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Assessment of the quantities of herbicides and nutrients brought down by the river Charente to the coast and modelling of the dispersion of atrazine in the Marennes-Oléron bay

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Abstract: Our study aims at making progress the estimate of herbicide and nutrient inputs to the Marennes-Oleron bay which could influence summer oysters mortalities, and to bring a better understanding of the impact on coastal ecosystems by modelling the dynamics of these compounds in the shellfish-farming area. The development of a strategy adapted to the river Charente and its estuary reveals that agricultural activity on the watershed area is omnipresent, as well on the level of the nitrogen as on the one of herbicides contributions. It is thus necessary to specify Charente fluxes, which is the main tributary of the Marennes-Oleron bay, in order to better characterize its impact on shellfish-farming activity. Hydrodynamic modelling will constitute an invaluable help in the risk assessment with respect to pesticides, by specifying the periods of the high and low concentrations of these molecules and the biotope exposure durations.

Résumé : *Estimation des quantités d'herbicides et de nutriments apportées par la Charente au milieu côtier et modélisation de la dispersion d'atrazine dans la Baie de Marennes-Oléron.* Cette étude vise à faire progresser l'estimation des apports d'herbicides et de nutriments au bassin de Marennes-Oléron susceptibles d'influencer les épisodes de mortalité estivale des huîtres, et à apporter par la modélisation une meilleure compréhension de la dynamique de ces composés dans la zone de production conchylicole. La mise au point d'une stratégie d'étude adaptée au fleuve Charente et à son estuaire révèle que l'influence de l'activité agricole sur le bassin versant est omniprésente, tant au niveau des apports d'azote que d'herbicides. Il est donc nécessaire de préciser les flux apportés par la Charente, principal affluent du bassin de Marennes-Oléron, afin de mieux caractériser son impact sur l'activité conchylicole. L'utilisation d'un modèle de dispersion constituera une aide précieuse dans l'évaluation du risque vis à vis des produits phytosanitaires, en précisant les niveaux de présence de ces molécules et les durées d'exposition du biotope.

Keywords: Herbicides; Nutrients; Fluxes; Modelling; River Charente; Marennes-Oléron bay.

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Introduction

The reasons for undertaking this study are all related to the water quality of the Charente River and its impact on coastal ecosystems, but the immediate aim was undoubtedly to understand the phenomena involved in the summer mortality of oysters in the Marennes-Oléron bay, one of the most controversial regional ecological problems. In fact, the presence of herbicides such as triazines and phenyl-ureas has added to an already complicated debate on the reasons for the fall in oyster productivity, the causes of which have not been fully elucidated. Limited information relative to the inputs of pesticides into the basin and their dynamics in this complex and fragile ecosystem, and on their direct and indirect impact on shellfish, has in the past led to conflicts between shellfish growers and inland land users in the use of the freshwater resources. The difficulty arises from the fact that a large number of factors are likely to have an impact, either on their own, or more probably in a combined and synergistic manner. Several studies have in fact shown that oysters are naturally very weakened at this time of year, just after the period of gametogenesis. Meteorological and/or hydrological factors have also been proposed as determining phenomena in oyster physiology. The limit to the trophic capacity of the basin, resulting from its over-exploitation, has also been mentioned as an aggravating factor (Soletchnik et al., 1999). Finally, the general decrease in water quality, the presence of pollutants such as heavy metals (Miramand et al., 2002), pesticides (Munschy, 1995; Dupas, 1996), bacteria and viruses (Le Roux et al., 2002) have been studied, but up until now no clear relation has been demonstrated. Our research therefore naturally became part of the project called : *Impact of micro-pollutants (heavy metals and pesticides) on ecosystem functioning: application to the intertidal mud-flats of the Marennes-Oléron bay* of the CNRS Programme “Environnement Vie et Société” (PEVS).

Our contribution consists of three parts. The first attempts to quantify as precisely as possible the inputs of herbicides and nutrients brought down by the Charente river to marine coastal waters and to detect the temporal trends that have occurred over the decade 1993-2002. The second, that is a preliminary to modelling, has been used to confirm the relative stability of various herbicides (triazines and phenyl-urea) under two hydrological regimes on a transect across the estuary. Because of the mixing of fresh and salt waters, the adsorption and degradation kinetics can in fact be significantly modified. In the third part, a simulation of the dispersion of atrazine in the Marennes-Oléron bay has been conducted using the MARS2D hydrodynamic model developed by Ifremer.

Materials & Methods

Firstly, we decided on the main herbicides to be studied in relation to various criteria such as their use, toxicity, ecotoxicity, mobility and physico-chemical characteristics. A list of 29 molecules was drawn up. This included 22 active ingredients, belonging to various chemical families of herbicides such as triazines, phenyl-ureas and chloroacetanilides. Four of these active ingredients (atrazine, simazine, diuron and isoproturon) are included in the list of priority substances in the European Framework Directive on Water in marine coastal environment of 23 October 2000. In addition to these 22 studied active ingredients, we added 7 metabolites (or degradation products): desethyl-atrazine (DEA), desisopropyl-atrazine (DIA), desethyl-terbuthylazine (DET), dichlorophenyl-methyl-urea (DPMU), dichlorophenyl-urea (DPU), isopropyl-phenyl-methyl-urea (IPMU) and isopropyl-phenyl-urea (IPU). Some of these are also included in the regional priority list. All the molecules in this list were detected only in the dissolved phase because of their low capacity to be adsorbed onto suspended particles.

Water samples were collected at weekly intervals from 2000 to 2003, at the limit between the river and estuarine environments, i.e. at the tidal limit which is located at St Savinien on the river Charente and at the Ecluses de Carillon on the river Boutonne (Fig. 1).

Water samples were also collected upstream at 5 stations on the river Charente: Chalonne, Nersac, Sireuil, Bourg and Brives, at monthly intervals between 1993 and 2002 (Fig. 1). This sampling was used to detect year-to-year trends and place the inputs calculated for 2001-2002 within the context of the decade.

Assays were then conducted by HPLC-UV as indicated by Dupas et al. (1996). The daily discharges of the Charente were provided by the DIREN Poitou-Charentes, which operates several gauging stations distributed throughout the watershed. This time series, combined with the measurement of the concentrations enabled us to calculate the crude quantities of dissolved herbicides brought down to the estuary by the weighted estimation method of Verhoff et al. (1980).

Results and Discussion

Assessment of the quantities of nutrients and herbicides input by the Charente

Nitrogen and phosphorus. The low concentrations of phosphates present as far down as the estuary are certainly the result of the efforts made in the catchment in terms of

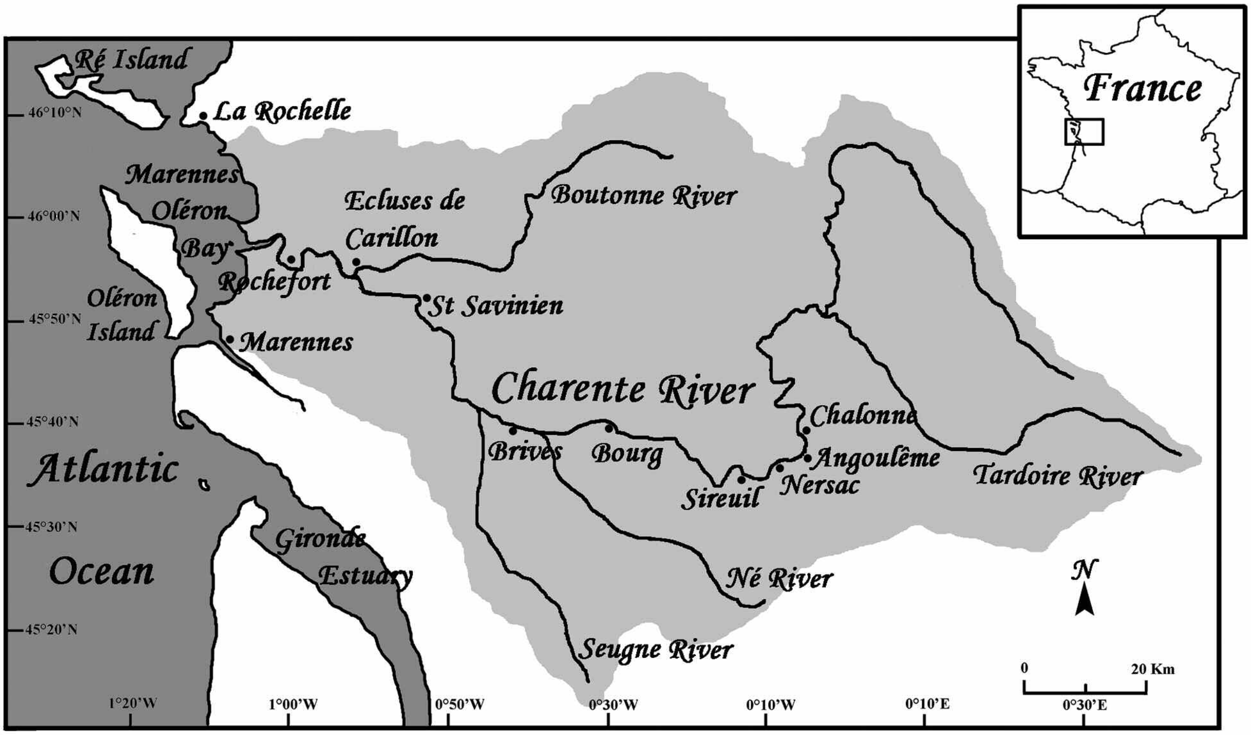

Figure 1. Sampling sites in the Charente watershed.
Figure 1. Localisation des sites d'échantillonnage sur le bassin versant de la Charente.

water purification. On the other hand, the much higher nitrogen concentrations in the waters of the Charente, 92% of which on average is in the form of nitrate nitrogen, is a certain sign of the importance of agricultural activity in its watershed (Munaron, 2004). The Charente is therefore a river that is completely unbalanced in trophic terms with an N/P ratio much higher than 16 and is subject to phenomena of eutrophication (proliferation of opportunistic macrophytic green algae and phytoplankton) that with the increasingly long period of low summer water levels, leads to prolonged stagnation of the waters. The N/P ratio has also tended to increase since 1993 (Fig. 2). Examination of the data indicates that the quantities of nitrogen provided by the Charente have remained stable in the last ten years, whereas those of phosphorus have tended to decline, due to improvements in waste water treatments, thus explaining the slow increase in the N/P ratio. In fact, in addition to the regenerated benthic production, the Charente is the main source of nutrients for the Marennes-Oléron bay (Ravail-Legrand, 1993). The substitution of the nutrient element that limits primary production, which has been demonstrated since the 1990s by Soletchnik et al. (1998), has therefore led us to ask three questions. Is the diminishing trend in phosphorus inputs by the Charente since 1993 about to increase in amplitude ? What effects would this have on the trophic status of the Marennes-Oléron bay ? Are the trophic resources currently sufficient to meet the requirements of the stock of shellfish being reared in the basin (124,000 tons in 1995) ? These will be the major problems to be faced in forthcoming years on the Charente coastline that reveal the great complexity of the upstream/downstream relation, between development and the sustainability of shellfish activity within the Marennes-Oléron bay and the efforts that are being made in the catchment in terms of restoration of surface water flows and the reduction of nutrient-laden flows.

Herbicides. For most of the molecules, the peak concentrations occur regularly and especially at times when treatments are applied within the watershed. There is therefore no time of year when at least one herbicide or degradation product does not occur at concentrations of at least 0.1 $\mu g.l^{-1}$ in the waters of the Charente.

We have also shown that the probability of these molecules occurring can be very high at spraying times, when the soils are highly saturated with water, because at these times the lightest rainfall event will lead to a simultaneous increase in both concentrations and discharges. A flood on the Charente during a spraying time generally leads to exceptional quantities of active ingredients and metabolites. This situation occurred in May 2001, when more than

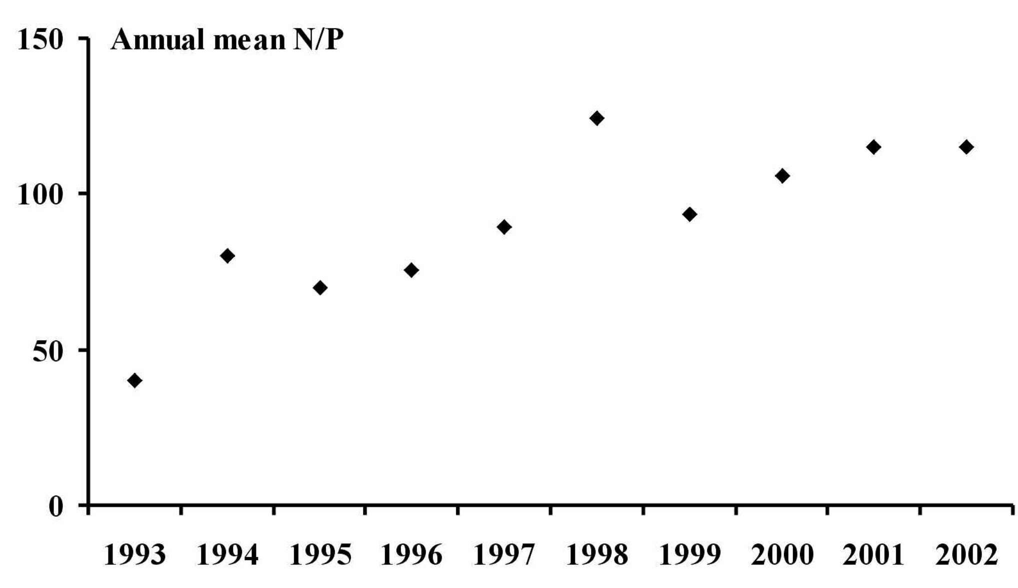

Figure 2. N/P annual mean ratio in the Charente river at Bourg-Charente.
Figure 2. Evolution des rapports N/P moyens annuels dans les eaux de la Charente à Bourg-Charente.

400 kg of herbicides were carried down to the estuary in one month by the Charente. The other risk periods in terms of the occurrence of these molecules in the river's water are as follows : i) at spraying times when the level of soil saturation is low, so that rainfall generally leads to very little surface runoff or groundwater flows. The water therefore becomes very concentrated in herbicides and the concentrations in the Charente can be particularly high (from 0.2 to 0.6 $\mu g.l^{-1}$) because of the low dilution. Even though the discharges remain low (20 to 80 $m^3.s^{-1}$), the quantities transported can be moderately high, as was the case in May and June 2002, when respectively 60 and 100 kg of herbicides were provided by the Charente; ii) at spraying times when the soil saturation levels are high, since the slightest rainfall can lead to the Charente flooding. This results in the transport of large quantities especially of metabolites (as in the winter floods of January to March 2001, when between 90 and 200 kg of herbicides were transported per month).

The Charente can therefore transport variable quantities of herbicides each year to its estuary, with quantities reaching more than 1360 kg in 2001 (Fig. 3) and about 510 kg in 2002 (Fig. 4) as a result of variable meteorological and hydrological conditions. As the first of these two years was one of the wettest of the decade (1993-2002) whereas the second was one of the driest, we can estimate that the values for quantities transported represent the range of variation for the annual quantities of herbicides transported by the Charente (for the 29 products studied).

Summer (July, August and September) is the period when the quantities of herbicides provided by the Charente are the lowest, because this is outside the time of most intensive spraying and the soil saturation levels are usually very low at this time. We estimate that between 12 and 30 kg of herbicides are provided per month during summer.

Following the analysis of the pesticides data collected on the Charente from 1993 to 2002, we can confirm that a decrease in the concentrations and quantities of atrazine and simazine has occurred in the last ten years, even though these two products are found almost constantly in the Charente, together with their metabolites, DEA and DIA, respectively.

This decrease in the last ten years is the result of a series of restrictions on use that have been put in place up to the present day, and that led to a complete ban on the use of these two active ingredients in 2003. As for the phenylureas, currently no molecule is found systematically. However, it seems that the use of diuron (from April to June) and isoproturon (from January to March) has become increasingly common in recent years. In the case of diuron, the reason is probably the ban or restrictions on the use of other active ingredients used in vineyards (terbuthylazine and simazine). The results of analyses conducted in 2002 also demonstrated, that for the first time on the Charente, two degradation products of diuron, DPMU and DPU have occurred, although at relatively low concentrations (0.1 $\mu g.l^{-1}$ but up to 0.37 $\mu g.l^{-1}$ in May 2002 on the Boutonne). These examples show that in addition to monitoring active ingredients in waters, it is essential to also monitor metabolites of herbicides when these have a mobility, remanence or toxicity at least as great as the parent-molecule. If not,

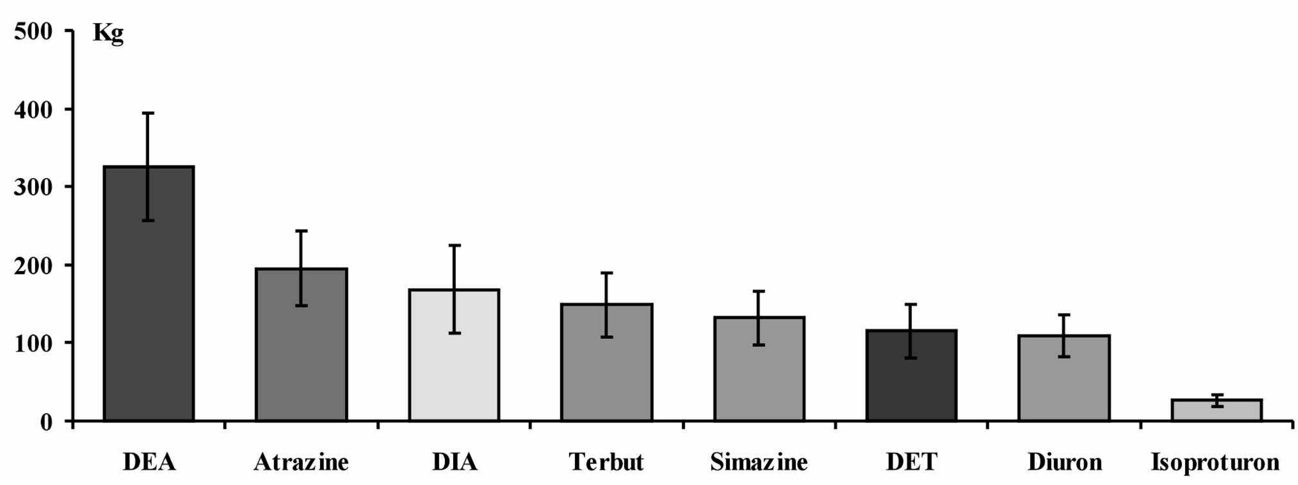

Figure 3. Herbicide inputs from the river Charente to the Marennes-Oleron bay during 2001.
Figure 3. Flux bruts d'herbicides apportés par la Charente au bassin de Marennes-Oléron au cours de l'année 2001.

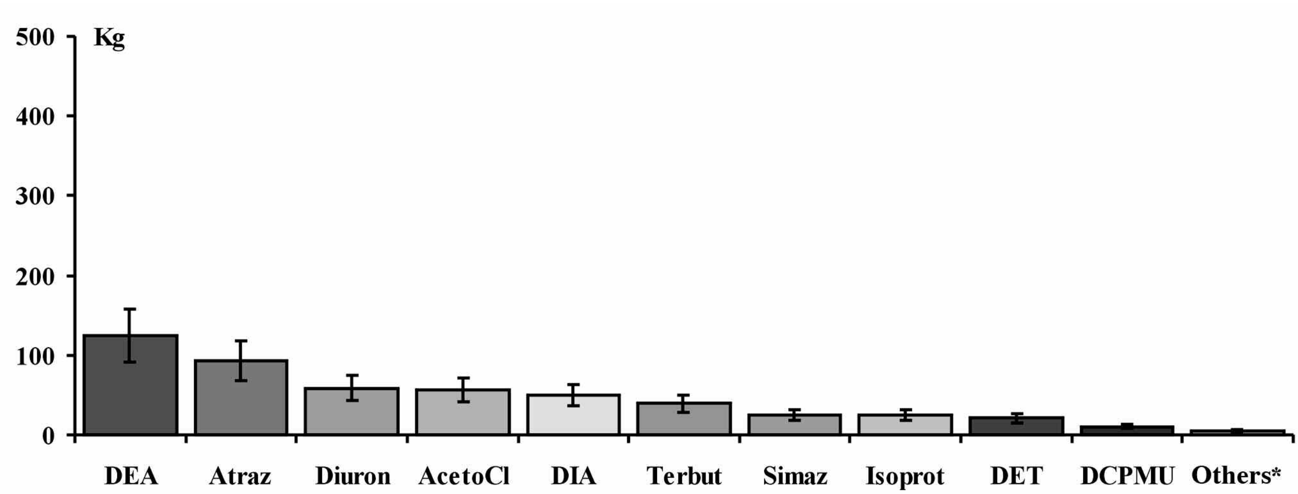

Figure 4. Herbicide inputs from the river Charente to the Marennes-Oleron bay during 2002. * *: (Chlortoluron + DCPU + linuron)*
Figure 4. Flux bruts d'herbicides apportés par la Charente au bassin de Marennes-Oléron au cours de l'année 2002. * *: (Chlortoluron + DCPU + linuron).*

part of the problem remains masked, the assessments would therefore be incomplete and the conclusions of the studies falsified.

Characterization of the geochemical behaviour of herbicides during their traverse of the estuary

It is important to determine whether the transfer of herbicides in the transition zone between the inland and marine environments is influenced by the mixing of fresh and saline waters (dilution phenomenon) or whether other factors also affect their fate by, for example, amplifying the phenomena of adsorption or degradation. We therefore conducted two sampling programmes in May 2000 and March 2002, by monitoring a water-mass as it became gradually diluted. These two periods differed significantly in hydrological terms, the discharges of the Charente being 190 and 75 $m^3.s^{-1}$, respectively. They reflected two different circumstances that can occur in the Charente estuary (the first being a rapid transfer of the transported materials and the second a much slower transfer). The results obtained showed that only atrazine seemed to have a consistent behaviour from one year to another in the Charente estuary, in relation to the different meteorological/hydrological and biogeochemical conditions occurring at the two sampling times.

This is why we chose this substance thereafter to illustrate the dispersion of a herbicide in the Marennes-Oléron bay (Munaron, 2004).

Simulation of the dispersion of atrazine in the Marennes-Oléron bay

Four events, corresponding to scenarii encountered in the last two years of the study (2001-2002) were simulated (Munaron et al., 2003). The very different character of these two years, particularly in terms of hydrology, allowed us to simulate very varied scenarii, typified by high, moderate and low quantities transported, on the basis of a realistic data set collected during the study (in terms of discharges and meteorology and in terms of the herbicide concentrations present in the waters of the Charente). These simulations confirmed the fact that there is a clear relation between the use of herbicides on agricultural land and their occurrence in the natural marine and estuarine environments (the highest concentration of atrazine in the Marennes-Oléron bay, of the order of 0.12 $\mu g.l^{-1}$, was effectively recorded during the times of spraying). Furthermore, they showed that the discharges of the Charente determined the extent of the atrazine plume in the basin, so that the atrazine present in the estuary was expulsed during floods, but in contrast was retained when the discharges were lower.

The extent of the plume was greatest in the estuary during flood episodes on the Charente, when it could affect all the zone located on the north side of the estuary mouth (the western limit of the plume at this time being situated at the line of Fort Boyard), but also and especially the mud-flat areas on both sides of the estuary (the Brouage mud-flat to the south and those of Aunis and Chatelaillon to the north). Residual currents then gradually led the plume toward the south toward the Pertuis de Maumusson, where it was forced to travel along the eastern coast, i.e. toward the Brouage and Marennes mud-flats. The calculated exposure times indicate that in general, the exposure to concentrations of more than 0.1 $\mu g.l^{-1}$ of atrazine is rather rare, except during periods of spraying. At these times, the calculated exposure times to a concentration of > 0.1 $\mu g.l^{-1}$ of atrazine can reach 35 days in the Charente estuary (during low discharges), 20 days at the estuary mouth, 14 days at the mud-flats close to the estuary and up to 5 days in the areas furthest from the mud-flats on either side of the estuary (also during floods).

Hydrodynamic simulations using Mars2D software have enabled us to determine the concentrations and exposure times that result from the dispersion of atrazine in the Marennes-Oléron bay. They show that at certain times, the waters of the Marennes-Oléron bay can have high atrazine concentrations (up to 0.12 $\mu g.l^{-1}$). This herbicide can then come into contact initially with non-targeted species (suspended micro-algae, the benthic macro-fauna, farmed filter-feeding shellfish and oyster larvae) for a sufficiently long time to lead eventually to toxicity effects. It is still impossible at present to determine whether this compound leads either to inhibition of photosynthesis in certain phytoplankton species, thereby modifying phytoplankton populations, or whether it causes an overall reduction in primary production, or the appearance of malformation in oyster larvae, leading to the low settlement rates that have frequently been observed.

Conclusions and Perspectives

Following all these results, many perspectives can be discerned from our work, some of which are currently being developed.

Extend the diagnosis of inputs of contaminants to the Charente coast

The same problem exists in all the bays and creeks along the Charente coast. For example, the inputs to the Sèvre-Niortaise estuary could have an impact on shellfish farming in the Aiguillon bay and Seudre River also influence the water quality in the south of the Marennes-Oléron bay. It is therefore necessary to comprehensively take into account all of the inputs from estuaries and creeks to the sea. Special attention has been given throughout our work to obtaining realistic estimates of the quantities transported by the Charente and in developing a methodology that can be applied to other estuaries in the region. The application of this methodology to the upstream parts of the Sèvre-Niortaise river (collaboration between Cemagref and DIREN, with the installation of an automated sampling station) and downstream in the Seudre (collaboration between Ifremer and Cemagref, with the installation of a point sampling programme at times when the shellfish are particularly sensitive) is already in place.

Widen the range of contaminants being detected and develop more comprehensive ecotoxicological approaches

Because of all the pressures that are being exerted on coastal and marine environments, especially in the Marennes-Oléron bay, a more holistic approach to the contamination of coastal areas has become essential. Very often, studies (of which ours is an example) only focus on a single chemical compound or family of contaminants, because of the lack of resources, so that it is then difficult to characterize the effects on ecosystems. No correlation is apparent, either because the concentrations are too low in the coastal environment, or because other contaminants can occur simultaneously and interfere with the results. Furthermore, synergistic and combined effects are beginning to be reported in the literature between several contaminants (of the same or different families) that occur in trace quantities in waters. It has been shown that the cumulative impact of dozens of herbicides at environmental concentrations on micro-algae is much greater than the effect of each one taken singly. Why not test new correlations between the cumulative effects of the cocktail of contaminants present in the Marennes-Oléron bay and the suspected changes in the communities of phytoplanktonic species, the phenomena of summer mortalities or even the decreased settlement of oyster spat? These new ecotoxicological approaches are currently being developed on the Brouage (Marennes-Oléron) mud-flat, as part of the PEVS (Programme Environnement Vie et Société of the CNRS). They are based on the concentrations and exposure times obtained in this study and focus particularly on the genotoxic impact of atrazine on oysters (aneuploidy) and on the combined effects of cocktails of pesticides (including atrazine) on the immunodeficiency of shellfish (Bouilly et al., 2003). These more comprehensive and more realistic approaches should provide concrete advances in terms of risk assessment and of the effects related to the simultaneous occurrence of cocktails of contaminants in the water. In this study area, a major advance has been made with the development of passive captors, whose use is in our opinion a priority because of the information provided on the concentrations (< 0.1 $ng.l^{-1}$) of a wide range of contaminants (metals, and water- and fat-soluble compounds).

Acquiring a better understanding of the geochemical behaviour of herbicides in the estuarine environment

The behaviour of herbicides in the estuarine environment has been studied on many occasions, but has never been studied during periods of low summer water levels, when the transit times are long and mixing by tides is incessant. There is no evidence to confirm in these circumstances, that the normally conservative behaviour of herbicides is constant from one year to another. It will however be essential to have suitable detection techniques, allowing us to descend to quantification levels of the order of a nanogram per litre (e.g. HPLC, or GC-MS). Furthermore, how can we estimate the half-lives of herbicides in the estuarine environment? This question is for the moment unanswered. The currently available techniques using mesocosms, and therefore closed systems, does not seem to be suitable because the very property of an estuary is that it is an open ecosystem.

Further improving the realism of the Mars2D model

This research has enabled us to test the latest developments of Mars2D model in the Charente channel area. The model has been considerably improved compared to earlier versions. By gaining realism, it has thus been able to answer the questions posed by our work. Nevertheless, the very fact of using it has revealed improvements that could be made, which will be essential, if we want to use it for other types of molecules, and over a wider area, such as the Pertuis coastal waters. The hydrodynamic part of the model must be improved by including the inputs from the Seudre and the Gironde, which could have a major influence on the salinity and water quality in the Marennes-Oléron bay. Similarly, the effect of the tides must be simulated since only a single amplitude is currently taken into account, whereas in certain cases differences are observed according to the tidal cycle. The relatively shifting bathymetry of the intertidal zone can also be a significant error factor. It is therefore essential to improve each of these points in order to obtain a reliable tool that gives a faithful representation of the advection and dispersion phenomena that take place in the bay. Starting from this, together with the ecotoxicological results and data concerning the contaminants brought down from the watershed, the model could be used as an efficient risk assessment tool relating to the contaminants in the waters of the Marennes-Oléron bay.

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