

## WATER TOXICITY AND PESTICIDES LOADS IN WATER AND SEAFOOD IN THE EBRO RIVER DELTA DURING RICE CULTIVATION

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This work presents the results obtained in a monitoring study carried out in the Ebro river delta (NE, Spain) where surface water samples have been analysed for both toxicity and pesticides in an attempt to disclose the causes of the seafood mortality episodes observed yearly in this area at spring time. Eight pesticides have been analysed also in seafood.

Target pesticides (a total of 22) included 6 triazines, 4 phenylureas, 4 organophosphorous, 1 anilide, 2 chloroacetylanilides, 1 thiocarbamate and 4 acid herbicides. Analysis was performed by fully automated on-line solid phase extraction-liquid chromatography-electrospray-tandem mass spectrometry (SPE-LC-ESI-MS/MS). 16 of the 22 pesticides were determined in positive ionization mode (PI) using PLRP-s cartridges for extraction and 6 pesticides were measured in negative ion mode (NI) after SPE with Hysphere Resin GP cartridges. Method detection limits in river water varied between 0.07 and 7.58 ng/L for diazinon and fenitrothion, respectively. Recovery percentages were higher than 70% for all compounds except malathion (64%), desethylatrazine (44%) and fenitrothion (36%).

Analysis of pesticides (a total of 8) in seafood was performed by gas chromatography-mass spectrometry with electron impact ionization (GC/MS-EI). Oysters and mussels were first dried (lyophilization) and blended (with mortars).

Toxicity of samples was evaluated using 3 standard methods based on *Daphnia magna*, *Selenastrum capricornutum*, and *Vibrio fischeri*. These organisms were selected because they represent 3 different organization levels in the aquatic chain and because of their different sensitivities towards the different groups of pesticides.

Surface water samples (a total of 62) were collected in selected days in April and May 2008 from six different locations: the two northern and southern bays (Fangar and Alfacs) forming the delta, and four main draining channels discharging the output water from the rice fields into them (Figure 1). The seafood samples (a total of 11) were collected from the two bays, Fangar and Alfacs.



Figure 1: Map of sampling at the Ebro river delta (NE, Spain).

Results showed that about 50% of the pesticides investigated presented individual concentrations above 100 ng/L and four locations presented (in many cases) levels of total pesticides higher than 5000 ng/L. The most ubiquitous compounds were bentazone and MCPA and the highest levels observed corresponded to malathion (5825 ng/L) and MCPA (4197 ng/L). With respect to the maximum allowable concentrations (MAC) proposed by the EU for atrazine, alachlor, diuron, isoproturon and simazine in inland and other surface waters (2008/C 71 E/01 - Common Position (EC) No 3/2008 of 20 December 2007), only alachlor was found to exceed the proposed limit of 700 ng/L in two of the samples investigated.

Good agreement was observed between pesticides concentration (in water and seafood), toxicity, and mortality episodes of seafood (oyster and mussel). Most of the measured toxicity responses were explained theoretically using an additive approach with the concentrations of the pesticides measured in water by LC-MS/MS and multiplied by TUs (toxicological units) of each pesticide. Modulation of toxicological responses can be attributed to synergistic effects, matrix effects and possible presence of metals. The most representative organism was, as expected, *Daphnia magna*, a micro crustacean.

Comparing the sides of the river delta, the left side was the more contaminated and toxic, both at the output and at the bay.

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