Dissipation of Rice Herbicides in Surface Waters of the Camargue (Rhône River Delta, France): Experimental Study and Modelling

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Introduction

The Ile de Camargue basin is the central part of the Rhône Delta in the south of France between the two branches of the river. The higher parts of this area are devoted to agricultural land, mainly rice fields. 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 of the Nature Reserve Camargue. Both, the water of Fumemorte canal and Vaccarès lagoon, were studied here (Fig.1). They differ mainly in their salinity and organic matter content.

Bentazone, Dichlorprop, MCPA and Pretilachlor are post-emerging herbicides applied in rice fields from mid April to mid June.

Objectives:

Only few studies about the fate of herbicides in estuarine waters have been conducted so far. The main purposes of current study were:

✓Studying the photodegradation under natural sunlight and the hydrolysis of those herbicides in water from the canal and the Vaccarès lagoon

✓Modelling the environmental fate of those herbicides with the model MASAS which links the fundamental chemical properties of the pesticides in question to a half-life time in the aquatic environment (Fig.2).

✓Comparing experimental results and model findings with previous field data (2004-2006)

Fig. 1: Location of sampling sites within the study area

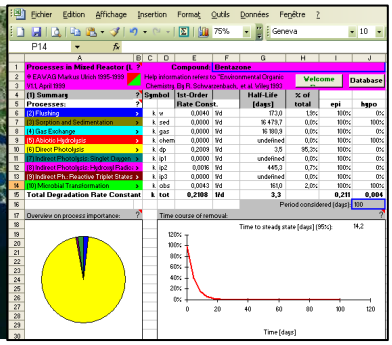
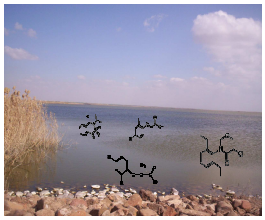


Fig. 2: The model MASAS [2] running on an Excel spreadsheet

Material and Methods

Photodegradation experiments under natural sunlight: The experiments were conducted using two different solutions of pesticides: Solution (1): contained Bentazone, Dichlorprop and MCPA; solution (2) contained Alachlor alone (used as a surrogate for the similar Pretilachlor). The final concentration of the pesticides was 0.5E-4M in filtered Vaccarès and Canal water samples. The same solutions but in high purity water was used for estimation the direct photolysis of those samples were exposed to natural sunlight in summer conditions in Marseille. Controls were run in the dark yielding hydrolysis half-life times.



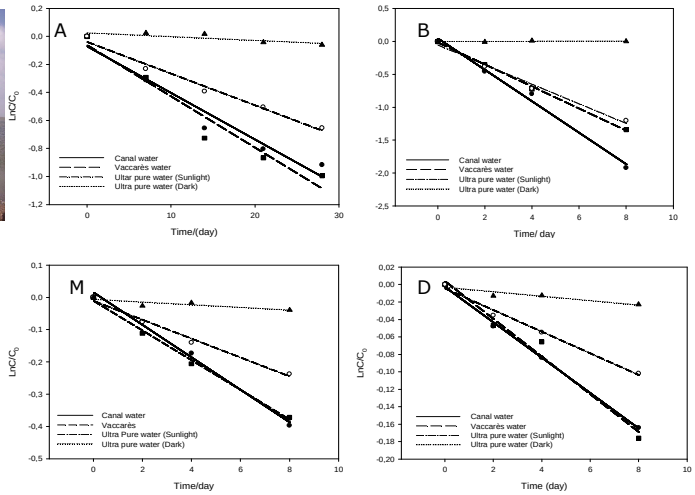


Fig.3: Photodegradation of herbicides(0.5E-4M) in water from (●) Canal and (■) Vaccarès, (○) Ultra pure water samples under natural sunlight july, 2008. and (▲) Ultra pure water (Dark). A: Alachlor, B: Bentazone, M: MCPA, D: Dichlorprop.

Results

Degradation experiment: The loss of herbicides could be described using a first –order kinetic equation. None of the studied herbicides showed a significant degradation by hydrolysis during the course of the experiment. So the attenuation of those herbicides in natural estuarine waters from Camargue cannot be a result of hydrolysis process. (Fig. 3).

Model simulations with MASAS: According to MASAS, photolysis accounts for more than 95% of the loss rate of Bentazone (T1/2=3.3 days), and for more than 89% of the one of MCPA (T1/2=6.8 days). Microbial transformation accounts for 85% of Alachlor dissipation (T1/2=19.5 days). DCPP degraded much slower in our experiment (T1/2=35 days) compared to what MASAS predicted (12 days) (Table 1, Fig.4). Sorption+Sedimentation as well as gaz exchange (volatilization) were negligible for all compounds.

	Half-life time ($T_{1/2}$) day			
	Alachlor	Bentazone	MCPA	DCPP
Photodegradation (Natural sunlight)	21.0-23.1	2.17-4.08	13.9-15.1	31.5 -34.6
Modelling (MASAS)	19.5	3.3	6.8	12
Field data 2004-2006	5-9 (Pretilachlor)	10-15	6.0-13.5	10.0

Table 1: Half-live times of the herbicides obtained experimentally compared with those calculated by the MASAS software and those obtained from field data.

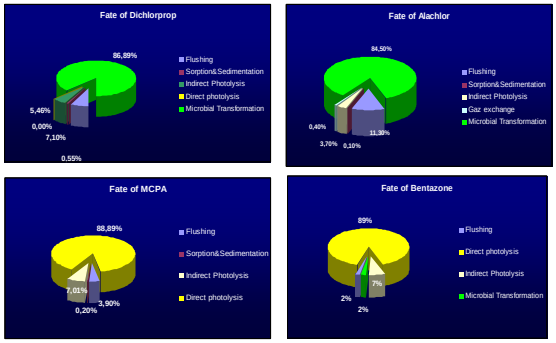


Fig. 4: Results from the MASAS model: Main Processes responsible for attenuation of herbicides concentrations

Conclusions

The photodegradation experiments showed a rapid removal of Bentazone, and intermediate to slow removals of the other three herbicides in both Canal and lagoon water.

The MASAS model suggests that biodegradation in the aqeous phase accounts for high percentages of the removal of Alachlor and Dichlorprop. Sorption and sedimentation, gaz exchange, flushing and abiotic hydrolysis have a minor role in attuenuation of the studied herbicides.

A pretty good correlation exists between the model predictions and the field observations, although there are knowledge gaps concerning the modelling of complex indirect photochemistry.

Cited references

[1] 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.

[2] 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. Software 10, 177-198.