parent pesticides from the environment, include hydrolysis, photolysis, and biodegradation. Phase-transfer processes include the transfer from the dissolved phase to the vapour phase (i.e., volatilization) and transfer from the dissolved phase to the particulate phase (i.e., sorption), with possible subsequent deposition to the bed sediments.

Monitoring of pesticides residues in water bodies is costly and time consuming. A previous thesis devoted to monitoring pesticides in the surface waters of the Camargue (Comoretto, 2009) gave a detailed picture of the spatial and temporal distribution of various pesticides, but yielded little insight into their behaviour and fate. Alternatively, modelling is considered unavoidable to understand the fate and behaviour of pesticides. MASAS (Modelling of Anthropogenic Substances in Aquatic Systems), is an useful software for this objective as it links the fundamental chemical properties of the herbicides in question to the characterizations of the aquatic environment.

This thesis will focus on the fate of water soluble rice herbicides in non- target compartments (surface waters) such as irrigation/drainage canals (Fumemorte Canal) and surrounding water bodies (Vaccarès lagoon). Accordingly, the processes that control herbicides behaviour and fate are those processes that are specific to surface waters. In this context, the main objectives of this study were:

- Characterizing the photochemical reactivity represented by hydroxyl radical, singlet oxygen and dissolved organic matter triplet state with pesticides in estuarine surface waters.

- Elucidating the photochemical and biodegradation processes occurring in the surface waters of Camargue and determining how they influence the degradation of rice herbicides.

- Modelling the fate and transfer of herbicides in the aquatic environment of the Camargue

Chapter 2: Literature review

2.1. The Camargue

Located in the Mediterranean, Camargue is Western Europe's largest river delta. A rough triangle, whose base is formed by 80 km of sandy sea coast running east-west, extends over an area of 145.300 hectares between the two gulfs of Aigues-Mortes in the west and Fos in the east. The Camargue is bounded on the north at Arles, where the Rhône river divides into two branches: the Grand Rhône and the Petit Rhône. These two arms divide the Camargue into three sectors.

- The western sector "Petite Camargue", known also as La Camargue Gardoise, extends west of the Petit Rhône to the Canal du Rhône à Sète.
- The central sector "Grande Camargue", at the mouth of the Rhône. The Grande Camargue is actually an island and known as the "Île de la Camargue".
- The plain of the Camargue on the east of the Grand Rhône.

Our work will focus on the Île de la Camargue where the aquatic ecosystem around a shallow, coastal lagoon (Vaccarès lagoon) is the largest coastal wetland of Western Europe (Roche et al., 2002). It is internationally recognized as a biosphere reserve within the framework of the UNESCO’s Man and the Biosphere (MAB) Programme. A central area of this wetland is the Reserve the Camargue, an area covering 13.000 ha protected in the framework of French Regional Nature Parks (http://www.reserve-camargue.org/). The Ile de Camargue bears an exceptional biological diversity and is a home of a wide variety of aquatic organisms. Also it is regarded to be among the most important wintering and breeding sites for water birds in Europe (Health and Evans, 2000).

The Rhône delta can be divided into 6 hydrological units (Fig. 1): Camargue major, Roquemaure, Fumemorte, Japon, Saintes Maries and Sigoulette. The north and south east of the delta (Camargue major and Japon) are devoted to intensive flooded rice cultivation. In this zone (310 km^2), irrigation water is pumped from the Rhône river and drainage water is returned to the river (SD 1) or directly to the salt works (SD 2) by pumping. Tourism activities (Saintes-Maries and Sigoulette) prevail in the western part of the delta. The eastern section of the delta (see Fig. 1) naturally drains into the Vaccarès lagoon by low slope ditches, mainly the Fumemorte and the Roquemaure ditches (see arrows in Fig. 1). In this zone (87 km2) agriculture is mainly flooded rice cultivation plus cattle breeding. Sea/lagoons exchanges occur at the “Grau de la Fourcade”.

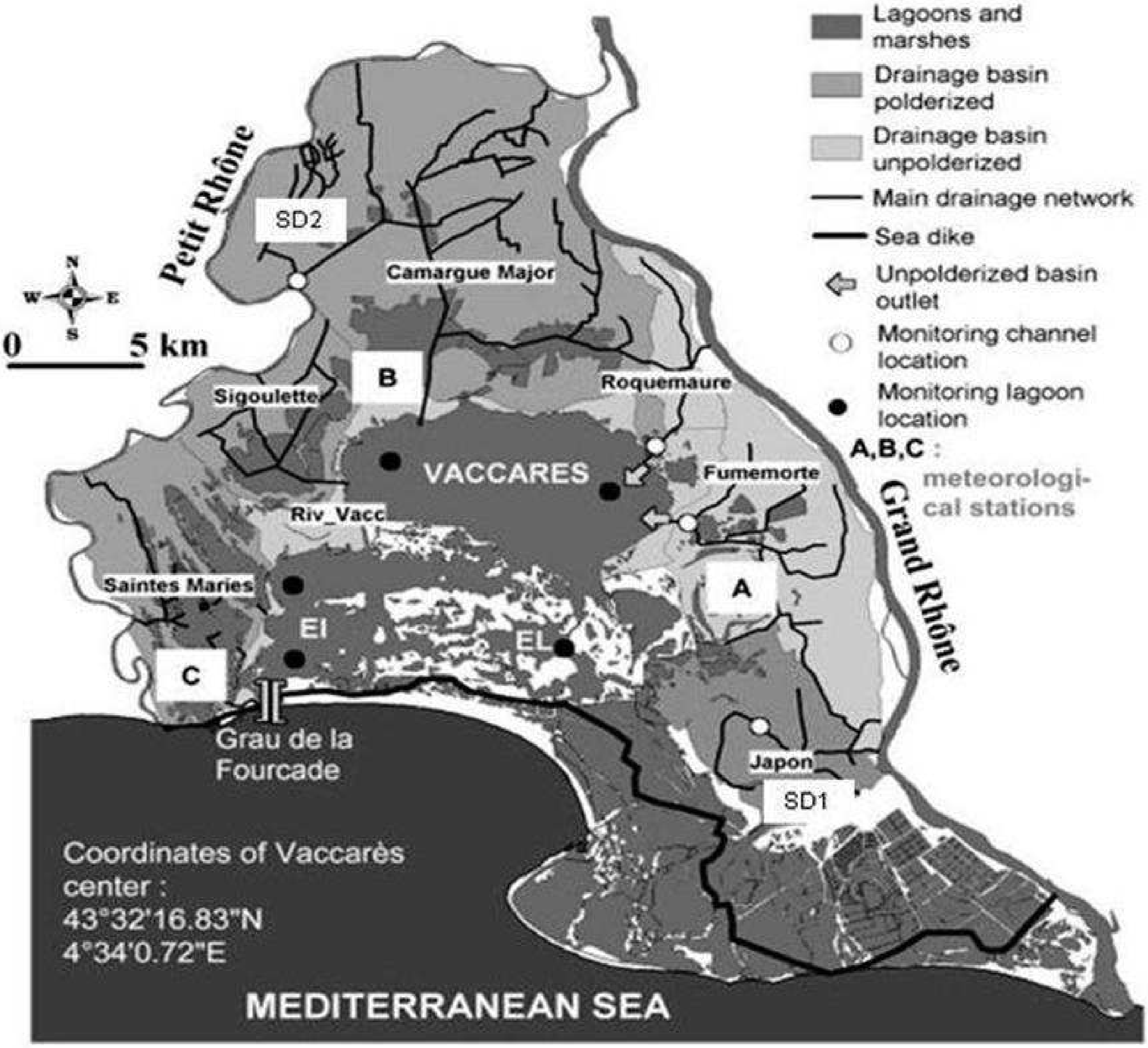

Figure 1. Rhône delta (Camargue) and sampling sites, Vaccarès lagoon and Fumemorte Canal.

The permanent surface waters in the Reserve de Camargue (10800 ha when their water level is at sea level) can be divided into two sub-systems: the Vaccarès lagoon and two lower lagoons. The lower lagoons which are separated from the Mediterranean Sea by a dike can be divided into two sub units: “Etang de l'Impérial” and “Etang du Lion” (EI and EL in Fig.1). Only the Impérial lagoon is directly connected to the Mediterranean Sea by a sluice gate at “la Grau de la Fourcade” where flow is controlled by mankind.

2.2 Rice Cultivation in Camargue

It is quite certain that rice has been introduced in the European countries during the early period of Arab domination of southern European regions, at first in the Seville area (Spain) in the eighth century and later in Sicily (Italy) and Camargue in France (Ferrero and Vidotto 2008). The harvested area in France fluctuated between 32’000 ha in 1961 and 5’000 ha in 1980; it has now stabilised around 21’000 ha for the last few years, see figure 2, (Centre Français du Riz, 2010). Therefore, France is not considered as top rice producer in Europe as Italy and Spain have higher productions which together contribute more than 80% of the total rice production in Europe (Ferrero and Vidotto 2008).

The Camargue is the main area of rice production in France and represents 98% of French rice production. The harvest in Camarage was about 126’600 tonnes in 2009 for an area of 21’100 ha with average yield of 6 t/ha (Figure 3, Centre Français du Riz, 2010).

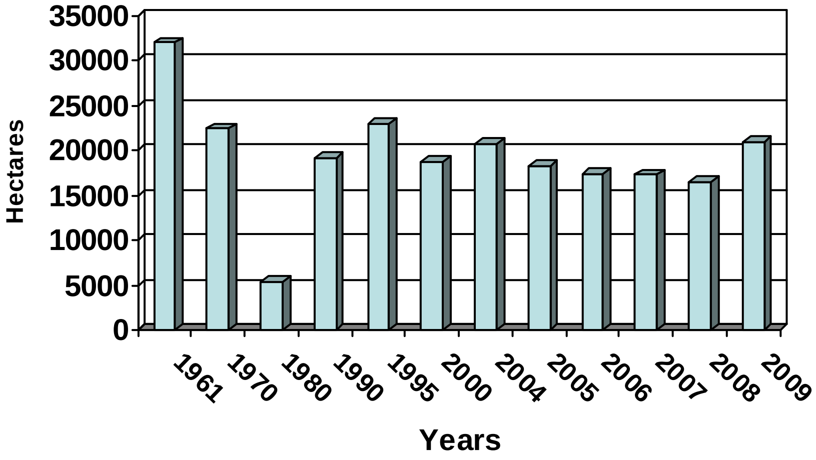

Figure 2. Evolution of the harvested area of rice paddy in France (Centre Français du Riz, 2010).

Rice has particularly strong ecological, thermal and hydrological requirements. In Camargue, rice is grown under irrigation with only one cultivation per year. Rice is directly seeded in soil from April to May and harvested in October. After seeding, the soils are flooded by water taken from the Rhône river, and the water is maintained in a layer ranging from 5 to 10 cm (Figure 4). The water is permanently renewed, with residences times in the fields of 9-18 days (Comoretto et al, 2008).

The Camargue area is characterized by a high solar radiation, and average temperature 10-12ºC during rice germination and from 20–25ºC during crop flowering. This climate is favourable for high photosynthetic rates and high rice yields. The Camargue area is frequently swept by the mistral (strong north wind).

The salinity and nature of the soils are factors which influence the utilisation of the delta land for agricultural purposes. Salt concentrations are high across much of the delta, especially in the low-lying lands, where the preference is given to crops whose method of cultivation has a desalinating effect which makes rice the dominant crop (www.parc-camargue.fr). The alluvial soil is silty in the east and sandy in the west. These soils are rich in calcareous material (15–45%), thus having pH values ranging from 7.5 to 8.5 (Audebert and Mendez del Vilar, 2007).

Most of the irrigation water for rice fields in Camargue originates from the Rhône River which provides the necessary fresh water for rice cultivation. A network of canals has been built for carrying river water. These canals deliver water to the rice fields while other canals allow for correct draining. However, the residence time of water in rice fields is short from 9 to 18 days (Comoretto, 2008). In the eastern part of the Ile de Camargue and around the Vaccarès lagoon, the runoff of rice paddies is directly discharged to the lagoon system, whereas in the northern and south-eastern parts, the runoff of agricultural areas (including rice paddies) is primarily returned to the Rhône River and discharged to the Mediterranean sea (Chauvelon et al., 2003).

2.3 Constraints to sustainable rice production in Camargue

The constraints in irrigation ecosystems include losses from weeds, insects and diseases. Pesticides in their different forms (herbicides, insecticides, fungicides, etc.) are therefore very important for rice production. It has been estimated that without herbicides for weed control, the yield loss can be as high as about 90% (Oerke *et al.*, 1994). Herbicides account for more than 80% of the total consumption of pesticides utilized for crop protection, with a total spending of about 787 million of Euros in France during 2006-2007 and 872 million of Euros in 2007-2008 (UIPP, 2009).

Rice management practices in Camargue have been developed during the last 60 years. The introduction of pre-emergence herbicides in mid 1965 made rice cultivation shift from transplanting to direct seeding. However, the yield was somewhat stable about 3-4 t/ha, until using laser equipments to level off the fields slope and using new herbicides as well. Those factors increased the yield by 40 % form 1980 to 1990 (Carlin et al., 2004). See figure 3.

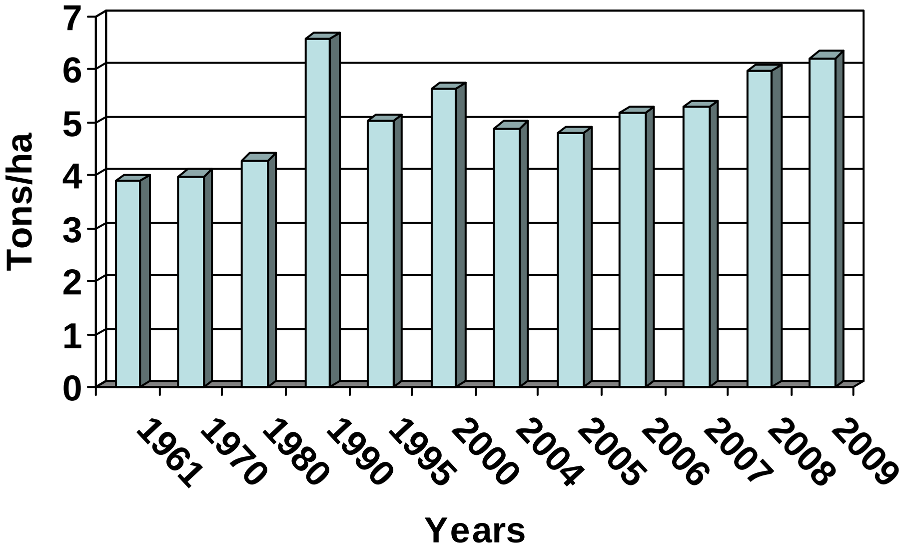

Figure.3. France rice paddy yield per hectare (Centre Français du Riz, 2010).

Rice fields constitute a favourable environment to growth and development of weeds particularly aquatic species. In European rice fields, weeds such as *Echinochloa* species, *Alisma* species are considered the most noxious organisms affecting rice production. The *Echinochloa* species are primarily controlled with various foliar post-emergence herbicides. Of sixty species of weeds in Camargue, about twenty species consider a major problem in rice fields. Some of them are reported below.

–*Echinochloa* species:	*E. crus-galli, E. oryzoides.*
– *Heteranthera* species:	*H. reniformis , H.reniformis – fleur, H. limosa*
–Weedy rice:	*Oryza sativa*
– *Alisma* species	

Weed management constitutes a strong constraint, as the availability of allowed herbicides is more and more limited and there are several consequences. Repeated applications of the same herbicides can cause the development of weeds resistant to those herbicides. Centre Française de Riz (CFR) reported that, in 2009, the control of *Echinochloa* and the *Cypéracéeses* by the inhibitors of the ALS enzyme such as Azimsulfuron and Bensulfuron-methyl, was insufficient or even has no efficacy. These herbicides inhibite the acetolactate synthase (ALS), which is a key enzyme in the biosynthesis of branched amino-acids (valine, leucine, and isoleucine, Vulliet et al., 2004). Further bad news is the evolution of new weeds, which had not been reported before in Camargue, such as *Leptochloa*, recently found in several rice fields.

At the end of 2009, the weed control was based on two systematic applications, and sometimes three applications.

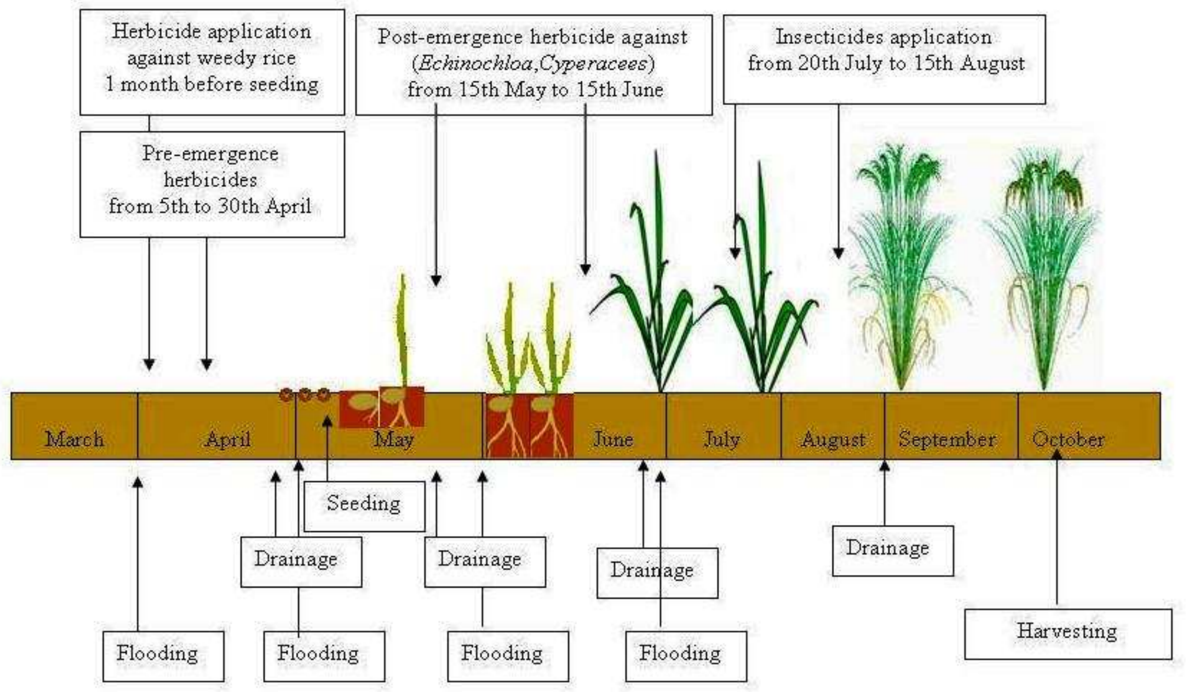

Figure 4. Water management in Camargue rice fields and rice pesticide applications. Recommendations by the Centre Français du Riz, 2009.

2.4 Herbicides and rice weed management

The concentration and persistence of herbicides in the environment depend on several factors including crop and soil type and application rate and the physicochemical properties of the compound. According to their application time, herbicides could be described by pre and post emergence (Fig. 5). Pre-emergence herbicides are used to prevent the germination of weed seeds. These herbicides control weeds by inhibiting cell division in the young root system. The failure to develop a root system results in the death of the young seedling weed shortly after germination. In contrast, post-emergence herbicides work by destroying already established weeds. As weed germinations occur over long period, pre-emergence herbicides are applied to soil and are designed to bind to upper soil components and to have long residence times caused by significant partitioning constants to soil (log K_{ow} values range from 0 to 4). While post-emergence herbicides are plant (crop or weed) applications, and their partitioning constants between soil and water are lower (log K_{ow} values between -2 to 2, figure 5, Coleman et al., 2002).

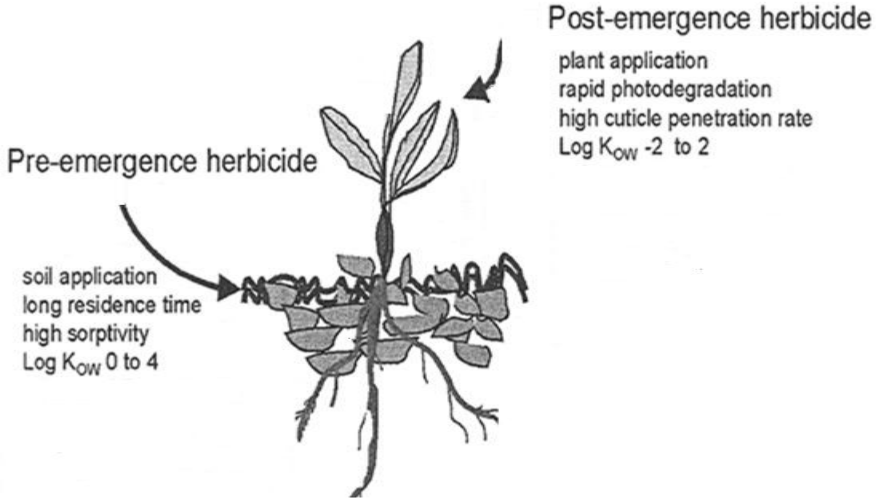

Figure 5. Type of herbicides (pre and post emergence) and some differential properties. From Coleman et al., (2002)

2.5 Herbicide application in Camargue

Pre-emergence herbicides (oxadiazon, molinate, pretilachlor) are applied before rice seeding and up to three weeks after seeding. Post-emergence herbicides (bensulfuron-methyl, propanil, cyhalofop-butyl, azimsulfuron, bentazone, MCPA and dichlorprop) are sprayed from mid-May to mid-June. Insecticides (tebufenozide and alpha-cypermethrin) are used in late July or in early August according to forecast and occurrence of insects, Table 1, Figure 4.

Management of weedy rice (termed "crodo")

The control of weedy rice (so-called crodo) is based on anticipated preparation and flooding of the soil (March-April), permitting to stimulate the germination of the rice crodo, followed by application of pre-emergence herbicide (Oxadiazon). Rice seeding takes place three to four weeks after herbicide application, Figure 4.

Table 1: Applied Pesticides in rice fields in Camargue 2003&2004&2005 and application rate according to CFR recommendation

Pesticides			**Rate of application g a.i./ha ***	**Date of application**
Name	**Active substance**			
SOFIT	Pretilachlore	Herbicide	1000	From April 5 to 30
RONSTAR	Oxadiazon	Herbicide	500	From April 5 to 30
ORDRAM	Molinate	Herbicide	4500	From 15 May to 15 June
-	Propanil	Herbicide	3600	From May 15 to June 15
GULLIVER	Azimsulfuron	Herbicide	25	From May 15 to June 15

-	Cyhalofop-butyl	Herbicide	300	From May 15 to June 15
LONDAX	Bensulfuron-methyl	Herbicide	60	From May 15 to June 15
ASGARAN	Bentazone	Herbicide	1914	From May 15 to June 15
CALLIO M400	2,4 MCPA	Herbicide	1200	From May 15 to June 15
-	Dichlorprop	Herbicide	700	From May 15 to June 15
-	Tébufénozide	Insecticide	144	From July 20 to August 15
-	Alphamethryne	Insecticide	15	From July 20 to August 15

* a.i: active ingredient

2.6 Pesticides detected in Camargue:

The requirement for large amounts of irrigation water used for rice cultivation increases the potential for contamination of the receiving surface water bodies with pesticides by runoff or controlled drainage (Boesten and Van der Linden 1991). Various studies related to Vaccarès Lagoon, demonstrated that this ecosystem is exposed to a wide range of organic chemicals such as pesticides, agricultural inputs, industrial products and hydrocarbons (Oliveira Ribeiro et al., 2005; Roche et al., 2000, 2002a,b).

These chemicals represent a potential risk for non-target organisms including humans. A monitoring study in the Ile de Camargue targeting currently used pesticides and their degradation products revealed that numerous pesticides were detected in the lagoons. Among the pesticides detected, rice herbicides constitute the major group of pesticides (90% of the detection rates) while the pesticides transported by the Rhône river water dissolved phase only accounted for 10% (Comoretto et al., 2007). The herbicides pretilachlor, oxadiazon, MCPA and bentazone were found at the highest frequencies into the effluent waters of ditches with maximum concentration levels of 1.2, 0.8, 2.5 and 1.6 µg/L, respectively (Comoretto et al., 2007). There were two main peaks of contamination. The first one in April corresponded to the use of pre-emergence herbicides (oxadiazon and pretilachlor) and the second one in June was related to the post-emergence herbicides (MCPA and bentazone). These concentration peaks were well correlated with the application period time and rapid pesticide transfers (1–2 weeks) from fields to lagoons were observed (Comoretto et al., 2007, 2008).

A recent biomonitoring study conducted in irrigation and drainage channels, which drained water from the Rhone river to rice fields, using the Asian clam, *Corbicula fluminea*, as bioindicator showed that many lipophilic chemicals were identified in *Corbicula* tissues, including pesticides used in rice fields (pretilachlor, oxadiazon), pesticides presumed in use in the Rhône basin [diuron and its metabolite 3,4 dichloroaniline (3,4-DCA)] and organochlorine pesticides (OCPs) banned for several decades. In addition, also polychlorinated biphenyls (PCBs) were highly bioaccumulated in *Corbicula* (Roche et al., 2009).

An earlier study by the same authors also reported that the draining ditches from the rice fields bring a number of persistent organic agrochemicals into the major water body of this natural reserve, the Vaccarès lagoon, especially organochlorine (OC) insecticides such as lindane (Roche et al. 2002a).

2.7 Importance of wetlands in pesticides attenuations

Though wetlands are valuable resources, there is relatively little information about environmental fate of pesticides in these systems. According to statistical calculations conducted using about 3000 scientific publications from 1973 to 2009, a total of 68% of the publications were devoted to the natural wetlands, but only 2% of them dealt with the fate of pesticides in artificial wetlands; Thereafter, the proportion of the publications concerning pesticides fate in both the artificial and natural increased and reached 8% (Gregoire et al., 2009). The fate and behaviour of the wide variety of contaminants that enters these systems are not fully understood, yet this knowledge is needed to comprehensively optimize and run these systems (Tack et al., 2007). Interest in the use of constructed and natural wetlands as a low cost and sustainable option for treatment of polluted water with organic pollutants such as pharmaceuticals (carbamazepine, ibuprofen and naproxen), caffeine, and pesticides (mecoprop, MCPA, atrazine, terbutylazine, chlorpyrifos and carbaryl) has significantly increased over the last decades (Miller and Chin, 2002; Sherrard et al., 2003; Tack et al., 2007; Matamoros et al 2008; Lin et al 2008; Vymazal 2009).

2.8 Fate and Behaviour of Pesticides in the Environment

Many processes are involved in the dissipation of pesticides in the environment. Once applied to a field, pesticides are distributed in the environment by phase-transfer processes. These processes are characterized by the pesticide molecule remaining intact. They include sorption and sedimentation, movement of the soil in runoff, movement into the air by volatilisation, movement downward in the soil by leaching. Transformation processes which change its chemical structure, include chemical or photochemical and biochemical processes mediated by microorganisms. Chemical processes generally occur in water, soil or the atmosphere and follow several reactions: oxidation, reduction, hydrolysis, and photolysis, figure 6. According to Allarad and Neilson (2008), the complementary roles of both abiotic and biotic degradation processes should always be taken into consideration. As abiotic reactions may be the first step in the degradation of an organic molecule, the transformation products may be resistant to further chemical transformation so that their ultimate fate is dependent upon subsequent microbial reactions.

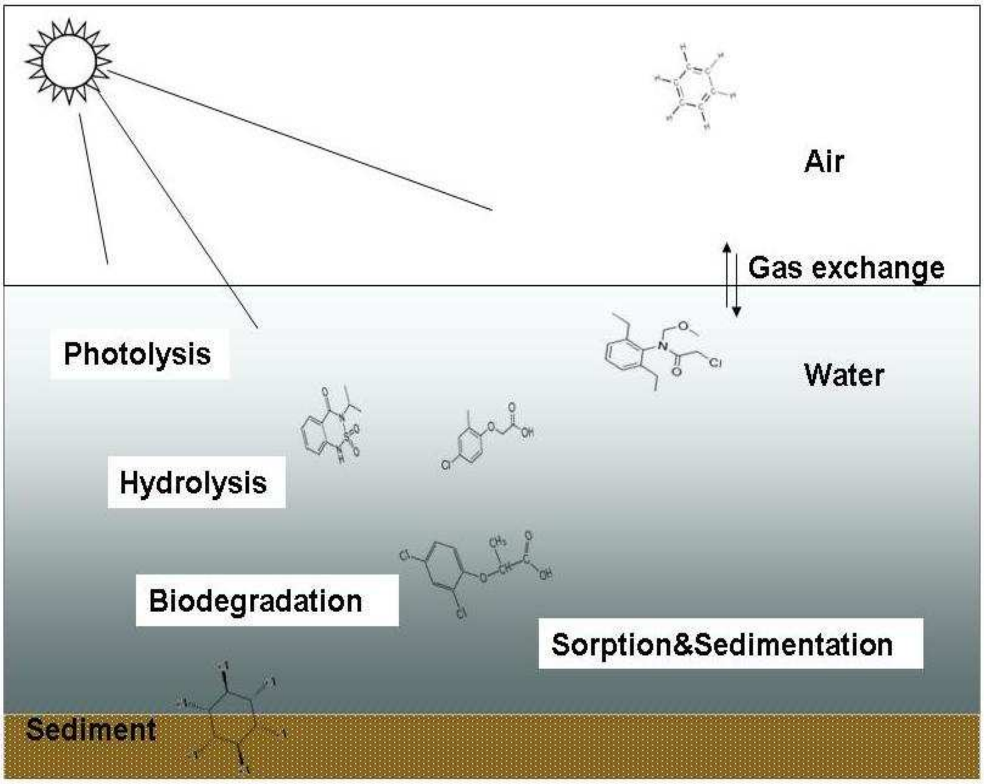

Figure 6. Elimination processes of pesticides in surface water

The fate and behaviour of pesticides in the environment depend on their chemical and physical properties and on the nature of the environment in which the pesticide is distributed. The main differences between behaviour of organic chemicals in the environment are attributable to their physical-chemical properties. The key properties are recognized as solubility in water, vapour pressure, Henry's low constant, the partition coefficients between air, water and soil organic matter, dissociation constant in water and susceptibility to degradation or transformation reactions. The partitioning coefficient between water and octanol is often used to estimate the similar partitioning coefficient between water and soil organic matter (Schwarzenbach et al, 2003). Below follows a summary of important equilibrium constants used for estimation the environmental fate and behaviour of chemicals ((Mackay et al., 2006; Dunnivant and Anders; 2006; Clark 1994).

-Solubility in water: Defines a chemical's water solubility, in presence of a pure phase (solid or liquid) at equilibrium. Chemicals that have high solubility will remain in water and tend to not be resorbed by the pure phase.

-Partition coefficients: Partition coefficient is an indicator of the environmental fate of a chemical since it gives a general idea of how a chemical will be distributed among different phases (gaseous, aqueous, and solid) in the environment.

- Octanol/water partition coefficient ($K_{ow)}$): is defined as the ratio of a chemical's concentration in octanol divided by its concentration in water. K_{ow} is generally expressed in (Log K_{ow}) and the values range from -3 to 7. K_{ow} is used in correlations to describe partitioning from water into lipids of fish and other organisms and into natural organic carbon such as humic material. It is also used to correlate toxicity data for a variety of chemicals. K_{ow} is an important description of chemical hydrophobicity or lipophilicity, as octanol is commonly used as a surrogate for lipids and organic matter in the environment.

-Sorption coefficient (K_d): is sediment-water or soil-water distribution coefficient. It shows how pollutants adsorb to a solid phase.

-Organic carbon-water partition coefficient (K_{oc}): is the key to the estimation of soil-water and sediment-water partition coefficients for many compounds. K_{OC} is then an important parameter to describe the potential for movement or mobility of pesticides in soil, sediment and groundwater.

-Vapor pressure: is defined as the pressure that a chemical in the gas phase exerts over its pure phase at a given temperature. Pesticides with high vapor pressures may become environmental problems because they can volatilize and disperse over a large area.

-**Henry's law constant (K_H)** is the ratio of the equilibrium vapour pressure to aqueous solubility of a substance at a given temperature. K_H is important in environmental chemistry, perhaps more important than vapour pressure, for estimating the volatilisation of pollutants from water. It used to describe the equilibrium partitioning of a pollutant between the gas and liquid phase. Due to frequent changes of units for pressure, its units are often poorly unified, and units of atm-L/mol, or Pa.m3/mol or others are encountered in literature.

2.9 Transformation processes

Photolysis

Photochemical reactions are important pathways of degradation of organic contaminants such as pesticides in surface waters. Photolytic transformations of pesticides are caused by the absorption the energy (Photons) from sunlight. The earth's atmosphere filters out light with wavelengths shorter than 290 nm; only wavelengths greater than this reach the earth's surface. Two basic types of reactions may occur. Pesticides can undergo direct reaction via absorption of solar radiation, which is referred to as direct photolysis causing a chemical transformation, such as cleavage of bonds, dimerization, oxidation, hydrolysis, or rearrangement (Zepp and Cline, 1977; Clark, 1994; Larson et al., 1997).

The importance of direct photolysis depends on the capacity of a pesticide to absorb light at wavelengths present in solar radiation above 290 nm. Since sunlight reaching the Earth’s surface contains only a very small amount (3-5%) of short wavelength UV radiation represented mainly by UV-A (315–400 nm) with varying amounts of UV-B (280–315 nm), the direct photodegradation of pesticides by sunlight is expected to be, in general, of only limited importance. In Figure 7, UV-Vis spectra of four herbicides found in the Camargue are shown, and one notes that only one compound, Bentazone, has a significant UV absorption. However, direct photolysis alone is sometimes efficient in defining the lifetime of many photolabile compounds in surface waters and yields a number of transformation intermediates rather than complete removal (Vione et al. 2005, Vione et al. 2010). Direct photolysis is also considered important for compounds that react relatively slowly (10^{-7} to 4×10^{-8} M^{-1} s^{-1}) with $HO^{\bullet}$, such as nitrophenols and those compounds containing multiple halogens or oxygen atoms and few hydrogen atoms (Haag and Yao, 1992, Litter, 2005).

The rate of direct photolysis is determined by light intensity and the extent of light absorption and reaction quantum yield of the molecule or quantum efficiency (Zepp and Cline, 1977) Schwarzenbach et al. (2003) defines reaction quantum yield as

$$\Phi = \frac{\text{Number of molecules transformed}}{\text{Number of photons absorbed by the system due to the presence of the molecule}}$$

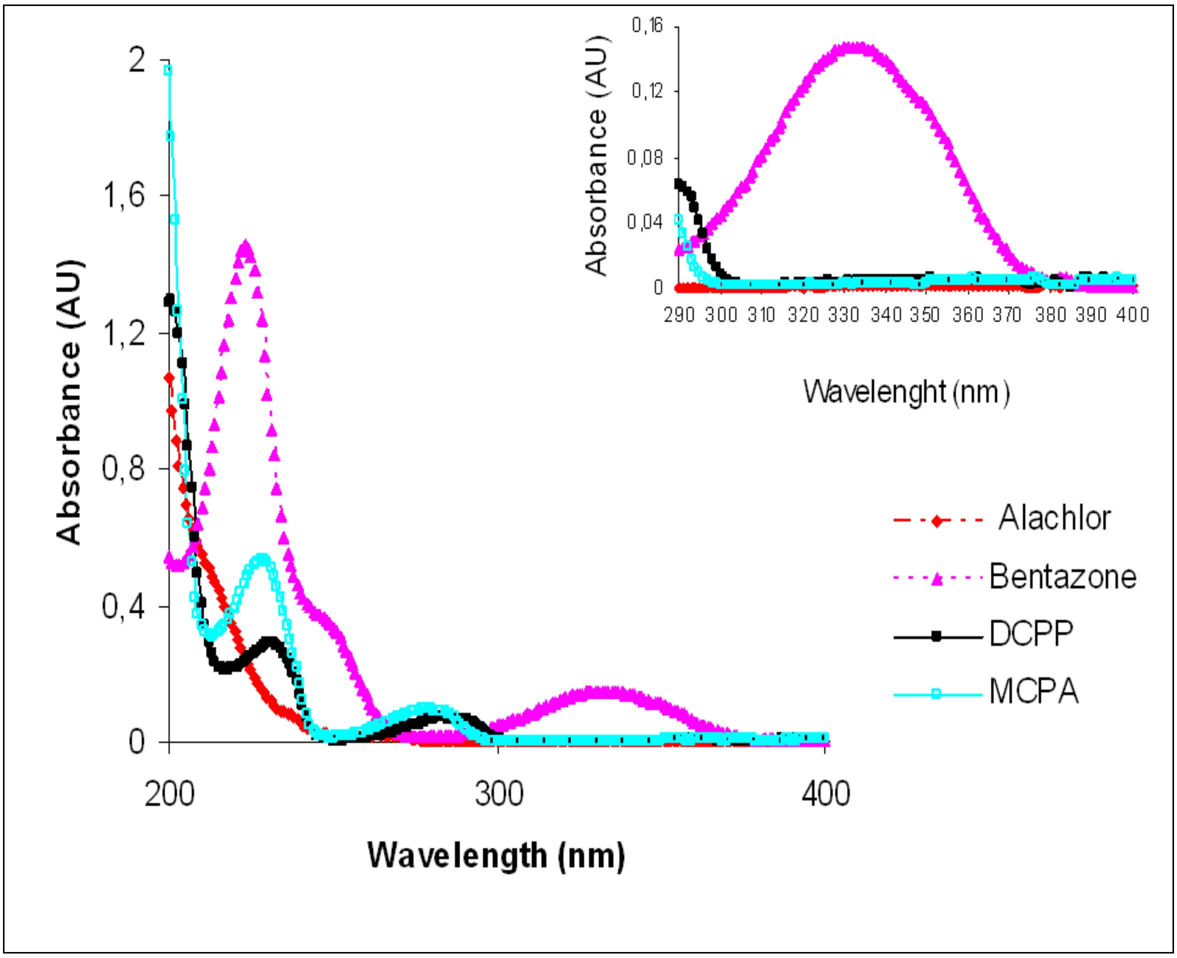

Figure 7. UV-Vis spectra for Alachlor, Bentazone, Dichlorprop (DCPP) and MCPA in pure water.

Alternatively, pesticides are subject to degradation by indirect photolysis. Indirect photolysis is usually a photoinduced oxidation reaction. Sunlight excites a photon absorber, such as nitrate, nitrite or colored dissolved organic matter (so- called chromophores, Fig 8), which in turn react with dissolved oxygen to form potential photoreactants such as singlet oxygen ($^1O_2$) (Haag and Hoingé,1986), hydroxyl radical ($HO^{\bullet}$) (Draper and Crosby, 1984), superoxide anion (O_2^-), peroxy radical ($ROO^{\cdot}$), and hydrogen peroxide (H_2O_2).

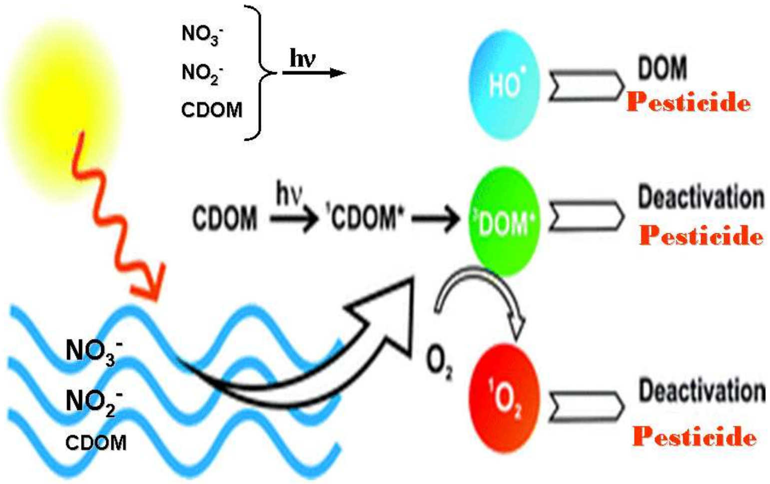

Figure 8: Indirect photolysis in aquatic environment and chromophores (nitrate, nitrite and colored dissolved organic matter, CDOM).

The occurrence of several reactive photooxidants and the calculation of their their steady-state concentrations has been reported previously by Hoigné (1990), Schwarzenbach (2003) and Vione et al. (2006).

These highly short-lived reactive species attack dissolved organic matter, dissolved oxygen, or pesticides, if present. Another type of indirect photolysis, triplet photosensitization (Zepp et al., 1985) occurs when a photon absorber, such as humic acid, transfers excess energy to a pesticide molecule, which then photodegrades. The efficiency of such reactions depends on the number of reactive species produced by excitation of the chromophores as well as on the ability of these species to react with the contaminant. Indirect phototransformations may be the dominant degradation processes in the case of contaminants that absorb terrestrial sunlight poorly or that are stable against direct photolysis. The type of photoinduced reaction is dependent on the structure of the pesticide and specific environmental conditions. (Richard and Canonica, 2005).

Significance of photolysis in rice fields

The clear and shallow water in wetlands filters very little of the incident light and allows both photochemical processes to occur within the water column and at the sediment-water interface. Wetlands are generally abundant in potential photosensitizers such as natural dissolved organic matter (DOM) and nitrate, which are capable of absorbing sunlight and catalyzing the transformation of organic compounds by indirect photochemical pathways. Indeed, wetland waters have been reported to have greater near-surface photoreactivity than other natural waters (Valentine and Zepp 1993). Miller and Chin (2002, 2005) reported the ability of wetland waters to promote the photoinduced degradation of agrochemicals (Alachlor, Carbaryl).

Hydrolysis

Hydrolysis is an important abiotic degradation process for many pesticides in aquatic environments. Hydrolysis is the chemical (sometimes biologically mediated) reaction of a pesticide with water, usually resulting in the loss of a lateral functional chain and in the formation of new C-OH or C-H bonds. Consequently, the parent compound, in hydrolysis reaction, is transformed into more polar products that have quite different properties. Therefore, the products have different environmental behaviours than the starting chemical (Schwarzenbach et al., 2003). Hydrolysis reactions can be a result of direct attack by the water molecule (H_2O), the hydronium ion (H_3O^+), or the hydroxide ion (OH^-). These are termed neutral, acid, and base hydrolysis, respectively (Larson et al., 1997). However, at the pH values around neutrality that is typical of surface waters neutral hydrolysis is dominant (Vione et al., 2010).

The hydrolysis of pesticides in aquatic environment obeys pseudo-first-order kinetics (neutral hydrolysis), and second –order kinetics for acid and base catalized hydrolysis (Scharzenbach et al., 2003). The observed hydrolysis rate of a certain chemical compound A therefore, (k_{obs}) can be expressed by overall rate of hydrolysis as shown in (eq. I) (Jørgensen and Bendoricchio 2001; Katagi, 2002).

$$d[A]/dt = k_H \times [A] = k_A [H^+] [A] + k_B [OH^-][A] + k_N [H_2O][A]$$

where k_H is a pseudo first-order rate constant at a given pH, while k_A and k_B are second-order rate constants, because the reaction depends on the concentration of two reactants, $[H^+]$ and

[A], or [OH^-] and [A], k_N is the second-order rate constant for neutral reaction of a chemical compound with water, which may be expressed as a pseudo first-order rate constant.

The hydrolysis rate is influenced by several factors. The strongest factor is pH. Some hydrolysis reactions work better in slightly basic or acidic environments. Temperature also is an important factor (Arrhénius law) where the rate constant k of chemical reactions depends on of the temperature T and activation energy E_a as shown below:

$$k=A\, e^{-Ea/RT}$$

A chemical's reactivity is the most important factor determining whether hydrolysis will occur. This reactivity is largely determined by the substituent bonded to the main body of pesticide (Clark, 1994). The common pollutant chemicals are likely to undergo hydrolysis includes the alkyl halides, where in this reaction an alkyl halide has been converted to an alcohol, the halogen has been released as a negatively charged halide ion ((Eq. (I)). Other compounds that may undergo hydrolysis include esters and ester analogues (Hemond and Fechner 2000). Hydrolysis converts esters into the "parent" organic acid and an alcohol ((Eq. (II)).

$$H_2O + R\text{–}X \rightarrow R\text{–}OH + H^+ + X^- \qquad \text{(Eq. I)}$$

$$H_2O + R_1COOR_2 \rightarrow R_1\text{-}COOH + R_2\text{-}OH \qquad \text{(Eq. II)}$$

Biodegradation

Biodegradation is the general term for biologically mediated reactions as either direct or cometabolic. It is believed that degradation by microbes (bacteria, fungi, algae) accounts for over 90% of all degradation reactions in the environment and is the nearly exclusive breakdown pathway in most surface soils, near plant root zones (micorrhyzae), and in nutrient-rich waters (Alexander,1981).

Catabolic microbial reactions transform pesticides in a series of enzyme-catalyzed reactions, predominantly oxidations or reductions, which convert organic compounds into energy and carbon to sustain microbial growth. In a typical catabolic redox reaction, an organic carbon compound serves as an electron donor that microbes use as a food source. The transfer of an electron from the donor to an electron acceptor proceeds through multiple reaction steps that generate energy, carbon and other elements, for microbial cell growth (Weiner, 2008). A cometabolic reaction requires the presence of a second electron donor (carbon source) to serve as the source of energy because the microbial oxidations of organic substances of interest fail to support growth of the microorganism. Therefore the organic substance of interest enters into the process and is transformed though microorganisms derive no particular benefit from the degradation of this compound (Larson et al., 1997, Rittmann and McCarty, 2001).

Biodegradation is a continuous process in aquatic environments (Pagga, 1997). Therefore, surface waters are good environments for pesticide breakdown, especially when micro-organisms are able to attach on surfaces, such as the sediment–water interface. However, in natural systems, the rate of microbial degradation of a pesticide will depend on type on chemical structure, and environmental conditions, and the microorganisms present. The environmental conditions such as temperature, nutrient supply, similarity of the compound to other food sources, pH, oxygen availability and salinity determine the species and viability of the microorganisms present (Larson et al., 1997; Warren et al., 2003). It is generally known that salts are detrimental to biological treatment systems including wetlands by causing plasmolysis and/or loss of cell activities, thereby lowering the system performance (Glenn, 1995).

2.10 Phase Transfer Processes

Phase-transfer processes involve the movement of a pesticide from one environmental matrix to another. The important processes that can occur in surface water environments include water-to-solid transfer (sorption), water-to-biota transfer (bioaccumulation), and water-to-air transfer (volatilisation from water). Although the physical movement of the chemical is involved, these transfer processes should not be confused with transport processes. Transfer processes are important on the scale of molecular distances. Once the organic chemical has passed through the environmental compartment boundary, it may undergo transport over much larger distances. The phase-transfer processes of sorption and volatilisation largely control the overall transport of many pesticides in surface waters (Larson et al., 1997).

Sorption and Sedimentation:

The process in which chemicals become associated with solid phases is generally referred to as sorption. It is adsorption if the molecules attach to a two-dimensional surface, while it is absorption if the molecules penetrate into a three-dimensional matrix (Hemond and Fechner 2000). Sorption could influence directly or indirectly the degradation of the pesticide as chemical reactivity of a sorbed pesticide is significantly different from that in solution. Since molecular transfer is necessary for the uptake of organic pollutants by organisms, the bioavailability of a given compound and thus its rate of biotransformation or its toxic effects are affected by sorption processes. Moreover, some sorbed molecules are substantially shaded from incident light; therefore, these molecules may not experience direct photolysis processes. Moreover, when present inside solid matrices, they may never come in contact with short-lived photooxidants like hydroxyl radicals (Schwarzenbach et al., 2003, Warren et al., 2003).

Smalling and Aelion (2004) reported that sorption of pesticides to suspended solids and to sediment organic carbon reduced the decay rates of pesticides in water systems. While another study demonstrated an inverse relationship between decay rates and the amount of organic matter (Warren et al., 2003). However, in some cases sorption accelerates the abiotic degradation rate (Ying and Williams, 2000).

Natural organic matter and sorption

Natural organic matter, present in soils, sediments, ground waters and surface waters, potentially acts as a sorbent and plays therefore an important role in the overall sorption of many organic chemicals. Natural organic matter is somewhat polar in that it contains numerous oxygen-containing functional groups including carboxy-, phenoxy-, hydroxy-, and carbonyl-substituents (Schwarzenbach et al., 2003).

Sorption of many hydrophobic chemicals (sorbate) is often described by a constant normalized for the organic carbon content (K_{oc}, Warren et al., 2003). Accordingly, the organic carbon–water partitioning coefficient could be estimated by (Eq I, II)). K_{oc} is the preferred value for determining a soil's ability to adsorb, than K_d (sorption coefficient), since it considers the organic content of the soil.

$$Koc = \frac{\text{chemical concentration sorbed to organic carbon (mg/g)}}{\text{chemical concentration in water (mg/ml)}} \qquad \text{(Eq. I)).}$$

$$Koc = \frac{\text{Kd} \times 100}{\text{\% organic carbon}} \qquad \text{(Eq. II))}$$

Correlations have been developed for several partition coefficients for neutral organic chemicals as a function of chemical properties such as solubility in water, K_{ow} and vapour pressure. Noteworthy is the use of K_{ow} to estimate K_{oc} the organic carbon partition coefficient. Table 2 shows some correlations for different chemical classes.

Table 2. Equations to estimate K_{oc} from K_{ow}, (Hemond and Fechner 2000).

Equation	**Correlation(r^2)**	**Chemical classes represented**
$\log K_{oc} = 0.544 \log K_{ow} + 1.377$	0.74^a	Wide variety, mostly pesticides
$\log K_{oc} = 1.029 \log K_{ow} - 0.18$	0.91^a	Variety (insecticides, herbicides, fungicides)
$\log K_{oc} = 0.524 \log K_{ow} + 0.855$	0.84^a	Substituted phenylureas and alkyl-phenylcarbamates

The sorption behaviour of pesticides is determined by the complex interrelationship between the physiochemical properties of the pesticides involved and environmental conditions under which sorption to natural organic matter (NOM) occurs. Sorption of weak acids and bases are generally affected by pH. For example, MCPA exist as charged species at pH values approximately >3.7. Acidic pesticides are proton donors, which at high pH one or more pH unit above the p*Ka* of the acid, become anions due to dissociation. And at ambient pH values, natural organic matter (NOM) tends to exhibit predominantly negatively charged adsorption surfaces primarily due to the presence of carboxylic acid groups. Therefore, NOM primarily acts as a cation exchanger. This means that negatively charged organic compounds will sorb more weakly to NOM than their neutral counterparts.

Volatilisation:

Pesticides can be transferred from the dissolved aqueous phase to the vapor phase in the atmosphere as a result of volatilisation from water. This transfer is controlled by the pesticide's molecular diffusion coefficients in air and water, and its Henry's Law constant. Thomas (1990) has suggested that the importance of volatilisation for a given chemical can be generalized from its Henry's Law constant alone. For pesticides that have a Henry's Law constant less than 3×10^{-7} atm-m^3/mole, volatilisation from surface water is unimportant. For pesticides that have a Henry's Law constant greater than 10^{-5} atm-m^3/mole volatilisation is significant for all waters (Larson et al., 1997).

2.11 Studied Herbicides and their Physicochemical Properties

Polar acidic herbicides such as bentazone and phenoxy acides (MCPA, dichlorprop) are an important class of pesticides and used in the control of a wide variety of weed in many crops. They are largely used in rice farming in the Camargue. Bentazone has the potential to contaminate surface water because of both its mobility in runoff water from treated crops, and its pattern of use on rice, which involves either direct application to water, or application to fields prior to flooding. Alachlor is considered to be a model molecule for examining indirect photolysis due to its lack of reactivity by either direct photolysis or dark reaction pathways (Miller and Chin, 2005). Alachlor and pretilachlor both belong to the chloroacetanilide class of herbicides differing only in a propyl group instead of a methyl group on the ether side of the molecule. Pretilachlor has been used extensively in paddy fields in the Camargue. The substitution of alkoxyalkyl can influence the reactivity and the mechanism of the reaction of hydrolysis significantly, (Carlson et al, 2006). Consequently, Pretilachlor is more persistent than Alachlor.

For the reasons explained above, four herbicides (alachlor, bentazone, MCPA and dichlorprop) were chosen for this study.

All physicochemical properties of the studied herbicides (Table 3) were obtained from the FOOTPRINT database (eu-footprint, 2009) and the handbook of Mackay et al. (2006), unless otherwise indicated. The FOOTPRINT database contains reviewed data on about 800 pesticides.

Alachlor

Alachlor, 2-chloro-N-(2, 6-diethylphenyl)-N-(methoxymethyl) acetanilide, is a selective pre-emergence herbicide **Fig. 9** of the chloroacetanilide family and has been used widely since 1969 for weed control of annual grasses and broad-leaved weeds in different crops such as corn, cotton, peanuts, peas, sunflower, and soybeans, (Chesters et al., 1989). Several studies of the environmental biotic and a biotic degradation have been reported.

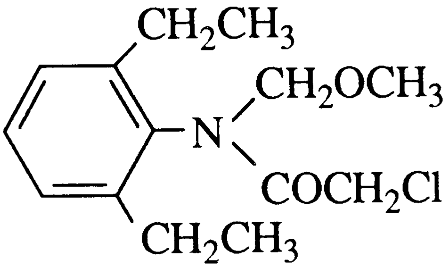

Figure 9: Chemical structure of Alachlor

Mode of action and selectivity

Alachlor is a growth inhibitor affecting root elongation due to THE inhibition of cell division. Chloroacetanilides herbicides influence the biochemical and physiological processes include protein and lipid synthesis, respiration and photosynthesis. The selective phytotoxicity of alachlor is based on the lack of metabolic deactivation in susceptible plants (Chesters et al.,1989).

Environmental Fate, Rate Constants(k), and Half-Lives of Alachlor

Alachlor is highly mobile and moderately persistent. These two characteristics are generally observed in chemicals that reach ground water and surface water. The major dissipation routes for the chemical appear to be microbially mediated degradation and leaching. Alachlor is stable to abiotic processes (hydrolysis, photolysis in aqueous media). Volatilisation is not a significant cause of losses due to its value of vapour pressure which is relatively low, (Reregistration Eligibility Decision, 1998; Carlson et al, 2006). Earlier studies have shown that alachlor disappears through various mechanisms, including biotransformation, photochemical decay (Chesters 1989). However, it was suggested that biotransformation may be central to alachlor fate in most aerobic systems (Novick and Alexander, 1985; Graham et al., 2000). Ramesh and Maheswari (2004) found that $t_{1/2}$ values calculated for alachlor dissipation in model ecosystem in water were 3.3 and 3.4 days in India.

Biodegradation

The reported half- life of Alachlor biodegradation in surface water: $t_{1/2}$ = 23 d for 0.244 µg/mL in river water at 23°C with biodegradation rate $k_{biodeg.}$ = 0.030 d^{-1}(Mackay et al., 2006)

Novick & Alexander (1985) reported that biodegradation $t_{1/2}$ > 6 weeks for 0.01–1.0 µg /mL in sewage effluent lake water at 28°C, where microorganisms converted 18-21% of alachlor to four to six subproducts by cometabolism.

Galassi et al (1996) found that alachlor is rather persistent since its biodegradation is lower than 50 % after 28 d of incubation in river water. Field experiments using mesocosms reported that half lives ranged from 16 to 122 days with the highest rate in hypereutrophic waters (Knapp et al., 2003).

Most degradation studies in soils indicate that alachlor disappears relatively rapidly. The $t_{1/2}$ under aerobic conditions is, generally under 30 days and in most field studies, 4-24 days. Biodegradation via co-metabolism is the most important process by which alachlor is lost from most soils and surface waters (Galassi et al., 1996)

Photolysis:

Alachlor showed high stability in deionized water when exposed to natural sunlight irradiation for a period of 5 days (Gustavo and Damià, 1996). Another study reported half-lives at the surface water of 2.3-25 days in summer midday sunlight (40°N), assuming an 8-h irradiation period (Miller and Chin 2005). Chiron and co-workers (1995) found that the alachlor analytical grade was depleted within 10 h upon irradiation with a xenon arc lamp in distilled water.

Indirect photolysis:

Miller and Ping Chin (2005) found that indirect photolysis is an important process of alachlor degradation in natural wetlands. A calculated rate constant k_{OH} for reaction with hydroxyl radical is 7×10^{9} M^{-1} s^{-1} (Haag and Yao, 1992).

Hydrolysis

It was reported that $t_{1/2}$ of alachlor is 0.5 day at 20^{o}C and pH 7 (Eu-footprint, 2009), which is different from values reported by Carlson and co-workers (2006); $t_{1/2}$ 19, 20 and 22 days at pH 5, 7 and 8, respectively.

The rate of acid- and base-catalyzed hydrolysis was reported by Carlson and co-workers (2006).

k_{obs} (2 - 4) $\times10^{-10}$ s^{-1} and 0, 2.45 $\times10^{-6}$ s^{-1} (1.96 N HCl, 25 °C), respectively.

k_{obs} 2.22 $\times10^{-5}$ s^{-1} and 2.95 $\times10^{-5}$ s^{-1} (1.96 N NaOH, 25 °C), respectively.

Unlike alachlor, little is known about the fate of pretilachlor. Vidotto and al, 2004 reported that the adsorption on the sediments considers the process involved in pretilachlor disappearance with half-life of 4.68-6.77 days in rice field water, and 15 - 28.76 days in sediment of rice field. The k_{oc} of pretilachlor is 628, compared to 124 for alachlor. Pretilachlor was reported, in eu.footprint.org, to be stable to hydrolysis at 20^{o}C and pH 7.

Bentazone

Bentazone (3-isopropyl-1H- 2,1,3-benzothiadiazin-4(3H)-one 2,2-dioxide), chemical structure shown in Fig. 10, is a post-emergence herbicide used in early spring to early summer for controlling weeds in corn fields, paddy fields, and orchards. Its selectivity is based on the ability of the crop plants to metabolize bentazone quickly to 6-OH- and 8-OH-bentazone and conjugate these with sugars, while weeds do not, so that photosynthesis is disrupted and the weeds die (Huber and Otto, 1994).

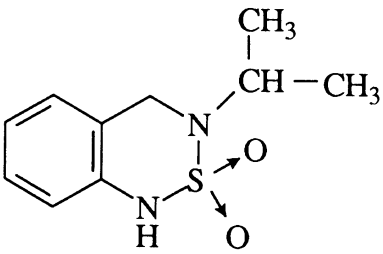

Figure 10: Chemical structure of bentazone

Most of the available reports state that bentazone exhibits little sorption in soil and has a relatively high mobility (Li et al., 2003). Bentazone appears to be stable to hydrolytic degradation at pH 5, 7 and 9 at 25°C (eu-footprint, 2009). Bentazone, however, has the potential to be degraded rapidly by photolytic degradation in water at pH 7 with half life ranged from 2.6 to 3.8 days because it absorbs light above 290 nm (Fig. 4). A similar value (4 days) was also reported in (eu-footprint, 2009) as half life time of bentazone photolysis in water at pH 7. Based on the fate studies reviewed, the reported half life time for biological degradation of bentazone in water is 161 days (European Commission report, 2000).

MCPA & Dichlorprop

Both chemicals are chlorophenoxyalkanoic acids, an important group of systemic herbicides. MCPA (4-chloro-o-tolyloxyacetic acid, Fig. 11) was introduced during the 1940s. It is a selective systemic post –emergence herbicide against broadleaf weeds absorbed by leaves and roots. MCPA is used to control annual and perennial weeds in cereals, rice, vines, peas, potatoes, asparagus, grassland and turf.

In the 1950s and 60s, dichlorprop 2-(2,4-dichlorophenoxy)propanoic acid (Fig. 12) was found to be more effective than the chlorophenoxyacetic acids. Dichlorprop is used as herbicide and growth regulator. It controls annual broadleaf and grass weeds and also to controls aquatic weeds.

Being anionic species at pH >3.7, they do not sorb to soil, they tend to be discharged to surface waters.

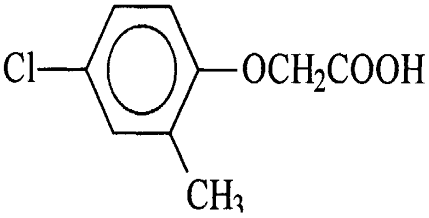

Figure 11: Chemical structure of MCPA

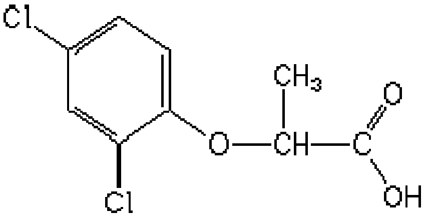

Figure 12: Chemical structure of dichlorprop

MCPA is highly water soluble and has a low affinity for most soil types, which gives it the potential to leach and contaminate groundwaters. MCPA undergoes microbial degradation in aerobic conditions; therefore, it is only slightly persistent in soil and water. Reported half life time dissipation is 4 days in rice field waters and 17 days in dilute aqueous solution under laboratory irradiation (Soderquist and Crosby 1975). ^{14}C-MCPA was stable to hydrolytic degradation at pH 5, 7 and 9 at 25°C for 30 days. The photodegradation half-life time of MCPA in water was reported to be 25.4 days (European commission, 2005).

Different rate constants for reaction with hydroxyl radical were reported. Mabury and Crosby (1996) calculated k_{OH} of 1.70×10^9 M^{-1} s^{-1} for reaction with hydroxyl radical, in irradiated field water both in the laboratory and sunlit rice paddies. Another study reported 2.21×10^{10} M^{-1} s^{-1} (Fdil et al. 2003).

Environmental Fate of dichlorprop

Available environmental fate data indicates that dichlorprop is non-persistent to moderately persistent. The primary routes of dissipation appear to be photodegradation in water, microbial-mediated degradation, ($t_{1/2}$ = 14 days) in aerobic terrestrial and aquatic environments, and leaching (RED, 2007). Dichlorprop is very persistent to hydrolysis hydrolyse at 20^{o}C and pH 7 (eu-footprint, 2009).

Table 3: Physicochemical Properties of the studied herbicides

Property	Alachlor	Bentazone	MCPA	Dichlorprop
CAS No.	15972-60-8	25057-89-0	94-74-6	120-36-5/7547-66-2
Molecular Formula	$C_{14}H_{20}ClNO_2$	$C_{10}H_{12}N_2O_3S$	$C_9H_9ClO_3$	$C_9H_8Cl_2O_3$
Molecular mass (g mol^{-1})	269.77	240.3	200.62	235.06
Water Solubility (25°C mg/L)	240	570	29390	350
Dissociation constant (pKa) at 25^{o}C	0.62	3.28	3.73	3
Vapor pressure at 25oC (mPa)	2.9	0.17	0.4	0.01
Henry's Law Constant (Pa.m3/mol at 25°C)	1.31×10^{-06}	7.20×10^{-05}	5.50×10^{-05}	8.8×10^{-06}
Octanol/Water Partition Coefficient (Log K_{OW})	3.09	0.35	-0.81	2.29
Sorption Partition Coefficient, K_{OC}:	124	51	74	170

Chapter 3: Photochemistry & Photoinduced Reactive Species

Several reactive species (Hydroxyl radical, singlet oxygen and chromophore organic matter triplet state, superoxide ion/hyproperoxyl radical ($O_2^{\bullet -}/HO_2^{\bullet}$), carbonate radicals ($^{\bullet}CO_3^{-}$) can be produced upon irradiation of photosensitizers such as DOM itself, nitrate, nitrite, and Fe(III) present in natural waters by sunlight (Draper and Crosby, 1984; Haag and Hoigné, 1986; Zepp et al., 1981; Richard and Canonica, 2005, Vione et al., 2009). They may be referred to as photo-oxidants because they induce oxidative transformations of natural water components and micropollutants. This Chapter will deal with the following photogenerated reactive species in aquatic environments: $HO^{\bullet}$, $^1O_2$, and $^3CDOM^*$.

3.1 Hydroxyl Radical

Hydroxyl radical $HO^{\bullet}$ is a potential oxidant and reacts at nearly diffusion-controlled rate with many organic compounds in water. It is known to be most reactive with electron-rich aromatic organic compounds due to its electrophilicity and nonselectiveness toward C-H bonds (Buxton et al., 1988; Zepp et al., 1985). Hydroxyl radicals ($HO^{\bullet}$) can be generated by several mechanisms in natural waters:

- Photolysis of nitrite and nitrate (Brezonik and Fulkerson-Brekken 1998; Vione et al., 2005; Richard and Canonica, 2005). Photolysis of nitrite and nitrate ions considers a relevant source of hydroxyl radicals in natural waters. Though nitrite is usually present in the environment at a lower concentration than nitrate, but its higher molar absorptivity and photolysis quantum yield can make it a competitive photoreactant under environmental conditions. The nitrite irradiated at 250–400 nm essentially results in the formation of $NO^{\bullet}$ and $O^{\bullet -}$ (Eq. 1), where the latter species can be protonated to form $HO^{\bullet}$ (Eq. 2). Nitrate considers as the key source of •OH in natural waters, and nitrate photochemistry results in two main pathways producing reactive hydroxyl radical and nitrogen dioxide (Eq. 3+4).

- Fenton reaction of H_2O_2 and Fe^{2+} (Eq. 5) is often cited as possible source of $OH^{\bullet}$ in sunlighted freshwaters (Zepp et al., 1992).

- Direct photolysis of dissolved organic matter (DOM) (Eq. 6+7).

$$NO_2^{-} + h\nu \rightarrow NO^{\bullet} + O^{\bullet -} \qquad \text{Eq. 1}$$

$$O^{\bullet -} + (H^{+}) \rightarrow HO^{\bullet} \qquad \text{Eq. 2}$$

$$NO_3^{-} + h\nu \rightarrow NO_2^{\bullet} + O^{\bullet -} \xrightarrow{H_2O} NO_2^{\bullet} + HO^{\bullet} + HO^{-} \qquad \text{Eq. 3}$$

$$NO_3^{-} + h\nu \rightarrow NO_2^{-} + O^{\bullet} \qquad \text{Eq. 4}$$

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + OH^{-} + {}^{\bullet}OH \qquad \text{Eq. 5}$$

$$CDOM + h\nu \rightarrow {}^{3}CDOM^{*} \qquad \text{Eq. 6}$$

$$^{3}CDOM^{*} + H_2O + h\nu \rightarrow CDOM\text{-}{}^{\bullet}H + {}^{\bullet}OH \qquad \text{Eq. 7}$$

- Photolysis of hydrogen peroxide (H_2O_2) is another potential source of $HO^{\bullet}$ (Buxton et al., 1988). Hydrogen peroxide is produced in significant concentrations in many natural waters from the disproportionation of superoxide anion ($O_2^{\bullet -}$). The latter results from reduction of molecular oxygen (O_2) by photoexcited dissolved organic matter (DOM) (O'Sullivan et al., 2005). However, the concentration of $O_2^{\bullet -}$ in sunlit surface waters is considered to be too low to induce appreciable transformations of organic contaminants (Richard and Canonica, 2005). Figure 13, shows the oxygen reactive species ($O_2^{\cdot -}$, $HO^{\cdot}_2$, H_2O_2 and ${}^{\cdot}OH$) generation by sequential reduction of molecular oxygen.

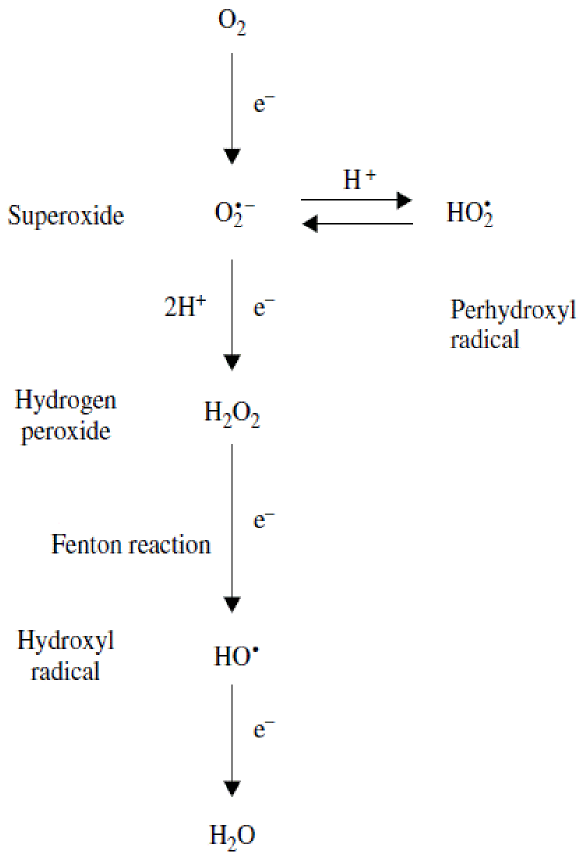

Figure 13. Formation of oxygen reactive species ($O_2^{\cdot -}$, $HO^{\cdot}_2$, H_2O_2 and $^{\cdot}OH$) by sequential reduction of molecular oxygen. (From Smirnoff, 2005).

In addition to the chromophores that generate hydroxyl radical, there are the scavengers of $HO^{\bullet}$ present naturally in freshwater. Therefore, as a result of a balance between $HO^{\bullet}$ rates of production and rates of consumption the steady-state condition for $[^{\bullet}OH]_{ss}$ is reached. The main •OH scavengers are carbonate and bicarbonate, DOM, and nitrite to a lesser extent (Brezonik and Fulkerson-Brekken, 1998; Vione et al., 2006).

It is important to know, in sunlit natural waters, the contribution of those sensitizers toward $HO^{\bullet}$ production. Vione and co-workers (2006, 2010) reported that the relative role of CDOM, nitrate, and nitrite as photochemical sources of $HO^{\bullet}$ would be in the order: CDOM > NO_2^- >NO_3^-. This finding was based on the absorption spectra of nitrate (NO_3^-) and nitrite (NO_2^-) ions in aqueous solutions, which have environmentally significant maxima in the UVB (305 nm) and UVA (355 nm), respectively (Mack and Bolton, 1999). In contrast, the absorption of radiation by CDOM shows an exponential decay from the UV through the visible. Moreover, the attenuation of sunlight in the water column of surface waters is expected to affect the $HO^{\bullet}$ sources. Generally the visible radiation is able to penetrate more deeply than the UV.

3.2 Reaction rate constant

The reactivity of pesticides with radical oxidants is best evaluated by competition kinetic methods. A competition kinetics model was initially proposed by Gurol and Nekouinaini (1984), and later used in other studies (Buxton et al., 1988; Yao and Haag, 1991). The rate constants constitute a key parameter in modelling pesticides degradation through indirect photolysis in natural waters. The rate constants for pesticides obtained by competition kinetics can be incorporated into computer model to compare the importance of the photochemical processes to other dissipation pathways occurring simultaneously in the ecosystem (Mabury and Crosby, 1996; Armbrust, 1999; Benitez et al., 2007). Second-order rate constants with organic compounds range: 10^{8}-10^{10} M^{-1} s^{-1} (Buxton et al., 1988). Interestingly, a database of chemical reactivity rate constants toward hydroxyl radical and singlet oxygen is available on http://www.rcdc.nd.edu/Solnkin2/

A variety of $HO^{\bullet}$ generating techniques were used for measuring the rate constants. Of these techniques:

- Fenton's system (either by photolysis of $Fe(OH)^{2+}$ and H_2O_2 or by dark reaction of Fe^{II} with H_2O_2); the later one is appropriate for compounds that react slowly with $HO^{\bullet}$ and are light- sensitive.
- Ozone decomposition. Ozone is a specific and efficient oxidant for the purification of drinking waters and some industrial wastewaters and it is also a source of hydroxyl radicals (Benitez et al., 2007). This method can be used only for compounds that do not react with ozone directly and limited solubility of ozone in water results in low conversions for compounds that react slowly with $HO^{\bullet}$ because ozone itself becomes a competitor for $HO^{\bullet}$ produced (Yao and Haag, 1991)

Experimental measurements of $k_{HO^{\bullet}}$

The reaction of a compound (pesticide) with hydroxyl radical can be expressed as:

$HO^{\bullet} + P \rightarrow \text{products}$

And reaction kinetic is: $V = -dP/dt = k_P[HO^{\bullet}][P]$ (Eq. 8)

Where P: pesticide concentration, and k_p: reaction rate constant of a pesticide with hydroxyl radical. By integration the Eq. 8 we write:

$\ln[P]_0/[P]_t = k_P[HO^\bullet]t$ (Eq. 9)

Similarly for the reference compound (competitor)

$\ln [R]_0/[R]_t = k_R[HO^\bullet]t$ (Eq. 10)

Then by dividing Eq. (9) by Eq. 10 we get:

$\ln [P]0/[P]t = (kp/k_R) \ln [R]_0/[R]_t$ from which we could calculate kp, figure 14-15, by assuming that concentration of HO• will reach a photostationary state and that the production rate will not vary during the course of the experiments. In the following, an example is illustrated (own unpublished data). The examples shows how the rate is obtained for one herbicide (bentazone) by competition with reference compound (2-HBA), Fig 14, and then for another herbicide (MCPA) by using dichloprop as competitor compound, Fig 15 .

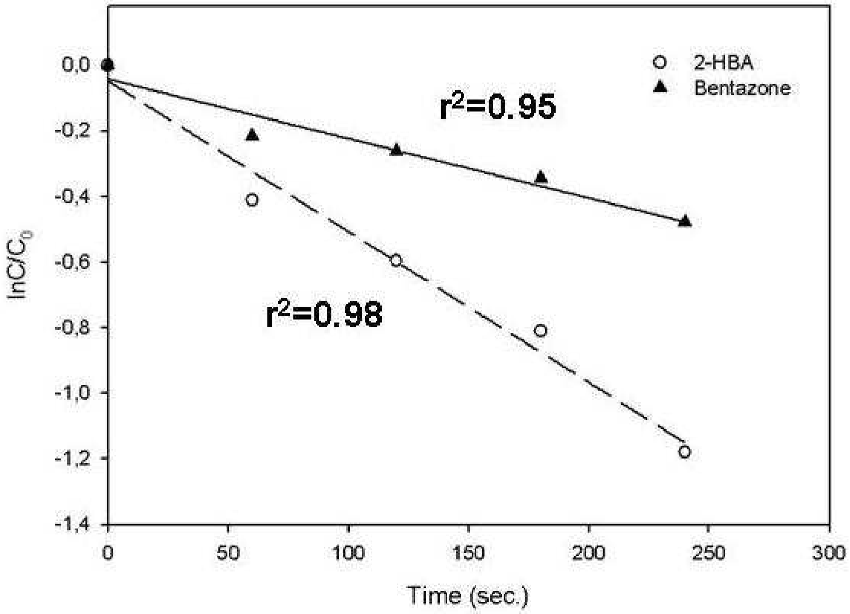

Figure14. Competition of bentazone with the reference compound 2-Hydroxybenzoic acid (2-HBA)

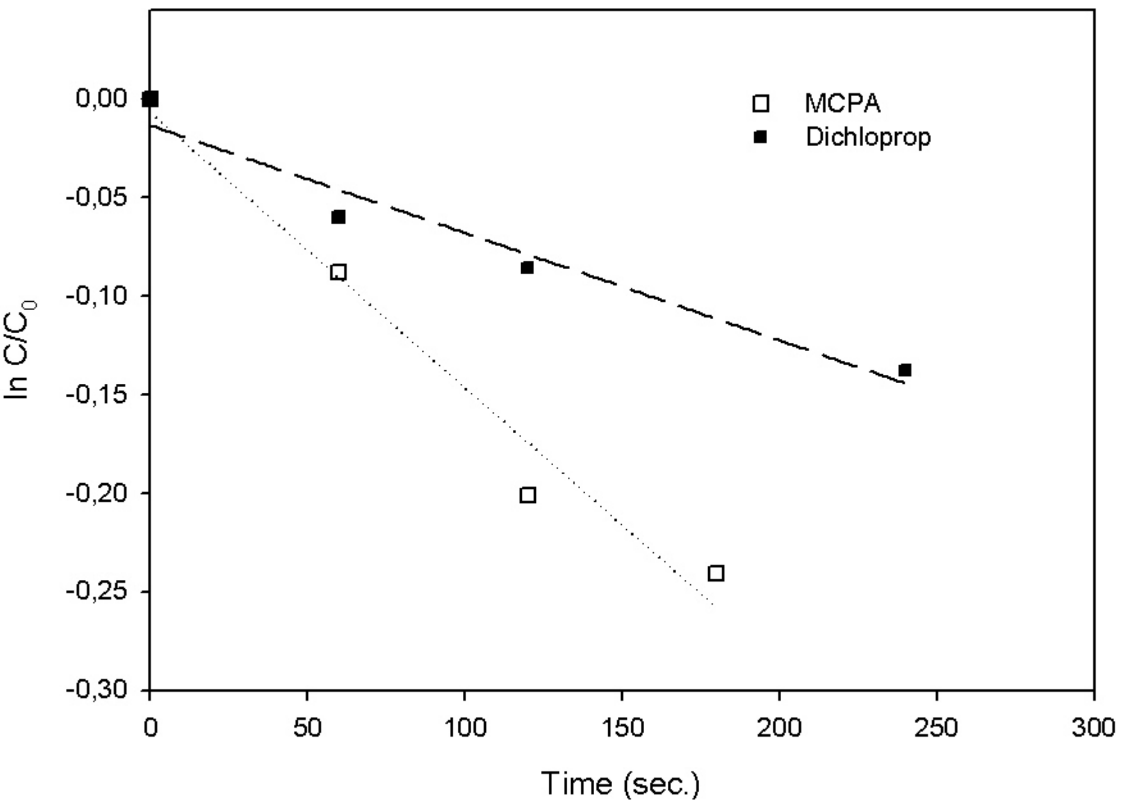

Figure 15. Relative rate of reaction for MCPA and dichlorprop with hydroxyl radical

3.3 Singlet Oxygen

Singlet oxygen ($^1O_2$) is formed by energy transfer from dissolved organic material (DOM) triplets to dissolved oxygen O_2 (Zepp et al., 1981; Haag and Hoigné, 1986). Once formed in natural waters, $^1O_2$ is rapidly quenched back to the ground state by water. And the first order rate constant of singlet oxygen deactivation, *k*d, is 2.5 × 10^5 s^{-1} (Eq. 11), so it is present in low steady state concentration ($[^1O_2]_{ss} < 10^{-12}$ M in natural water during sunshine Haag and Hoigné, 1986). In the presence of $^1O_2$-labile substrates that may exist in DOM, reaction and physical quenching of $^1O_2$ by DOM could serve as additional sinks for $^1O_2$. Thus, DOM may act as both the sensitizer and substrate for $^1O_2$ in natural waters.

$$^1O_2 \xrightarrow{K_d} O_2 \qquad \text{Eq. (11)}$$

$^1O_2$, a selective oxidant, represent an important degradation pathway for specific types of chemical structures. Those compounds contain highly electron rich double bonds or have functional groups easily oxidizable, such as alkyl sulphides and thiones or some phenolate ions (Scully and Hoigné 1987). Among pesticides, ethiofencarb (Sulfur pesticide) could react with $^1O_2$ yielding ethiofencarb sulfoxide (Vialaton and Richard, 2000). However, the reactivity of most pesticides and many other organic contaminants with singlet oxygen is relatively low (several orders of magnitude below the diffusion limit). This is supported by a recent study of Dell'Arciprete and co-workers (2010) which found that neonicotinoid pesticides chemically react with $^1O_2$ with rate constants ranging from 1×10^6 to 4×10^7 M^{-1} s^{-1}.

3.4 Excited Triplet States of the CDOM

In addition to photoinduction of several reactive species, CDOM can induce phototransformation through the direct reactions of its excited triplet states ($^3CDOM^*$) with organic compounds in aquatic environment (Haag and Hoigné, 1986; Vialaton and Richard 2002). Transformations of organic chemicals in surface waters therefore are initiated through light absorption by chromophores present in dissolved organic material (DOM). The fraction of the dissolved natural organic matter DOM pool that interacts with sunlight is referred to as chromophoric dissolved organic matter (CDOM) (O'Sullivan et al., 2005). Several studies undertaken so far have shown that chromophoric components of the DOM pool can enhance the photolysis of numerous organic compounds and herbicides. Zepp et al. (1985) first demonstrated that humic triplets (important chromophore of DOM pool) could be involved in energy transfer reaction.

It is known that to predict the half-life time of an organic compound in the aquatic environment, knowledge about the reaction rate constant of a given compound with the reactive species together with steady- state concentration of the reactive species is required. The problem with $^3CDOM^*$ is that CDOM is not a species of definite chemical composition alongside with the variable chromophores of the DOM. Accordingly, Canonica and co-workers (1995) used in their studies aromatic model ketones (for example benzophenone) as photosensitizer or chromophore. They proposed that this chromophore is the main reactive transient responsible for the transformation of electron-rich phenols in aqueous solutions of humic and fulvic acids and in natural waters irradiated with UVA and visible light. It was suggested that the short-lifetime $^3CDOM^*$ triplet reacts with phenols by electron abstraction and/or hydrogen transfer. These transformation mechanisms were also suggested for the three phenylurea herbicides fenuron, monuron, and diuron based on irradiation experiments with humic acids at 365 nm (Aguer and Richard, 1996, 1999).

Moreover, results from laboratory and field experiments indicated that, in surface waters, the photosensitized transformation of phenylurea herbicides may be significant and occurs primarily by an initial one-electron oxidation due to excited triplet states (^{3}CDOM*) constituents (Gerecke et al 2001). The assessment of the transformation kinetics with ^{3}CDOM* represents a major issue, but recent investigations, reported by Halladja and co-workers (2007), opened up new perspectives in this area and provided evidence for the direct reaction of the electron-rich phenol (2,4,6-Trimethylphenol) with humic triplet excited states.

From the literature mentioned above, CDOM plays a role in photosensitized transformation. However, CDOM has also an inhibition effect on the transformation of organic compounds. The photodegradation of pesticide (atrazine, imazaquin, iprodione) under UV–visible radiation (280–480 nm) was investigated in aqueous solutions with different kinds of humic substances (HS) added to samples by Garbin et al. (2007). The presence of HS showed a positive effect in increasing pesticide degradation except for imazaquin, for which HS decreased the photolysis rate. This inhibition effect was observed with high HS concentration in the solution (50mg/l). It was suggested that the high absorbance of HS in the UV–visible region decreases the rate of pesticide direct photolysis. Moreover, HS are on the one hand sources of hydroxyl radicals which increases the pesticides degradation provided the pesticide susceptible to $^{\cdot}$OH attack. On the other hand, the HS also react with the photogenerated hydroxyl radical resulting in decreasing the photolysis rate of pesticide molecule. More evidence about the inhibition of the reaction of hydroxyl radical with polycyclic aromatic hydrocarbons (PAHs) by dissolved natural organic matter was also reported by Lindsey and Tarr (2000).

3.5 Experimental section

Additional information about the photochemical materials is mentioned below to complete the information reported in the following article.

The photochemical studies were conducted using a medium pressure Hg lamp Fig. (16) which has maximum emission wavelengths at (313, 366, 406, 436, 546 and 578 nm, Fig. 17)

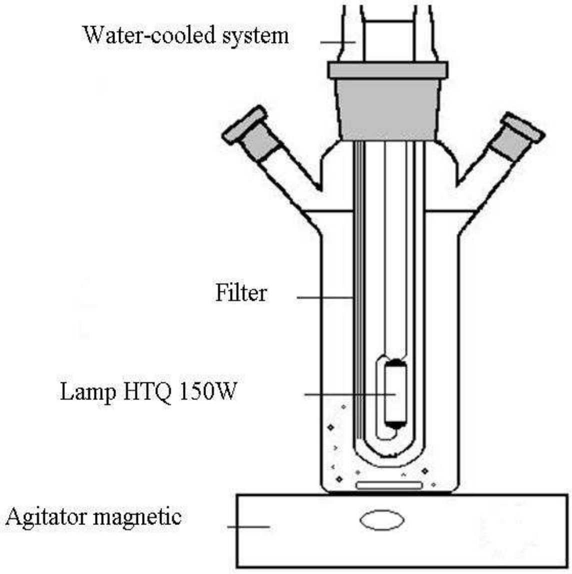

Figure 16. Glass photoreactor with medium pressure Hg lamp and filter cut off (λ<290 nm).

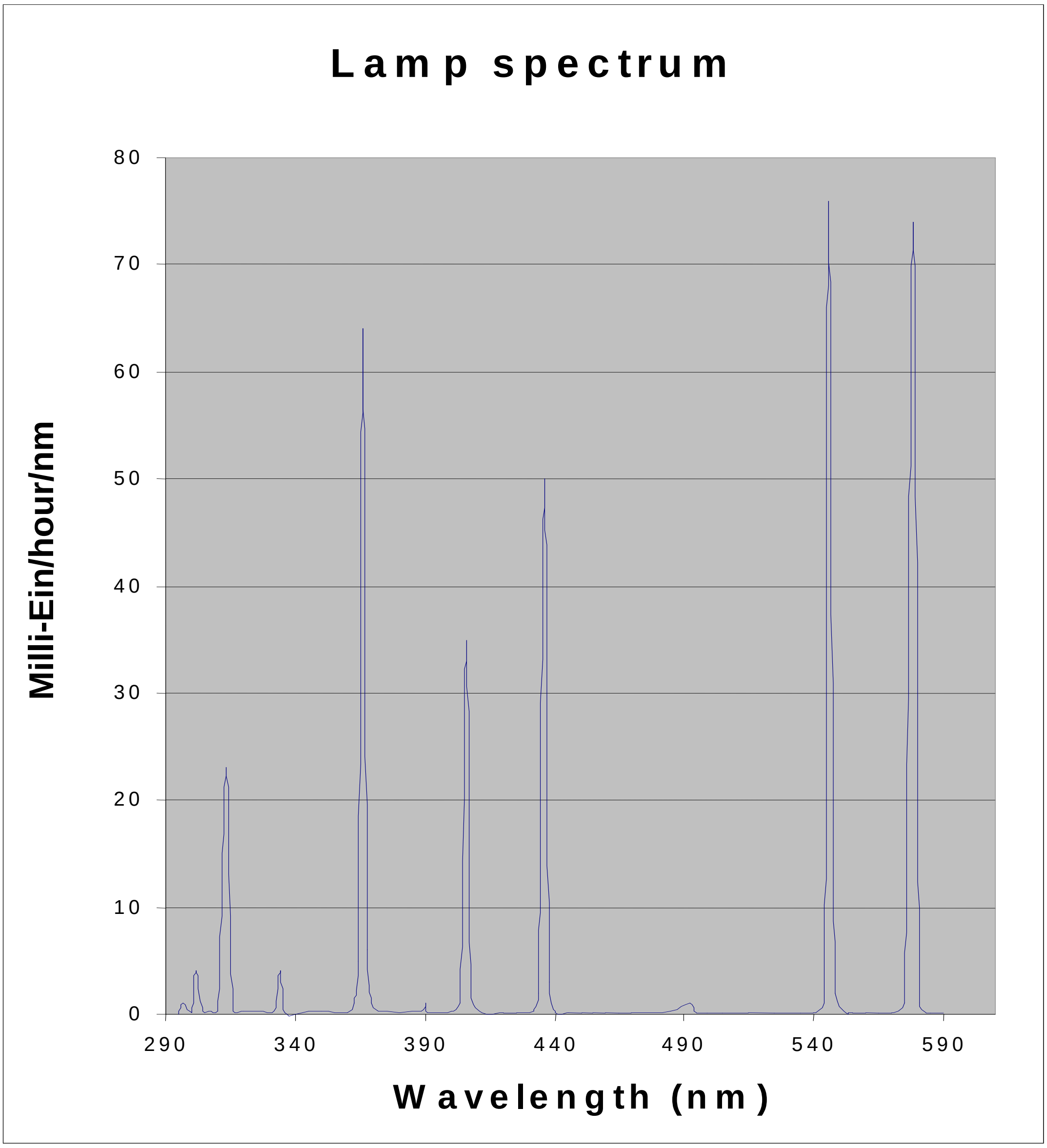

Figure 17. Emission spectrum of the medium-pressure mercury lamp adopted for irradiation experiments.

Article 1

Reactive photoinduced species in estuarine waters. Characterization of hydroxyl radical, singlet oxygen and dissolved organic matter triplet state in natural oxidation processes

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Reactive photoinduced species in estuarine waters. Characterization of hydroxyl radical, singlet oxygen and dissolved organic matter triplet state in natural oxidation processes

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This paper describes the reactive photo-induced species (RPS) hydroxyl radical ($HO^{\bullet}$), singlet oxygen ($^1O_2$) and chromophoric dissolved organic matter triplet state ($^3CDOM^*$) in fresh water (Canal Fumemorte) and estuarine water (Vaccarès), sampled in the Camargue region, southern France. Experiments were conducted with a medium-pressure Hg lamp in a glass photoreactor ($\lambda > 290$ nm, 220 W m^{-2} irradiance between 290 and 400 nm). Steady-state concentration and initial production rate of RPS were determined for $HO^{\bullet}$ and for $^1O_2$. $HO^{\bullet}$ and $^1O_2$ were indirectly identified in the presence of benzene and furfuryl alcohol, respectively, as specific probes. The steady-state measured concentration of $HO^{\bullet}$was $(1.72 \pm 0.01) \times 10^{-16}$ M and $(9.41 \pm 0.12)\times10^{-17}$ M for Vaccarès and Canal waters samples, respectively, and the respective concentrations of $^1O_2$ was $(2.06 \pm 0.22) \times 10^{-13}$ M and $(5.44 \pm 0.04) \times 10^{-14}$ M. The interference of $^3CDOM^*$ or other species in the determination of $^1O_2$ with furfuryl alcohol, and of $^1O_2$ in the quantification of $^3CDOM^*$ with 2,4,6-trimethylphenol was also quantitatively assessed. We developed a kinetic model describing the solar photo-transformation of xenobiotic organic compounds induced by the three different photooxidants $HO^{\bullet}$, $^1O_2$ and $^3CDOM^*$.

Introduction

Aqueous photochemistry is an important process for the transformation of endogenous and exogenous organic components in natural waters. Under solar irradiation, photochemical transformations in aquifers, defined here as natural oxidation processes (NOP), involve direct and indirect photochemical reactions. In direct photolysis, organic compounds absorb radiation themselves and undergo chemical changes. In indirect photochemical pathways, chromophoric dissolved organic matter (CDOM), nitrate, nitrite and Fe(III) act as sensitizers by absorbing radiation, then inducing indirect degradation of surrounding organic compounds. Several important intermediates play a key role in the photodegradation pathways, including the reactive photoinduced species (RPS) $HO^{\bullet}$, $^1O_2$, $ROO^{\bullet}$, $HOO^{\bullet}$, $O_2^{\bullet-}$, $CO_3^{\bullet-}$, $NO_2^{\bullet}$, e_{aq}^-, and $^3CDOM^*$.[1,2] Particularly, $HO^{\bullet}$, $^1O_2$ and $^3CDOM^*$ are of prime importance for their contribution to organic fate in sunlit aquifers.[3] Hydroxyl radical is one of the most reactive free radicals, reacting at nearly diffusion-controlled rate,[4] that is involved in the mineralization of organic compounds. $HO^{\bullet}$ has a central role in advanced oxidation processes (AOPs), following the definition by Glaze *et al.*:[5] AOPs are near-ambient temperature and pressure water treatment processes that involve the generation of $HO^{\bullet}$ in sufficient quantity to affect water purification. In sunlit natural water, $HO^{\bullet}$ is mainly produced by photolytic reactions involving NO_2^-, NO_3^-,[6] and irradiated CDOM.[7–9] Additionally, Fe(III) has also been reported to enhance $HO^{\bullet}$ production *via* the photo-Fenton reaction,[10,11] or from the photoreduction of Fe(III) hydroxocomplexes.[12,13] The photoproduction rate of $HO^{\bullet}$ in many river waters and seawaters has been determined to be in the order $6–150 \times 10^{-12}$ M s^{-1} and $4–50 \times 10^{-12}$ M s^{-1}, respectively.[14] It is noteworthy that $HO^{\bullet}$ is also efficiently consumed by natural dissolved organic matter, which limits its steady-state concentration in waters illuminated by sunlight.[3] CDOM is known to promote organic pollutant degradation in sunlight[8] *via* its excited triplet states, which induce electron transfer with organic compounds, or *via* singlet oxygen ($^1\Delta_g$) produced from energy transfer of $^3CDOM^*$ to molecular oxygen.[8,15] Photochemical processes are strongly related to the chemical composition of water, because of the possible reaction between RPS and intrinsic components of natural water.[3,16] A major parameter in natural water is the concentration of chloride that distinguishes marine water from fresh water. The oceans, covering 71% of the Earth's surface, form a significant reservoir and reaction medium for exogenous contaminants, particularly in coastal water. In estuarine areas, the ionic composition of river water is strongly modified by chloride enrichment due to the proximity of seawater. Chloride may affect the photochemistry of exogenous organics and lead to the production of chloro derivatives.[17] Additionally, it has been reported that estuarine waters contain higher DOM compared to river water.[18] To our best knowledge the RPS $HO^{\bullet}$, $^1O_2$ and $^3CDOM^*$ have never been studied and identified together in freshwater samples and nor in estuarine waters.

The aim of this study was then to quantify the primary RPS in estuarine waters and to determine their production kinetics in real samples in order to bring a comprehensive method to

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model photochemical reactions in natural waters characterized by high salinity and high DOM. The specific probes benzene, furfuryl alcohol and 2,4,6-trimethylphenol (TMP) were used to characterize the reactive species $HO^•$, $^1O_2$ and the triplet states of CDOM, respectively.

Experimental

Chemicals

All reagents and chemicals were purchased commercially from the following suppliers: 2,4,6-trimethylphenol (TMP) and furfuryl alcohol (FFA) (98%) from Alfa Aesar; NaN_3 (99%), methanol and acetonitrile from Sigma-Aldrich; isopropanol from Carlo Erba. All chemicals and reagents were used without further purification. All glassware and plastic were acid washed with HCl (5%) and rinsed with distilled water followed by Milli-Q water prior to use. HPLC eluents were prepared with Milli-Q water.

Water samples

Two sampling sites from Camargue were adopted, taking water from about 15 cm below the surface. Estuarine water was taken from Vaccarès, and fresh water samples were collected in Canal Fumemorte (04° 38′ 11″ E, 43° 31′ 25″ N; hereafter referred to as "Canal"). Water was then filtered through 0.45 μm pore-size membranes, and stored at 4 °C in the dark until analysis. Storage and all measurements were performed at the natural water pH. Sample analysis is presented in Table 1. Spectra were recorded in a cell with 1 cm optical path length. UV-Vis spectra of the samples are presented in Fig. 1. It is noticeable that the Vaccarès sample shows a much higher absorption than the Canal one. This can be attributed to the higher organic matter content of the Vaccarès sample (see Table 1) for wavelength values down to 230–240 nm where CDOM dominates the absorption.[7,9] Interestingly, the absorbance ratio of the two samples is much higher than the non-purgeable organic carbon (NPOC) ratio. This implies that the specific absorbance of CDOM is higher in the case of Vaccarès. Below 230 nm other water components would also play a very important role (*e.g.* nitrate, nitrite and Fe species).[6,7,9] Nitrate and nitrite cannot account for the difference as they are more concentrated in the case of Canal. In contrast, the higher Fe concentration of the Vaccarès sample could play a role below 230 nm.

Table 1 Physical and chemical parameters of water samples. Error intervals represent $\mu \pm \sigma$

Sample	Canal	Vaccarès
Sampling date	28 April 2008	28 April 2008
Cl^-/M	$(1.18 \pm 0.03) \times 10^{-3}$	$(1.90 \pm 0.05) \times 10^{-1}$
NO_3^-/M	$(4.36 \pm 0.03) \times 10^{-5}$	$(1.64 \pm 0.01) \times 10^{-5}$
NO_2^-/M	$(9.57 \pm 0.05) \times 10^{-7}$	$(8.26 \pm 0.05) \times 10^{-7}$
Fe (ppb)	3.81 ± 0.90	22.81 ± 3.06
NPOC/mg(C) L^{-1}	19.83 ± 0.30	32.11 ± 0.60
pH	7.81	8.01
Conductivity/mS	0.62	36.50
Salinity/g L^{-1}	0.10	26.20
$r_{HO^•}$/M s^{-1}	$(1.52 \pm 0.01) \times 10^{-11}$	$(1.93 \pm 0.01) \times 10^{-11}$
$[HO^•]_{ss}$/M	$(9.41 \pm 0.12) \times 10^{-17}$	$(1.72 \pm 0.01) \times 10^{-16}$
$\sum_i k_i[S_i]$/s^{-1}	$(1.62 \pm 0.03) \times 10^5$	$(1.12 \pm 0.01) \times 10^5$
$r_{^1O_2}$/M s^{-1}	$(1.36 \pm 0.01) \times 10^{-8}$	$(5.14 \pm 0.54) \times 10^{-8}$
$[^1O_2]_{ss}$/M	$(5.44 \pm 0.04) \times 10^{-14}$	$(2.06 \pm 0.22) \times 10^{-13}$

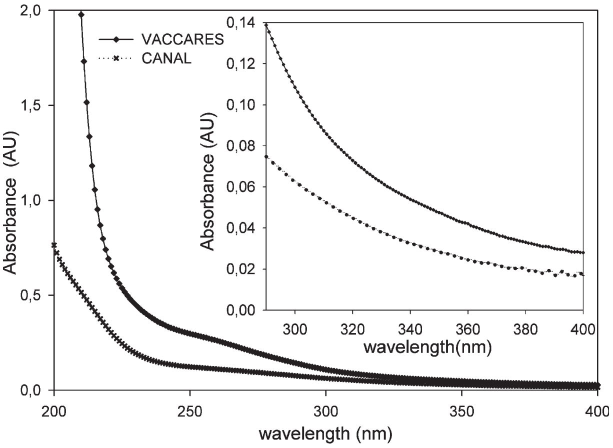

Fig. 1 UV-Vis spectra for Canal and Vaccarès water samples collected on 28 April 2008.

Irradiation experiments

Stationary photolysis experiments were carried out in a cylindrical immersion-type glass photoreactor (0.5 L; Heraeus TQ 150 Model) equipped with a water-cooled medium-pressure Hg lamp (glass cut off ($\lambda < 290$ nm), maximum emission wavelengths at 313, 366, 406, 436, 546 and 578 nm). The incident, volumetric photon flux in solution was 1.0×10^{-4} einstein L^{-1} s^{-1}. The irradiance between 290 and 400 nm was around 220 W m^{-2}. The radiation path length inside the reactor was 2 cm. The whole assembly was wrapped with aluminium foil. Upon irradiation, aliquots were removed at various time intervals and analyzed by HPLC-UV. Each experiment was carried out in triplicate.

Analytical determinations

pH was measured by a pH meter ORION model 420A. The measures of iron were performed by ICP-AES with a JY2000 ULTRACE apparatus (Jobin Yvon Horiba). ICP-AES conditions: Plasma argon flow 12 L min^{-1}, plasma power 1000 W, nebulisation pressure 3.2 bars. The standard solutions were supplied by Aldrich (concentration of metal 1000 mg L^{-1} in acidified solution containing 1% HNO_3). The identification of Fe was performed at 260 nm. UV-Vis absorption spectra of water samples were recorded using a spectrophotometer model Agilent 8453 and ChemStation software (quartz cells, 1 cm path length). Anions (NO_3^-, NO_2^-, Cl^-) were analyzed with a DIONEX ICS 3000 Ion chromatograph, equipped with an Autosampler AS 40, a gradient pump, a Dionex Ion Pac AS11-HC 4 × 250 mm anion exchange column, a Dionex IonPac AG 11-HC 4 × 5 mm guard column, a ASRS-ULTRA 300–4 mm suppressor, and two detectors: Ultimate 3000 Photodiode Array Detector UV/VIS and a conductimetric one at 35 °C. The eluents were H_2O and 100 mM NaOH. Flow rate was 1.5 mL min^{-1}. Elution gradient: 0–16 min (NaOH 1.3%/H_2O 98.7%); 16–29 min (from NaOH 1.3% to NaOH 60%). The retention times were (min): Cl^- (13.64), NO_3^- (21.8). NO_2^- concentration was measured by the sulfanilamide method.[19]

Organic carbon was quantified as NPOC with 5050A/SSM 5000 Shimadzu carbon analyzer, after acidification of the sample with concentrated $HClO_4$ and a 20 min air purge to eliminate CO_2. Three measures were systematically acquired for each experiment, and averaged to give the final value. HPLC analysis was carried out by a Hitachi HPLC chromatograph equipped with a L-2400 UV detector and using a RP-C18 LiChrospher column (Merck; length 250 mm, diameter 4.6 mm, particle size 5 µm). Samples were eluted with a mixture of acetonitrile (ACN) and water acidified with orthophosphoric acid (0.1%) at a flow rate of 0.8 mL min^{-1}. The percentage volume of ACN/acidified water was 20 : 80 and 60 : 40 for FFA and TMP, respectively. Retention times (min)/detection wavelength (nm) were: FFA (7.06/218), 6-hydroxy(2H)pyran-3(6H)-one (pyranone) (4.30/218), TMP (9.97/205). Benzene consumption and phenol formation were monitored with the same HPLC apparatus. Samples were eluted with a 40 : 60 mixture of ACN/water. Retention times (min)/detection wavelength (nm) were: phenol (4.62/210), benzene (9.50/210).

Methodology

The adopted methology was to measure $HO^•$ with the formation of phenol from benzene as a probe reaction (95% yield),[9,14] $^1O_2$ upon transformation of FFA plus control experiments (quenching with azide),[15] and ^{3}DOM* with the phototransformation of TMP.[8] The errors associated to the relevant quantities ($\pm\sigma$) were derived from the goodness of the fit of the theoretical kinetic functions to the experimental data or, where relevant, from the rules of error propagation.

Results and discussion

Measurement of hydroxyl radical

Hydroxyl radicals were identified and quantified in natural water samples with the benzene probe as described by Vione *et al.*[9] Benzene was chosen as a model compound for examining indirect photolysis due to its fast reaction with $HO^•$ (second-order rate constant 7.8×10^9 M^{-1} s^{-1})[4] and to its lack of reactivity by direct photolysis. The transformation reaction of benzene to phenol was monitored as a function of time assuming that phenol was produced only upon reaction between benzene and $HO^•$ (95% yield). This hypothesis is justified by the fact that natural waters afford limited interference on this reaction by other reactive transients.[20] Applying the steady-state approximation to $[HO^•]$ the rate of benzene reaction is given by:

$$\frac{\mathrm{d[phenol]}}{\mathrm{d}t} = k'_{\mathrm{B}}[\mathrm{HO}^\bullet][\mathrm{benzene}] = \frac{k'_{\mathrm{B}} r_{\mathrm{HO}^\bullet}[\mathrm{benzene}]}{\sum_i k_i[S_i] + k_{\mathrm{B}}[\mathrm{benzene}]} \qquad (1)$$

where k_B is the second-order rate constant for the reaction between benzene and $HO^•$ (7.8×10^9 M^{-1} s^{-1}), and $k'_B = 0.95k_B$. S_i is a generic $HO^•$ scavenger present in the natural water sample, having rate constant k_i for reaction with $HO^•$. $r_{HO^•}$ is the rate of $HO^•$ photoformation. The reaction of phenol with $HO^•$ was not considered because only the initial rates were taken into account. Eqn (1) was resolved for low concentration of benzene to determine $[HO^•]$ (denominator becoming equal to $\sum_i k_{S_i}[S_i]$ by neglecting the reaction of benzene with $HO^•$ compared to the reaction of S_i with $HO^•$) and at high concentration of benzene to determine $r_{HO^•}$ (denominator equal to k_B[benzene] by neglecting the reaction of S_i with $HO^•$ compared to the reaction of benzene with $HO^•$). The time evolution of phenol upon irradiation of the two natural water samples in the presence of benzene at different initial concentrations is shown in Fig. 2. The initial formation rate of phenol was calculated as the slope of the tangent at $t = 0$ to the curve fitting the experimental concentration values of phenol. Following the procedure of Vione *et al.*,[9] $[HO^•]$ was determined from the tangent at $t = 0$ to the curve representing the initial formation rate of phenol as a function of [benzene] (Fig. 3). The values of $r_{HO^•}$, $[HO^•]$ and $\sum_i k_{S_i}[S_i]$ are reported in Table 1. The associated errors are referred to the goodness of the fit of the theoretical curves (eqn (1)) to the experimental data shown in Fig. 3.

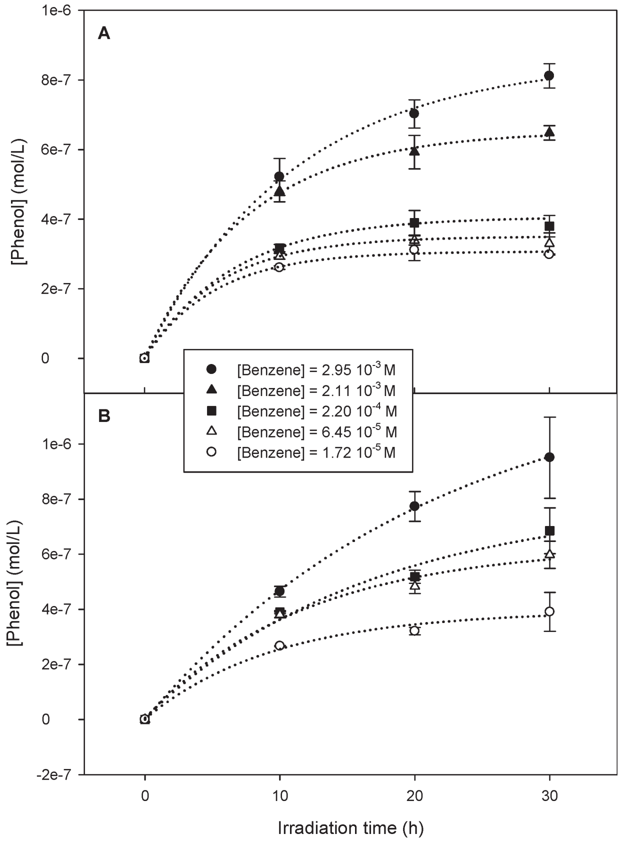

Fig. 2 Time evolution of phenol upon irradiation of water from (A) Vaccarès and (B) Canal for different concentration values of benzene. SD is given for three replicates.

The adopted procedure is based on the hypothesis of a selective reaction of $HO^•$ with benzene. Phenol could also be produced from alternative sources like $^1O_2$ and humic acids *via* the triplet state ^{3}CDOM*. However, $^1O_2$ is weakly reactive toward benzene,[21] and the addition of $HO^•$ scavengers in excess is able to completely quench the formation of phenol from benzene upon irradiation of humic acids or lake water.[20] The deduced steady-state $[HO^•]$ in the Vaccarès water sample ($(1.72 \pm 0.01) \times 10^{-16}$ M) was about 1.8 times higher than that of Canal ($(9.41 \pm 0.12) \times 10^{-17}$ M). The overall scavenging rate constant ($\sum_i k_{S_i}[S_i]$) values were $(1.12 \pm 0.01) \times 10^5$ and $(1.62 \pm 0.03) \times 10^5$ s^{-1} for the Vaccarès and Canal water samples, respectively (Table 1).

Dissolved organic matter is most likely the main scavenger of $HO^•$ in the two samples. In contrast, chloride even at elevated

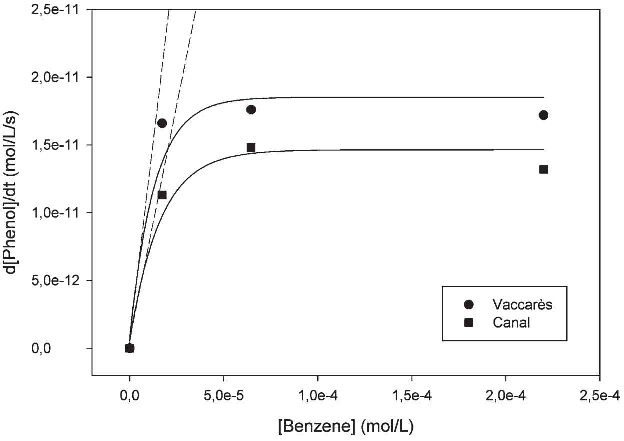

Fig. 3 Comparative initial formation rate of phenol upon irradiation of water from Vaccarès and Canal, as a function of the initial benzene concentration. The tangents representing the $\lim_{[\text{benzene}]} \rightarrow 0\{\mathrm{d}[\text{phenol}]/\mathrm{d}t \times [\text{benzene}]^{-1}\}$ give access to [HO$^\bullet$].

concentration is extremely unlikely to be a significant HO$^\bullet$ scavenger at neutral to basic pH. While significant consumption of hydroxyl radicals by Cl^- is operational under acidic conditions, no scavenging could be detected at circumneutral pH in the presence of chloride at concentration up to at least 1 M.[9,17] Interestingly, the lower scavenging rate constant of the Vaccarès sample in the presence of higher NPOC suggests that the Vaccarès organic matter is considerably less reactive toward HO$^\bullet$ than the Canal one.

Also interesting is the higher $r_{\mathrm{HO}^\bullet}$ in the case of Vaccarès. Among the possible HO$^\bullet$ sources, nitrate is much more concentrated in Canal, and the concentration of nitrite is similar in the two samples but slightly higher for Canal. Moreover, note that $[\mathrm{NO_3}^-][\mathrm{NO_2}^-]^{-1}$ is <100 in both cases, which suggests a more important role of nitrite as HO$^\bullet$ source compared to nitrate.[6] Of the other possible species that could be involved in the photoinduced generation of HO$^\bullet$, CDOM and Fe are more concentrated in the Vaccarès sample. The two compounds together could be involved into photo-Fenton reactions, which would therefore be presumably more important in the estuarine sample. However, it should be pointed out that the photo-Fenton process is for instance the prevailing HO$^\bullet$ source in the Satilla river (USA), characterized by high Fe levels (5–14 μM) and relatively acidic pH (<7).[22] In the present case, even in the Vaccarès sample the concentration of Fe is sub-μM and the pH is quite high. Under basic conditions the generation of HO$^\bullet$ by the Fenton reaction is inhibited,[23] for which reason the Vaccarès sample could hardly be considered as an ideal system for the photo-Fenton process to be an important source of HO$^\bullet$. Additionally, the generation rate of HO$^\bullet$ upon direct irradiation of Fe(III) species under neutral to basic conditions is quite low.[24] Another possibility is that the high generation rate of HO$^\bullet$ in the Vaccarès sample is due to the presence of more concentrated and more active CDOM (see Fig. 1 and Table 1), which could produce hydroxyl radicals directly upon irradiation.[9]

Involvement of singlet oxygen ($^1\mathrm{O}_2$)

Under solar irradiation, natural waters are known to produce hydroxyl radical and singlet oxygen. Consequently, these reactive species should be involved in the transformation pathways of organic compounds (R) that are present in water. The relevant processes are described in eqn (2)–(3), where P_1 and P_2 are the photoproducts of the reaction of R with HO$^\bullet$ and $^1\mathrm{O}_2$, respectively. The reactivity of the organic compound R with RPS may be affected by various scavengers present in the natural water matrix (S_i, S_j), which can compete with R for reaction with the photogenerated transients (eqn (4)–(5)). The equations representing the oxidation rate of R (r_R) and the reaction rates of HO$^\bullet$ ($r_{\mathrm{HO}^\bullet}$) and $^1\mathrm{O}_2$ ($r_{^1\mathrm{O}_2}$) are given by eqn (7)–(9), where k_1 is the second-order rate constant of the reaction of R with HO$^\bullet$, k_2 that with $^1\mathrm{O}_2$, k_i and k_j the second-order rate constants of the reaction of the scavenger S_i and S_j with HO$^\bullet$ and $^1\mathrm{O}_2$, respectively. Finally, k_d is the first-order rate constant for the deactivation of $^1\mathrm{O}_2$ in water ($2.5 \times 10^5\ \mathrm{s}^{-1}$).[25]

$$R + \mathrm{HO}^\bullet \xrightarrow{k_1} P_1 \tag{2}$$

$$R + {}^1\mathrm{O}_2 \xrightarrow{k_2} P_2 \tag{3}$$

$$S_i + \mathrm{HO}^\bullet \xrightarrow{k_i} P_i \tag{4}$$

$$S_j + {}^1\mathrm{O}_2 \xrightarrow{k_j} P_j \tag{5}$$

$${}^1\mathrm{O}_2 \xrightarrow{k_d} \mathrm{O}_2 \tag{6}$$

$$r_R = -\frac{\mathrm{d}[R]}{\mathrm{d}t} = k_1[R][\mathrm{HO}^\bullet] + k_2[R][{}^1\mathrm{O}_2] \tag{7}$$

$$r_{\mathrm{HO}^\bullet} = (k_1[R] + \textstyle\sum_i k_i[S_i])[\mathrm{HO}^\bullet] \tag{8}$$

$$r_{^1\mathrm{O}_2} = (k_2[R] + k_\mathrm{d} + \textstyle\sum_j k_j[S_j])[{}^1\mathrm{O}_2] \tag{9}$$

Note that under the steady-state conditions that are operational for HO$^\bullet$ and $^1\mathrm{O}_2$ in surface waters, $r_{\mathrm{HO}^\bullet}$ and $r_{^1\mathrm{O}_2}$ would also represent the formation rates of the relevant species under irradiation.

The characterisation of $^1\mathrm{O}_2$ was carried out with furfuryl alcohol (FFA), which is known to react with singlet oxygen ($k_2 = 1.2 \times 10^8\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$) to give the corresponding 6-hydroxy(2H)pyran-3(6H)-one (pyranone) in 85% yield.[15] The initial rate of FFA photooxydation (r_FFA) was measured for several initial FFA concentrations. Assuming that FFA reacts with both hydroxyl radical and singlet oxygen, r_FFA can be expressed as follows (note that $R = \mathrm{FFA}$ in eqn (2)–(3)):

$$r_\mathrm{FFA} = \frac{r_{\mathrm{HO}^\bullet} k_1[\mathrm{FFA}]}{\sum_i k_i[S_i] + k_1[\mathrm{FFA}]} + \frac{r_{^1\mathrm{O}_2} k_2[\mathrm{FFA}]}{\sum_j k_j[S_j] + k_2[\mathrm{FFA}] + k_d} \tag{10}$$

In this equation, the fitting variables are $r_{^1\mathrm{O}_2}$ and $\sum_j k_j[S_j]$. The variables $r_{\mathrm{HO}^\bullet}$ and $\sum_i k_i[S_i]$ were deduced from the measurement of HO$^\bullet$ in the presence of benzene (see above). The preliminary fit of the experimental data with eqn (10) (data not shown) yielded $\sum_j k_j[S_j] << k_2[\mathrm{FFA}] + k_\mathrm{d}$, which suggests that the term $\sum_j k_j[S_j]$ can be neglected.

The irradiation of FFA (0.25×10^{-4} M) in natural waters indicated that FFA depletion reached 44.5% and 21.1% after 240 min for the Vaccarès and Canal water samples, respectively (Fig. 4). Only a small percentage of FFA reacted under irradiation, compared to Richard and co-workers who obtained 80% FFA removal in similar conditions after 200 min of irradiation in laboratory-grade water in the presence of fulvic acid.[15]

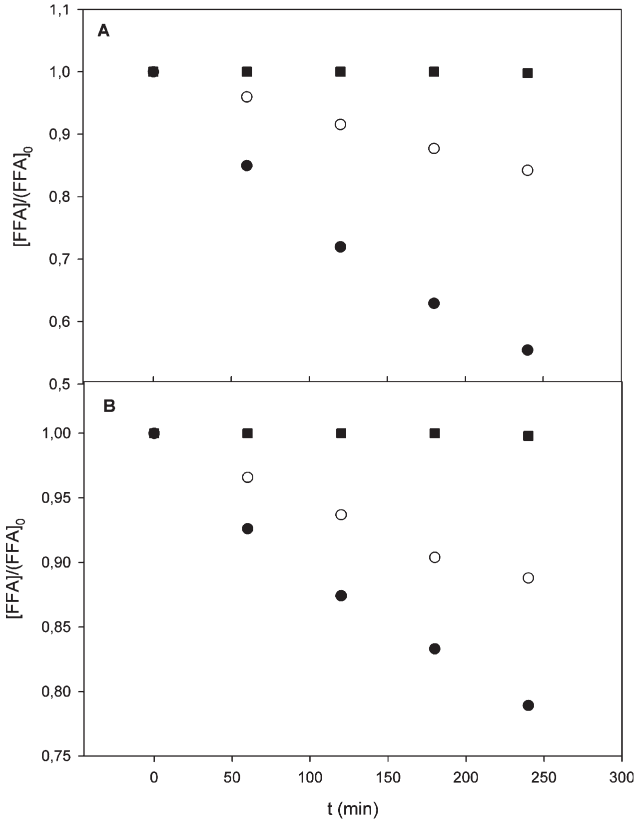

Fig. 4 Normalized evolution of FFA *vs.* time under polychromatic light in (A) Vaccarès water and (B) Canal water. (■) FFA (0.25×10^{-4} M) in milliQ water, (●) FFA (0.25×10^{-4} M) in real water; (○) FFA (0.25×10^{-4} M) in real water + sodium azide (3×10^{-3} M).

The low degradation yields observed here could be explained by the lower photochemical reactivity of whole CDOM samples compared to fulvic acids, or by the matrix effect of the natural waters because of the presence of dissolved antioxidants.[26] The control of the reaction in milliQ water indicated that FFA did not undergo direct phototransformation under irradiation. The effect of the azide anion (3×10^{-3} M) is also reported in Fig. 4. Azide is known to react with $HO^{\bullet}$ and $^1O_2$ with second-order rate constants $k_3 = 1.4 \times 10^{10}$ M^{-1} s^{-1} [27] and $k_4 = 7.8 \times 10^{8}$ M^{-1} s^{-1},[28] respectively. In the presence of the azide, eqn (10) would be modified as follows:

$$r_{FFA} = \frac{r_{HO^{\bullet}} k_1[FFA]}{\sum_i k_i[S_i] + k_1[FFA] + k_3[N_3^-]} + \frac{r_{^1O_2} k_2[FFA]}{\sum_j k_j[S_j] + k_2[FFA] + k_d + k_4[N_3^-]} \qquad (11)$$

Eqn (11) foresees a 90% inhibition of FFA degradation in the presence of 3 mM N_3^-, but the experimental data (Fig. 4) show that the decrease of FFA was only partially inhibited for both the Vaccarès sample (65%) and the Canal sample (47%). These results indicate that [FFA] continued decreasing, albeit to a reduced extent, when $^1O_2$ and $HO^{\bullet}$ were quenched by azide. The oxidation of N_3^- in the studied system is expected to produce the azide radical $N_3^{\bullet}$, which shows significant reactivity toward many substituted phenols. Interestingly, no reactivity data of $N_3^{\bullet}$ with FFA or other alcohols are reported,[29] which suggests that $N_3^{\bullet}$ would not be involved to a significant extent in the transformation of FFA. It is therefore hypothesized that additional reactive species, possibly $^3CDOM^*$ or organic matter-derived radicals (*e.g.* $RO^{\bullet}$ and/or $ROO^{\bullet}$),[3] could be involved in FFA depletion upon irradiation of natural water.

The next section discusses in greater detail the hypothesis that the residual transformation of FFA in the presence of the azide is due to the reaction with $^3CDOM^*$, or other species generated upon irradiation and transformation of organic matter.

Involvement of species derived from dissolved organic matter in the transformation of FFA

If the degradation of FFA is carried out by $^3CDOM^*$, the process would take place according to the following eqn (12)–(15):[30,31]

$$CDOM + h\nu \rightarrow {}^3CDOM^* \; [r_{^3CDOM^*}] \qquad (12)$$

$$^3CDOM^* \rightarrow CDOM \; [k^*] \qquad (13)$$

$$^3CDOM^* + FFA \rightarrow Products \; [k_5] \qquad (14)$$

$$^3CDOM^* + O_2 \rightarrow CDOM + {}^1O_2 \; [k_6] \qquad (15)$$

The chemistry of species such as $RO^{\bullet}$ and/or $ROO^{\bullet}$ is not known in sufficient detail to enable the setting up of a similar reaction scheme, but equivalent reactions could possibly be operational.

The role of the interfering species has been approximately assessed from the difference (r_{diff}) between the experimental (Table 2) and the calculated (eqn (11)) FFA rates in the presence of the azide. It was possible to obtain $r_{diff} = 7 \times 10^{-6}$[FFA] for Canal and $r_{diff} = 3 \times 10^{-6}$[FFA] for Vaccarès.

Under the hypothesis that the difference between the experimental and the calculated values is due to $^3CDOM^*$, and applying the steady-state approximation to [$^3CDOM^*$], an exact expression for r_{diff} would be:

$$r_{diff} = \frac{r_{^3CDOM^*} k_5[FFA]}{k_5[FFA] + k_6[O_2] + k^*} \qquad (16)$$

where $r_{^3CDOM^*}$ and k^* are the formation rate of $^3CDOM^*$ and the deactivation rate constant of $^3CDOM^*$, respectively. It would also be $k_5[FFA] << k_6[O_2] + k^*$.[30] Considering that the involvement of $^3CDOM^*$ is not demonstrated, eqn (16) can be more generically written as $r_{diff} = \alpha[FFA]$ (α has units of s^{-1}). The rate data of FFA without sodium azide would then be given by the sum of the contributions of $HO^{\bullet}$, $^1O_2$, and $^3CDOM^*$ or other species. The following, simplified fitting function was obtained:

Table 2 Experimental rate of FFA phototransformation in the absence (r_{FFA}) and in the presence (r_{FFAq}) of sodium azide (3×10^{-3} M) in the Canal and Vaccarès water samples

	Canal		Vaccarès	
$[FFA]/10^6$ M	r_{FFA}/ 10^{-10} M s^{-1}	r_{FFAq}/ 10^{-10} M s^{-1}	r_{FFA}/ 10^{-10} M s^{-1}	r_{FFAq}/ 10^{-10} M s^{-1}
25	4.0	2.1	10.3	2.9
50	8.2	4.5	19.0	3.9
100	15.8	8.1	36.5	6.4
200	24.3	4.8	46.9	8.7

$$r_{\mathrm{FFA}} = \frac{r_{\mathrm{HO^\bullet}} k_1[\mathrm{FFA}]}{\sum_i k_i[S_i] + k_1[\mathrm{FFA}]} + \frac{r_{^1\mathrm{O}_2} k_2[\mathrm{FFA}]}{k_2[\mathrm{FFA}] + k_d} + \alpha[\mathrm{FFA}] \qquad (17)$$

considering that $\sum_j k_{sj}[S_j] << k_d$.[31,32] From the experimental data of r_{diff} one gets $\alpha = 7 \times 10^{-6}\ \mathrm{s}^{-1}$ for Canal and $3 \times 10^{-6}\ \mathrm{s}^{-1}$ for Vaccarès. Fig. 5 reports the experimental rates of r_{FFA} *vs.* [FFA] for the Canal and Vaccarès waters (solid squares). The dashed lines represent the fit with eqn (17), where $r_{^1\mathrm{O}_2}$ was the only fit variable. It was found that $r_{^1\mathrm{O}_2} = (1.36 \pm 0.01) \times 10^{-8}\ \mathrm{M\ s^{-1}}$ and $(5.14 \pm 0.54) \times 10^{-8}\ \mathrm{M\ s^{-1}}$ for Canal and Vaccarès, respectively. The errors represent the goodness of the fit of eqn (17) to the experimental data. The dotted line indicates what would be the model without taking into account the contribution of ^{3}CDOM* or other interfering species (α[FFA] term in eqn (17)). It is apparent that the contribution of the interfering agents is much more important in the case of Canal, for which the value of α was more than double compared to Vaccarès. The fact that $r_{^1\mathrm{O}_2}$ is higher for Vaccarès compared to Canal is consistent with the higher NPOC (see Table 1) and even more with the higher content of CDOM (see Fig. 1) of Vaccarès. Indeed, $^1\mathrm{O}_2$ is produced by the excited triplet states ^{3}CDOM* (reaction 15). It is also possible to derive the steady-state $[^1\mathrm{O}_2]$ in the absence of FFA or the azide. Consider eqn (9) with $[R] = 0$ and $\sum_j k_{sj}[S_j] << k_d$,[31,32] from which one gets $[^1\mathrm{O}_2] = r_{^1\mathrm{O}_2} k_d^{-1}$. The steady-state $[^1\mathrm{O}_2]$ values thus derived are reported in Table 1.

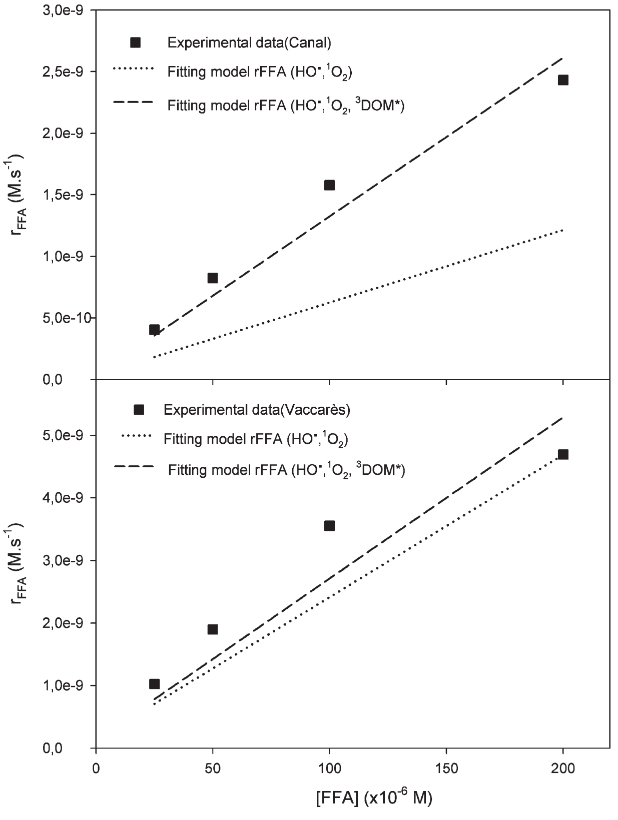

Fig. 5 Fitting model of r_{FFA} taking in account the three RPS in (A) Canal and (B) Vaccarès water samples. FFA concentrations: 0.25, 5.0, 1.0 and 2.0×10^{-4} M.

Quantitation of ^{3}CDOM*

2,4,6-Trimethylphenol (TMP) has successfully been used to probe the photosensitising properties of natural waters. This electron-rich phenol is readily transformed upon irradiation in the presence of chromophoric dissolved organic matter or humic substances.[30,33] TMP can react with singlet oxygen ($k_2 = 6.3 \times 10^7\ \mathrm{M^{-1}\ s^{-1}}$),[34] triplet states or other radicals (*e.g.* HO•). However, it has been reported that the rate of TMP phototransformation in the presence of humic or fulvic acids was not affected by the presence of the azide, confirming the negligible involvement of $^1\mathrm{O}_2$ under such conditions.[35] The formation of ^{3}CDOM* was specifically determined from the irradiation of TMP in Vaccarès and Canal water samples. Fig. 6 reports the transformation rate of TMP at different initial concentrations upon irradiation of the natural water samples. The transformation rate r_{TMP} can be written as follows:

$$-\frac{\mathrm{d}[\mathrm{TMP}]}{\mathrm{d}t} = \frac{r_{^3\mathrm{CDOM^*}} k_{\mathrm{TMP}}[\mathrm{TMP}]}{k_{\mathrm{TMP}}[\mathrm{TMP}] + k_6[\mathrm{O}_2] + k^*} + \frac{r_{^1\mathrm{O}_2} k_2[\mathrm{TMP}]}{k_2[\mathrm{TMP}] + k_{\mathrm{d}}} \qquad (18)$$

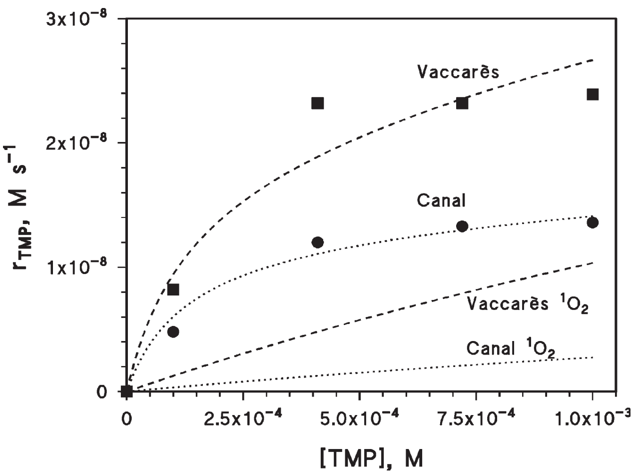

Fig. 6 Plot of r_{TMP} *vs.* [TMP] for Canal and Vaccarès water samples. Experimental data and fitting curves.

The reaction rate constant of TMP with hydroxyl radicals was neglected, based on previous findings that $k_1[\mathrm{HO^\bullet}] << k_{\mathrm{TMP}}[^3\mathrm{CDOM^*}]$ in natural waters,[30] where k_{TMP} is the second-order reaction rate constant between TMP and ^{3}CDOM*.

The fit of the experimental data was carried out with eqn (18), with $k_2 = 6.3 \times 10^7\ \mathrm{M^{-1}\ s^{-1}}$, $k_{\mathrm{d}} = 2.5 \times 10^5\ \mathrm{s^{-1}}$, $k_6[\mathrm{O}_2] + k^* = 5 \times 10^5\ \mathrm{s^{-1}}$,[25] $r_{^1\mathrm{O}_2} = (1.36 \pm 0.01) \times 10^{-8}\ \mathrm{M\ s^{-1}}$ and $(5.14 \pm 0.54) \times 10^{-8}\ \mathrm{M\ s^{-1}}$ for Canal and Vaccarès, respectively, and $r_{^3\mathrm{CDOM^*}}$ and k_{TMP} as fit variables. The fit yielded $r_{^3\mathrm{CDOM^*}} = (1.8 \pm 0.3) \times 10^{-8}\ \mathrm{M\ s^{-1}}$ and $k_{\mathrm{TMP}} = (4.8 \pm 4.4) \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$ for Vaccarès, $r_{^3\mathrm{CDOM^*}} = (1.4 \pm 0.1) \times 10^{-8}\ \mathrm{M\ s^{-1}}$ and $k_{\mathrm{TMP}} = (3.0 \pm 1.1) \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$ for Canal. Fig. 6 also reports the calculated contribution of $^1\mathrm{O}_2$ to the transformation of TMP in the two samples, which is definitely not negligible in the case of Vaccarès. It is noticeable the elevated error on k_{TMP} in the case of the Vaccarès sample. However, a further fit carried out on the same data by taking fixed $k_{\mathrm{TMP}} = 3.0 \times 10^9\ \mathrm{M^{-1}\ s^{-1}}$ as for Canal yielded a very similar $r_{^3\mathrm{CDOM^*}} = 1.9 \times 10^{-8}\ \mathrm{M\ s^{-1}}$. The determination of $r_{^3\mathrm{CDOM^*}}$ from the Vaccarès data can therefore be considered as sufficiently robust.

Interestingly, in the case of Canal it is $r_{^3\mathrm{CDOM}^*} \approx r_{^1\mathrm{O}_2}$, which is reasonable because ^{3}CDOM* is the main source of $^1O_2$ in surface waters.[15,30] However, for the Vaccarès sample one finds $r_{^3\mathrm{CDOM}^*} < r_{^1\mathrm{O}_2}$. Possible explanations are: (i) the addition of the azide to the Vaccarès sample was able to quench both $^1O_2$ and some of the interfering species. The role of these species would be underestimated from the azide data and, as a consequence, one would overestimate $r_{^1\mathrm{O}_2}$. (ii) TMP was not able to react with the whole of ^{3}CDOM* in the Vaccarès sample, possibly because some transients would preferentially react with O_2 to yield $^1O_2$, even with TMP in large excess. One should assume that such peculiar transients are particularly common in the estuarine sample. (iii) The adopted literature value of k_d is too elevated. Note that the model fit to the data of Fig. 5 would be largely improved by adopting a lower value of k_d. In that case $r_{^1\mathrm{O}_2}$ would be considerably lower. Interestingly, in cases (i) and (ii) one has to assume a rather peculiar behavior of the estuarine sample.

Expected transformation kinetics of model substrates

The data obtained or available for $HO^\bullet$ ($r_{\mathrm{HO}^\bullet}$ and $\sum_i k_i[S_i]$), $^1O_2$ ($r_{^1\mathrm{O}_2}$ and k_d) and ^{3}CDOM* ($r_{^3\mathrm{CDOM}^*}$ and $k_6[O_2] + k^*$) can be used for the assessment of the transformation kinetics of model substrates in the two water samples under the adopted irradiation conditions. It would therefore be possible to compare the relative importance of the different transformation pathways. Unfortunately, while a wide data set is available for the reactivity of the dissolved molecules with $HO^\bullet$, that with ^{3}CDOM* has been studied for relatively few compounds (mainly phenylurea herbicides and sulfonamides),[8] for which additionally there is no data concerning the (presumably low, however) reaction rate constant with $^1O_2$. Table 3 reports the reaction rate constants with $HO^\bullet$ of two amino acids (tyrosine and histidine), 4-chlorophenol (4CP) and the corresponding phenolate (4CP$^-$), and the phenylurea herbicides diuron and fenuron.[4,36,37] For phenylureas the reaction rate constants with ^{3}CDOM* are also reported,[38] while for the other compounds the rate constants with $^1O_2$ only are available.[36,39]

Let R be a generic compound dissolved in water. Under reasonable pseudo-first order conditions, the half life time of R for reaction with $HO^\bullet$, $^1O_2$ and ^{3}CDOM*, respectively, is expressed by:

$$t_{1/2}^{R,\mathrm{OH}^\bullet} = \frac{\ln 2 \sum_i k_i[S_i]}{k_{R,\mathrm{OH}^\bullet} r_{\mathrm{OH}^\bullet}} \tag{19}$$

$$t_{1/2}^{R,^1\mathrm{O}_2} = \frac{\ln 2 k_\mathrm{d}}{k_{R,^1\mathrm{O}_2} r_{^1\mathrm{O}_2}} \tag{20}$$

$$t_{1/2}^{R,^3\mathrm{CDOM}^*} = \frac{\ln 2 (k_6[\mathrm{O}_2] + k^*)}{k_{R,^3\mathrm{CDOM}^*} r_{^3\mathrm{CDOM}^*}} \tag{21}$$

where $k_\mathrm{d} = 2.5 \times 10^5$ s^{-1},[21] and k_6 $[O_2] + k^* = 5 \times 10^5$ s^{-1}.[25] The values of $r_{\mathrm{HO}^\bullet}$, $\sum_i k_i[S_i]$, $r_{^1\mathrm{O}_2}$ and $r_{^3\mathrm{CDOM}^*}$ for the Vaccarès and Canal samples are reported in Table 1, together with the associated errors. The values of the reaction rate constants of the different model compounds (substrates) with the transient species $HO^\bullet$, $^1O_2$ and ^{3}CDOM*, and the corresponding half-life times of the substrates are reported in Table 3. They are expressed in hours of continuous irradiation under the adopted device. The UV irradiance was 220 W m^{-2}, namely around 7 times more intense than the irradiance of sunlight at noon during the summer solstice at mid-latitude.[40] Also note that the errors associated to the half-life times have been derived by error propagation, from the relevant quantities reported in Table 1, and rounded to the precision of the $t_{\frac{1}{2}}$ values.

In the case of $k_{\mathrm{R},^3\mathrm{CDOM}^*}$, the main problem is that CDOM is not a species of definite chemical composition. Accordingly, the relevant reaction rate constants can only be measured relative to model molecules that are representative of the nature of CDOM. It has been reported that 3′-methoxyacetophenone (MAP) and benzophenone (BP) can be used to this purpose.[38] The reactivity of the relevant excited triplet states toward fenuron and diuron is quite different, with MAP being considerably less reactive than BP. For this reason Table 3 reports an interval for the values of $k_{^3\mathrm{CDOM}^*}$, with the upper end corresponding to $k_{^3\mathrm{BP}^*}$ and the lower end to $k_{^3\mathrm{MAP}^*}$.

From the $t_{\frac{1}{2}}$ data reported in Table 3 it is apparent that, first of all, the photochemical reactivity of the Vaccarès (estuarine, brackish) sample is higher compared to Canal (freshwater). The difference is highest for the reaction with $^1O_2$, and lowest for ^{3}CDOM*. It is remarkable that the estuarine sample is photochemically more reactive than the riverine/freshwater one. The most plausible explanation is the higher occurrence and reactivity of CDOM in the studied estuarine sample, which in the case of the Rhône river would be combined with a delta where the water is quite shallow. Higher intrinsic photoreactivity and shallow water would combine together in producing a delta environment where photochemical processes could play a very important role, also considering that such an environment is located in the Mediterranean region where sunlight is abundant. Such a

Table 3 Rate constants for the reaction of some model substrates with $HO^\bullet$, $^1O_2$, and ^{3}CDOM*.[36–39] The interval in the case of ^{3}CDOM* shows the different reactivity of ^{3}BP* and ^{3}MAP* with diuron and fenuron. The corresponding values of $t_{\frac{1}{2}}$ for the Vaccarès (V) and Canal (C) samples are based on the reported literature rate constants, the results of the irradiation experiments carried out in this work, and eqn (19)–(21). The values of $t_{\frac{1}{2}}$ are expressed in hours of continuous irradiation under the adopted device. n/a = not available

	Tyrosine	Histidine	4-CP	4-CP$^-$	Diuron	Fenuron
$k_{^\bullet\mathrm{OH}}$/M^{-1} s^{-1}	1.3×10^{10}	5.0×10^9	7.6×10^9	4.1×10^9	5×10^9	7×10^9
$k_{^1\mathrm{O}_2}$/M^{-1} s^{-1}	9.0×10^6	6.6×10^7	6.0×10^6	1.9×10^8	n/a	n/a
$k_{^3\mathrm{CDOM}^*}$/M^{-1} s^{-1}	n/a	n/a	n/a	n/a	$(9–520) \times 10^6$	$(8.1–200) \times 10^7$
$t_{\frac{1}{2}}^{\;^\bullet\mathrm{OH}}$(C)/h	160 ± 5	410 ± 10	270 ± 10	500 ± 15	410 ± 10	290 ± 10
$t_{\frac{1}{2}}^{\;^1\mathrm{O}_2}$(C)/h	390 ± 5	54 ± 1	590 ± 10	19 ± 1	n/a	n/a
$t_{\frac{1}{2}}^{\;^3\mathrm{CDOM}^*}$(C)/h	n/a	n/a	n/a	n/a	13–760	3.4–85
$t_{\frac{1}{2}}^{\;^\bullet\mathrm{OH}}$(V), h	90 ± 1	220 ± 2	150 ± 1	270 ± 3	220 ± 2	160 ± 2
$t_{\frac{1}{2}}^{\;^1\mathrm{O}_2}$(V)/h	100 ± 10	14 ± 1	160 ± 20	4.9 ± 0.5	n/a	n/a
$t_{\frac{1}{2}}^{\;^3\mathrm{CDOM}^*}$(V)/h	n/a	n/a	n/a	n/a	10–590	2.7–66

result strengthens the previous findings that the Rhône delta is a very useful field photochemical reactor, where for instance the photoinduced nitration processes can be easily detected.[41]

As far as the relative reactivity with $HO^\bullet$ and $^1O_2$ is concerned, in both samples tyrosine and 4CP are expected to react faster with the hydroxyl radical, histidine and the 4-chlorophenolate with singlet oxygen. In the case of the compounds that react faster with $HO^\bullet$, the reactivity with $^1O_2$ is of secondary importance but it is not negligible. In contrast, for the molecules that react faster with $^1O_2$, the reaction with $HO^\bullet$ is unimportant. Note that $4CP^-$, in analogy with many chlorophenolates, would also undergo direct photolysis to a significant extent.[36,42–44]

In the case of the two phenylurea pesticides chosen as model substrates, the comparison of the reactivity with $HO^\bullet$ and with $^3CDOM^*$ should take into account the relatively large interval of $t_{\frac{1}{2}}^{^3\mathrm{CDOM}^*}$. Such an interval depends on the choice of BP and MAP as model molecules for CDOM. By comparison with $t_{\frac{1}{2}}^{HO^\bullet}$ one gets that, in the case of diuron, the reaction with the hydroxyl radical is more important if the reactivity of $^3CDOM^*$ is more similar to that of $^3MAP^*$, while $^3CDOM^*$ is a more significant sink if its reactivity resembles that of $^3BP^*$. In case the reaction with $HO^\bullet$ is more important, it would be around twice as fast as that with $^3CDOM^*$. In the opposite case, the reaction with $^3CDOM^*$ could out-compete that of $HO^\bullet$ by an order of magnitude or more.

In the case of fenuron the reaction with $^3CDOM^*$ is expected to be more important compared to $HO^\bullet$, irrespective of the hypothesized reactivity of $^3CDOM^*$ ($^3BP^*$-like or $^3MAP^*$-like). Accordingly, the present results confirm the findings of Canonica and coworkers that $^3CDOM^*$ is a very important sink of phenylurea herbicides in surface water.[8] However, under definite circumstances of CDOM photoreactivity and with certain substrates (*e.g.* diuron), the reaction with $HO^\bullet$ cannot be neglected as a sink.

Conclusions

In this study, for the first time to our knowledge, the photochemical formation of $HO^\bullet$, $^1O_2$ and $^3CDOM^*$ was determined in both a freshwater and an estuarine environment (Canal and Vaccarés samples, respectively). The estuarine sample contained more organic matter as measured by NPOC, as expected, but interestingly the organic matter of the estuarine sample also showed a higher intrinsic absorption of radiation. As a consequence, the absorbance ratio between the estuarine and the freshwater sample is higher than the ratio of NPOC, which could make the CDOM in the estuarine sample considerably more photoreactive.

The reported CDOM features in the two samples are reflected in the respective photochemical activity as measured by the formation of $HO^\bullet$, $^1O_2$, and $^3CDOM^*$. The formation rates of all these species are considerably higher in the estuarine sample, where the indirect photolysis of organic contaminants could therefore be faster. Such a finding is somewhat expected in the case of $^1O_2$ and $^3CDOM^*$ that are produced by irradiated colored organic matter. The radical $HO^\bullet$ is also produced by nitrate and nitrite, which have equal to higher concentration in the freshwater sample. It can therefore be inferred that the higher photoproduction of $HO^\bullet$ in the estuarine sample can be accounted for by irradiated CDOM. Overall, the transition from the Rhône freshwater to the delta results in more favorable conditions for photochemistry, because of the combination of higher intrinsic reactivity, shallower water columns and longer residence time of water.[41]

In this work it was also shown that the quantification of $^1O_2$ through the degradation of FFA suffers from some interference by $^3CDOM^*$ or other species such as $ROO^\bullet$ and/or $RO^\bullet$. At the same time, the determination of $^3CDOM^*$ using TMP is also sensitive to the interference by $^1O_2$. However, it was possible to overcome the problem upon addition of NaN_3 to the FFA system, which allowed for the quantification of the contribution of the interfering species to the degradation of FFA. In a similar way, $^1O_2$ is able to react with TMP and therefore to interfere with the determination of $^3CDOM^*$. The knowledge of the formation rate of $^1O_2$ allows its inclusion into the kinetic model that describes the degradation of TMP, and the measurement of the formation rate of $^3CDOM^*$ is therefore possible despite the interference. Interestingly, Fig. 6 shows that the reaction rate between TMP and $^1O_2$ increases linearly with [TMP], while the total transformation rate of TMP (r_{TMP}) has a less-than-linear increase with [TMP]. The consequence is that the interference by the reaction between TMP and $^1O_2$ becomes more important at elevated [TMP].

The procedure depicted in the present paper (measurement of $^1O_2$ with FFA, of other interfering species with FFA + NaN_3, and inclusion of $^1O_2$ into the kinetic model of TMP degradation to exactly quantify $^3CDOM^*$) could therefore be useful for future studies into the quantification of $^1O_2$ and $^3CDOM^*$ upon irradiation of surface waters.

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Notes and references

1 S. S. Walse, S. L. Morgan, L. Kong and J. L. Ferry, Role of dissolved organic matter, nitrate, and bicarbonate in the photolysis of aqueous fipronil, *Environ. Sci. Technol.*, 2004, **38**, 3908–3915.

2 R. Huie and P. Neta, Kinetics of one-electron transfer-reactions involving ClO_2 and NO_2, *J. Phys. Chem.*, 1986, **90**, 1193–1198.

3 C. Richard and S. Canonica, Aquatic phototransformation of organic contaminants induced by coloured dissolved natural organic matter, *Handb. Environ. Chem.*, 2005, **2m**, 299–323.

4 G. Buxton, C. Greenstock, W. Helman and A. Ross, Critical-review of rate constants for reactions of hydrated electrons, hydrogen-atoms and hydroxyl radicals ($^\bullet OH/^\bullet O^-$) in aqueous-solution, *J. Phys. Chem. Ref. Data*, 1988, **17**, 513–886.

5 W. Glaze, J. Kang and D. Chapin, The chemistry of water-treatment processes involving ozone, hydrogen-peroxide and ultraviolet-radiation, *Ozone Sci. Eng.*, 1987, **9**, 335–352.

6 C. Minero, S. Chiron, G. Falletti, V. Maurino, E. Pelizzetti, R. Ajassa, M. E. Carlotti and D. Vione, Photochemical processes involving nitrite in surface water samples, *Aquat. Sci.*, 2007, **69**, 71–85.

7 P. Vaughan and N. Blough, Photochemical formation of hydroxyl radical by constituents of natural waters, *Environ. Sci. Technol.*, 1998, **32**, 2947–2953.

8 S. Canonica, Oxidation of aquatic organic contaminants induced by excited triplet states, *Chimia*, 2007, **61**, 641–644.

9 D. Vione, G. Falletti, V. Maurino, C. Minero, E. Pelizzetti, M. Malandrino, R. Ajassa, R. Olariu and C. Arsene, Sources and sinks of hydroxyl radicals upon irradiation of natural water samples, *Environ. Sci. Technol.*, 2006, **40**, 3775–3781.

10 B. Voelker and B. Sulzberger, Effects of fulvic acid on Fe(II) oxidation by hydrogen peroxide, *Environ. Sci. Technol.*, 1996, **30**, 1106–1114.

11 B. Voelker, F. Morel and B. Sulzberger, Iron redox cycling in surface waters: effects of humic substances and light, *Environ. Sci. Technol.*, 1997, **31**, 1004–1011.

12 I. Pozdnyakov, Y. Sosedova, V. Plyusnin, V. Grivin, D. Vorob'ev and N. Bazhin, Optical spectra and kinetic characteristics of radicals formed upon the photolysis of aqueous solutions of a $FeOH_{aq}{}^{2+}$ complex and phenol, *Russ. Chem. Bull.*, 2004, **53**, 2715–2722.

13 I. Pozdnyakov, Y. Sosedova, V. Plyusnin, E. Glebov, V. Grivin, D. Vorobyev and N. Bazhin, Photodegradation of organic pollutants in aqueous solutions caused by $Fe(OH)_{aq}{}^{2+}$ photolysis: Evidence of OH radical formation, *Int. J. Photoenergy*, 2004, **6**, 89–93.

14 K. Takeda, H. Takedoi, S. Yamaji, K. Ohta and H. Sakugawa, Determination of hydroxyl radical photoproduction rates in natural waters, *Anal. Sci.*, 2004, **20**, 153–158.

15 S. Halladja, A. Ter Halle, J. P. Aguer, A. Boulkamh and C. Richard, Inhihition of humic substances mediated photooxygenation of furfuryl alcohol by 2,4,6-trimethylphenol. Evidence for reactivity of the phenol with humic triplet excited states, *Environ. Sci. Technol.*, 2007, **41**, 6066–6073.

16 S. Canonica and P. G. Tratnyek, Quantitative structure-activity relationships for oxidation reactions of organic chemicals in water, *Environ. Toxicol. Chem.*, 2003, **22**, 1743–1754.

17 S. Chiron, C. Minero and D. Vione, Photodegradation processes of the Antiepileptic drug carbamazepine, relevant to estuarine waters, *Environ. Sci. Technol.*, 2006, **40**, 5977–5983.

18 S. Mylon, K. Chen and M. Elimelech, Influence of natural organic matter and ionic composition on the kinetics and structure of hematite colloid aggregation: Implications to iron depletion in estuaries, *Langmuir*, 2004, **20**, 9000–9006.

19 J. Rodier, in *L'analyse de l'eau, eaux naturelles, eaux résiduaires, eau de mer*, Dunod, Paris, 7th edition, 1984, p. 1365.

20 D. Vione, V. Lauri, C. Minero, V. Maurino, M. Malandrino, M. E. Carlotti, R. I. Olariu and C. Arsene, Photostability and photolability of dissolved organic matter upon irradiation of natural water samples under simulated sunlight, *Aquat. Sci.*, 2009, **71**, 34–45.

21 S. H. Chien, M. F. Cheng, K. C. Lau and W. K. Li, Theoretical study of the Diels-Alder reactions between singlet (^1D_g) oxygen and acenes, *J. Phys. Chem. A*, 2005, **109**, 7509–7518.

22 E. M. White, P. P. Vaughan and R. G. Zepp, Role of the photo-Fenton reaction in the production of hydroxyl radicals and photobleaching of colored dissolved organic matter in a coastal river of the southeastern United States, *Aquat. Sci.*, 2003, **65**, 402–414.

23 S. J. Hug and O. Leupin, Iron-catalyzed oxidation of arsenic(III) by oxygen and by hydrogen peroxide: pH-dependent formation of oxidants in the Fenton reaction, *Environ. Sci. Technol.*, 2003, **37**, 2734–2742.

24 S. Chiron, S. Barbati, S. Khanra, B. K. Dutta, M. Minella, C. Minero, V. Maurino, E. Pelizzetti and D. Vione, Bicarbonate-enhanced transformatino of phenol upon irradiation of hematite, nitrate and nitrite, *Photochem. Photobiol. Sci.*, 2009, **8**, 91–100.

25 M. A. J. Rodgers and P. T. Snowden, Lifetime of $O_2{}^1D_g$) in liquid water as dermined by time-resolved infrared luminescence measurements, *J. Am. Chem. Soc.*, 1982, **104**, 5541–5543.

26 S. Canonica and H. U. Laubscher, Inhibitory effect of dissolved organic matter on triplet-induced oxidation of aquatic contaminants, *Photochem. Photobiol. Sci.*, 2008, **7**, 547–551.

27 N. Motohashi and Y. Saito, competitive measurement of rate constants for hydroxyl radical reactions using radiolytic hydroxylation of benzoate, *Chem. Pharm. Bull.*, 1993, **41**, 1842–1845.

28 F. Wilkinson and J. Brummer, Rate constants for the decay and reactions of the lowest electronically excited singlet-state of molecular-oxygen in solution, *J. Phys. Chem. Ref. Data*, 1981, **10**, 809–1000.

29 P. Neta, R. E. Huie and A. B. Ross, Rate constants for reactions of inorganic radicals in aqueous solution, *J. Phys. Chem. Ref. Data*, 1988, **17**, 1027–1230.

30 S. Canonica and M. Freiburghaus, Electron-rich phenols for probing the photochemical reactivity of freshwaters, *Environ. Sci. Technol.*, 2001, **35**, 690–695.

31 J. Hoigné, Formulation and calibration of environmental reaction kinetics: Oxidations by aqueous photooxidants as an example, in *Aquatic Chemical Kinetics*, ed. W. Stumm, Wiley, New York, 1990, pp. 43–70.

32 D. Vione, D. Bagnus, V. Maurino and C. Minero, Quantification of singlet oxygen and hydroxyl radicals upon UV irradiation of surface water, *Environ. Chem. Lett.*, 2009, DOI: 10.1007/s10311-009-0208-z.

33 B. C. Faust and J. Hoigné, Sensitized photooxidation of phenols by fulvic acid and in natural waters, *Environ. Sci. Technol.*, 1987, **21**, 957–964.

34 P. G. Tratnyek and J. Hoigné, Photo-oxidation of 2,4,6-trimethylphenol in aqueous laboratory solutions and natural waters: kinetics of reaction with singlet oxygen, *J. Photochem. Photobiol., A*, 1994, **84**, 153–160.

35 J.-P. Aguer, D. Tétégan and C. Richard, Humic substances mediated phototrensformation of 2,4,6-trimethylphenol: a catalytic reaction, *Photochem. Photobiol. Sci.*, 2005, **4**, 451–453.

36 M. Czaplicka, Photo-degradation of chlorophenols in the aqueous solution, *J. Hazard. Mater.*, 2006, **134**, 45–59.

37 F. Javier Benitez, F. J. Real, J. L. Acero and C. Garcia, Kinetics of the transformation of phenyl-urea herbicides during ozonation of natural waters: Rate constants and model predictions, *Water Res.*, 2007, **41**, 4073–4084.

38 S. Canonica, B. Hellrung, P. Müller and J. Wirz, Aqueous oxidation of phenylurea herbicides by triplet aromatic ketones, *Environ. Sci. Technol.*, 2006, **40**, 6636–6641.

39 A. L. Boreen, B. L. Edhlund, J. B. Cotner and K. McNeill, Indirect photodegradation of dissolved free amino acids: the contribution of singlet oxygen nd the differential reactivity of DOM from various sources, *Environ. Sci. Technol.*, 2008, **42**, 5492–5498.

40 D. Vione, V. Maurino, C. Minero, M. E. Carlotti, S. Chiron and S. Barbati, Modelling the occurrence and reactivity of the carbonate radical in surface freshwater, *C. R. Chim.*, 2009, **12**, 865–871.

41 S. Chiron, C. Minero and D. Vione, Occurrence of 2,3-dichlorophenol and of 2,4-dichloro-6-nitrophenol in the Rhône River Delta (Southern France), *Environ. Sci. Technol.*, 2007, **41**, 3127–3133.

42 D. Vione, C. Minero, F. Housari and S. Chiron, Photoinduced transformation processes of 2,4-dichlorophenol and 2,6-dichlorophenol on nitrate irradiation, *Chemosphere*, 2007, **69**, 1548–1554.

43 S. Chiron, L. Comoretto, E. Rinaldi, V. Maurino, C. Minero and D. Vione, Pesticide by-products in the Rhône delta (Southern France). The case of 4-chloro-2-methylphenol and of its nitroderivative, *Chemosphere*, 2009, **74**, 599–604.

44 G. Grabner, C. Richard and G. Kohler, Formation and reactivity of 4-oxocyclohexa-2,5-dienyldiene in the photolysis of 4-chlorophenol in aqueous solution at ambient temperature, *J. Am. Chem. Soc.*, 1994, **116**, 11470–11480.

Chapter 4: Modelling and MASAS*light*

Plant protection products (PPPs) have an important role in agricultural production and food security, and ensuring their safety to man and the environment is of paramount importance. Understanding the fate and behaviour of PPPs is therefore necessary for toxicological assessment and eventually for development of new chemicals.

The Eurepean Plant Protection Product Directive (91/414/EEC) emphasises the need of models to calculate predicted environmental concentrations of active substances of plant protection products (PPPs). To this end, both monitoring and modelling the pesticide fate at the appropriate temporal and spatial scales is necessary. There is a complementary role of monitoring and modelling, as the later serves as a guideline for setting up environmental monitoring programs. However, monitoring of pesticides residues in water bodies is costly and time consuming. Models are indispensable tools to be used in the applied environmental sciences for predictions of the pesticides fate and behaviour.

Many models have been developed to assess the fate of pesticides. Let us first clarify a few terms encountered in environmental modelling which are shown in Fig.18:

- **Mathematical model**: The description of the environmental processes by a set of mathematical equations. Having formulated a mathematical model, the model must be solved.
- **Simulation:** finding a solution (analytically or numerically) to the mathematical equations.
- **Simulation tool**: The solution is implemented in a computer or program software.

Mathematical models are usually divided into two fundamentally different types of models used in understanding chemical fate (Andrew ford, 1999, Jørgensen and Bendoricchio 2001, Webster et al., 2005):

- Static models: to predict concentrations of a chemical compound partitioning between different phase in the environment at equilibrium. Static models consider a steady-state condition of an ecosystem averaged over long time (almost infinite time).

- Dynamic models: are quite different, as the variables or their interactions are functions of time. Process-based models are a substitute for real systems linking together processes to estimate the expected chemical behaviour

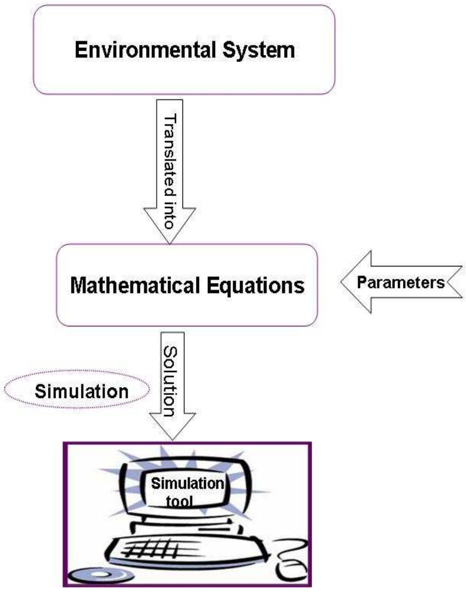


Figure18. A simple view of modeling steps in environmental modelling.

4.1 Modelling environmental processes

Once released in fields, pesticides become part of agricultural ecosystems and their fate is determined by physical, chemical and biological processes. The description of these processes is translated into mathematical terms. These approaches lead to differential equations, which are related to the change of a variable, like concentration. In formulating models of chemical and environmental processes, one of the most important principals is the material balance. Mass balances are simply representations of the first law of conservation, namely that matter can neither be created nor destroyed. Mass balance usually considers the fate of substances entering and leaving a system in various ways. The modelling approach to the mass balance tries to simplify the system with some general assumptions (completely mixed aquatic system). Environmental models usually contain two kinds of processes:

(1) Reaction processes (Physicochemical properties and transformation processes).

(2) Transport processes.

These processes are linked by the concept of mass balance. Accordingly, there are three environmental processes or pathways to be considered in a mass balance model; transformation or degradation processes, advection processes that move the chemical out of the modelled system, and exchange processes between environmental media or compartments. The mass balance is thus fundamental and when coupled with other forms of a defining relationship, can be used with very great effect in forming mathematical process models, which are powerful in describing quite complex process phenomena (Richter et al., 1996; Schwarzenbach et al., 2003; Webster et al., 2005).

There are many models used to evaluate the fate and behaviour of pesticides which are varied in their complexity, in processes treated and in their approach and purpose. Some researchers use a simple mass-balance approach, whereas others have attempted to model the in-lake processes in detail.

We are interested in MASAS, (Modelling of Anthropogenic Substances in Aquatic Systems), developed by Ulrich and co-workers (1995). Models included are based on a dynamic one-dimensional vertical lake model describing the time-dependent concentration of a compound in the water column and in the sediment.

MASAS is useful for estimating the fate and behaviour of chemicals in lakes as it links the fundamental chemical properties of the herbicides in question to the characterizations of the aquatic environment. The primary herbicide transport and transformation processes, simulated in the model, include flushing, sorption and sedimentation, gas exchange, photolysis, hydrolysis, and biological degradation (Ulrich et al, 1995). It reports the contribution of each process to the overall aquatic dissipation processes, Fig .19.

4.2 Description of MASAS-*light*

MASAS-light is a collection of different tools for the assessment of the behaviour of chemical compounds in lakes and rivers. Models included are based on a dynamic one-dimensional vertical lake model describing the time-dependent concentration of a compound in the water column and in the sediment. It contains several simple mathematical models, Figure 19:

- One-box model
- Two-box model
- Combi-box model
- River model

Further, it provides the tool **Processes** that allows users an easy evaluation of the impact of different elimination processes and reports the contribution of each process the overall aquatic dissipation processes.

- Flushing
- Sorption/sedimentation
- Gas exchange
- Hydrolysis
- Direct photolysis
- Indirect photochemical transformation (singlet oxygen, hydroxyl radicals, reactive triplet states)
- Microbial transformation

Processes are linked to a database that stores data of various compounds. MASAS*light* is based on the textbook "Environmental Organic Chemistry" by Schwarzenbach, Gschwend and Imboden, Wiley 1993.

4.3 Evaluation of the elimination processes:

For determination the dominant elimination processes responsible for a given compound, we used Processes and One-Box Model, as we consider a well-mixed water body. Each process requires certain input parameters which were obtained either experimentally or from references.

-Flushing:

The elimination rate constant by flushing k_w was calculated for the Vaccarès lagoon by dividing the mean seasonal discharge of water from the Vaccarès lagoon to its neighbour lagoons by the volume of the lagoon. The water flow is unknown, but we know both the mean residence time of the water (t) days and the volume of water system (V) m^3, therefore the $Q= V/ t$

Other elimination processes volatilization, sedimentation as input parameters for MASAS were explained in article (2).

4.4 Modelling results

The result show up as the degradation rate constant for each processes with corresponding half life time and also the total the rate constant together with contribution percentage of each process to the overall elimination, Fig. 20.

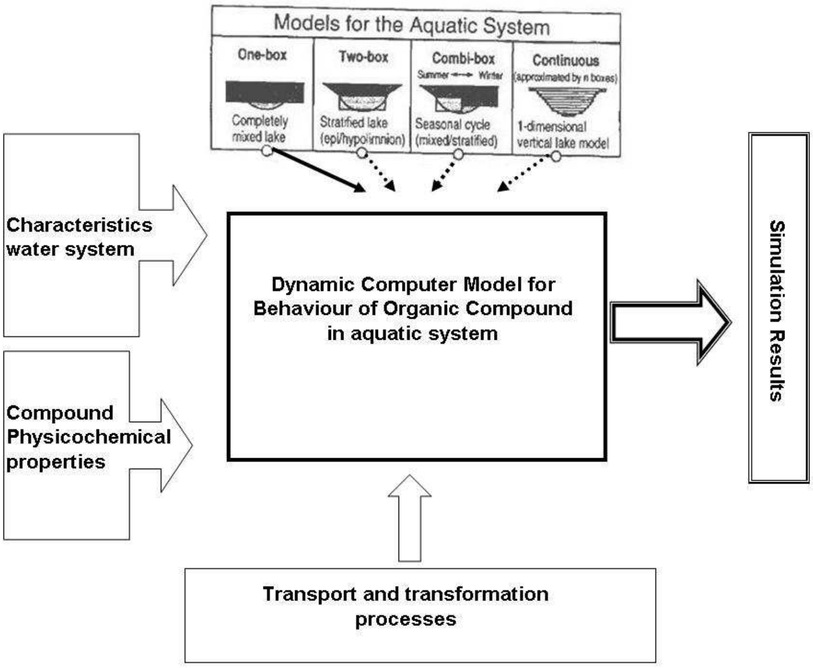
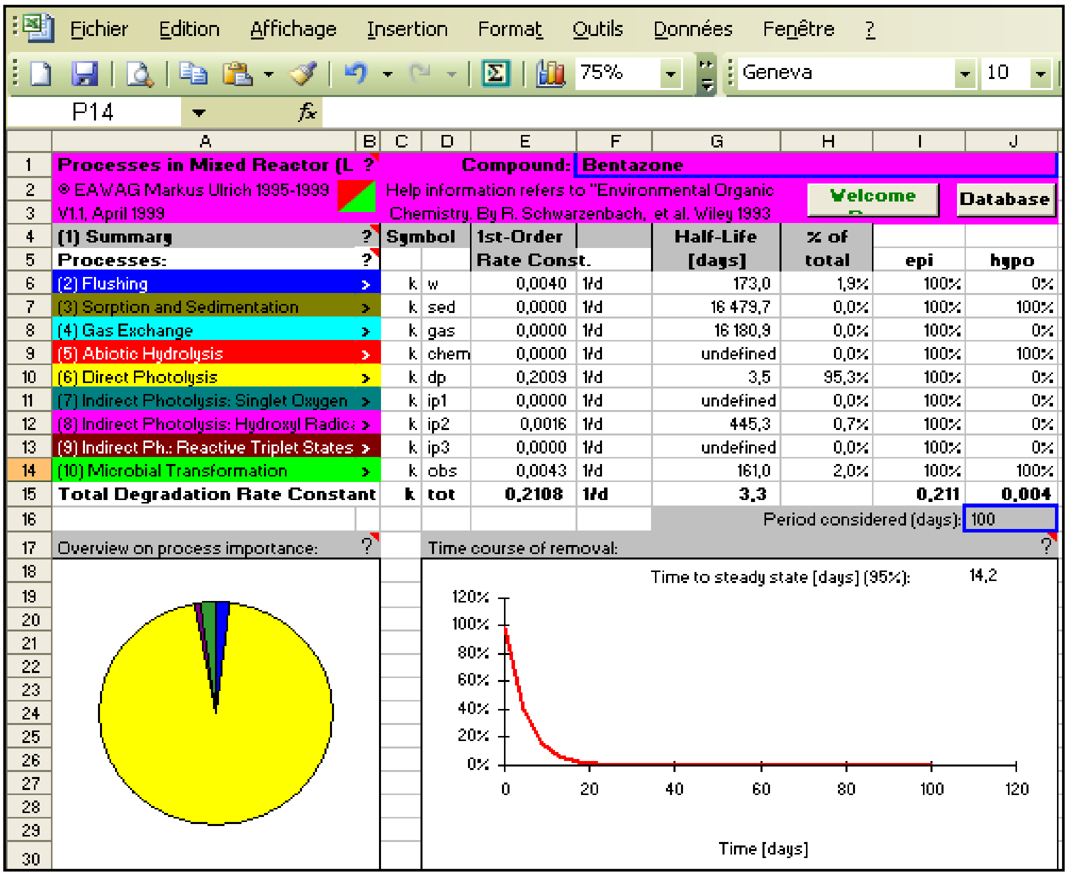


Figure 19. Main elements of MASAS simulation tool (Ulrich et al, 1995).



Processes in Mixed Reactor (L ? Compound: Bentazone

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V1.1, April 1999

Help information refers to "Environmental Organic Chemistry. By R. Schwarzenbach, et al. Wiley 1993

(1) Summary ?	Symbol		1st-Order		Half-Life	% of		
Processes: ?			Rate Const.		[days]	total	epi	hypo
(2) Flushing >	k	w	0,0040	1/d	173,0	1,9%	100%	0%
(3) Sorption and Sedimentation >	k	sed	0,0000	1/d	16 479,7	0,0%	100%	100%
(4) Gas Exchange >	k	gas	0,0000	1/d	16 180,9	0,0%	100%	0%
(5) Abiotic Hydrolysis >	k	chem	0,0000	1/d	undefined	0,0%	100%	100%
(6) Direct Photolysis >	k	dp	0,2009	1/d	3,5	95,3%	100%	0%
(7) Indirect Photolysis: Singlet Oxygen >	k	ip1	0,0000	1/d	undefined	0,0%	100%	0%
(8) Indirect Photolysis: Hydroxyl Radic: >	k	ip2	0,0016	1/d	445,3	0,7%	100%	0%
(9) Indirect Ph.: Reactive Triplet States >	k	ip3	0,0000	1/d	undefined	0,0%	100%	0%
(10) Microbial Transformation >	k	obs	0,0043	1/d	161,0	2,0%	100%	100%
Total Degradation Rate Constant	**k**	**tot**	**0,2108**	**1/d**	**3,3**		**0,211**	**0,004**

Period considered (days): 100

Overview on process importance: ?

Time course of removal: ?

Time to steady state [days] (95%): 14,2

Figure20. Summary of MASAS model processes running on an Excel spreadsheet (Ulrich et al, 1995).

Article 2

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

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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 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.

Key words: photochemistry; biodegradation; MCPA; dichlorprop; bentazone; lagoon.

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, 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 ($HO^{\bullet}$), 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 different 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 gL^{-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 μgL^{-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 park lies in the center of the Île de Camargue and covers 85,000 hectares 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 gL^{-1} in the canal water and about 25 gL^{-1} in the Vaccarès lagoon. Two different types of water samples were selected to elucidate if there is any or possible impact of water type on biodegradation and photodegradation. Ultravioletvisible (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, 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 mgCL^{-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. $FeSO_4.7H_2O$ 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 mLmin^{-1} (10mm 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 mLmin^{-1}. Details of HPLC conditions are given in Table 1. The limit of detection was 25 ± 3 μgL^{-1}. Three blank samples were obtained by spiking ultra pure water with the studied herbicides to give final concentrations of 10 μgL^{-1}. The average recoveries ranged from 83 to 90% for bentazone, MCPA and, dichlorprop, with relative standard deviations of 3 – 4%.

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 $k_{(^{\cdot}OH)}$ 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 $FeSO_4.7H_2O$ (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 ($k_{(^{\cdot}OH)} = 1.7 \times 10^{10}\ M^{-1}s^{-1}$, 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 OH radicals. To eliminate the interference of by-products, the measurements were done within 5 minutes. 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 $k_{(.OH)}$ for each herbicide was calculated according the following equation:

$$\ln (P_t/P_0) = \ln (R_t/R_0) \times (k_P/k_R) \qquad \text{(eq. 1)}$$

where P_0 and P_t represent herbicide compound concentration at the initial and at any reaction time, respectively, R_t and R_0 those of the reference compound, and k_P, k_R are second-order reaction rate constants of herbicide and reference compound with OH radical, respectively. The herbicide MCPA was included to compare with other literature results, by using dichlorprop as reference compound as its rate constant was determined previously.

2.7. Aerobic biodegradation

The experiment was based on the guideline ISO/DIS 14592-1 (International Organisation of Standardization, 1999) and the guideline from OECD (Test No. 309, 1999). In brief, the aerobic biodegradability of those herbicides was determined in a shake flask system in 1 L of water in the dark at 25 ± 2°C. Herbicides were applied at 10 μgL^{-1} in this study. This is only slightly higher than typical herbicide peak concentrations found in the Fumemorte canal from 2004-2006 (Comoretto, 2009). The test flasks were closed by loose cotton wool plugs that prevent contamination from air, wrapped with aluminum foil and incubated under aerobic conditions and continuous agitation (75 rpm). The oxygen concentration and pH were measured regularly and were fairly constant (5.9 ± 0.11 mgL^{-1}, pH 8.7 ± 0.1). The test lasted for 60 d. The removal of the tested herbicides was analyzed by HPLC after SPE. The following biotic flasks and abiotic controls were run: water samples with biotic activity for each site were run in triplicate containing a concentration of 10 μgL^{-1} of the tested herbicides. Two flasks of canal and lagoon water sample with sodium benzoate, at 10 μgL^{-1} were used to measure a microbial activity toward a reference compound. The possible abiotic degradation of the herbicides was tested in two ways in a flask with ultra pure water, and in two flasks of canal and lagoon water in which the biotic activity was inhibited by adding sodium azide (NaN_3) at 10 gL^{-1}.

2.8. Modeling phase transfer processes with the model MASAS (Modeling of Anthropogenic Substances in Aquatic Systems)

The use of modeling tools has become essential to evaluate the environmental fate of herbicides. MASAS, developed by Ulrich and co-workers (1995), is useful for this purpose as it links the fundamental chemical properties of the herbicides in question to the characterizations of the aquatic environment. The software MASAS was used to estimate elimination rate constants for herbicides in the Vaccarès lagoon by volatilization, sedimentation and flushing.

3. Results

3.1 Modeling the elimination by volatilization, sedimentation and flushing

The elimination rate constant for volatilization from the lagoon is obtained using the two-film model implemented in MASAS (eq. 2 + 3):

$$k_{gas} = v_{a\text{-}w}\, A/V \qquad \text{(eq. 2)}$$

where A is the surface area of the Vaccarès lagoon (89 $*10^6$ m^2) and V is its Volume 96 $*10^6$ m^3, and $v_{a\text{-}w}$ is the air-water transfer velocity (unit m d^{-1}, eq. 3).

$$v_{a-w} = \frac{1}{v_w{}^{-1} + v_{air}{}^{-1} H^{-1}} \qquad \text{(eq. 3)}$$

The $v_{a\text{-}w}$ was estimated for each compound as a function of its dimensionless Henry coefficient H, which were 2×10^{-13}, 1.1×10^{-8} and 5.6×10^{-5} for bentazone, MCPA and dichlorprop, respectively. We used the double boundary layer theory (Schwarzenbach et al. 2003) and an average wind speed u_{10} of 5.2 ms^{-1} at 10 m above ground of two meteorological stations (Höhener et al. 2010). The relations $v_{air} = 0.5 + 0.185\, u_{10}$ (Münnich et al. 1978) and $v_w = 1.75*10^{-4}((6.1+0.63\, u_{10})\wedge 0.5)\, u_{10}$ (Mackay and Yeun. 1983) for the air-side and the water-side boundaries, respectively, were used.

The elimination rate constant for sedimentation k_{sed} is obtained with eq. 4:

$k_{sed} = F_{sed} f_{oc} K_{OC} A/V$ (eq. 4)

In eq. 4, F_{sed} is the settling flux of particles in the Camargue (1.8 $gm^{-2}d^{-1}$) from Hensel et al. (1998), f_{OC} is the fraction of organic carbon in the sediment (0.1 g_{OC} g^{-1}, highest value of 8 sediment samples from Vaccarès lagoon analyzed by a TOC analyser), K_{OC} are the partitioning coefficients of the compounds between organic carbon and water, in $Lkg^{-1}{}_{OC}$: bentazone 51, MCPA: 74 and dichlorprop: 170 (eu-footprint, 2009). Furthermore, the elimination rate constant by flushing k_w (0.002 d^{-1}) was calculated for the Vaccarès lagoon by dividing the mean seasonal discharge of water from the Vaccarès lagoon to its neighboring lagoons (180,000 m^3 per day, Höhener et al, 2010) by the volume of the lagoon.

3.2. Photodegradation under natural sunlight

The loss of bentazone could be described as a sum of different first-order kinetic processes as plots of (ln $[\text{bentazone}]_t / [\text{bentazone}]_0$) versus time and were linear (Fig. 1a). The observable rate constant of herbicide degradation is defined as (eq. 5):

$k_{obs} = k_{dp} + k_{ip} + k_{hyd}$ (eq. 5)

which includes the first order decay constant of direct k_{dp} (d^{-1}) and indirect photolysis k_{ip} (d^{-1}) and the first order decay constant of hydrolysis k_{hyd} (d^{-1}). The overall half-life times for bentazone were 2.17 ± 0.25 and 4.08 ± 0.32 d for canal and lagoon water samples, respectively. In ultra pure water incubated in the dark, hydrolysis of bentazone was found to be negligible. The half-life time for bentazone in ultra pure water under natural sunlight was measured to be 5.12 ± 0.7 d. The disappearance of MCPA under natural sunlight was slower than for bentazone (Fig. 1b). The half life times were 13.86 ± 0.80 and 15.07 ± 1.10 d in canal and lagoon water samples, respectively. Direct photolysis contributed to 50 and 46% percent to overall photolysis. The half-life time for hydrolysis was greater than 160 d. Photolysis was even less significant for dichlorprop compared to the previous compounds (Fig. 1c). Its half-life times were 31.5 ± 1.2 and 34.6 ± 1.5 d for lagoon and canal water samples, respectively. Direct photolysis contributed 54% and 60% to overall photolysis. The half-life time for hydrolysis was found to be greater than 265 d.

3.3. Hydroxyl radical rate constant $k_{(^{\cdot}\mathrm{OH})}$

The measured rate constants for the reaction of OH radical with bentazone, MCPA and dichlorprop were shown in Table 2, together with literature data. Our values were higher than those reported in the literature for MCPA and dichlorprop by 1.5 and 3 times, respectively. Bentazone was less reactive toward $^{\cdot}$OH than MCPA and dichlorprop. Haag and Yao (1992) reported that a factor of 2 is acceptable for the purposes of the estimation of oxidation rates. We adopted then the higher value because a good agreement was obtained between the modeled rate constants upon reaction of those herbicides with OH radicals and those of indirect photodegradation under natural sunlight for MCPA and dichlorprop.

3.4. Biodegradation test

Sodium azide inhibited the degradation of all 3 herbicides (data not shown). In biotic flasks with canal water, MCPA and dichlorprop were significantly degraded with very short lag periods (Fig. 2a). The bentazone concentration remained constant. Half-lives for biodegradation of the herbicides studied in canal water sample were 6.9 ± 0.5 d (dichlorprop) and 8.3 ± 0.7 d (MCPA). In water from the lagoon, all herbicide concentrations were > 80 % of initial concentration until day 26 (Fig. 2b). MCPA and dichlorprop decreased thereafter somewhat, but not bentazone. In the period from 2 to 60 d, the half-life times were 39.6 ± 1.4 d and 46.2 ± 1.6 d for MCPA and dichlorprop, respectively. Sodium benzoate was completely degraded in both water samples within 2 d (results not shown). The control flasks with herbicides in ultra-pure water yielded some small losses due to hydrolysis and volatilization. This abiotic degradation was too slow to be significant for bentazone (82% remaining), taking into account the analytical variability. A relatively constant concentration of MCPA was maintained until the end of the test. However, abiotic degradation was responsible for disappearance of about 30% of the initial concentration of dichlorprop (Fig. 2c). Nevertheless, abiotic degradation was not a significant degradation pathway of all herbicides.

4. Discussion

4.1. Reactivity of herbicides

Bentazone was found to be the most reactive compound with an overall half-life time of 2.2 d in canal water and 4 d in lagoons. The main processes responsible for bentazone dissipation were shown to be direct photolysis (81%), and indirect photolysis (17%). The European commission data (2000) reported that the half-life time DT50 of bentazone subject to photolytic degradation in water at pH 7 was in the range of 2.6-3.8 d. Our results confirm these values. The total experimental half-life time for MCPA was 10.1 d in lagoon water. The major factors responsible for MCPA dissipation in the lagoon (Tab. 3) are direct photolysis (34%), indirect photolysis (33%) and microbial transformation (25%). A study on the fate of MCPA reported a half-life time of 12-16 d in Thames river water under sunlight (Stangroom et al. 1998). Soderquist and Crosby (1975) observed MCPA dissipation with about 5 d in water drained from rice fields. They suggested that microbial degradation contributed to the MCPA dissipation under field conditions. A half-life time of 16.7 d was found for dichlorprop (Tab. 3). Microbial transformation accounted for 36%, direct photolysis and indirect photolysis for 30% and 22%, respectively. Available environmental fate data indicate that dichlorprop is non-persistent to moderately persistent. (half-life time = 14 d) in aerobic terrestrial and aquatic environments (U.S.EPA, 2007). The primary routes of dissipation reported in literature are photodegradation in water and microbial-mediated degradation. Also, investigations under aerobic conditions in column experiments using aquifer material and low concentrations of dichlorprop (approximately 25 μgL^{-1}), reported that its degradation is likely to occur after lag periods of 20-30 d with degradation rates of 1.3 ± 2.6 $\mu gL^{-1}d^{-1}$ (Tuxen et al. 2000).

4.2. Comparison with field results

The total experimental and modeled half-life times of three herbicides in this study were in the same order of magnitude to those obtained by field observations in the Vaccarès lagoon during the period 2004-2006 which ranged from 5 to 15 d. For bentazone, a higher reactivity was found in the laboratory compared to the “apparent” reactivity in the lagoon. It is difficult to assess field dissipation rates when the duration and magnitude of the herbicide input functions are not known precisely (Höhener et al, 2010). Bentazone, for example, decreased apparently in the lagoon with half-life times between 10 to 15 d. This is a result of combining reactivity in the lagoon with continuous release from the canals. However, when a half-life time of 4 d is used to model bentazone in the lagoon with the model described in Höhener et al. (2010), the bentazone concentrations in the lagoon would not exceed 0.05 μgL^{-1}, whereas measured concentrations were frequently between 0.1 and 0.2 μgL^{-1} (Comoretto, 2009).

4.3. Photodegradation under in situ conditions

The light conditions for the photodegradation experiments in glass vials were different to those really applied in the lagoon, which has a mean depth of approximately 1 m and a natural turbidity. MASAS allows the assessment of direct photolysis in water bodies of varying thickness and turbidity and was used to estimate the overestimation of degradation rates under direct exposure. These calculations showed that the overestimation is by about a factor of 2.5

to 3, depending on turbidity. This is in agreement with findings of Stangroom et al. (1998) who applied a factor of two for correcting direct exposure to in situ conditions in a river to provide an estimate of half-life time for the flat natural water body. Assuming that photolysis is 3 times slower in the lagoon, then the bentazone half-life time (12 d) would match well with the field observations. The relative contribution of microbial degradation to the overall degradation rates of MCPA and dichlorprop would increase.

4.4. Contribution of OH radical to overall indirect photolysis

The initial formation rate of hydroxyl radical $R_{.OH}$ in lagoon water was measured with a medium-pressure Hg lamp in a glass photoreactor by Al Housari et al. (2010). It is possible therefore to calculate the outdoor persistence of the studied herbicides due to reaction with $^{\cdot}$OH. The measured rate constants of each herbicide $k_{p,^{\cdot}OH}$ values were combined with values of $R_{^{\cdot}OH}$ in the model of Vione et al. (2009) after dividing the latter value by 10 since the irradiance of the used lamp is 10 times higher than that of sunlight (eq. 6).

$$(t_{1/2})_{SSD} = (\ln 2 \times V \times \sum_i K_i[S_i]\ ) / (3.6 \times 10^4 \times R_{.OH} \times k_{p,^{\cdot}OH}) \qquad \text{(eq. 6)}$$

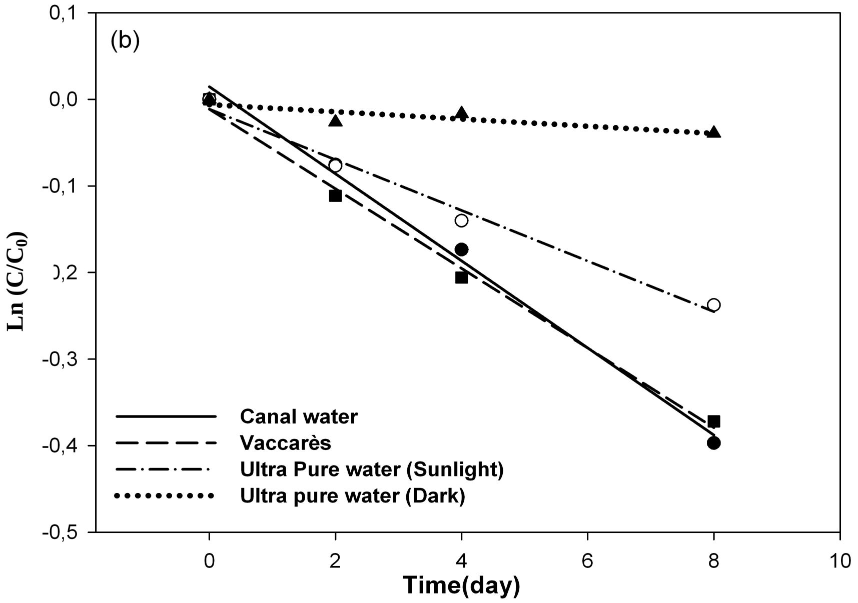
Here, $(t_{1/2})_{SSD}$ is the half-life time for a herbicide converted in units of summer sunny days (SSD, taking 15 July at 45° N latitude as reference) and by dividing by 10 h = 3.6×10^4 s. $V = S \times d$ is the volume (in liters) of water contained in a cylinder of surface $S = 12.6$ cm^2 and height d (average depth for thoroughly mixed water bodies; $d = 100$ cm). $\sum_i K_i[S_i]$ represents the overall $^{\cdot}$OH scavenging rate constant (Al Housari et al, 2010). The modeled half-life times of the studied herbicides upon reaction with $^{\cdot}$OH were about 131.5, 28.6 and 67.5 d for bentazone, dichlorprop and MCPA, respectively. The respective elimination rates are then 0.005, 0.01 and 0.024 d^{-1}. The contribution of $^{\cdot}$OH to the overall photodegradation rate can be obtained by dividing those elimination rates by the rate of photolysis (direct + indirect) from Table 3. $^{\cdot}$OH radical was then predicted to contribute to < 3% of the overall observed photodegradation rate of bentazone, while it was more important for MCPA (52%) and dichlorprop (45%) degradation (Tab. 3). Note that the studied herbicides were not irradiated under the lamp but under natural sunlight, which gave shorter half-life time as the herbicides would also react with other photogenerated species (e.g. CDOM*, $^1O_2$) and undergo direct photolysis.

4.5. Contribution of biodegradation

Biodegradation was significantly more important in the canal than in the lagoon water. More than 80% of initial concentration of MCPA was degraded in canal water compared to 60% in Vaccarès lagoon water. However, the residence time of the water in the canals is only in the order of 1-2 d, and therefore biodegradation in the canals of the Camargue is not a major issue. The initial period before the onset of herbicides degradation was longer in the Vaccarès lagoon than in canal, which means that the biodegradation behavior was most likely influenced by the salinity of lagoon water. Microbial degradation did not contribute to bentazone dissipation. This is in agreement with the reported results of Willard. (1977) where aerobic aquatic degradation showed that ^{14}C-labelled bentazone applied to rice paddy water remained intact for the 36 d of the study.

5. Conclusions

Findings from laboratory experiments, coupled with model estimations for sedimentation and volatilization, could improve the understanding of the fate of acidic herbicides after being discharged from paddy fields to the nearby canals and the Vaccarès lagoon. Sorption and sedimentation, gas exchange, flushing and abiotic hydrolysis had a minor role in the natural attenuation of the studied herbicides. Consequently, biodegradation and photodegradation competed for herbicide dissipation. However, biodegradation was dramatically slowed down in lagoon water with respect to canal water, and photodegradation was definitively the main route responsible for dissipation of acidic herbicides in Vaccarès lagoon. There is a need to investigate the phototransformation products of acidic herbicides in brackish lagoon waters because some of them have already been found to be of concern due to their potential (eco)toxicity (Vione et al., 2007; Chiron et al., 2009).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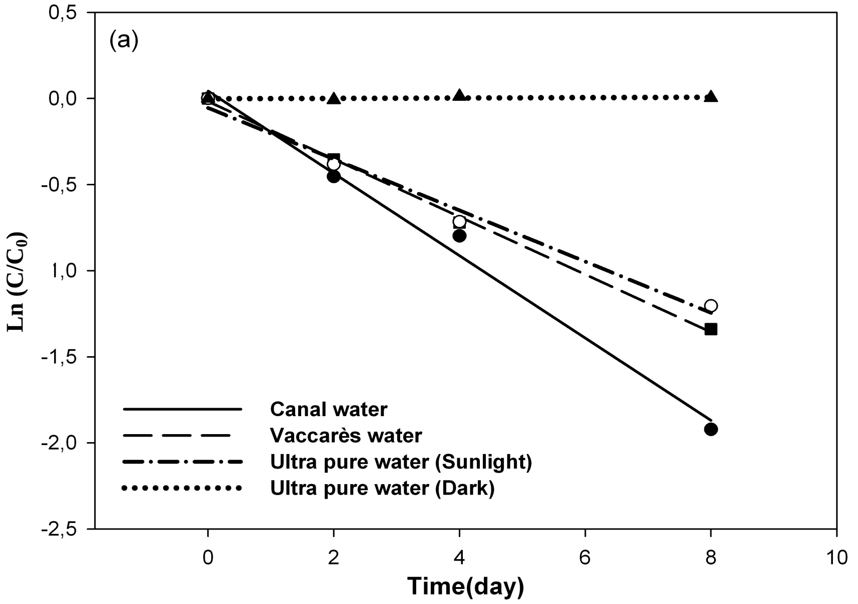
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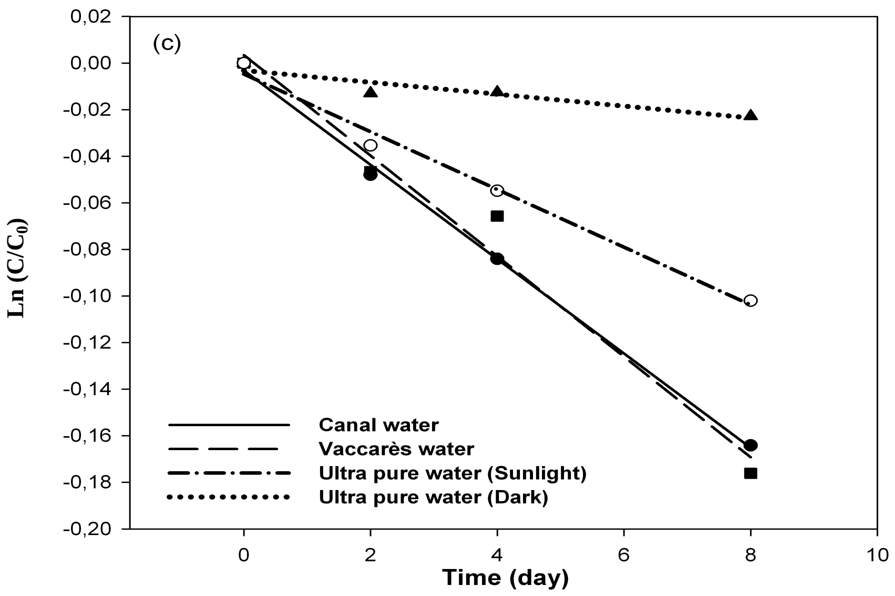
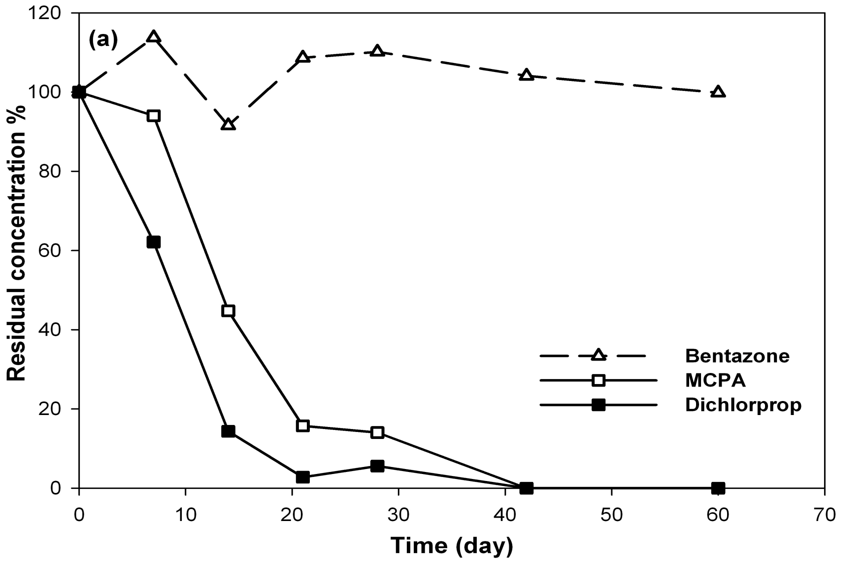


Fig. 1. Photodegradation kinetics in (●) canal and (■) lagoon water samples, (○) in ultra pure water under natural sunlight in July 2008 of a) bentazone, b) MCPA and c) dichlorprop. (▲) ultra pure water (dark control). Results are means of three replicates.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Residual concentration %
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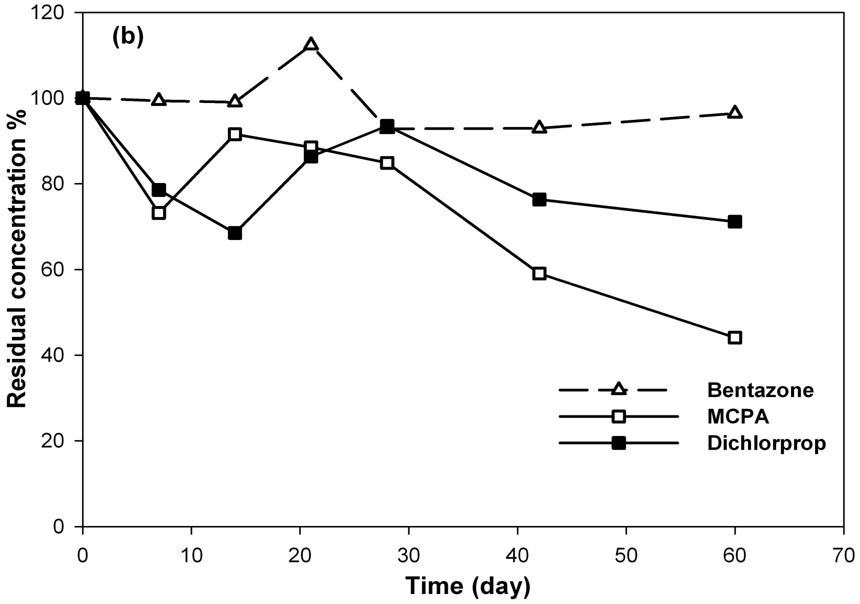
Bentazone
MCPA
Dichlorprop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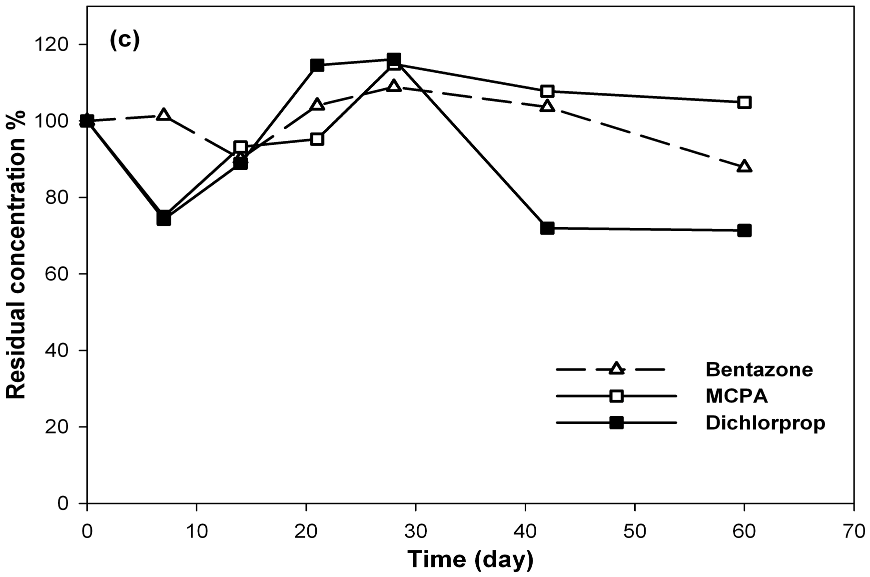

Fig. 2. Biodegradation kinetics of bentazone (Δ), MCPA (□) and dichlorprop (■) at 10 µgL^{-1} in a) canal water, b) lagoon water and c) ultra pure water used as reference in the biodegradation test. Results are means of three replicates, with relative standard deviations of 5%. Error bars are not shown here.

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

Chemicals	Mobile phase	Wavelength (nm)	Flow rate (mLmin^{-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

Table 2**.** Second-order kinetic rate constants of herbicide reaction with hydroxyl radical.

Compound	$k_{\bullet OH}$ (M^{-1} s^{-1})	Literature
Bentazone	$8.37 \pm 0.26 \times 10^{9}$	n.f.
MCPA	$3.85 \pm 0.23 \times 10^{10}$	2.21×10^{10} ref.a
Dichlorprop	$1.63 \pm 0.08 \times 10^{10}$	4.66×10^{9} ref.a

n.f. not found in literature, ref a: (Fdil et al. (2003).

Table 3**.** Summary of elimination rate constants for herbicides in the Vaccarès lagoon.

Elimination rate		Bentazone [d^{-1}]	MCPA [d^{-1}]	Dichlorprop [d^{-1}]
Flushing	k_w	0.002	0.002	0.002
Abiotic hydrolysis	k_{hyd}	$0.001 \pm 1x10^{-4}$	$0.004 \pm 5x10^{-4}$	$0.0026 \pm 5x10^{-4}$
Direct photolysis	k_{dp}	$0.14 \pm 2x10^{-2}$	$0.023 \pm 2x10^{-2}$	$0.012 \pm 1x10^{-3}$
Indirect photolysis	k_{ip}	$0.03 \pm 1x10^{-2}$	$0.022 \pm 8x10^{-3}$	$0.0096 \pm 1x10^{-2}$
Microbial degradation	k_{bio}	stable	$0.018 \pm 2x10^{-3}$	$0.015 \pm 1x10^{-3}$
Volatilization	k_{gas}	<0.001	<0.0001	<0.0001
Sorption + sedimentation	k_{sed}	<0.0001	<0.0001	<0.0001
Total (sum of all k)	k_{tot}	0.173	0.0685	0.0412
Half-life time (d)	$t_{1/2}$	4.0 d	10.1 d	16.7 d
Field data (2004-2006)	$t_{1/2}$	(10-15 d)	(6-13.5 d)	(10 d)
Reactivity with $^{\cdot}OH$	$t_{1/2}$	(131.5 d)	(28.6 d)	(67.5 d)
Overall $^{\cdot}OH$ contribution		< 3%	52%	45%

References

Al Housari F, Vione D, Chiron S, Barbati S. Reactive photoinduced species in estuarine waters. Characterization of hydroxyl radical, singlet oxygen and dissolved organic matter triplet state in natural oxidation processes. Photochem Photobiol Sci 2010;9(1):78-86.

Amphlett CB, Adams GE, Michael BD. Pulse radiolysis studies of deaerated aqueous salicylate solutions. Advances in Chemistry Series1968;81:231-50.

Chauvelon P, Tournoud MG, Sandoz A. Integrated hydrological modeling of a managed coastal Mediterranean wetland (Rhône delta, France): initial calibration. Hydrol Earth Syst Sci 2003;7:123-31.

Chiron S, Minero C, Vione D. Photodegradation processes of the antiepileptic drug carbamazepine, relevant to estuarine waters. Environ Sci Technol 2006;40:5977–83.

Chiron S, Comoretto L, Rinaldi E, Maurino V, Minero C, Vione D. Pesticide by-products in the Rhône delta (Southern France). The case of 4-chloro-2-methylphenol and of its nitroderivative. Chemosphere 2009;74:599–604

Comoretto L, Arfib B, Chiron S. Pesticides in the Rhône river delta (France): Basic data for a field based exposure assessment. Sci Total Environ 2007;380:124-32.

Comoretto L, Arfib, B, Talva R. Chauvelon P, Pichaud M, Chiron S, Höhener P. Runoff of pesticides from rice fields in the Île de Camargue (Rhône river delta, France): Field study and modeling. Environmental Pollution 2008;151(3):486-93.

Comoretto, L., 2009. L’étude des herbicides dans la phase dissoute des eaux superficielles Camarguaises. Apport, transfert et devenir. Thèse doctorale (Ph D Thesis), Université de Provence, Marseille, 190 pp.

Eu-footprint.org, FOOTPRINT : creating tools for pesticide risk assessment and management in Europe : The FOOTPRINT Pesticide Properties Database.2009. HYPERLINK « http ://www.eu-footprint.org/ppdb.html » http ://www.eu-footprint.org/ppdb.html

European Commission Directorate-General Health & Consumer Protection. Nov. 2000.

Fdil F, Aaron JJ, Oturan N, Chaouch A, Oturan MA. Photochemical degradation of chlorophenoxyalcanoic herbicides in aqueous media. Rev Sci Eau 2003;16:123-42.

Giroto JA, Teixeira ACSC, Nascimento CAO, Guardani R. Photo-Fenton removal of water-soluble polymers. Chemical Engineering and Process 2008;47:2361-9.

Haag WR, Yao CCD. Rate constants for reaction of hydroxyl radicals with several drinking water contaminants. Environ Sci Technol 1992;26:1005-13.

Hemond HF, Fechner-L JE. Chemical fate and transport in the environment. 2nd ed. Academic Press, London 2000.

Hensel PF, Day JW, Pont D, Day JN. Short-term sedimentation dynamics in the Rhône River Delta, France: The importance of riverine pulsing. Estuaries 1998;21:52-65.

Höhener P, Comoretto L, al Housari F, Chauvelon P, Pichaud M, Chérain Y, Chiron S Modeling anthropogenic substances in coastal wetlands: application to herbicides in the Camargue (France), Environmental Modeling and Software 2010;25:1837-44.

ISO/DIS 14592-1 Water quality evaluation of the aerobic biodegradability of organic compounds at low concentrations- Part 1: Shake flask batch test with surface water or surface water/sediment suspensions. International Organisation of Standardization 1999.

Mackay D, Yeun ATK, Mass transfer coefficients correlations for volatilization of organic solutes from water, Environ Sci Technol 1983;17:211-33.

Miller PL, Chin YP. Indirect photolysis promoted by natural and engineered wetland water constituent: Processes leading to alachlor degradation. Environ Sci Technol 2005;39(12):4454–62.

Miller PL, Chin YP. Photoinduced degradation of carbaryl in a wetland surface water. J Agric Food Chem 2002;50:6758–65.

Münnich KO, Clarke WB, Fischer KH, Flothmann D, Kromer B, Roether W, Siegenthaler U, Top Z and Weiss W. Gas exchange and evaporation studies in a circular wind tunnel, continuous radon measurements at sea, and tritium-helium-3 measurements in a lake, in : H. Favre and K. Hasselmann (ed), Turbulent fluxes through the sea surface, wave dynamics and predictions, Plenum, New York.1978, p. 151-65.

OECD- Organization for the Economic Cooperative and Development. OECD Guidelines for testing of chemicals. Aerobic and anaerobic transformation in aquatic sediment. Paris: OECD publications ;1999.

Schwarzenbach RP, Gschwend PM, Imboden DM. Environmental Organic Chemistry, 2nd ed. Wiley, Hoboken, New Jersey; 2003.

Soderquist CJ, Crosby DG. Dissipation of 4-chloro-2-methylphenoxyacetic acid (MCPA) in rice field. Pest Sci 1975; 6:17-33.

Stangroom SJ, Macleod CL, Lester JN. Photosensitized transformation of the herbicide 4-Chloro-2-methylphenoxy acetic acid (MCPA) in water. Wat Res 1998;32(3):623-32.

Tam NFY, Guo CL, Yau WY, Wong YS. Preliminary study on biodegradation of phenanthrene by bacteria isolated from mangrove sediments in Hong Kong. Marine Pollut Bull 2002;45:316-24.

Tao L, Yue W, Lingyan J, Jianbo L, Silu Y, Qi Z. Study of atrazine degradation in subsurface flow constructed wetland under different salinity. Chemosphere 2008;72:122–28.

Tuxen N, Tüchsen PL, Rügge K, Albrechtsen HJ, Bjerg PL. Fate of seven pesticides in an aerobic aquifer studied in column experiments. Chemosphere 2000;41:1485-94.

Ulrich MM, Imboden DM, Schwarzenbach RP. MASAS- A user-friendly simulation tool for modeling the fate of anthropogenic substances in lakes. Environmental Software1995; 10:177-98.

U.S. Environmental Protection Agency (EPA) Registration Eligibility Decision for dichlorprop-p (2,4-DP-p); 2007. EPA/738/R-07/008.

Vione D, Minero C, Housari F, Chiron S. Photoinduced transformation processes of 2,4-dichlorophenol and 2,6-dichlorophenol on nitrate irradiation Chemosphere 2007;69;10:1548-54.

Vione D, Das R, Rubertelli F, Maurinoa V, Minero C, Barbati S, Chiron S. Modeling the occurrence and reactivity of hydroxyl radicals in surface waters: Implications for the fate of selected pesticides. Intern J Environ Anal Chem 2009;90:260-275.

Walse SS, Morgan SL, Kong L, Ferry JL. Role of dissolved organic matter, nitrate, and bicarbonate in the photolysis of aqueous fipronil. Environ Sci Technol 2004;38: 3908−15.

Willard JI Aerobic Aquatic Metabolism of ^{14}C-bentazone in Rice water. In Pesticides Residues in Food 1977; (Evaluation 1991 Part 1- Residues). P 651.

Fate of Alachor in the coastal lagoons of the Camargue (Rhône River Delta, France)

Alachlor was studied together with the other acidic rice herbicides but was not included in the paper 2, the data is provided here.

-Photodegradation of alchlor under sunlight

The photodegradation of alachlor under sunlight fit with a second -order kinetic, which yielded linear plots of $1/C-1/C_0$ versus time, Fig.1. Half life times were estimated by the equation 1 for lagoon and canal water samples, respectively, which were 11.20 and 18.2 days. Alachlor degradation by hydrolysis was not significant during the course of the experiment; the half-life time of hydrolysis is larger than 250 days.

$t_{1/2} = \ln(2)/k_{obs}$ Eq. 1

In summary, the following elimination rate constants were estimated for alachlor (Table 1).

Table 1. Experimentally determined rate constants for alachor photodegradation upon irradiation under natural sunlight, and for hydrolysis.

	kobs (day-1)		**kd (day-1)**	**ki (day-1)**		**khyd (day^{-1})**
Herbicide	Canal	Lagoon		Canal	Lagoon	
Alachlor	0.038±0.003	0.062±0.006	0.027±0.003	0.011±0.003	0.036 ±0.003	0.002

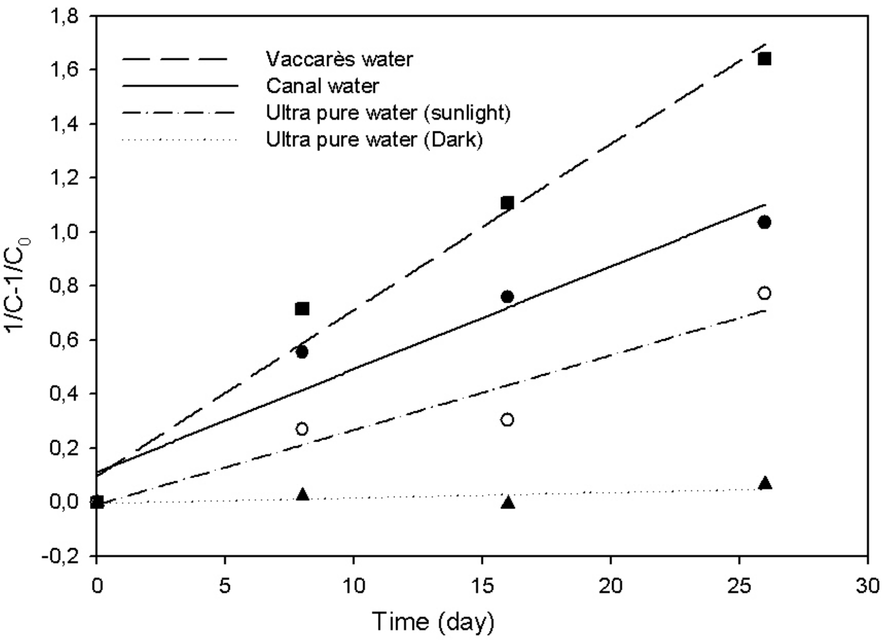

Figure. 1. Alachlor photodegradation in (●) Canal and (■) Lagoon, (○) Ultra pure water samples under natural sunlight from july 8th to august 7th, 2008. (▲)Ultra pure water (Dark).

Biodegradation of alchlor

Alachlor underwent a slow decrease to 50% of initial concentration, in canal water sample, after 60 days, with a lag time of 31 days. The half-life time after the lag period was 9.9 days. However, alachlor biodegradation was quite low ($t_{1/2}$ 22.4 day with 28 days lag time) in lagoon water, Fig.2. These results suggest that biological degradation was not a significant degradation pathway of alachlor.

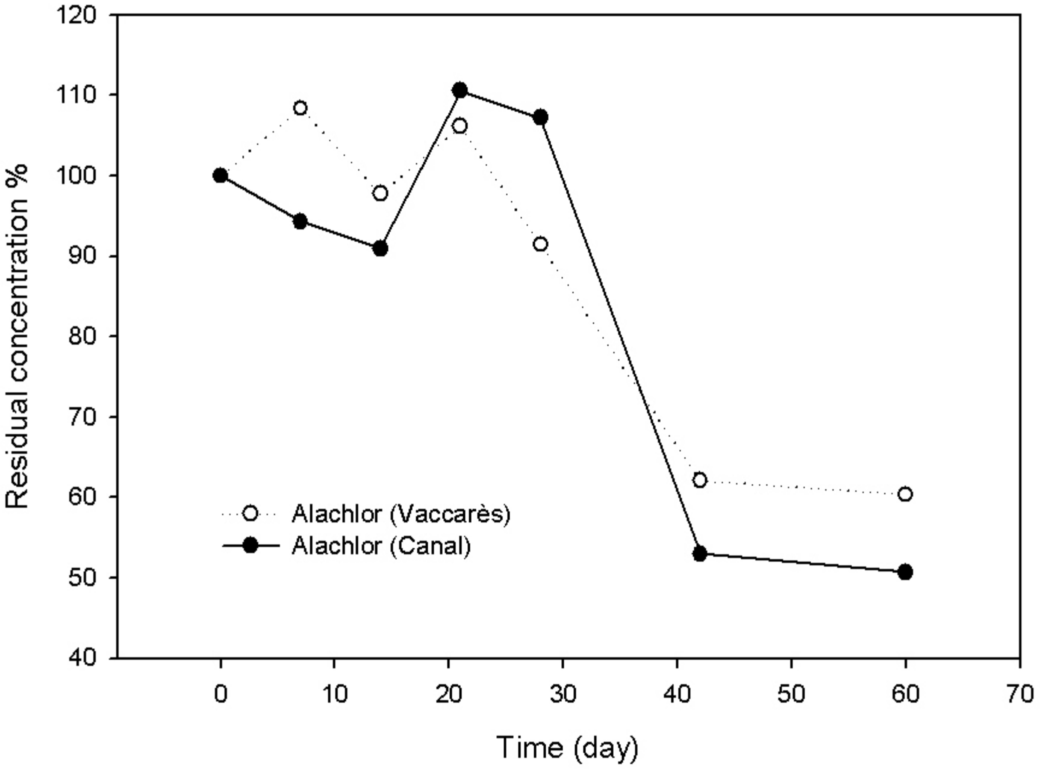

Figure. 2. Microbial transformation of alachlor in lagoon and Canal water samples

Our findings are in agreement with Miller and Ping Chin (2005) which found that indirect photolysis is an important process of alachlor degradation in natural wetlands. Moreover, Galassi and co-workers (1996) found that alachlor is rather persistent since its biodegradation is lower than 50 % after 28 d of incubation in river water.

Another previous study reported a slow direct photolysis of alachlor as it absorbs radiation weekly above 290 nm (Chiron et al. (1995). Gustavo et al.(1996) reported that alachlor showed a high stability in deionized water when exposed to natural sunlight irradiation for a period of /5/days. However, our experiment conditions lasted 28 days.

In the EU footprint database (eu-footprint.org, 2009), alachlor is reported to hydrolyse with a half-life time of 0.5 days, whereas pretilachlor would have a hydrolysis half-life time of about 200 days. Obviously, the alachlor hydrolysis data in the database is wrong. Because of the variability and inhomogenity of the literature data, it is difficult to correctly assess the fate of herbicides in natural surface waters using models. The software MASAS was used to estimate elimination rate constants of alachlor in the Vaccarès lagoon by volatilization, sedimentation and flushing. And then added to the rate constants of photodegradation and biodegradation processes, Table 2. The total rate constant k_{tot} is 0.096 and half life time of 7.22 days, those finding fall in the range of pretilachlor field half life time (5-7) days, and in agreement of results from previous studies: field experiments using large mesocosms reported that alachlor half lives ranged from 16 to 122 days with the highest rates occurring in hypereutrophic waters (Graham et al.2000, Knapp et al, 2003).

This work showed that photochemical decay is the main process responsible for alachlor dissipation in Vaccarès lagoon, while the other processes are not significant.

Table 2. Elimination rate constant of alachlor in Vaccarès lagoon

Elimination rate		Alachlor [d^{-1}]
Flushing	k_w	0.002
Abiotic Hydrolysis	k_{hyd}	0.002
Direct Photolysis	k_{dp}	0.027
Indirect photolysis	k_{ip}	0.036
Microbial degradation	k_{bio}	0.03
Volatilization	k_{gas}	0.0002
Sorption + Sedimentation	k_{sed}	<0.0001
Total	k_{tot}	0.096
Half-life time (days)		7.22
Field data (2004-2006)		(5-9 days) Pretilachlor
Reactivity with $^{\cdot}$OH Half-life time		(532.4 days)

Chapter 5:

In the following papers, the chemical model for the herbicide MCPA was integrated with hydrodynamic model set up by Höhener and co-workers. 2010

Article 3

Modeling anthropogenic substances in coastal wetlands: Application to herbicides in the Camargue (France

Patrick Höhener, Laetitia Comoretto, Fadi al Housari, Philippe Chauvelon, Marc Pichaud,
Yves Chérain and Serge Chiron

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Modeling anthropogenic substances in coastal wetlands: Application to herbicides in the Camargue (France)

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ABSTRACT

The purpose of this work was to develop a coupled hydrological and chemical model that can simulate time-dependent concentrations of pesticides and their degradation products in shallow coastal water bodies of variable volumes. The model was applied to simulate the exposure of two herbicides, oxadiazon and MCPA, in three interconnected lagoons which form the coastal wetlands of the Camargue. These shallow lagoons and adjacent marshes are of international importance for the preservation of biodiversity. The chemical fugacity and reactivity are modeled in these complex ecosystems as in classical fate models for well-mixed lakes, but additionally water exchanges between the lagoons, seawater intrusion, variable evaporation rates and fluctuating water volumes of the lagoons are incorporated. Analytical solutions for coupled differential equations for the water volumes of the lagoons, the salinities, and the concentrations of pesticides were derived and evaluated using the software Maple. The model was calibrated using salinity data and was able to simulate measured concentrations of oxadiazon and MCPA and two subsequent degradation products of MCPA in the main lagoon in Camargue. Interestingly, model simulations differed from real observations in the two smaller lower lagoons, and the model served tracking so far unknown entry paths of herbicides into these lagoons.

Software availability

The software developed in this work is an annotated MAPLE worksheet which is distributed for free (to be downloadable on the Journal's website). The software MAPLE (Maple Inc., Waterloo, Ontario, CA) in version 9 or higher is needed to run the worksheet. Developer: Patrick Höhener, for contact information see title page of manuscript.

1. Introduction

Numerous models have so far been developed to model the fate of anthropogenic chemicals in aquatic systems like lakes, ponds, rivers, or water-submerged rice fields (Di Guardo et al., 1994; Reichert, 1994; Mackay and Webster, 2003). A well documented example is the model MASAS ("Modelling Anthropogenic Substances in Aquatic Systems") developed by Ulrich et al. (1994, 1995). This model describes how anthropogenic substances undergo volatilization, sorption and sedimentation, neutral, acid and alkaline hydrolysis, direct and indirect photolysis, and biodegradation in either completely mixed or stratified water bodies such as lakes and ponds. Since all these processes also occur in coastal wetlands and lagoons, an attempt was made to use MASAS in the lagoons of the Camargue in order to predict the fate of pesticides. However, coastal lagoons differ from lakes and ponds by two major facts: they are generally very shallow and undergo significant volume changes between wet and dry seasons, and their salinity can change drastically due to seawater intrusion and evaporation. A significant volume reduction of a lagoon results in enrichment of pollutants, which MASAS and many other models can not simulate. Several numerical models for water, salt and nutrient dynamics in coastal lagoons are available (Magbanua et al., 2003; Umgiesser et al., 2003; Dias and Lopes, 2006; Ebrahimi et al., 2007; Zacharias and Gianni, 2008) but do not address the specific question of xenobiotics and their degradation products. In the Camargue, a long record of water volume and salinity measurements represents an excellent data base to validate a model taking into account variable water volumes. This is done by checking

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whether salinity predictions match with observed salinities. However, it must be noted that the salinity in coastal wetlands is influenced by either seawater intrusion or evaporation, and can thus increase to levels higher than the salinity in seawater during summer months. Models used for modeling pesticides in rice paddies such as PCPF-1 (Watanabe and Takagi, 2000), PADDY (Inao and Kitamura, 1999) or RICEWQ-VADOFT (Miao et al., 2003; Karpouzas et al., 2005a,b) are adapted to the specific irrigation situation in submerged rice fields and were developed to predict surface water runoff of pesticides at the farm level. Those models do, however, not predict pesticide concentrations in lagoons of variable volumes and salinity.

The aim of this work was to propose a model that is capable to describe the fate of anthropogenic substances in interconnected lagoons of variable volumes and variable salinity. The model should incorporate the processes from MASAS (Ulrich et al., 1995) but extend its application to shallow well-mixed water bodies which are shrinking under high evaporation rates. It should allow rapid computations of predictions for pesticide dissipation in the lagoons on ordinary personal computers. The model should be calibrated with data on water volumes and salinity and then predict measured concentrations of two herbicides in the lagoons reasonably.

2. Study area

The Île de Camargue basin is the central part of the Rhône delta in the south of France (Chauvelon et al., 2003), spreading between the two branches of the Rhône river (Fig. 1). The Camargue regional nature park lies in the center of the Île de Camargue and covers 85,000 ha of lagoons, marshes and other lands separated by the Mediterranean Sea by a dike. The lagoons and adjacent marshes are of international importance for the preservation of biodiversity. The lagoons are very little influenced by tidal forcing. Frequent strong winds lead to a homogenization of salt concentrations within each lagoon and force water exchanges between the lagoons. The modeled area (Fig. 2) is the area in the southern Central part of the Camargue, the **H**ydrologic **S**ystem of the **C**amargue (HSC) (Chauvelon et al., 2003). This system is defined as three interconnected lagoons, which are the Vaccarès lagoon, the Impériaux lagoon, and the complex Lion/Dame lagoons (treated as one lagoon, called Lion/Dame in the model). The Vaccarès lagoon is the only one receiving runoff from rice farming, which carries the main load of pesticides. The lagoon has a mean depth of 0.98 m when the water level is equal than the sea level, and a maximum depth of about 2 m (see bathymetry in the Supporting Information). Impériaux is the only lagoon exchanging water with the sea, according to fluxes determined at the "Grau de la Fourcade". All lagoons receive rainfall, which can represent a minor load of pesticides.

Sea-lagoon exchanges are mainly controlled by 13 sluices gates in the dike at a location called 'Grau de la Fourcade', where gates can be opened and closed. The flow of water is calculated from measured hourly data (water levels, status of gates), and during the cropping season, the overall flow is mainly directed from the sea to the lagoons. Agricultural land borders the park to the North and

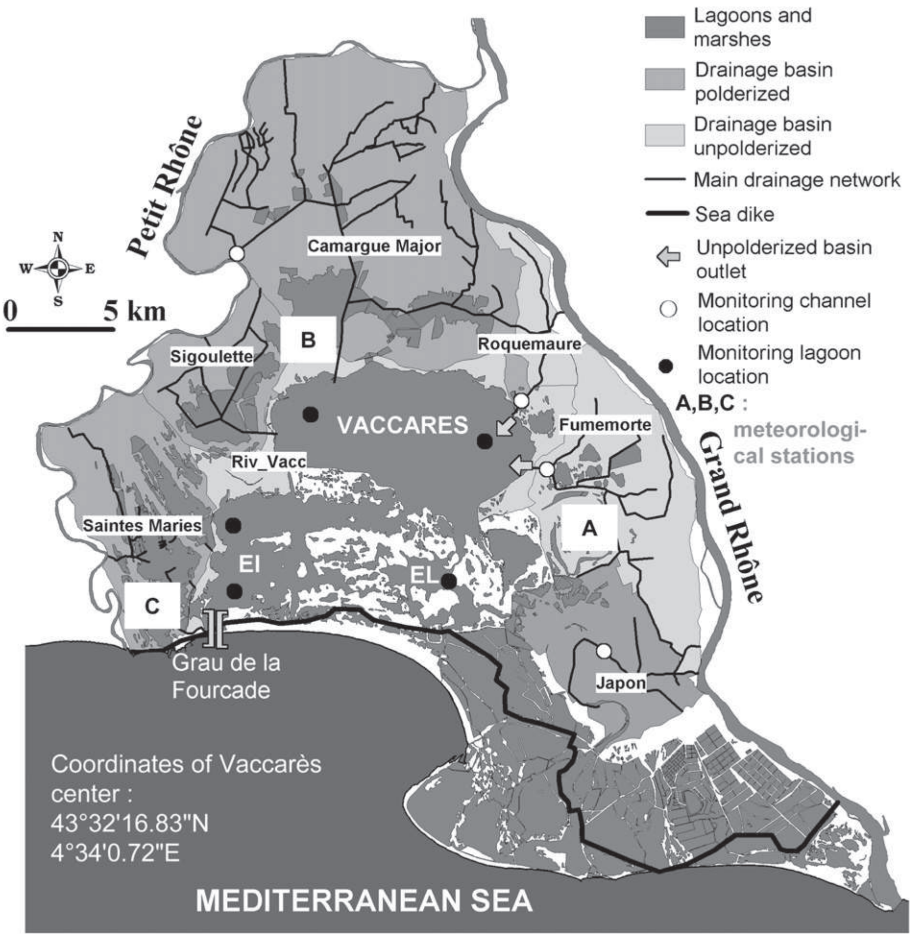

Fig. 1. Map of the modeled area in the Rhône delta, with sampling locations for pesticides in channels and lagoons (adapted from Comoretto et al., 2007). The three lagoons studied are the lagoon Etang de Vaccarès, the Etang des Impériaux (EI), and the Etang de Lion/Dame (EL).

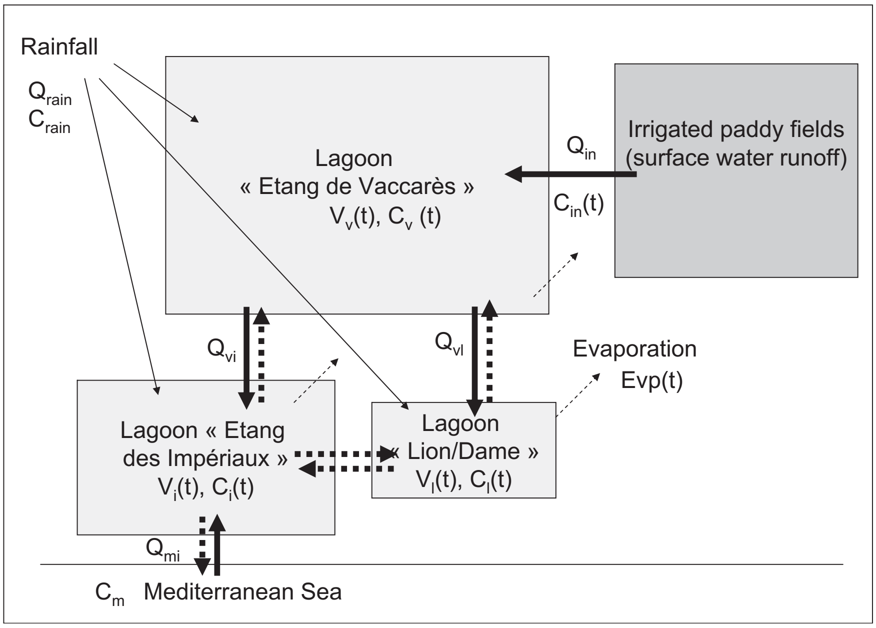

Fig. 2. Set-up of the hydrologic model "Hydrologic System of the Camargue" HSC. Arrows show predominant water fluxes (black arrows) during cultivation season from mid March to August, and optional water fluxes (broken arrows) in other seasons. *Q* designates fluxes, *V*(*t*) variable water volumes, and *C*(*t*) variable concentrations, either of salt or of pesticides.

South-East, and most of it is devoted to intensive flooded rice cultivation. The rice parcels are irrigated during the crop period (from mid-April or early May, to September) by irrigation pumping stations taking water from both arms of the river Rhône (Comoretto et al., 2008). The discharge of irrigation induced drainage water to the lagoons in the park is about 480,000 m^3 per day during the crop period. This counterbalances partially the salinity increases in the lagoons due to high evaporation rates and due to seawater intrusion, but carries a load of anthropogenic substances into the preserved area. Therefore, there is an ongoing debate on the management of water in this area.

3. Monitoring data

The water fluxes to and from the lagoons were measured in the field by hydrologic techniques which were described in more detail previously (Chauvelon et al., 2003). Rainfall, wind speed, humidity and temperature were continuously recorded (hourly data) at two stations (A and B, shown in Fig. 1). Another anemometer measured wind speed and direction 10 m above the soil at the station C near the sea outlet (Fig. 1). Water evaporation was estimated from averaged data from the meteorological stations using the Penman method (Chauvelon et al., 2003). Stocks of salts in the lagoons were calculated from monthly salinity measurements and water volumes estimations by the Nature Reserve of the Camargue.

A field survey targeting various pesticides and their degradation products used in the rice fields on the Île de Camargue between March and October from 2004 to 2006 permitted to document concentration peaks of these compounds in three lagoons in the Camargue regional nature park (Comoretto et al., 2007; Chiron et al., 2009; Comoretto, 2009). Four herbicides were found to be present in highest concentrations in channels and lagoons: Oxadiazon + Pretilachlor in April and May, and MCPA and Bentazone in June/July (Comoretto et al., 2007; Comoretto, 2009). In this study, we chose to model Oxadiazon and MCPA in order to represent both time periods with the compound for which the data base was most complete. Water samples for analysis of dissolved pesticides were sampled approximately bi-weekly during three seasons of cropping from mid-April to September in 4 channels receiving runoff from rice fields, and at 5 locations in the three lagoons in Camargue (Fig. 1). The two channels Fumemorte and Roquemaure drain unpolderized area in the east of the Vaccarès lagoon and discharge directly into this lagoon, whereas water from the two other channels is mainly pumped back to the river Rhône. Before analysis by HPLC-MS, the water samples were filtered. Details about the sampling procedures and the analytical method were published previously (Comoretto et al., 2007; Comoretto, 2009). In 2005, pesticide concentrations also were measured in rainfall sampled at three times between April and June (Chiron et al., 2009; Comoretto, 2009). We used arithmetic means of the concentrations of herbicides or degradation product in rainfall from 2005 in the model.

4. Model description

The model developed in this work describes three independent water bodies with variable volumes to cope with the specific situation of the hydrologic system of the Camargue. A priori, another configuration could be treated as well. The water volumes in all lagoons depend on a number of in- and outflows from or to other lagoons with rate Q_i, on rainfall, and on net evaporation. These flows are shown in Fig. 2 and Table 1. The main inflow to the Vaccarès lagoon is the Fumemorte channel, where discharge was measured continuously. An extrapolation of this discharge to other channels with lower contributions was made based on the area of the drained basins. The volume of the Impériaux lagoon depends further on seawater inflow, which was estimated from the increase of salt stocks in the Impériaux lagoon between March and October. Rainfall was further accounted for, and similarly to the other inflows, rainfalls was assumed to be evenly distributed throughout the season. Analytical equations of the form of equation (1a) (volume) and (1b) (concentration) were established for each lagoon, in with subscripts *i* stand for any water flow contribution and *j* for the names of the lagoons:

Table 1
Overview on model parameters for unspecific parameters (top) and parameters specific for each lagoon (bottom). Subscripts are v (Vaccarès), *i* (Impériaux), l (Lion/Dame), m (Mediterranean sea), and in for inflow of runoff from rice farms.

Parameter	Symbol	Unit	Value	Taken from
Inflow of drainage water	Q_{in}	$m^3\ day^{-1}$	480,000	Measurements in channel Fumemorte, and extrapolation
Seawater inflow	Q_{mi}	$m^3\ day^{-1}$	45,000	Estimated based on salt stock increase in Impériaux lagoon
Rainfall[a]	Rain	$mm\ day^{-1}$	0.6	100 mm/season distributed evenly every day
	Q_{rain}	$m^3\ day^{-1}$	65,000	
Flow Vaccarès-Impériaux	Q_{vi}	$m^3\ day^{-1}$	11,040	Adjusted to meet volume and salinity criterion
Flow Vaccarès-Lion	Q_{vl}	$m^3\ day^{-1}$	7400	Adjusted
Flow Impériaux-Lion	Q_{il}	$m^3\ day^{-1}$	2400	Adjusted
Salinity in seawater	$C_{s\ mi}$	$g\ L^{-1}$	38	(Obaton, 1998)
Salinity in irrigation water	$C_{s\ in}$	$g\ L^{-1}$	0.75	Average of measurements in Fumemorte channel

Parameter	S	Unit	Values			Taken from
			Vaccarès	Impériaux	Lion/Dame	
Initial volume	$V_{j(0)}$	$10^6\ m^3$	96	13.4	4.4	Data reserve[b]
Volume change[c]	loss	(%)	-13 ± 7	-26 ± 5	-38 ± 13	Data reserve[b]
Surface area	A_j	$10^6\ m^2$	88.9	17.05	4.1	Taken as constant with time
Initial salinity	$C_{js(0)}$	$g\ L^{-1}$	13.6	18.6	16.4	Data reserve[b]

[a] Salinity in rain was set to zero. All initial concentrations of pesticides in the lagoons were set to zero as well.

[b] The "Reserve de Camargue" publishes monthly measurements of water levels and salinity of the three lagoons on http://www.reserve-camargue.org/. Water levels were transformed to volumes using bathymetric curves from the Reserve de Camargue.

[c] mean ± standard deviation of averaged data from 2004 to 2006.

$$\frac{\delta V_{j(t)}}{\delta t} = \sum_i Q_i \qquad (1a)$$

$$\frac{\delta C_{j(t)}}{\delta t}V_{j(t)} + \frac{\delta V_{j(t)}}{\delta t}C_{j(t)} = \sum_i Q_i C_{i(t)} - k_j V_{j(t)} C_{j(t)} \qquad (1b)$$

where $C_{j(t)}$ are time-dependent concentrations in inflows denominated with subscript i or in the lagoons denominated with subscript j, $V_{j(t)}$ is water volume in the lagoon, Q_i are water fluxes to or from the lagoons, and k_j is a first order rate constant for the overall chemical reactivity of a compound of interest in each lagoon. This rate constant has been estimated using the existing fate model for chemical in well-mixed lakes MASAS (Ulrich et al., 1995), including sedimentation, gas exchange, chemical and biological degradation, and photolysis, as described in detail in the Supporting Information section. The rate constants k_j depend on the mean depth of the modeled water body, and for each of the 3 lagoons, a slightly different k_j is used based on an average mean depth of the lagoon at mid season. Note that the degradation rate constant does not depend on salinity. This was supported by experimental work on photodegradation (al Housari et al., 2010). The following boundary conditions for solving the coupled equations were needed:

1) Initial volumes of lagoons: $V_{j(0)}$, which are given with other model parameters such as water fluxes and rainfall in Table 1.
2) Initial concentrations: $C_{s(0)}$ for salinity, $C_{p(0)}$ for pesticide concentration, $C_{dp(0)}$ for degradation product (Table 1).
3) The time-dependent concentration of pesticides in surface water runoff discharging into the Vaccarès lagoon $C_{p,\ in}(t)$ was represented by a normal distribution (eq. (2)):

$$C_{p,in}(t) = C_{p,background} + C_{p,0}\exp\left(-0.5\sigma(t-t_0)^2\right) \qquad (2)$$

where $C_{p,\ background}$ is a constant pesticide concentration, $C_{p,\ 0}$ is the concentration of pesticide in runoff at the maximum of the peak, s is the variance, and t_0 is the time of the peak maximum.

4) The time-dependent evaporation rate of water from a free surface $ET_{(t)}$ was calculated with a quadratic function which yielded a maximum evaporation rate in early summer (eq. (3)):

$$ET_{(t)} = ET_0 + \kappa \cdot t + \psi \cdot t^2 \qquad (3)$$

where ET_0 is the evaporation for t_0 in mid march (2 mm day^{-1}), and κ and ψ are correction factors for later times. This quadratic function matched well estimated daily values of evaporation which were obtained from measurements of temperature, wind speed and solar irradiation at two meteorological stations in the area (Fig. 3). The evaporation fluxes of water from each lagoon were obtained by multiplying $ET_{(t)}$ with the surface of each lagoon (Table 1).

The system of equations was solved by solving first the three coupled equations for the volumes (eq. (1a)) using the appropriate boundary conditions, and subsequently the system of three coupled equations for the concentrations of the lagoons (eq. (1b)) using the *dsolve* functionality of the software Maple (Maple Inc., Waterloo, Ontario, CA). This yielded analytical solutions for the time-dependent volumes and concentrations of pesticides for the specific boundary conditions chosen. The *dsolve* functionality of Maple software also can resolve systems of equations numerically. In the results section, it is shown that model results were the same when the system of coupled differential equation was resolved by a true analytical or a numerical procedure. However, after numerical solution, the evaluation of results needed much less computation time for drawing concentration-time curves, and therefore we used only the faster numeric resolution procedure further

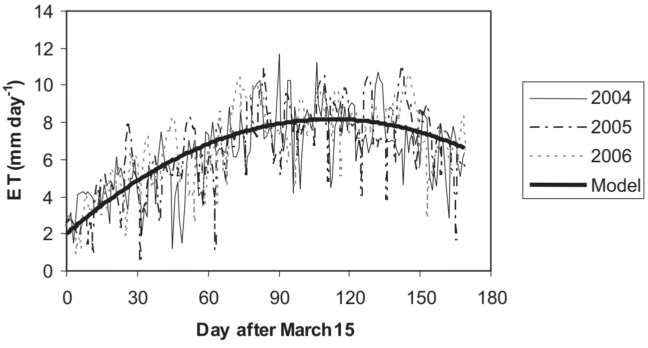

Fig. 3. Daily evaporation rate estimated from meteorological data for 2004–06, and analytical equation used in the model to simulate the data (eq. (3), with $\kappa = 0.11$ and $\psi = 4.9\ 10^{-4}$).

calculations. A maple worksheet containing all calculations is shown in the supporting information section.

The computation of time-dependent concentrations of a degradation product in the Vaccarès lagoon is performed with equation (4):

$$\frac{\delta C_{\mathrm{dp(t)}}}{\delta t}V_{\mathrm{v(t)}}+\frac{\delta V_{\mathrm{v(t)}}}{\delta t}C_{\mathrm{dp(t)}} = aV_{\mathrm{v(t)}}k_{\mathrm{proddp}}C_{\mathrm{vp(t)}}-\sum_i Q_iC_{\mathrm{vdp(t)}} - k_{\mathrm{degdp}}V_{\mathrm{v(t)}}C_{\mathrm{dp(t)}} \tag{4}$$

where $k_{\mathrm{prod\ dp}}$ and $k_{\mathrm{deg\ dp}}$ are first order rate constants for production and decay of the degradation product, a is a stoichiometric factor (g of degradation product/g of pesticide), $V_{\mathrm{v}(t)}$ is the variable volume of the Vaccarès lagoon, and $C_{\mathrm{v,p}(t)}$ is the pesticide concentration in Vaccarès lagoon. Two subsequent degradation products could be handled. An input of degradation product with the discharged drainage water was considered since the degradation product is formed upgradient of the lagoons in the rice fields (Chiron et al., 2009).

5. Results

5.1. Calibration of model with salinity data

The system of analytical equations for the three lagoons was first calibrated with data on water level and salinity changes. The goal was to meet the average water volume and salinity changes observed from 2004 to 2006, when herbicide concentrations were monitored. In the months of March from 2004 to 2006, the Vaccarès lagoon had an average mean level of +0.1 m above sea level. This corresponded to an average volume of $96{,}10^6$ m^3 (Table 1). The lagoon lost in the average 13 ± 7% of water until the end of August due to evaporation and discharge to the other lagoons. The salinity increased in the average from 13.6 to 15.5 g L^{-1} in August and dropped to 14.3 g L^{-1} in September (Fig. 3). The two other lagoons, which received no significant freshwater inputs, had water losses of 26 ± 5% (Impériaux) and 38 ± 13% (Lion/Dame), and final salinities of up to 52 and 41 g L^{-1}, respectively (Fig. 3). However, the stock of salt did only increase in the Impériaux lagoon, and not in the Lion/Dame lagoon, and therefore no seawater intrusion is taken into account for the latter. To calculate water volume changes and salinity in the lagoons, the model was run with the parameters given in Table 1. The three fluxes of water between the lagoons which were not known were manually adjusted in order to get the best match of modeled vs. observed water volume changes and salinity changes. After fine-tuning, the computed volumes of the lagoons by end of August corresponded well with the volumes observed at that date. The modeled salinity in the Vaccarès corresponded equally well with the observed salinity (Fig. 4). The model matched the observed salinity in the Impériaux and Lion lagoons also quite well from March to July, whereas in August, the modeled salinities were underestimating the observed ones.

5.2. Time-dependent variations of the herbicide oxadiazon

Oxadiazon is a pre-emergence herbicide used in rice fields in spring. According to (Comoretto et al., 2007), 5200 ha are treated in the basin of the Île de Camargue, with 500 g ha^{-1} of active ingredient, which makes a total amount of about 2600 kg of oxadiazon used annually. The concentrations of oxadiazon in 4 channels with surface water runoff from rice fields approached highest values of almost 4 μg L^{-1} in early May and decreased later (Fig. 5). To model the time-dependent input of oxadiazon into the Vaccarès lagoon, we adjusted manually a normal distribution (eq. (2)) to the data. This function does not decrease to zero toward the end of the season, but simulates a permanent background concentration of 0.2 μg L^{-1} in the channel water. Oxadiazon is a strongly sorbing compound (Ying and Williams, 2000), and slow desorption from paddy soils is a tentative explanation for long-lasting input (Comoretto et al., 2008). When the time-dependent concentration is multiplied by the water discharge and integrated throughout the season, the total load of oxadiazon to the Vaccarès lagoon by surface water is 67 kg in the model. In 2005, a concentration of 0.03 μg L^{-1} was measured in rain, and this adds an additional load of 0.3 kg to the 3 lagoons. No other loads are considered in the model. The model simulations for the time-variant concentrations of oxadiazon in the Vaccarès lagoon are shown in Fig. 6, along with measured concentrations from the years 2005 and 2006.

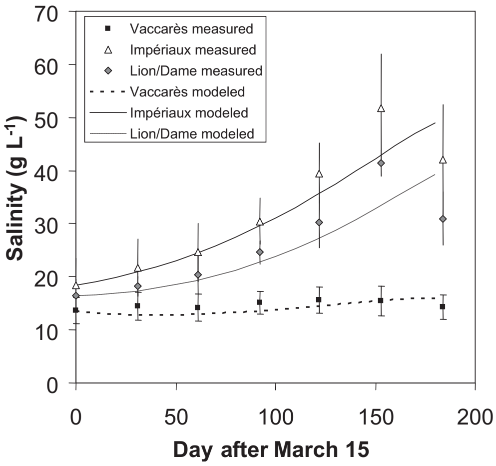

Fig. 4. Arithmetic means of salinity data from 2004 to 2006 for the three lagoons (symbols) with standard deviation representing inter-annual variations, and modeled salinity increases (lines).

5.3. Time-dependent concentrations of MCPA and its two degradation products

MCPA (4-chloro-2-methylphenoxy-acetic acid, Fig. 7) is a post-emergence herbicide used in Camargue on 5000 ha of rice fields at a rate of 1200 g active ingredient per hectare (Comoretto et al.,

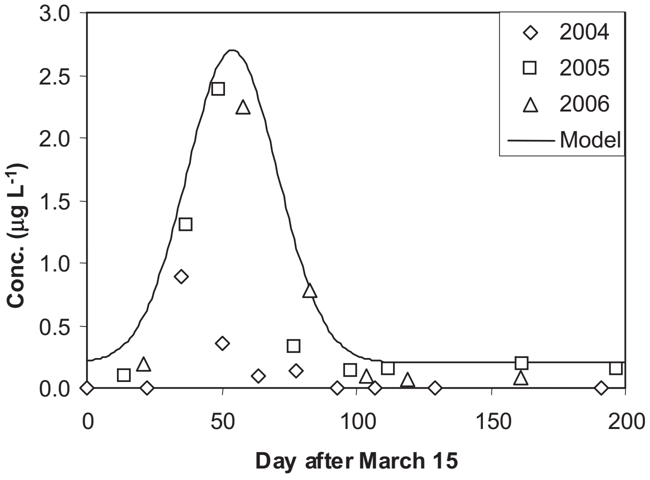

Fig. 5. Measured concentrations of Oxadiazon in channels receiving surface water runoff from rice fields in the Camargue, and normal distribution curve used in the model to simulate the data.

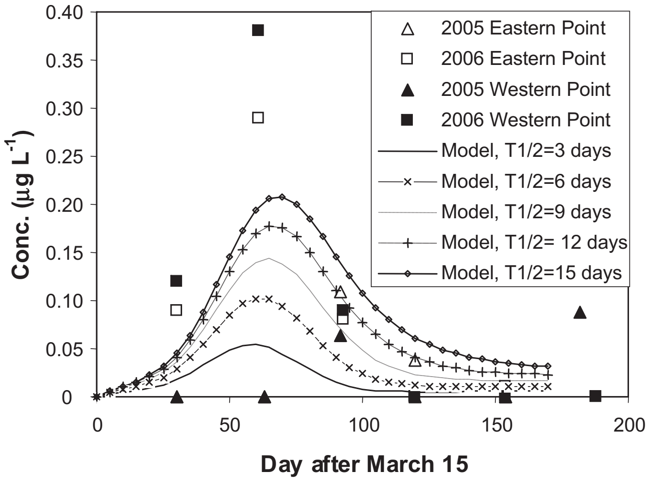

Fig. 6. Measured concentrations of Oxadiazon in the Vaccarès lagoon from 2005 to 2006, and independent model simulations based on the salinity-calibrated model and 5 different half-life times.

Table 2
Best parameters for normally-distributed input functions of herbicides and degradation products to the Vaccarès lagoon, and half-life times used in the model for the Vaccarès lagoon.

		Oxa–diazon	MCPA	CMP	CMNP
Date of peak maximum		May 8 (day 57)	June 18 (day 95)	June 18 (day 95)	June 18 (day 95)
Peak maximum	$\mu g\ L^{-1}$	2.7	2.2	1.32	0.88
Variance σ		0.0035	0.01	0.01	0.01
Peak duration	days	65	40	40	40
Half-life time in lagoon k_j[a]	days	3 to 15	14.4	8	22

[a] see Supporting Information, Table S1 for derivation of half-life times.

2007), mainly in June. This compound undergoes photocatalyzed degradation to 4-chloro-2-methylphenol (CMP) and can undergo subsequent photonitration to 4-chloro-2-methyl-6-nitrophenol (CMNP) in the water of the Vaccarès lagoon (Chiron et al., 2009).

During exposure of MCPA in water from Vaccarès lagoon to natural sunlight in July at Marseille, a half-life time of 14.4 days was measured (al Housari et al, 2010). The half-life times of CMP and CMNP were estimated in the field which showed that CMP degrades more rapidly than its parent compound MCPA, whereas the CMNP degrades more slowly (Chiron et al., 2009). The values of the degradation constants $k_{deg\ dp1}$ and $k_{deg\ dp2}$ in the model were set to values corresponding to the following half-life times: CMP: 8 days, CMNP: 22 days (Table 2). The values of the production rate constants were set equal to the degradation rate constants of the parent compounds, assuming that photodegradation represents the unique degradation pathway. Measurements of the concentrations of the products CMP and CMNP in channels and in rainwater reported in (Chiron et al., 2009) allowed to set appropriate concentrations values in the model. The input concentrations of both products followed the same normal distribution as MCPA (Fig. 8), but the concentrations were decreased to 60% (CMP) and 40% (CMNP), respectively. C_{rain} was set as 0.1 $\mu g\ L^{-1}$ for both degradation products. The model simulations gave results as shown in Fig. 9.

The concentrations of MCPA in channels in the Camargue were highest in second half of June between days 93 and 104 and reached 1.5 $\mu g\ L^{-1}$ (Fig. 8). The normal distribution adopted for the model had a somewhat higher peak (Table 2), since we assume that a bi-weekly sampling campaign is unlikely to have a sampling day precisely at the day of the highest peak concentration. In the Vaccarès lagoon, the highest measured concentrations were approaching 0.18 $\mu g\ L^{-1}$ between days 93 and 122 in 2004 and 2006, whereas in 2005 they were always much lower for unknown reasons (Fig. 9). Our model simulation had a peak concentration of 0.14 $\mu g\ L^{-1}$ on day 105 (Fig. 9). The agreement between model simulation and measurement was acceptable, given the fact that measured concentrations were near the method detection limit of 0.02 $\mu g\ L^{-1}$ and thus somewhat variable. In Fig. 9, it is further documented that model results were not different when the systems of coupled analytical equation were solved analytically or numerically in the MAPLE software.

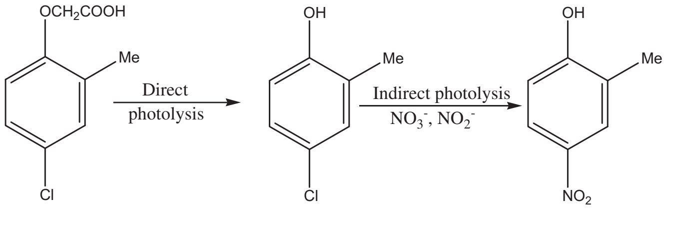

Fig. 7. Transformation of MCPA by direct photolysis to CMP and then by indirect photolysis to CMNP.

5.4. *Modeling the herbicide concentrations in the two lower lagoons*

The simulated concentrations of oxadiazon in the Impériaux lagoon were showing peak concentrations of less than 0.002 $\mu g\ L^{-1}$ (data not shown). This did not correspond with measured values of up to 0.26 $\mu g\ L^{-1}$ (Comoretto et al., 2007). Similar findings were found for the Lion/Dame lagoon. Also for MCPA, the model underestimated significantly the observed concentrations in the two lower lagoons.

6. Discussion

6.1. *Water volumes, salinity and model calibration*

The model is capable to reproduce salinity changes within the standard deviations from inter-annual differences. The model was

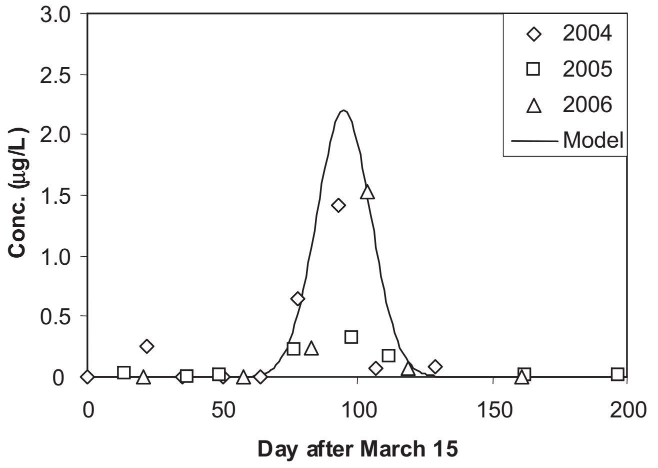

Fig. 8. Measured concentrations of MCPA in channels receiving surface water runoff from rice fields in the Camargue, and normal distribution function adopted manually to simulate the herbicide load in the model.

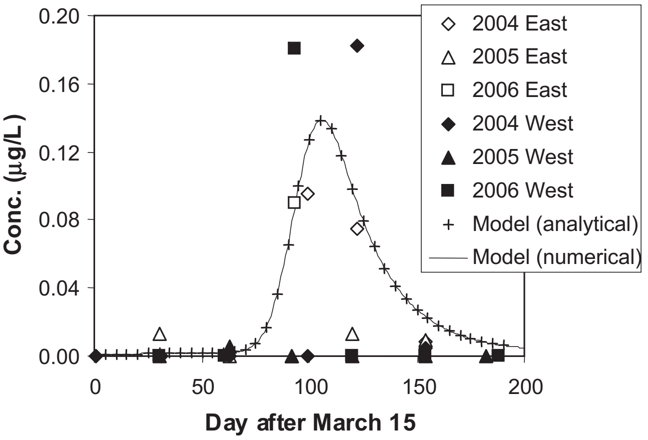

Fig. 9. Measured concentrations of MCPA in the Vaccarès lagoon from 2004 to 2006, and independent model simulations based on the salinity-calibrated model and a half-life time of 14.4 days. The model data obtained from the analytical and numerical resolution of the system of coupled equations are shown to be identical.

found to be quite sensitive on the fluxes of water between the lagoons, which were calibration parameters. When these fluxes were lowered by 20%, the water volume loss in the Impériaux lagoon increased from 25.4% loss to 27.4%, that in the Lion lagoon from 37.3% loss to 43.3%. The final salinities in the lower lagoons increase by 1 and 3 permille, respectively, when water flux is reduced by 20%. However, the model was not capable either of reproducing the drops in salinity observed after day 170 (September). Because of the low number on annual pesticide measurements, three years were averaged, and this did not allow using daily rainfall data in the model, but only an averaged rainfall distributed evenly across the whole modeled period. In the Camargue, rainfall is stronger in September than in July–August, and that's why the modeled salinity in September is overestimated.

6.2. *Herbicides*

The estimated overall elimination rate for oxadiazon (Supporting Information, Table S1) is quite uncertain due to the lack of information on photolysis. The model simulates curves for 5 different elimination half-life times of oxadiazon from 3 to 15 days. This yields concentration peaks of dissolved oxadiazon between 0.05 and 0.21 $\mu g\ L^{-1}$. The times of peak maxima shift progressively from day 60 to day 70 when the half-life time of oxadiazon elimination increases from 3 to 15 days. The observed peak maximum in the lagoon was between 0.3 and 0.4 $\mu g\ L^{-1}$, at day 61 in 2006. The model curves are all somewhat below actual measurements, but follow the time trend quite well. The model curves for the half-life times between 9 and 12 days seem to represent best the measured data. Literature data for photochemistry of oxadiazon (Ying and Williams, 1999) suggest rapid photolysis in distilled water under laboratory conditions (Ying and Williams, 1999). The database "eu-footprint.org" used for risk assessment of pesticides in Europe gives a photolysis half-life time of 5.9 days for oxadiazon at 40° latitude (eu-footprint.org, 2009). Our model suggests that in the Vaccarès lagoon, the photolysis half-life time is somewhat superior to this value due to the fact that the lagoon has a mean depth of about 1 m and carries some turbidity, which is known to slow down photolysis. An important observation is made when looking at simulated concentrations of the herbicide in the lagoon: the concentration decrease after the peak maximum does not reflect the true half-life time of degradation in the lagoon. It depends more on the decrease of the normally-distributed input function (Fig. 5). This shows the importance of having an accurate knowing of the boundary conditions, especially the load functions, when modeling the fate of chemicals in aquatic systems.

The application of the model to MCPA illustrated the need to model degradation products for the assessment of the overall impact of a chemical on the aquatic community. MCPA and its degradation products CMP and CMNP may have a combined effect due to their simultaneous presence {Chiron et al., 2009#2639}, and the model predicted this correctly. For the two subsequent degradation products, the model simulated peak concentrations of 0.09 $\mu g\ L^{-1}$ (CMP) and 0.23 $\mu g\ L^{-1}$ (CMNP, Fig. 10), which were somewhat lower than actually observed peak concentrations.

6.3. *Unknown entry routes in lower lagoons*

Additional inputs of about 3 kg of herbicide to the Impériaux lagoon and about 1.5 kg to the Lion/Dame lagoon would be required to attain the observed concentrations. At present, the input pathways are not known. The model was used to test four hypotheses for these unknown entry paths. As a first hypothesis, it was tested whether higher water exchange fluxes from the Vaccarès lagoon to the lower lagoons would explain the observed herbicide concentrations. However, when we simulated higher water fluxes, the model was not predicting anymore the correct salinity increases in the lower lagoons, and thus the hypothesis can be excluded. As a second hypothesis, it was assumed that the actual herbicide concentrations in rain were underestimated due to the low frequency of measurement. However, simulated concentrations in the lower lagoons are only getting close to real data when the concentrations in evenly-distributed rain are about 100-fold higher than the few measured values from 2005 (Chiron et al., 2009), and then the simulated concentrations of herbicides in the Vaccarès lagoon would exceed the observed values. Thus, the second hypothesis can be excluded as well. A third hypothesis concerns leaking channels in the area adjacent to the lower lagoons. This area is mainly polderized, and water from channels is pumped back to the Rhône river. This does not exclude that unnoticed leakage across channel walls and dikes can occur. When we included pesticide load by freshwater input into the lower lagoons at the expense of input from the Vaccarès lagoon, the simulated concentrations of pesticides could be matched with the observed

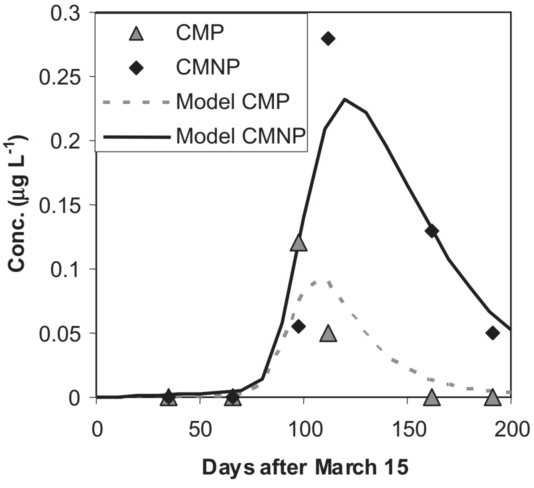

Fig. 10. Measured concentrations of the two subsequent degradation products of MCPA in the Vaccarès lagoon in 2005 (Chiron et al., 2009), and independent model simulations based on the salinity-calibrated model and the modeled curve for MCPA as shown in Fig. 8.

ones, but the salinity increases were too low and make this hypothesis also quite unlikely. Recent monitoring (Chauvelon, 2009) near the sea outlet at "Le Grau de la Fourcade" showed that some water flow from the Rhone river may occur during the summer season. Water is pumped in the river, then flows in channels to the surroundings of Saintes Maries to finally either reach the sea channel at "Grau de la Fourcade" where it can mix with seawater and enter the lagoon; or even directly into the Impériaux lagoon in some situations. By this way, some pesticides from the river, coming themselves from upstream rice fields drainage could enter again in the lagoon system. There is also the fourth hypothesis of an input by dry deposition. In the metropolitan area of Strasbourg (France), dry deposition had been found to account for between 4 and 60% of total deposition for 11 pesticides studied (Sauret et al., 2009). However, dry deposition was not measured in the Camargue. The shallow depth of the lower lagoons makes concentration increases higher after small mass loads, whereas in the deeper Vaccarès lagoon, these concentration increases would remain negligible. Still, the model is presently not capable of modeling correctly the lower lagoons. More work is needed to understand the dry deposition of herbicides on the lagoons in the Camargue area and to incorporate this into our model.

7. Conclusions

This study presents an analytical model that was aimed at simulating the fate of anthropogenic substances in coastal lagoons undergoing volume changes and combined freshwater-seawater inputs. While previous fate models for anthropogenic substance such as MASAS were written for well-mixed lakes of constant volume, this model extends modeling of well-mixed water bodies for time-variable water volumes, which is useful for shrinking lakes and ponds in arid regions. The model was shown here to realistically simulate the concentrations of the herbicide MCPA and two subsequent degradation products in the Vaccarès lagoon under the assumption of complete mixing. The Vaccarès lagoon is separated from the sea by a dike and other lagoons, and no evidence for large salinity gradients is so far known for this lagoon. For other lagoons which are more open to the sea and which can have important horizontal and vertical salinity gradients, the model would need to be refined. In that case, a discrete numerical model in 2- or 3 dimensions would be preferable and is currently developed. We also note that the model failed to realistically simulate two smaller lagoons for which more knowledge is needed to incorporate correctly all loads of pesticides. More work is needed to better understand the processes associated with the reactivity of pesticides, especially as concerns the indirect photolysis, including the influences on increasing salinity and increased concentrations of other compounds (iron, nitrate, nitrite, and others) on photolysis. Future modeling will thus tackle the coupling of hydrology, salinity and reactivity in coastal lagoons.

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Appendix. Supplementary material

The supplementary material associated with this article can be found in the on-line version at doi:10.1016/j.envsoft.2010.05.005.

References

al Housari, F., Vione, D., Chiron, S., Barbati, S., 2010. Reactive photoinduced species in estuarine waters. Characterization of hydroxyl radical, singlet oxygen and dissolved organic matter triplet state in natural oxidation processes. Photochem. Photobiol. Sci. 9, 78–86.

Chauvelon, P., Tournoud, M.G., Sandoz, A., 2003. Integrated hydrological modelling of a managed coastal Mediterranean wetland (Rhone delta, France): initial calibration. Hydrology Earth Syst. Sci. 7, 123–131.

Chauvelon, P., 2009. Gestion Intégrée d'une Zone humide littorale méditerranéenne aménagée: contraintes, limites et perspectives pour l'Ile de CAMargue (GIZCAM). Programme LITEAU 2, Ministère de l'Ecologie, de l'Energie, du Développement durable et de l'Aménagement du Territoire, Tour du Valat, Rapport de fin de contrat, Août 2009, 84 p + annexes.

Chiron, S., Comoretto, L., Rinaldi, E., Maurino, V., Minero, C., Vione, D., 2009. Pesticide by-products in the Rhône delta (Southern France). The case of 4-chloro-2-methylphenol and of its nitroderivative. Chemosphere 74, 599–604.

Comoretto, L., 2009. L'étude des herbicides dans la phase dissoute des eaux superficielles Camarguaises. Apport, Transfert et Devenir. Thèse doctorale thesis, Université de Provence, Marseille, 190 pp.

Comoretto, L., Arfib, B., Chiron, S., 2007. Pesticides in the Rhône river delta (France): basic data for a field-based exposure assessment. Sci. Total. Environ. 380, 124–132.

Comoretto, L., Arfib, B., Talva, R., Chauvelon, P., Pichaud, M., Chiron, S., Höhener, P., 2008. Runoff of pesticides from rice fields in the Ile de Camargue (Rhône river delta, France): field study and modeling. Environ. Pollut. 151, 486–493.

Di Guardo, A., Calamari, D., Zanin, G., Consalter, A., Mackay, D., 1994. A fugacity model of pesticide runoff to surface water: development and validation. Chemosphere 28, 511–531.

Dias, J.M., Lopes, J.F., 2006. Implementation and assessment of hydrodynamic, salt and heat transport models: the case of Ria de Aveiro Lagoon (Portugal). Environ. Model. Softw. 21, 1–15.

Ebrahimi, K., Falconer, R.A., Lin, B., 2007. Flow and solute fluxes in integrated wetland and coastal systems. Environ. Model. Softw. 22, 1337–1348.

eu-footprint.org, 2009. FOOTPRINT: Creating Tools for Pesticide Risk Assessment and Management in Europe: The FOOTPRINT Pesticide Properties Database. http://www.eu-footprint.org/ppdb.html.

Inao, K., Kitamura, Y., 1999. Pesticide paddy field model (PADDY) for predicting pesticide concentrations in water and soil in paddy fields. Pestic. Sci. 55, 38–46.

Karpouzas, D.G., Capri, E., Papadopoulou-Mourkidou, E., 2005a. Application of the RICEWQ-VADOFT model to simulate leaching of propanil in rice paddies in Greece. Agron. Sustain. Dev. 25, 35–44.

Karpouzas, D.G., Ferrero, A., Vidotto, F., Capri, E., 2005b. Application of the RICEWQ-VADOFT model for simulating the environmental fate of pretilachlor in rice paddies. Environ. Toxicol. Chem. 24, 1007–1017.

Mackay, D., Webster, E., 2003. A perspective on environmental models and QSARs. Sar Qsar Environ. Res. 14, 7–16.

Magbanua, B.S., Hawkins, J.C., Willis, G., 2003. Modeling compartmentalized lagoon systems under cyclic operation. Environ. Model. Softw. 18, 109–118.

Miao, Z.W., Cheplick, M.J., Williams, M.W., Trevisan, M., Padovani, L., Gennari, M., Ferrero, A., Vidotto, F., Capri, E., 2003. Simulating pesticide leaching and runoff in rice paddies with the RICEWQ-VADOFT model. J. Environ. Qual. 32, 2189–2199.

Obaton, D., 1998. Circulation et modelisation de la Méditerranée occidentale du golfe du Lion, Ifremer, Internal Report 98.03, Brest.

Reichert, P., 1994. Aquasim – a tool for simulation and data-analysis of aquatic systems. Water Sci. Technol. 30, 21–30.

Sauret, N., Wortham, H., Strekowski, R., Herckes, P., Nieto, L.I., 2009. Comparison of annual dry and wet deposition fluxes of selected pesticides in Strasbourg, France. Environ. Pollut. 157, 303–312.

Ulrich, M.M., Imboden, D.M., Schwarzenbach, R.P., 1995. MASAS – A user-friendly simulation tool for modelling the fate of anthropogenic substances in lakes. Environ. Softw. 10, 177–198.

Ulrich, M.M., Müller, S.R., Singer, H.P., Imboden, D.M., Schwarzenbach, R.P., 1994. Input and dynamic behavior of the organic pollutants tetrachloroethene, atrazine, and NTA in a lake – a study combining mathematical-modeling and field-measurements. Environ. Sci. Technol. 28, 1674–1685.

Umgiesser, G., Melaku Canu, D., Solidoro, C., Ambrose, R., 2003. A finite element ecological model: a first application to the Venice Lagoon. Environ. Model. Softw. 18, 131–145.

Watanabe, H., Takagi, K., 2000. A simulation model for predicting pesticide concentrations in paddy water and surface soil. I. Model development. Environ. Technol. 21, 1379–1391.

Ying, G.G., Williams, B., 1999. The degradation of oxadiazon and oxyfluorfen by photolysis. J. Environ. Sci. Health B 34, 549–567.

Ying, G.G., Williams, B., 2000. Laboratory study on the interaction between herbicides and sediments in water systems. Environ. Pollut. 107, 399–405.

Zacharias, I., Gianni, A., 2008. Hydrodynamic and dispersion modeling as a tool for restoration of coastal ecosystems. Application to a re-flooded lagoon. Environ. Model. Softw. 23, 751–767.

CHARPTER 6

GENERAL DISCUSSION

This work has demonstrated that photolysis (direct and indirect) is the main process responsible for the dissipation of acidic herbicides in the coastal lagoons of the Camargue. The importance of direct or indirect photolysis depends on the herbicide structure. Direct photolysis accounts for 82% of the overall photodegradation of bentazone, 65% of MCPA and 55% of dichlorprop. For alachlor the indirect photolysis is more relevant than the direct one and accounts for 60% of the overall photodegradation. The photoreactivity of estuarine waters represented by Vaccarès lagoon samples was generally more important than that of fresh waters from the Fumemorte Canal. The concentrations of hydroxyl radical and singlet oxygen were slightly higher in Vaccarès $(1.72 \pm 0.01) \times 10^{-16}$M and $(2.06 \pm 0.22) \times 10^{-13}$ M, respectively compared to those of the Canal $(9.41 \pm 0.12) \times 10^{-17}$ M, $(5.44 \pm 0.04) \times 10^{-14}$ M.

An accumulation of photodegradation products from MCPA in the Camargue has been reported previously (Chiron et al, 2009). Degradation products may be as non toxic, more toxic or less toxic the parent pesticides. Chiron et al. (2009) found that MCPA transformed to CMP and the later transformed to 4-chloro-2-methyl-6-nitrophenol (CMNP) upon *in situ* irradiation experiments. Chiron and co-workers (2009) suggested that the photonitration of CMP into CMNP involves nitrogen dioxide, generated from the photolysis of nitrate and from the photooxidation of nitrite by $^{\cdot}OH$. However, CMP disappeared about as quickly as MCPA, while CMNP was environmentally more persistent than the parent molecules. This is very relevant to the environmental risk associated with the occurrence of these compounds, because the nitration of chlorophenols reduces their acute toxicity but the nitroderivatives could have more marked long-term effects, associated with their genotoxicity.

Microbial transformation, which is in competition with photodegradation process, is the second most important factor involved in the attenuation of most acidic herbicides in Vaccarès lagoon, with contributions of 25-30% to total degradation, (Fig. 21) except for bentazone, which was found to be stable to biodegradation. The microbial transformation experiments revealed that the lag time was shorter in fresh water (Canal) than that of estuarine water. Consequently the biodegradation is faster. By combining these results with those of herbicides photodegradation under sunlight and rate constants of physical elimination processes obtained by MASAS we could understand the fate and the main factors responsible for acidic rice herbicides dissipation. Finally, our results indicated that sorption and sedimentation, gaz exchange, flushing and abiotic hydrolysis have a minor role in attenuation of the studied herbicides.

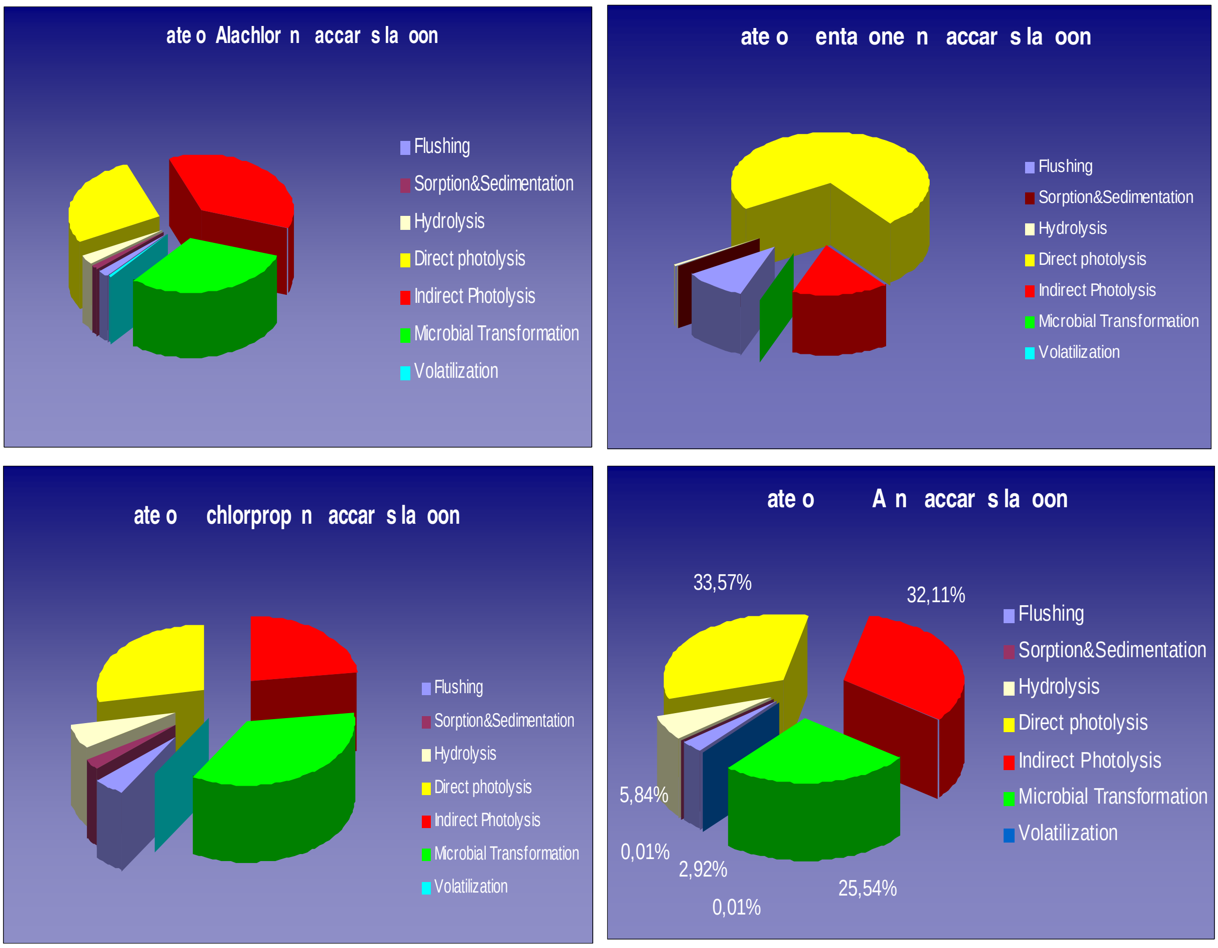

Figure 21. Summary of elimination processes responsible for alahlor, bentazone, MCPA and dichlorprop dissipation in Vaccarès lagoon.

CONCLUSIONS and OUTLOOK

Photodegradation under natural sunlight, and biodegradation experiments enabled us to better understand the behaviour of the studied herbicides in the coastal lagoons of Camargue, and to obtain information about the kinetics of degradation and the half-life times under natural conditions. Modelling by MASAS helped to reflect more closely the physical processes in real environmental situations.

Based on our results, one can conclude that a longer retention of the water in the canals or in constructed wetlands would decrease the pollution of the lagoon. Because the biodegradation rate in river water (Canal) is more rapid than in estuarine one and estuarine water has slightly higher near- surface photoreactivity. Moreover, our findings about fate and behaviour of the studies herbicides may be used for assessment of the potential environmental hazard. That’s why more work is needed to understand the fate and ecological impact of the photodegradation products in the lagoon

REFERENCES

Al Housari F, Vione D, Chiron S, Barbati S. Reactive photoinduced species in estuarine waters. Characterization of hydroxyl radical, singlet oxygen and dissolved organic matter triplet state in natural oxidation processes. Photochem. Photobiol. Sci. 2010;9(1):78-86.

Allarad A. S. and Neilson H. A. 2008. Environmental degradation and transformation of organic chemicals. Taylor & Francis, 6000 Broken Sound Parkway NW, 710 p.

Aguer J. P. and Richard C. 1996. Transformation of fenuron induced by photochemical excitation of humic acids. Pesticide Science 46, 151–155.

Aguer J. P. and Richard C. 1999. Influence of the excitation wavelength on the photoinductive properties of humic substance.eChemosphere 38, 2293–2301.

Alexander M. 1981. Biodegradation of chemicals of environmental concern. Science 211:132.

Armbrust K. L. 1999. Photochemical processes influencing pesticide degradation in rice paddies. Journal of Pesticide Science 24, 69-73.

Audebert A. and Mendez del Vilar P. 2007. Characterization of rice crop systems and rice sector organization in Camargue-France. In: A. Ferrero and F. Vidotto (Eds), Agro-Economical Traits of Rice Cultivation in Europe and India, page 278. Edizioni Mercurio, Vercelli, Italy.

Benitez F. J, Real F. J., Acero J. L., Garcia C. 2007. Kinetics of the transformation of phenyl-urea herbicides during ozonation of natural waters: Rate constants and model predictions. Water Research, 41, 4073–4084.

Boesten J. J. T. I., and van der Linden A. M. A.1991. Modelling the influence of sorption and transformation on pesticide leaching and persistence. J. Environ Qual. 20,425–435.

Boule P, Bahnemann W. D., and Robertson J. K. P. 2005. Handbook of Environmental Chemistry Vol. 2, Part M. 299–323.

Brezonik P. L., and Fulkerson-Brekken J. 1998. Nitrate-induced photolysis in natural waters: controls on concentrations of hydroxyl radical photo-intermediates by natural scavenging agents. Environ. Sci. Technol 32:3004–3010.

Buxton G. V., Greenstock C. L., Helman W. P., Ross A. B. 1988. Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (.OH/.O-) in aqueous solution. J Phys Chem Ref Data 17, 513–886.

Canonica S., Jans U., S, Stemmler K., and Hoigné J. 1995. Transformation kinetics of phenols in water: Photosensitization by dissolved natural organic material and aromatic ketones. Environ. Sci. Techno. 29, 1822–1831

Carlin A., Mouret J.-C., Dreyfus F., Marnotte P., and Hammond R. 2004. Riziculture biologique. Maîtrise des mauvaises herbes en Camargue. Brochure INRA-CIRAD-ONIC, 20 p.

Carlson D. L., Than K.D., and Roberts A. L. 2006. Acid- and Base-Catalyzed Hydrolysis of Chloroacetamide Herbicides. J. Agric. Food Chem. 54, 4740–4750

Centre Français du Riz. 2010. Bilan de la compagne 2009 Résultats variétaux. http://www.rizdecamargue.com/cfr/index.php.

Cervelli S. and Jackson R. 2008. Pesticide exposure assessment in rice paddies: The Lower-Tier Analysis page (91–123). In: Capri, E., and Karpouzas, D. G. (Eds), Pesticides risk assessment in rice paddies: theory and practice, page 255. Elsevier.

Chauvelon P., Tournoud M.G., and Sandoz A., 2003. Integrated hydrological modelling of a managed coastal Mediterranean wetland (Rhone delta, France): initial calibration. Hydrol. Earth Syst. Sci. 7, 123–131.

Chiron S., J. Abian M. Ferrer F. Sanchez-Baeza A. Messeguer and Barceló D. 1995. Comparative Photodegradation Rates of Alachlor and Bentazone in Natural Water and Determination of Breakdown Products. Environ. Toxicol. Chem. 14(8):1287–1298.

Chiron S, Comoretto L, Rinaldi E, Maurino V, Minero C, Vione D. 2009. Pesticide by-products in the Rhône delta (Southern France). The case of 4-chloro-2-methylphenol and of its nitroderivative. Chemosphere;74:599–604

Coleman J. O. D., Frova C., Schröder P., and Tissut M. 2002. Exploiting Plant Metabolism for the Phytoremediation of Persistent Herbicides. Enivron Sci& Pollut Res 9(1): 18–28

Clark D. J. 1994. Physical-Chemical Properties and Environmental Fate of Pesticides. Environmental Hazards Assessment Program. State of California. Environmental Protection Agency., California, 56 p.

Comoretto L., Arfib B., and Chiron S., 2007. Pesticides in the Rhône river delta (France): basic data for a field-based exposure assessment. Sci. Total Environ. 380, 124–132.

Comoretto L., Arfib B., Talva R., Chauvelon P., Pichaud M., Chiron S., and Höhener P., 2008. Runoff of pesticides from rice fields in the Ile de Camargue (Rhône river delta, France): field study and modeling. Environ. Pollut. 151, 486–493.

Comoretto, L., 2009. L'étude des herbicides dans la phase dissoute des eaux superficielles Camarguaises. Apport, Transfert et Devenir. Thesis, Université de Provence, Marseille, 190 p.

Chesters G, Simsiman G. V., Levy J, Alhajjar B. J, Rathulla R. N., and Harkin J. M. 1989. Environmental fate of alachlor and metolachlor. Rev Environ Contam Toxicol, 110,1–74.

Dell'Arciprete M.L., Santos-Juanes L., Arques A., Vercher R.F., Amat A.M, Furlong J.P., Mártire D.O., Gonzalez M.C. 2010. Reactivity of neonicotinoid pesticides with singlet oxygen. Catalysis Today 151,137–142

Draper W. M, and Crosby D. G. 1984. Solar photooxidation of pesticides in dilute hydrogen peroxide. J. Agric. Food. Chem. 32, 231–237.

Dunnivant M. F and Anders E. 2006. A basic introduction to pollutant fate and transport. Page 480. John Wiley & Sons, Inc., Hoboken, New Jersey.

Eu-footprint.org, FOOTPRINT : creating tools for pesticide risk assessment and management in Europe : The FOOTPRINT Pesticide Properties Database.2009. HYPERLINK « http ://www.eu-footprint.org/ppdb.html » http ://www.eu-footprint.org/ppdb.html

EU, 1998. Official Journal of the European Communities L330: Council Directive 98/83/EC on the quality of water intended for human consumption. pp. 32–54.

European Commission Directorate-General Health & Consumer Protection. Nov. 2000. Review report for the active substance bentazone.

European Commission Directorate-General Health & Consumer Protection. April, 2005. Review report for the active substance MCPA.

Fdil F, Aaron J J, Oturan N, Chaouch A, Oturan M A. Photochemical degradation of chlorophenoxyalcanoic herbicides in aqueous media. Rev Sci Eau 2003;16:123-42.

Ferrero A. and Vidotto F. 2008. Rice Cultivation in the E.U. Ecological Conditions and Agronomical Practices page (1–24). In: Capri, E., and Karpouzas, D. G. (Eds). Pesticides risk assessment in rice paddies: theory and practice, page 255. Elsevier.

Galassi, S., Provini, A., Mangiapan S. , Benfenati, E., 1996. Alachlor and its metabolites in surface water. Chemosphere 32:229-237.

Garbin J. R., Milori D., Simões L. M., da Silva T. L. W., Neto M. L. 2007. Influence of humic substances on the photolysis of aqueous pesticide residues. Chemosphere 66, 1692–1698.

Gerecke A. C., Canonica S., Muller S. R., Scharer, M. and Schwarzenbach R. P. 2001. Quantification of dissolved natural organic matter (DOM) mediated phototransformation of phenylurea herbicides in lakes. Environ. Sci. Technol. 35, 3915–3923.

Glenn E., 1995. Effects of salinity on growth and evapotranspiration of Typha domingensis Pers. Aquatic Botany 52, 75–91.

Graham C.W, Miley M K, deNoyelles Jr F, Smith VH, Thurman EM, Carter R. 2000.Alachlor transformation patterns in aquatic fieldmesoco sms under variable oxygen and nutrient conditions. Water Res, 34:4054–62.

Gregoire C., Elsaesser D., Huguenot D., Lange J., Lebeau T., Merli A., Mose R., Passeport E., Payraudeau S., Schütz T., Schulz R., Tapia-Padilla G., Tournebize J., Trevisan M., and Wanko A. 2009. Mitigation of agricultural non point-source pesticide pollution in artificial wetland ecosystems. Environ Chem Lett, 7, 205–231.

Gustavo A. P, and Damià. B. 1996. Comparative degradation kinetics of alachlor in water by photocatalysis with FeC13, TiO2 and photolysis, studied by solid phase disk extraction followed by gas chromatographic techniques. Journal of Chromatography A, 754,187–195

UIPP- Union des Industries de la Protection des Plantes. UIPP rapport d’activité 2008-2009.

Haag R. W. and Hoigné J. Singlet Oxygen in Surface Waters. l986. 3. Photochemical Formation and Steady-State Concentrations in Various Types of Waters. Environ. Sci. Technol 20, 341–348.

Haag R. W. and Yao C. C. D. J. 1992. Rate constants for reaction of hydroxyl radicals with several drinking water contaminants. Environ. Sci. Technol 26, 1005–1013.

Halladja S., Ter Halle A., Aguer J. P., Boulkamh A. and Richard C. 2007. Inhibition of humic substances mediated photooxygenation of furfuryl alcohol by 2,4,6-trimethylphenol. Evidence for reactivity of the phenol with humic triplet excited states, Environ. Sci. Technol. 41, 6066–6073.

Mackay D, Shiu W-Y, Ma K-C, and Lee S C. Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals, Second Edition. 2006 page 4216. Taylor & Francis Group, LLC 6000 Broken Sound Parkway NW, suite 300.

Health M, and Evans M. Important bird areas in Europe: priority sites for conservation. 2000. Vol. 2: southern Europe. Cambridge, UK: Birdlife international Ed.

Hemond H.F., and Fechner-L J. E. 2000. Chemical fate and transport in the environment. 2nd ed. Academic Press, 433p.

Hoigné, J. 1990. Reaction rates of processes in natural waters In: Aquatic chemical kinetics: Stumm, W., Ed.; Wiley: New York, page 43–70.

Huber R and Otto S., 1994. Environmental behaviour of bentazon herbicide. Rev Environ Contam Toxicol., 137, 111–34.

Jørgensen S. E. and Bendoricchio G. 2001. Fundamentals of Ecological Modelling. ELSEVIER SCIENCE Ltd The Boulevard, Langford Lane Kidlington, Oxford OX5 1GB, UK. (3rd Edition), page 530.

Katagi T. 2002. Abiotic hydrolysis of pesticides in the aquatic environment. Rev Environ Contam Toxicol 175:79–261.

Knapp, C.W., Graham, D.W., Berardesco, G., deNoyelles F Jr, Cutak BJ, Larive CK. 2003. Nutrient level, microbial activity, and alachlor transformation in aerobic aquatic systems. Water Res. 2003;37(19):4761-9.

Larson S. J., Capel D. P., and Majewski S. M. 1997. Pesticides in surface waters: Distribution, Trends, and Governing Factors. Page 373. In: Gilliom, R.J. (Ed.), Series of Pesticides in Hydrologic System, vol. 3. Ann Arbor Press, Inc. Chelsea, Michigan.

Li, K., Liu W, Xu D, and Lee S. 2003. Influence of Organic Matter and pH on Bentazone Sorption in Soils Agric. Food Chem. 51, 5362–5366.

Lin T., Wen Y., Jiang L., Li J., Yang S.,ZhouQ., 2008. Study of atrazine degradation in subsurface flow constructed wetland under different salinity. Chemosphpere 72, 122–128.

Lindsey M. and Tarr M. 2000. Inhibition of hydroxyl radical reaction with aromatics by dissolved natural organic Matter. Environ. Sci. Technol. 34, 444–449

Mabury S. A., and Crosby D. G. 1996. Pesticides reactivity toward hydroxyl and its relationship to field persistence. J. Agric. Food Chem., 44, 1920–1924.

Mack J., and Bolton, J. R. 1999. Photochemistry of nitrite and nitrate in aqueous solution: a review. J. Photochem. Photobiol. A: Chem. 128, 1–13.

Matamoros V, García J, and Bayona J. M. 2008. Organic micropollutant removal in a full-scale surface flow constructed wetland fed with secondary effluent. Water Research 42, 653 660.

Miller P. L., and Chin Y-P., 2002. Photoinduced Degradation of Carbaryl in a Wetland Surface Water. J. Agric. Food Chem., 50, 6758–6765.

Miller P. L., and Chin Y-P., 2005. Indirect Photolysis Promoted by Natural and Engineered Wetland Water Constituents: Processes Leading to Alachlor Degradation. Environ. Sci. Technol. 39, 4454–4462.

Novick, N. J. and M. Alexander (1985), Cometabolism of low concentrations of propachlor, alachlor, and cycloate in sewage and lake water. Appl. Environ. Microbiol., 49, 737-743.

Numabe A. and Nagahora S. 2006. Estimation of pesticide runoff from paddy fields to rural river. Water Sci Technol. 53, 139–46.

Oerke, E.-C., Dehne, H.-W., Schönbeck, F., Weber, A., 1994. Crop Production and Crop Protection—Estimated Losses in Major Food and Cash Crops. Elsevier, Amsterdam, 808 p.

Oliveira Ribeiro C.A., Vollaire Y., Sanchez-Chardi A., and Roche, H., 2005. Bioaccumulation and the effects of organochlorine pesticides, PAHs and heavy metals in eels (*Anguilla anguilla*) from the Camargue Biosphere Reserve, France. Aquat. Toxicol. 74, 53–69.

O'Sullivan D. W., Neale P. J., Coffin R. B., Boyd T. J., and Osburn C. L. 2005. Photochemical production of hydrogen peroxide and methylhydroperoxide in coastal waters. Marine Chemistry 97,14–33.

Pagga U., 1997. Testing biodegradability with standardized methods. Chemosphere 35, 2953–2972.

Ramesh A., and Maheswari S T. 2004. Dissipation of alachlor in cotton plant, soil and water and its bioaccumulation in fish. Chemosphere 54, 647–652

Richard C., and Canonica S. 2005. Aquatic Phototransformation of Organic Contaminants Induced by Coloured Dissolved Natural Organic Matter. Handbook of Environmental Chemistry, vol. 2, Part M 299–323

Rittmann B.E., and McCarty P.L. 2001. Environmental biotechnology: principles and applications. McGraw-Hill, New York, NY.

Roche, H., Buet, A., Jonot, O., and Ramade, F., 2000. Organochlorine residues in European eel (*Anguilla anguilla*), crusian carp (*Carassius carassius*) and catfish (*Ictalurus nebolosus*) from Vaccares lagoon (French National Reserve of Camargue)—effects on some physiological parameters. Aquat. Toxicol. 48, 443–459.

Roche H., Buet, A., and Ramade, F. 2002a. Relationships between persistent organic chemicals residues and biochemical constituents in fish from a protected area: the French National Nature Reserve of Camargue. Compd. Biochem. Physiol. C 133, 393–410.

Roche, H., Buet, A., and Ramade, F., 2002b. Accumulation of lipophilic microcontaminants and biochemical responses in eels from the Biosphere Reserve of Camargue. Ecotoxicology 11, 9–18.

Roche H., Vollaire Y. Martin E., Rouer C., Coulet E., Grillas P., Banas D. 2009. Rice fields regulate organochlorine pesticides and PCBs in lagoons of the Nature Reserve of Camargue Chemosphere75, 526–533

Smalling K.L., and Aelion C.M., 2004. Distribution of atrazine into three chemical fractions: impact of sediment depth and organic carbon content. Environ. Toxicol. Chem. 23, 1164–1171.

Schwarzenbach R. P., Gschwend P. M., and Imboden, D. M. 2003. Environmental Organic Chemistry; 2end edition. Wiley: New York, 1313 p.

Scully F. and Hoigné J., 1987. Rate constants for reactions of singlet oxygen with phenols and other compounds in water. Chemosphere 16, 681–694.

Sherrard R M., Bearr J. S., Murray-Gulde C. L., Rodgers J. H., Jr. and Shah Y. T. 2003. Feasibility of constructed wetlands for removing chlorothalonil and chlorpyrifos from aqueous mixtures. Environmental Pollution 127, 385–394.

Smirnoff N., 2005. Antioxidants and Reactive Oxygen Species in Plants. Blackwell Publishing Ltd., City, 302 p.

Soderquist C. J. and Crosby D. G. 1975. Dissipation of 4-chloro-2-methylphenoxyacetic acid (MCPA) in rice field. Pest. Sci. 6, 17-33

Tack G, De Pauw N, Du Laing G, Rousseau D. 2007. Contaminants in natural and constructed wetlands: pollutant dynamics and control. Sci Total Environ 380, 1–2

Valentine R. L., and Zepp R. G. 1993. Formation of CO from the photodegradation of terrestrial DOM in natural waters. Environ. Sci. Technol. 27, 409–412.

Vialaton D and Richard C., 2002. Phototransformation of aromatic pollutants in solar light: photolysis versus photosynsitized reaction under natural water conditions. Aquat.Sci. 64, 207–215.

Vione D., Maurino V., Minero C., and Pelizzetti E. 2005. Reactions induced in natural waters by irradiation of nitrate and nitrite ions. Handbook of Environmental Chemistry Vol. 2, Part M: 221–253.

Vione D., Falletti G., Maurino V., Minero C., Pelizzetti E., Malandrino M., Ajassa R., Olariu R.and Arsene C. 2006. Sources and sinks of hydroxyl radicals upon irradiation of natural water samples, Environ. Sci. Technol. 40, 3775–3781.

Vione D, Maurino V, Minero C, Carlotti M E., Chiron S, and Barbati S. 2009. Modelling the occurrence and reactivity of the carbonate radical in surface freshwater. C. R. Chimie, 12 865–871.

Vione D, Das R, Rubertelli F, Maurino V, and Minero C. 2010. Modeling of Indirect Phototransformation Reactions in Surface Waters 203–234. In: Pignataro B. (Ed.) Ideas in Chemistry and Molecular Sciences: Advances in Synthetic Chemistry. WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Vulliet E., Emmelin C., and Chovelon J. M., 2004. Influence of pH and irradiation wavelength on the photochemical degradation of sulfonylureas, J. Photochem. Photobiol. A: Chem., 163, 69–75.

Vymazal J. 2009. The use constructed wetlands with horizontal sub-surface flow for various types of wastewater. Ecological Engineering 35, 1–17.

Warren N., Allan I J., Carter J.E., House W.A, Parker A. 2003. Pesticides and other micro-organic contaminants in freshwater sedimentary environments- a review. Appl. Geochem. 18, 159–194.

Weiner E.R. 2008. Application of environmental aquatic chemistry. 2nd Ed. Taylor & Francis Group, 6000 Broken Sound Parkway NW, Suite 300.

Yao,D. C. C. and Haag W. R., 1991. Rate constants for direct reactions of ozone with several drinking water contaminants. Water Res. 25, 761–773.

Ying, G.G., and Williams, B., 2000. Laboratory study on the interaction between herbicides and sediments in water systems. Environ. Pollut. 107, 399–405.

Zepp R G. and Cline M.D, 1977. Rate of direct photolysis in aquatic environment. Environ. Sci.& Technol 11, 359–366.

Zepp R. G., Baughman G. L. and Scholtzhauer P. F. 1981. Comparison of photochemical behaviour of various humic substances in water: sunlight induced reactions of aquatic pollutants photosensitized by humic substance. Chemosphere 10, 109–177.

Zepp R. G., Scholtzhauer P. F., and Sink R. M. 1985. Photosensitized transformations involving electronic energy transfer in natural waters: role of humic substances. Environ. Sci. Technol 19,74–81.

Zepp R. G, Faust B.C., and Hoigne J. 1992. Hydroxyl radical formation in aqueous reactions (pH 3–8) of iron(II) with hydrogen peroxide: the photo-Fenton reaction, Environ Sci Technol 26, 313–319.

RESUME EN FRANÇAIS

INTRODUCTION

Le delta du Rhône est une vaste plaine alluviale recouverte d'étangs et de lagunes, parsemée de cultures diverses, principalement du riz (21'100 ha en 2009, Centre Français du Riz, 2010). La culture du riz demande d'importants volumes d'eau provenant du Rhône (la consommation moyenne par hectare de rizière est de 28'000 m^3/an). Des herbicides répandus en avril (pré levée, prétilachlor) et en juin (poste levée, bentazone ; MCPA et dichlorprop) sont utilisés dans la riziculture pour lutter contre les mauvaises herbes. L'étang de Vaccarès, qui est classé «réserve de biosphère» par l'UNESCO pour sa grande richesse biologique reçoit des pesticides directement issus des rizières par les canaux de drainage.

La Camargue, située à l'embouchure du Rhône, est une vaste plaine deltaïque alluviale de 1453 km^2. Elle forme un triangle qui a pour sommet Arles et pour base le littoral depuis le golfe de Fos à l'est jusqu'à Aigues-Mortes à l'ouest. En arrivant près d'Arles, le cours du Rhône (812 km de long) se divise en deux bras : le Petit Rhône bifurque vers l'ouest et le Grand Rhône s'oriente vers l'est. Ces deux bras séparent le pays camarguais en trois unités, on distingue alors :

- La Grande Camargue ou île de Camargue entre les deux bras du Rhône dont le cœur est le système Vaccarès. Le système Vaccarès est composé de deux sous systèmes : l'étang du Vaccarès et les étangs dit du bas, composés de l'étang de l'Impérial et l'étang du Lion. Ces étangs du bas restent connectés à la mer, par le Grau de la Fourcade.
- La Petite Camargue à l'ouest du Petit Rhône
- Le Plan du Bourg à l'est du Grand Rhône.

La Camargue, unique delta français de cette ampleur, se distingue en Europe par la richesse biologique de ses écosystèmes. Son rôle de relais vital pour l'avifaune lui a valu une reconnaissance internationale. Dès 1927, fut créée la Réserve Nationale de Camargue.

L'agriculture en Camargue procède d'une longue tradition. Autrefois exclusivement localisée dans la partie nord, elle a depuis l'endiguement et l'introduction de la riziculture, envahi toute la "Camargue fluviale" et les pourtours de la "Camargue marine".
Les cultures occupent la majeure partie de la Camargue fluvio-lacustre, soit un tiers de la superficie totale. Essentiellement des céréalières, elles accordent à la riziculture 80 % des terres labourables. L'élevage extensif de chevaux et de taureaux, bien que subissant la

réduction des secteurs de pacage, connaît une progression récente en tant que support des activités taurines et touristiques.

PROBLEMATIQUE ET OBJECTIFS DE L'ETUDE

La Camargue est le principal lieu de production du riz Français. Le riz a des exigences écologiques particulièrement fortes au niveau thermique et hydrique. Le mode de culture pratiqué en Camargue est basé sur la quasi-permanence d'une lame d'eau d'une hauteur de 5 à 10 cm sur le sol. La riziculture fournit l'eau douce nécessaire à l'équilibre de l'environnement du delta. Ce mode de culture de riz est peuvent donc augmenter le risque de contamination les sources d'eaux alentours par les pesticides appliquées pour lutter contre les herbes et les insectes de riz. D'après des travaux récents réalisés par Comoretto et al. (2009, 2008, 2007), la source principale de pollution par les pesticides en Camargue est la riziculture. De plus, cette pollution est de type pulsé et la durée des pics de pollution en avril et juin est estimée à deux semaines en tenant en compte la variabilité temporelle d'application d'une même matière active. Mais des informations manquantes sur le devenir métabolique de xénobiotiques sont nécessaires afin de mieux comprendre les processus impliqués dans la dégradation des herbicides en Camargue.

D'un point de vue scientifique, peu d'études sont consacrées au devenir des pesticides dans les eaux estuariennes. En autre, la plus part de ces études ont été focalisés sur la photochimie bien que la biodégradation dont impliqué dans l'atténuation des pesticides.

Alors la présente étude a pour les objectifs suivants :

- ✓ Etudier le devenir des herbicides de riziculture dans les eaux de surfaces de Camargue par la voie photochimique en caractérisant la réactivité photochimique des eaux saumâtres.
- ✓ Evaluer le rôle de la biodégradation des herbicides de riziculture par les micro-organismes.
- ✓ La modélisation de transfert et de devenir des herbicides de riziculture dans le milieu aquatique en Camargue.

L'ensemble des ces objectifs permettra à déterminer les processus principaux impliqués dans l'atténuation rapide des herbicides de riziculture.

ETUDES EXPERIMENTALES

1. La photochimie :

Dans l’écosystème aquatique, il y a deux modes de photodégradation qui peuvent être se produire à la surface des eaux superficielles; la photolyse directe et la photolyse indirecte. La photolyse directe se produit par l’absorption de la lumière par le pesticide. Par ailleurs, la photolyse indirecte ou induite se produit par l’absorption de la lumière par une molécule, autre que le pesticide, qui peut alors, soit transmettre l’énergie reçue au produit phytosanitaire et provoquer sa transformation, soit encore former par oxydation des espèces réactives qui agissent à leur tour sur le pesticide.

Pour la réalisation des études de caractérisation la réactivité photochimique des eaux, l'espèce réactive photo-induits (hydroxyl radical $HO^{\cdot}$, l’oxygène singlet $^1O_2$ et l'état triplé de la matière organique DOM^*) dans des eaux estuariennes (lagune Vaccarès) el des eaux douces (Canal Fumemorte) ont été déterminés en utilisant des composés modèles (Benzène, 'alcool furfurylique). Pour cela un réacteur photochimique a été utilisé. Le réacteur photochimique à immersion est équipé d’une lampe haute pression à vapeur de mercure, filtre dont permet l’élimination du rayonnement à des longueurs d’onde inférieures à 290 nm pour se rapprocher du spectre solaire et simuler ainsi les conditions naturelles, et un système de refroidissement par l’eau.

Cependant des manipes sur la dégradation par la voie de photolyse directe et indirecte des quatre herbicides bentazone, MCPA, dichlorprop, alachlor (un substitut de Prétilachlor) ont été menées à l’extérieur par le soleil en été. Les études cinétiques de la photolyse des herbicides mentionnées ont été effectuées avec une concentration initiale de 50 µM. L’évolution de la concentration des herbicides a été suivie par Chromatographie Liquide à Haute Performance HPLC équipé d’une colonne à phase inverse (RP18, LiChrospher 4.6 mm) de 25 cm de longueur et de un détecteur UV et un injecteur automatique.

En autre, Les constantes cinétiques de la réaction des herbicides bentazone, MCPA et dichlorprop avec les radicaux hydroxyles ont été déterminé par la méthode de Fenton par compétition avec un molécule de référence 2-hydroxybenzoic acid (2-HBA)

2. La Biodégradation

La procédure du ce test suit les normes OCDE (Test No. 309, 1999) pour les produits chimiques. L'essai a conduit dans des flacons cylindriques d'une capacité 1,0 litre, Dans chaque flacon de on introduit 10 µg L^{-1} des herbicides étudiées (bentazone, MCPA, dichlorprop, alachlor). Les flacons sont ensuite maintenus pendant 60 jours à une température de 25 ± 2°C dans l'obscurité avec une agitation continue, afin de maintenir les microorganismes en suspension et permet de maintenir correctement l'aérobiose. Le pH et la concentration d'oxygène sont mesurés périodiquement dans le système expérimental. La concentration de la substance d'essai (herbicide) à été mesurée en fonction de temps par l'HPLC après avoir extrait par la technique de solide phase d'extraction (SPE).

3. La Modélisation

La sorption et la sédimentation, et la volatilisation de bentazone, MCPA, dichlorprop,et l'alachlor ont été obtenus par le modèle informatique MASAS (Modélisation de Substances Anthropogéniques dans les Systèmes Aquatiques).

RESULTATS

Les Concentrations de l'hydroxyle radical et l'oxygène singlet ainsi que le rôle de l'état triplé de la matière organique DOM*de ont été déterminés. Les concentrations des HO$^\cdot$ et $^1O_2$ obtenus : (1,72 ± 0,01) × 10^{-16}M et (2,06 ± 0,22) × 10^{-13} M. Ces valeurs ont été comparées avec ceux d'eau fraîche (Canal). Les concentrations étaient (9,41 ± 0,12) ×10^{-17} M, (5,44 ± 0,04) ×10^{-14} M. Nous avons puis développé un modèle cinétique qui décrit la photo transformation composés organiques induit par les trois photooxidants motionnées.

La photodégradation des herbicides étudiés, menée à l'extérieur par le soleil, dans les deux échantillons d'eaux (lagune Vaccarès, Canal Fumemorte) suit une cinétique du premier ordre sauf l'alachlore (deuxième ordres). Le processus de dégradation est relativement rapide dans l'eau de Vaccarès que le Canal. Les temps de demi-vie varient entre 2,17 et 4,08 jours pour la bentazone, 13-15 jours pour le MCPA, 31,50-34,65 jours pour le dichlorprop et 11,20-18,20 jours pour l'alachlore.

Cependant, La biodégradation était plus lente dans l'étang de Vaccarès que le canal de Fumemorte ainsi que le temps de latence (Le temps nécessaire pour une dégradation de 10% de la concentration initiale de pesticide).

Le MCPA et le dichlorprop ont été biodégradés considérablement avec un temps de latence court, par contre la bentazone n'a montré aucune biodégradabilité et sa concentration a été restée constante pendant l'étude dans les deux échantillons d'eaux. Les demi-vies pour la biodégradation des herbicides étudiée dans l'échantillon de l'eau du canal Fumemorte étaient 6,9 ± 0,5 jour (dichlorprop) et 8,3 ± 0,7 jour (MCPA). Dans l'eau de la lagune, toutes les concentrations de l'herbicide étaient > 80% de concentration initiale pendant 26 jours. Les temps de la demi-vie calculés étaient 39,6 ± 1,4 jour et 46,2 ± 1,6 jour pour MCPA et dichlorprop, respectivement. Par contre, la biodégradation de l'alachlore n'a pas été significative pendant la durée de cette expérience. Le taux de biodégradation de cet herbicide été entre 50 et 60 % seulement de la concentration initiale.

Selon résultats de la volatilisation et la sédimentation modélisée par MASAS nous avons trouvé que ces processus ne jouent qu'un rôle minoritaire dans l'atténuation des herbicides étudiés.

Finalement, en effectuant un calcul de temps de demi- vie total de la photochimie et de la biodégradation présentée dans la partie expérimentale ainsi que les processus de volatilisation et sédimentation modélisée par MASAS nous avons trouvé que nous résultats sont du même ordre de grandeur de données sur terraine (2004-2006).

CONCLUSION GENERALE

Cette étude nous a fourni des informations de sur la photoréactivité, et sur les processus photochimiques ainsi que la biodégradation qui ont lieu dans les milieux aquatiques en Camargue. La photodégradation est donc considérée comme voie importante et le processus de dégradation majoritaire dans les processus de transformations abiotiques des herbicides de riziculture. La biodegradation à été très lente dans les eaux estuariennes (lagune Vaccarès) que dans des eaux douces (Canal Fumemorte). Par ailleurs, nous avons pu modéliser et constater que les la sédimentation, volatilisation et l'hydrolyse, sont des processus minoritaires par rapport la dégradation rapide des herbicides de riziculture.

Les travaux ont été valorisés en 3 articles :

Fadi ALHOUSARI, Davide VIONE, Serge Chiron, Patrick Höhener, Stéphane Barbati. 2010. Reactive Photoinduced Species in Estuarine Waters: Characterization of Hydroxyl Radical, Singlet Oxygen and Dissolved Organic Matter Triplet State. Photochem Photobiol Sci. 9(1):78-86.

Patrick Höhener, Laetitia Comoretto, Fadi Al Housari, Philippe Chauvelon, Marc Pichaud, Yves Chérain, Serge Chiron. 2010. Modeling anthropogenic substances in coastal wetlands: application to herbicides in the Camargue (France). Environmental

Modelling & Software (25) 1837-1844.

Fadi Al Housari, Patrick Höhener, Serge Chiron. 2010. Factors responsible for rapid dissipation of acidic herbicides in the coastal lagoons of the Camargue (Rhône River Delta, France)? Science of the Total Environment, (Accepted)