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► To cite this version:

Thierry Caquet, Nicolas Mazzella, François Delmas, H. Budzinski, J.F. Dubernet, et al.. Presence and effects of pesticides along estuarine continuums in the Bay of Vilaine area (Brittany, France): 1. Monitoring of environmental contamination. SETAC Europe 18th Annual Meeting, May 2008, Warsaw, Poland. pp.1, 2008. hal-02590535

HAL Id: hal-02590535

<https://hal.inrae.fr/hal-02590535>

Submitted on 15 May 2020

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Presence and effects of pesticides along estuarine continuums in the Bay of Vilaine area (Brittany, France).

1. Monitoring of environmental contamination.

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Introduction

Information about the presence and effects of pesticides in estuaries and associated coastal areas are scarce although there is evidence that such compounds may be present at some critical periods (*e.g.*, in spring, when reproduction of many animal species takes place). With a 10,400 km² area watershed, Vilaine is the most important river from northwest France. About 60 % of the watershed is used for intensive agricultural production. Data from previous monitoring programs showed that pesticides are frequently detected in Vilaine water at high levels. Therefore, this area was selected by the IMOPHYS (Integration of Molecular and Physiological responses to contaminants in coastal areas) French research consortium to implement a program on the presence and effects of pesticides in sites distributed along fresh- to marine water continuums.

Material and methods

Three sampling sites were chosen: one in freshwater (Arzal reservoir), one in the estuary within mussel farming area (Le Halguen in 2006, Les Granges in 2007) and one in the open sea, outside of the Vilaine plume (Le Maresclé).

Chemical contamination was assessed in 2006 and 2007 through the analysis of water samples collected in Arzal reservoir by an automatic flow-triggered sampler and of point samples for the other sites. Point samples were collected every two weeks from April to July and following high rain events (> 20 mm during one day/ > 30 mm cumulated rain on three consecutive days). Sediment and mussel (*Mytilus edulis*) samples were also collected in estuarine and marine sites in 2006.

Herbicides and their main metabolites were analyzed in water samples using HPLC-ESI-MS/MS or HPLC-FL. POPs (lindane, PAHs, PCBs, PBDEs), alkylphenolethoxylates (APEOs) and pharmaceuticals were analyzed in water (dissolved and particulate phases), sediment, and mussel samples using HPLC-MS/MS or GC-MS/MS.

On each date, the risk associated with pesticides was assessed by computing the value of the risk quotient (RQ_i) for each compound using the corresponding HC_{5-95%} value [1,2], excepted for Irgarol 1051 and acetochlor for which PNEC values were used. To assess mixture risk, the pesticides were grouped according to their mode of action (photosystem II-PSII inhibition and Long fatty acids chains-Lfac synthesis inhibitors)

$$RQ_i = \frac{MEC_i}{HC_{5-95\%,i}}$$

MEC_i = measured concentration of pesticide i
HC_{5-95%,i} = lower limit of the 95% CI of Hazardous Concentration of pesticide i for 5% of species

Results and discussion

Triazines (atrazine + DEA, simazine, Irgarol 1051), phenylureas (diuron, isoproturon) and chloroacetanilides (acetochlor, metolachlor) were frequently detected and quantified in Arzal. Elevated diuron and Irgarol 1051 concentrations suggested that the use of antifouling paints significantly contributed to the contamination of Vilaine.

Temporal changes of Risk Quotient values showed that herbicide-associated risk was frequently unacceptable in may-june for PSII-inhibiting compounds, due to high levels of diuron and Irgarol 1051.

Analyses performed on samples from estuarine sites showed that many herbicides were transferred in a conservative manner from the river to the estuary and diluted at high tide. Presence of pesticides in the marine control site indicated that other sources than Vilaine (*e.g.*, tidal streams) may be responsible for coastal contamination.

APEOs and POPs concentrations were low and they decreased along the fresh- to marine water continuum. PAHs were mainly of a pyrolytic origin, probably associated with motorboat use. The only pharmaceutical detected in quantifiable amounts was aspirin, with levels ranging from a few 10s to a few 100s ng/L in all the sites. Mussels contamination by POPs was moderate and identical between the two sampling sites.

Conclusions

Pesticides and related compounds used in antifouling paints frequently present an unacceptable risk for aquatic organisms in spring in Arzal reservoir. These compounds are transferred to the estuary where they may present a risk for aquatic organisms, especially mussels.

Acknowledgements

This programme is funded by the French National Research Agency (Grant #ANR-05-ECCO-010) within the framework of the INSU ECODYN programme

Sampling sites for the assessment of chemical contamination in Vilaine river and its estuary



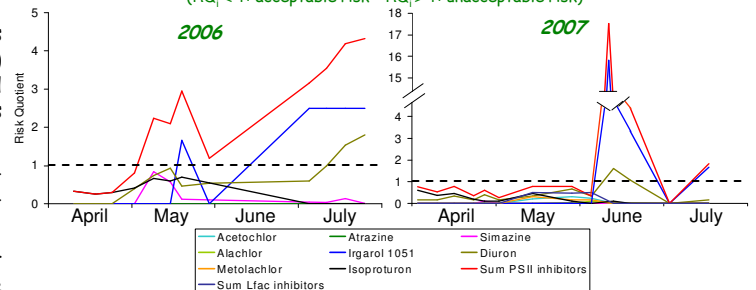
Point sampling of water in estuarine and marine sites



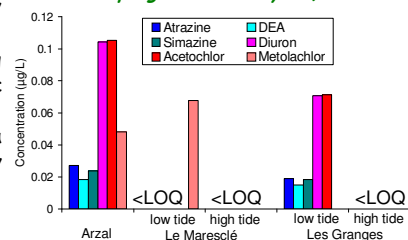
Automatic flow-triggered water sampler at Arzal reservoir



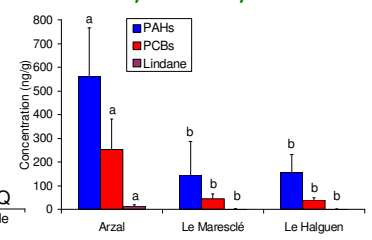
Risk Quotient values at Arzal (RQ_i < 1: acceptable risk - RQ_i > 1: unacceptable risk)



Herbicide concentrations in the various sampling sites on May 28, 2007



POPs concentrations in the particulate phase



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