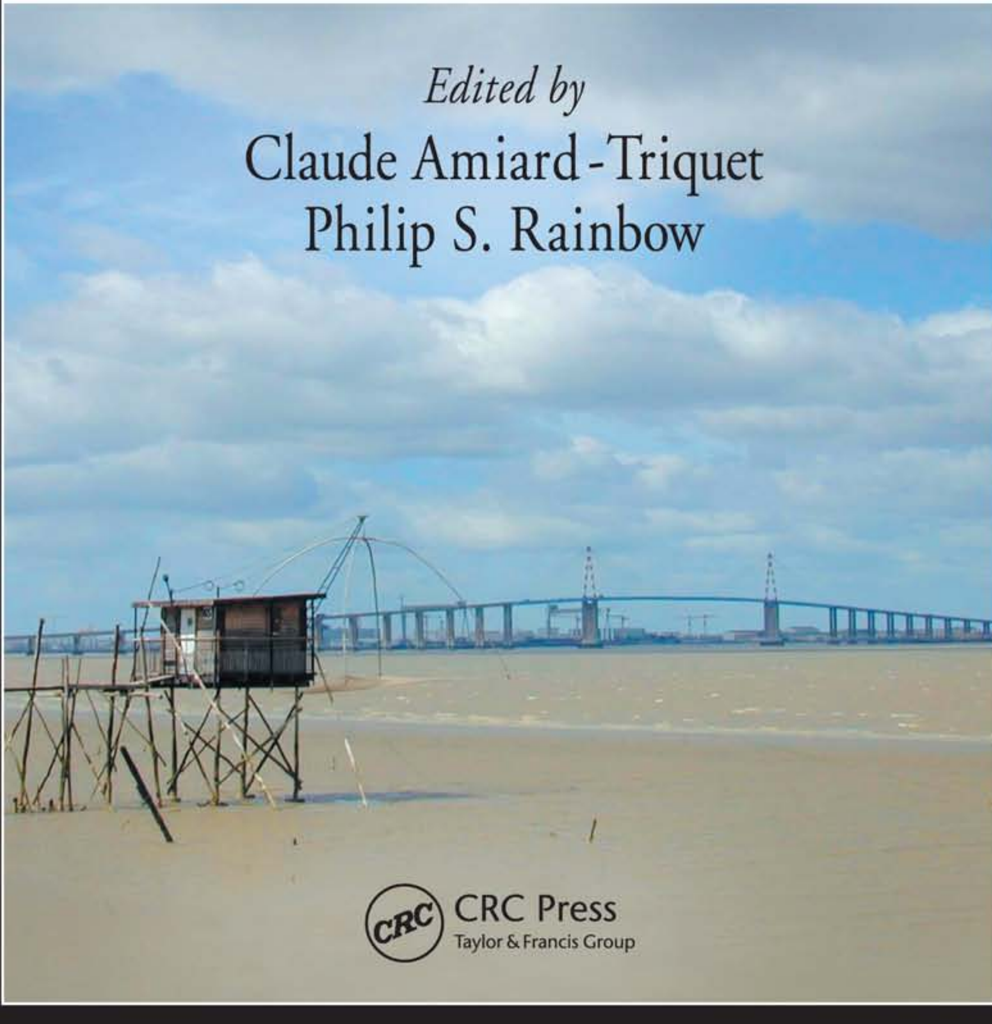
Environmental Assessment of Estuarine Ecosystems

A Case Study

Edited by

Claude Amiard-Triquet

Philip S. Rainbow



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Environmental Assessment of Estuarine Ecosystems

A Case Study

Environmental and Ecological Risk Assessment

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Preface

Estuaries are areas of high productivity, crucial in the life histories of many fish, invertebrates, and birds, for example, and the sustainability of estuarine biodiversity is vital to the ecological and economic health of coastal regions. On the other hand, estuarine ecosystems are exposed to toxic anthropogenic effluents transported by rivers from remote and nearby conurbations and industrial and agricultural concerns. It is important, therefore, to have techniques that enable society to assess the degrees of exposure of estuaries to anthropogenic toxic contamination and the significance of this exposure to the ecology of the biota living there, especially the effects on biota of commercial significance. This book describes a comparative multidisciplinary ecotoxicological study of two contrasting estuaries in France, using the results of this study to make generalisations on how different techniques might be used and interpreted in future studies assessing the ecotoxicological status of vital coastal ecosystems.

Multidisciplinary research has been carried out for years on the environmental status of the Seine estuary, France, which is one of the most important and most polluted estuaries in Northwest Europe. The comparatively clean Authie estuary nearby is not impacted by any significant human activity and can be considered a suitable reference site. Many of the contaminants accessible to chemical analysis to date have been determined in water, sediments, and biota at different levels of the food chain. The use of biochemical and physiological biomarkers, testifying to the local exposure of biota to toxins and their ecotoxicological effects, has been tested in species representative of the water column (e.g., the planktonic copepod *Eurytemora affinis*) and the sediment (the burrowing polychaete worm *Nereis diversicolor*). Further effects of contamination have been examined in different constituents of the biota: the abundance of cadmium and mercury-resistant bacteria in mudflats of the Seine; the community structures and photosynthetic capacities of microphytobenthos diatom communities; the abundance, diversity, and genus assemblage structures of foraminiferans and nematodes; and the physiological status and reproduction of copepods, worms, and estuarine fish.

Chemical stress is probably not the only reason for the observed changes, at least directly. In the Seine, land reclamation and harbour extension leading to the reductions of the surface areas of mudflats in the northern part of the estuary along with chemical stress may indeed have exerted negative effects on food availability for invertebrates and fish, impacting energy metabolism and inducing cascading effects on reproduction, populations, and communities of biota.

From a reverse view, the influence of biota on the fate of contaminants has also been investigated, for example, metals and their interactions with the sulfur cycle. The molecular quantification of the dsrAB gene that codes for an enzyme responsible for the production of hydrogen sulfide has been used to determine the degree of local microbial production of sulfides. Biogeochemical transformations in the upper layers of sediments have also been examined, taking into account both inorganic forms of sulfur such as sulfides and sulfates and fatty acids used as qualitative markers of microbial activity. Modelling has shown the influence of hydrodynamism on the profiles of dissolved compounds (oxygen, sulfates, sulfides) and of biological processes in the sediments, assessing the apparently less significant effects of bioturbation due to worm burrowing in a high energy estuary such as the Seine.

The main benefits of this study for coastal zone management and society include (i) the development of analytical tools for the determination of bioavailable forms of metals in interstitial waters; (ii) the validation of biochemical and physiological biomarkers in representative estuarine species; and (iii) recommendations for a comprehensive methodology to assess the health status of estuarine ecosystems. The outcome represents important new developments, particularly related to the application of the European Water Framework Directive. This work has been funded by the European Community's INTERREG, the French Ministry of Environment, and local partners, as well as by research institutions (CNRS, IFREMER, the Center for Estuarine and Marine Ecology of The Netherlands, The Natural History Museum of London, and several universities). This combination of funding sources underlines the double relevance of this book to both academic researchers and applied end users. It is our hope that this book will also serve as an important source of concrete examples for use in environmental science courses.

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1 Introduction

Claude Amiard-Triquet and Jean-Claude Dauvin

CONTENTS

1.1 ESTUARIES: CONFLICT OF BIOLOGICAL WEALTH AND ANTHROPOGENIC PRESSURE

Historically, estuaries have been areas of settlement for many human populations, resulting in a number of negative effects on the natural environment. For example, land reclamation, harbour extension, and dredging lead to decreased areas of wetlands that are very important for the protection of water quality as well as their floristic and faunistic interest. Water quality in estuaries and particularly in urbanized regions is decreasing as a consequence of anthropogenic activities, namely inputs of chemicals associated with industrial and domestic activities and pesticides and fertilizers originating from agriculture. In addition to such local contamination, estuarine ecosystems are exposed to toxic anthropogenic effluents transported by rivers constituting the whole river basin. Concomitantly, river transport is responsible for influxes of nutrients that underlie the biological wealth of estuarine areas, ensuring their role as nurseries for many commercial species. River transport of nutrients is also responsible for the high productivity of nearby coastal areas, allowing the establishment of mariculture enterprises. However the concomitant influx of nutrients and contaminants is a source of concern related to the growth and reproduction of cultivated species and represents a health risk related to the quality of seafood products. Thus estuaries are crucial in the life histories of many invertebrates and vertebrates and the sustainability of estuarine biodiversity is vital to the ecological and economic health of coastal regions.

Environmental monitoring of coastal and estuarine areas is based mainly on the measurement of chemicals that are perceived to be relatively easy to analyse (trace metals, DDT and its metabolites, γHCH, αHCH, some congeners of PCBs, and individual PAHs). These data may be useful in predicting potential biological effects, but only if contaminant levels are related to responses in biological systems. Threshold effect levels such as PNECs (predicted no-effect concentrations) may be derived from toxicological data, but a major limiting factor is that toxicological parameters are practically always determined for individual substances, without regard to potential interactions of different chemicals and classes of chemicals in the environment. In the cases of estuaries containing complex mixtures including many compounds (persistent organic pollutants) that are not yet accessible to analysis or are extremely expensive to analyse, we must develop strategies that allow us to assess whether ecosystems are under stress (Allan et al. 2006). On the other hand, ecological quality status may be determined using different biotic indices that have been recently reviewed (Dauvin et al. 2007) with a view to their use under the European Water Framework Directive (Water Framework Directive 2000).

Nevertheless, comprehensive methodologies have been proposed to determine pollution-induced degradations. The sediment quality triad approach has been proposed to assess the effects of chemical mixtures found in natural sediments (Chapman 1990). The triad includes chemistry to measure contamination, bioassays to measure toxicity, and *in situ* biological assessment to measure effects such as changes in benthic communities. A particular effort has been devoted to determining the ecotoxicities of sediments because, in aquatic environments, sediments are the main reservoirs for most organic and inorganic chemicals entering water bodies. This is also the reason this book treats sediments as key components for assessing interactions of chemicals and biota in estuarine ecosystems (Amiard-Triquet et al. 2007).

Not only do chemical analyses not provide access to all the toxic molecules of interest, but physico-chemical environmental conditions interfere with xenobiotics, modifying their chemical characteristics and thus their bioavailability. Bioassays have been widely used in recent decades, but their value in risk assessment is still a matter of concern because it is extremely complicated to extrapolate the biological responses of small numbers of standard species observed under simplified experimental conditions to many other species submitted to innumerable interactions in the field. Chapman (2002) proposed the inclusion of more “eco” in ecotoxicology and recommended a number of criteria to reach this aim including (1) the choice of the test species, ideally dominant or keystone species from the area being assessed as identified by community-based studies, for testing in laboratory or field; and (2) the selection of endpoints that are ecologically and toxicologically relevant. Few toxicological data have been obtained from estuarine species. Most bioassays were carried out with freshwater species, and some with marine species (EC 2003).

1.2 CHEMICAL CONTAMINATION AND BIOAVAILABILITY OF CONTAMINANTS

The chemical contamination of a given environment may theoretically be determined by measuring concentrations of molecules of interest in water, sediments, and organisms (Chapter 3). In the case of water samples, because of very low concentrations, extreme precautions are necessary to avoid secondary contamination and the time scales of change may be as short as diurnal. On the other hand, sediments, as the main reservoirs for many contaminants, exhibit high concentrations, are easily analysed, and represent records of past contamination. However, if surface sediments are collected, they respond to changes on time scales dictated by deposition (Chapter 2) and bioturbation rates (Chapter 15) (O'Connor et al. 1994). The use of organisms for monitoring chemical contamination is a worldwide and well established practice. In the water column, the species of interest are mainly filter-feeding bivalves among which mussels have given their name to Mussel Watch programmes (NAS 1980) that have been developed successfully in many countries (Beliaeff et al. 1998). However, the need to use biomonitors more representative of sedimentary compartments has been recognized (Bryan and Langston 1992; Diez et al. 2000; Poirier et al. 2006). Compared to water samples, the concentrations of contaminants in biomonitors are high enough to facilitate quantification. Compared to sediments, they can also play the role of integrative recorders and also reveal directly which fractions of environmental contaminants are readily available for bioaccumulation and subsequent effects.

Bioavailability is defined as the fraction of a chemical present in the environment that is available for accumulation in organisms. The environment includes water, sediments, suspended matter, and food. The questions of metal speciation and bioavailability in aquatic systems were reviewed in Tessier and Turner (1995). The distribution of metal species in different phases (sediment in suspension or deposited, interstitial water and water column), their transport, accumulation, and fate are governed by different physico-chemical and microbiological processes mainly related to carbon and sulfur cycles. Recent improvements of analytical tools (DET/DGT) now allow direct access to metal speciation, even in areas with very low levels of contamination (Chapter 5). Because sensitive analytical methods for organic contaminants were developed later, the state of their development is more restricted. Many hydrophobic organic xenobiotics (pesticides, PAHs, PCBs, etc.) have great propensities for binding to organic materials (humic acids, natural DOM) which modifies their bioavailability in water columns (see review by Haitzer et al. 1998). Bioavailability may be determined through three complementary approaches:

1. Chemical assessment of the distribution of the contaminant in different environmental compartments from which its fate would be forecast (see, for instance, Ng et al. 2005)
2. Measurements of bioaccumulated contaminants in biota exposed in the field (Chapter 3) or in the laboratory that reflect the bioavailable concentrations in the environment (a procedure that forms the bases of biomonitoring programmes such as Mussel Watch)
3. Measurements of biological responses (biochemical, physiological; see below) associated with accumulated doses in biota exposed to contaminants in the laboratory or in the field (Chapter 4)

When biological approaches are chosen, it is necessary to take into account the adaptive strategies of organisms (Chapter 7) that metabolize and/or eliminate different organic xenobiotics (Chapter 3) at different rates or store high concentrations of metals in detoxified forms (Chapter 4).

1.3 BIOACCUMULATION AND EFFECTS OF CONTAMINANTS AT DIFFERENT LEVELS OF BIOLOGICAL ORGANISATION

In addition to being affected by the physico-chemical characteristics of contaminants and their associated bioavailability, bioaccumulation depends upon a number of natural factors such as size, age, sexual maturity, and season. The influences of these factors have given rise to a number of studies based on their importance in the design of biomonitoring programmes and interpretation of biomonitoring data (NAS 1980). It is also well established that different species accumulate different contaminants to different degrees, and again the analytical techniques available to determine metals allowed earlier development of metal ecophysiology and ecotoxicology assays compared to assays for organic chemicals.

Briefly, living organisms are able to cope with the presence of metals by controlling metal uptake, increasing metal excretion, and/or detoxifying internalized metals (Mason and Jenkins 1995). Depending on the metal handling strategy, global concentrations in tissues may vary considerably, with lower concentrations generally observed in vertebrates compared to invertebrates. However, even in limited taxonomic groups (bivalves studied by Berthet et al. 1992; crustaceans studied by Rainbow 1998), strong interspecific differences have been shown. Adaptive strategies were reinforced in a number of species chronically exposed in their environment that become tolerant (Chapter 7) through physiological acclimation or genetic adaptation (Marchand et al. 2004; Xie and Klerks 2004). In vertebrates, tolerance to metals mainly results from metal binding to a detoxificatory protein such as metallothionein (MT). In invertebrates, biomineralization into insoluble form often co-exists with MT induction (see reviews by Marigomez et al. 2002; Amiard et al. 2006). It seems obvious that organisms have developed handling strategies for metals that are normally present at low doses in natural environments (several such metals are essential). However, many reports also exist of acquired tolerance in microalgae, crustaceans, and fish exposed to herbicides, organophosphorus insecticides, PCBs, PAHs, and other compounds (Amiard-Triquet et al. 2008). Numerous processes described may explain this tolerance, e.g., multi-xenobiotic resistance (Bard 2000) and induction of biotransformation enzymes (Newman and Unger 2003b). Because they are involved in increased elimination, these latter govern at least partly the concentrations of xenobiotics in biota. Both phylogeny and the chemical characteristics of contaminants influence accumulated chemical concentrations in organisms. It is generally accepted that vertebrates are more efficient than invertebrates in the biotransformation of organic xenobiotics. On the other hand, even in invertebrates, PAHs are relatively degradable, whereas the stability of PCBs and brominated flame retardants and their lipophilic characters are responsible for their bioaccumulation (Chapter 3), particularly in fatty tissues (Bernes 1998; Burreau et al. 1999; De Boer et al. 2000).

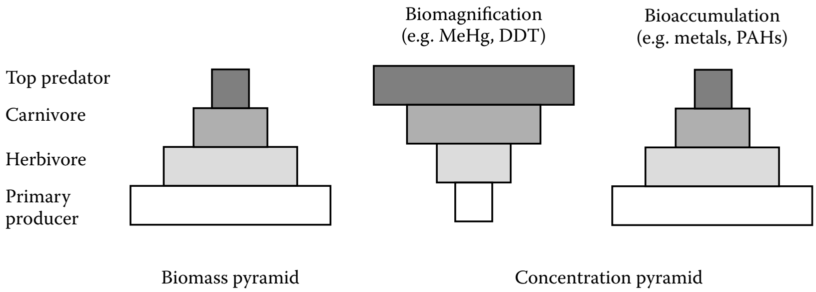


FIGURE 1.1 Biomagnification versus bioaccumulation in aquatic food chains.

One peculiar aspect of bioaccumulation is biomagnification in the food web. This has been a matter of concern since the demonstration in the 1960s that organochlorine insecticides and mercury concentrations were greatly enhanced in consumers belonging to higher trophic levels, including humans in the case of mercury (Newman and Unger 2003a; Drasch et al. 2004). In fact, the situation is variable and depends on the classes of contaminants considered (Figure 1.1). In most cases, the concentration pyramid is orientated like the biomass pyramid. This is the case for most metals along most aquatic food chains, except for elements like mercury that are, at least partly, in organometallic form in the environment and in the prey organisms. Metals in the diet contribute significantly to metal uptake in aquatic organisms (Wang 2002), but metals that are detoxified in insoluble granules are often released undigested in the faeces of predators, thus limiting transfer along food chains (Nott and Nicolaidou 1990).

Biomagnification is a situation in which the orientations of biomass and concentration pyramids are completely opposite. Due to their lipophilic characters, organic contaminants have high potentials for biomagnification but, the pattern is highly contrasted between those that are easily biodegraded (such as PAHs) and those which are very stable (such as PCBs) (Chapter 6). Among emerging contaminants, PBDEs share a number of chemical features characteristic of PCBs, and field studies have shown a clear tendency for PBDE biomagnification in food chains when the top predators are marine mammals or raptors. The pattern is not so clear when top predators are flatfish (Voorspoels et al. 2003), so it is important to increase our knowledge of the behaviour of these types of chemicals (Chapter 6).

Once incorporated into biota, chemicals can exert many different lethal or sublethal, acute or chronic responses, at different levels of biological organisation, from macromolecules to populations or communities. Recently, such a comprehensive approach has been applied to the assessment of the relative toxicity of estuarine sediments (Caeiro et al. 2005; Cunha et al. 2007). A battery of biomarkers (activities of liver ethoxyresorufin-O-deethylase, liver and gill glutathione S-transferases, muscle lactate dehydrogenase, and brain acetylcholinesterase) was examined in the fish *Sparus aurata* exposed for 10 days to sediments collected from different sites in the Sado estuary (Portugal). For all the enzymes assayed, significant differences were found among sites, allowing discrimination of different types or levels of contamination or both. The sediment ranking based upon these biomarkers agreed well with the ranking from a parallel study including chemical analysis of sediments, macrobenthic community analysis, amphipod mortality toxicity tests, and sea urchin abnormality embryo assays.

Similarly, the assessment of the chronic toxicity of estuarine sediments at different levels of biological organisation in the amphipod *Gammarus locusta* revealed a high consistency among chemical (bioaccumulation) and biochemical (metallothionein induction, DNA strand breakage, and lipid peroxidation) responses and effects on survival, growth, and reproduction (Costa et al. 2005; Neuparth et al. 2005). A similar design was used in a freshwater system to investigate effluent impacts using standard (*Daphnia magna*) and indigenous (*Gammarus pulex*) test species (Maltby et al. 2000). *In situ* bioassays carried out downstream of the discharge showed a reduction in *D. magna* survival, in *G. pulex* survival and feeding rate, and in detritus processing, consistent with biotic indices based upon macroinvertebrate community structure.

The present work involves a triad approach (Figure 1.2) based on several species: the copepod *Eurytemora affinis*, Chapter 10; the endobenthic worm *Nereis diversicolor*, Chapter 8; the European flounder *Platichthys flesus*, Chapter 11, along with higher taxa or functional groups (bacteria, Chapter 7; microphytobenthos, Chapter 7, Chapter 12; foraminiferans, Chapter 13; meiofauna, Chapter 14; macrofauna, Chapter 9) representative of the water column or the sedimentary compartment. In comparing multi-polluted and reference estuaries (see below), the objectives were (1) to establish causal relationships between bioaccumulated fractions of environmental pollutants; (2) to link biological effects at sub- and supra-individual levels; and (3) to provide tools to evaluate the health status of species important for the structure and functioning of the estuarine ecosystem.

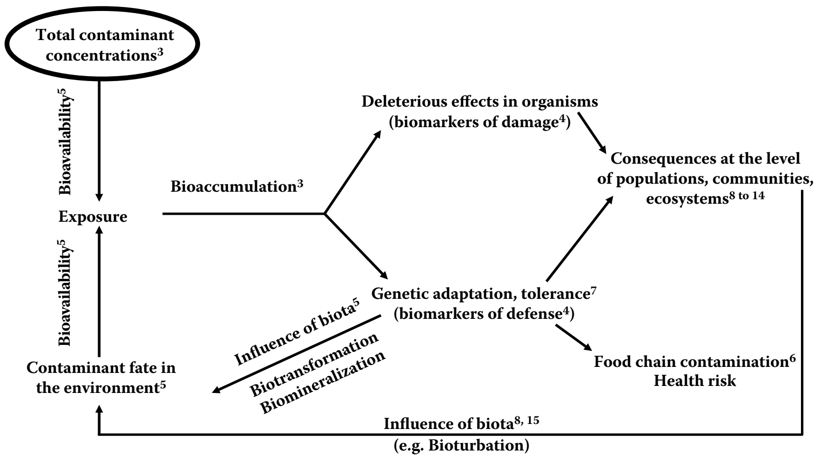


FIGURE 1.2 Links between exposure of marine organisms to contaminants, bioaccumulation, and subsequent effects at different levels of biological organization. Numbers in superscript refer to chapters.

1.4 PUTTING MORE "BIO" IN BIOGEOCHEMICAL CYCLES

The concept of the biogeochemical cycle recognizes the dynamism of multiple, complex processes that move, transform, and store chemicals in the geosphere, atmosphere, hydrosphere, and biosphere. This concept usually conjures up images of carbon, nitrogen, and phosphorus but it can be expanded to include most elements in the periodic table and even organic xenobiotics. Separate biochemical cycles can be identified for each chemical element but elements combine through chemical transformations to form compounds. Thus the biogeochemical cycle of each element or compound must also be considered in relation to the biogeochemical cycles of other elements or compounds. The biotic community may serve as an exchange pool (although it may seem more like a reservoir for some chemicals like calcium, bound in invertebrate shells over geological time scales) and serve to move chemicals from one stage of the cycle to another.

The role of bacteria in the major biogeochemical cycles was established many years ago (SCOPE 1983). The distribution of trace metal species in different phases, their transport, accumulation, and fate are controlled by different physico-chemical and microbiological processes that are mainly linked to carbon and sulfur cycles. While the importance of the carbon cycle is clearly recognized, the role of sulfur needs to be developed further. Sulfides likely play a crucial role in governing the bioavailability and toxicity of trace metals in sediments (Ankley et al. 1996; Lee et al. 2000). Sulfides, produced by the reduction of sulfates after oxidation of organic matter incorporated into sediments, react with many divalent transition metals to form insoluble precipitates (Allen et al. 1993). However, the acid-volatile sulfide (AVS) fraction may be rapidly released following changes in oxido-reduction conditions—such as oxidation due to microbial activity—that induce increased solubility and dissolved bioavailability of metals previously bound as insoluble sulfides (Svenson et al. 1998). Therefore, a multidisciplinary study was carried out to associate geochemical and microbiological expertise along with the use of fatty acids as markers of bacterial activities and of different sources of organic matter (Chapter 5).

In intertidal zones, microphytobenthos represent the major sources of primary production because turbidity restricts the development of phytoplankton in the water column. Microalgae are metal bioaccumulators and thus play a significant role in the biochemical cycle of microphytobenthos. In benthic communities of the coastal ecosystem of the Bay of Biscay, France, microphytobenthos was shown to be the main store for lead (75%) and significant for cadmium (30%) and copper (11%) (Pigeot 2001). Due to the fast succession of generations, microphytobenthos was much more important related to metal fluxes, representing 99% for lead, 98% for cadmium, 95% for copper, and 81% for zinc. Thus it was particularly important to investigate the responses of microphytobenthos to anthropogenic impacts in the Seine estuary and compare the impacts to the Authie reference site in terms of tolerance (Chapter 7) or in terms of community changes of a major microphytobenthic taxon, the diatoms (Chapter 12).

It is now accepted that bioturbation plays an important role in exchanges at the water–sediment interface. The presence of biogenic structures and the activities of endobenthic species deeply affect physical and geochemical properties of the substratum, thus influencing microbial communities and biogeochemical processes (Mermillod-Blondin et al. 2004). The impacts of benthic macrofauna on sediment mineralization rates and nutrient regeneration have served as foci of many studies (Heilskov and Holmer 2003). Numerous works have demonstrated the influence of bioturbation on denitrification through enhanced NO_3^- and O_2 supplies and coupled nitrification–denitrification (Gilbert et al. 1997, and references cited therein).

Bioturbation by infauna also affects different classes of pollutants (Ciarelli et al. 2000; Bradshaw et al. 2006; Ciutat et al. 2007). Among endobenthic species whose bioturbation activities influence the fates of contaminants, the common ragworm *Nereis diversicolor* plays an important role (Gilbert et al. 1996; Gunnarsson et al. 1999; Banta and Andersen 2003; Cuny et al. 2007; Granberg and Selck 2007). Particle mixing and burrow irrigation contribute to the transport and redistribution of pollutants. Enhancing the availability of molecular O_2 in bioturbated sediments stimulates microbial degradation of organic contaminants and, as mentioned above, through changes in oxido-reduction conditions, can influence metal speciation in relation to the sulfur cycle. Small species would have little impact on bioturbation and could not offset functions performed by larger species (Solan et al. 2004; Gilbert et al. 2007). However, meiofaunal bioturbation can affect cadmium partitioning in muddy sediments (Green and Chandler 1994).

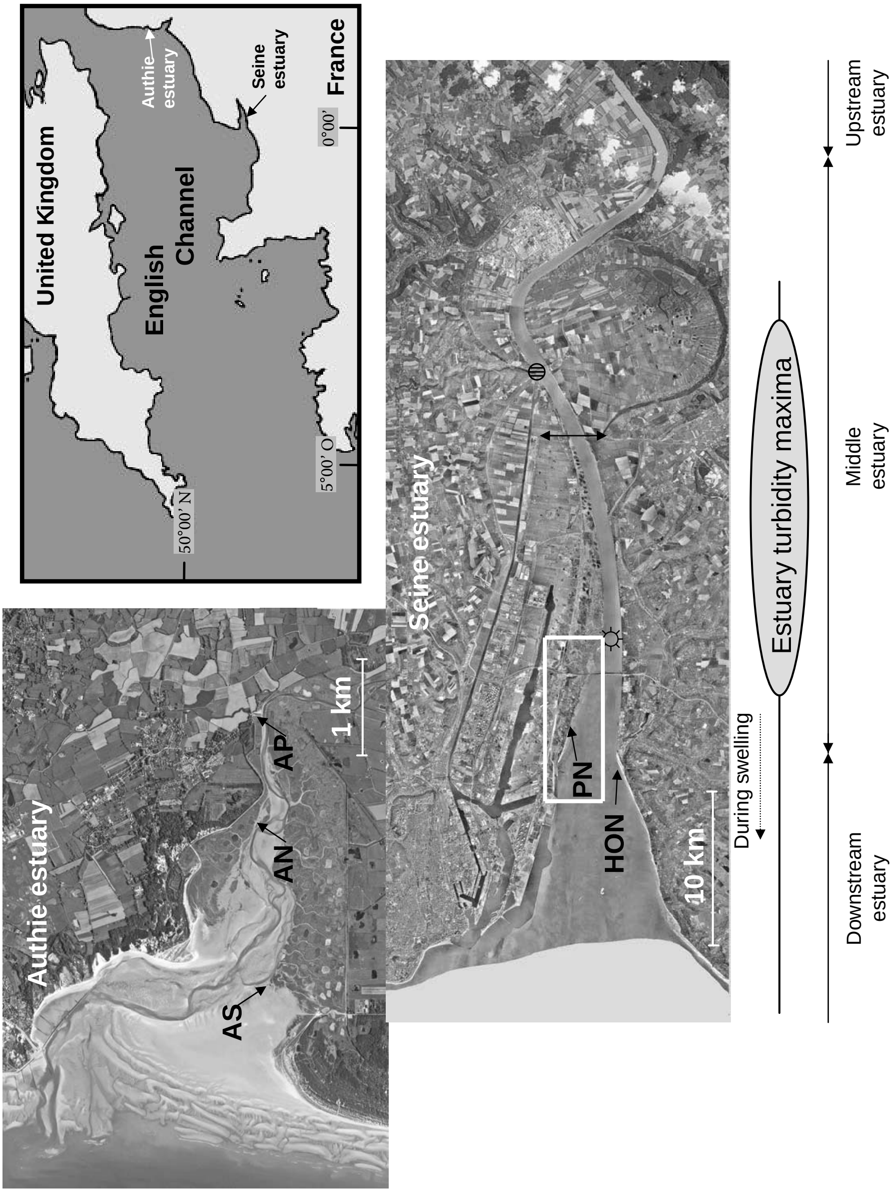
1.5 SITES OF INTEREST

A comprehensive method for assessing the health status of estuarine ecosystems was developed on the basis of a case study carried out in the multi-polluted Seine estuary and the comparatively clean Authie estuary, both situated on the French coast of the English Channel.

1.5.1 Main Characteristics of the Seine Estuary

The Seine estuary, situated on the English Channel, is one of the most important estuaries along the French Atlantic coast, along with the Loire and Gironde estuaries in the Bay of Biscay. The geographical zone of influence of the Seine estuary runs from just upstream of the Poses dam—some 160 km upstream of Le Havre, at the limit of the tidal penetration into the estuary—to the eastern part of the Bay of Seine. This zone can be divided into three sections (Figure 1.3): the fluvial, or upstream, estuary; the middle estuary; and the marine, or downstream, estuary. The first is a freshwater zone, extending from the Poses dam to Vieux Port; the second, situated between the fluvial and marine estuaries, is a mixing zone characterized by varying

FIGURE 1.3 (*see facing page*) Sites selected for studying interactions of sediment-bound contaminants and biota. AS = Authie South. AN = Authie North. AP = Authie port, Authie estuary. HON = Honfleur. PN = Pont de Normandie, Seine estuary. Sampling sites for studies in water column (Chapter 10): ☼ Pont de Normandie; ◍ Pont de Tancarville. White rectangle = *Nereis diversicolor* populations, 1987–2006 (Chapter 9). Position of salinity front ↕ and estuary turbidity maximum after Dauvin (2002).


United Kingdom
English Channel
Authie estuary
Seine estuary
France
50°00' N
5°00' O
0°00'
Authie estuary
AS
AN
AP
1 km
Seine estuary
PN
HON
10 km
During swelling
Estuary turbidity maxima
Downstream estuary
Middle estuary
Upstream estuary

salinity levels; the third is saltwater and runs from Honfleur to the eastern part of the Bay of Seine.

The freshwater flow of the river Seine at Poses is relatively small (480 $m^3.s^{-1}$ on average over the past 30 years), with high water volumes over 2220 $m^3.s^{-1}$ (autumn/winter) and low water flow under 100 $m^3.s^{-1}$ (at the end of the summer in September). The Seine estuary and its hydrodynamics are heavily influenced by tides that can reach nearly 8 m in magnitude downstream of Honfleur during the spring tides (Chapter 2). This megatidal regime causes a zone of maximum turbidity in the mixing zone (middle estuary) between the marine and fluvial sections of the estuary. This maximum turbidity zone traps suspended matter and, through the phenomena of desorption–adsorption, acts as a physico-chemical regulator for a number of elements and/or pollutants, particularly metals. It also leads to a decrease in the amount of oxygen entering the system from the oxidizing of organic matter trapped in the zone. Still, because the estuary waters are renewed by the tide, there is no anoxic zone in the downstream estuary.

The volume of seawater oscillating in this downstream section is always higher than the volume of freshwater, even during extreme floods. During the first extreme flood in autumn, most of the fine sediment and the associated contaminants that accumulate while the water flows are low are expelled into the Bay of Seine; these non-periodic paroxysmal events are, in fact, essential to the natural functioning of the estuary. Moreover, in addition to sediment arriving from upstream, sediment—mainly sand—may also be transported into the estuary from the Bay of Seine, resulting in a natural build-up of sediment in the estuary.

The estuary marks the administrative boundary between two regions (Haute-Normandie and Basse-Normandie) and three departments (Eure, Seine-Maritime, and Calvados). The Seine valley and its estuary are of major economic importance for France, notably because of the presence of two maritime ports. The Seine estuary lies at the discharge point of a watershed area covering 79,000 km^2. This area is home to 16 million people, and accounts for 50% of the river traffic in France, 40% of the country's economic activity, and 30% of its agricultural activities. In addition to the more than 10 million inhabitants of the Greater Paris area who contribute heavily to the Seine estuary's upstream inputs (mainly contaminants and purified waters), the area is also home to two other major river settlements—Rouen with 400,000 inhabitants and Le Havre with 200,000 inhabitants—and two maritime ports of international importance—Port Autonome de Rouen (PAR) and Port Autonome du Havre (PAH).

Despite the major national importance of the estuary and its highly degraded condition, it was not until the 1990s and the creation of the Seine-Aval (SA) multidisciplinary scientific programme that the knowledge base related to the Seine estuary began to grow significantly. The SA programme was designed to accomplish two important objectives: (1) to provide the knowledge needed to reveal how the estuarine ecosystem functions and (2) to develop the tools that local stakeholders require to make decisions about restoring the water quality in the Seine and preserving the natural habitats of the Seine valley. The programme was organised in three phases: SA 1 (1995–1999), SA 2 (2000–2003), and SA 3 (2004–2006) (Dauvin, 2006a and b).

Anthropogenic influences in the Seine estuary began in the mid-19th century and continue to this day. The estuary's ecosystems have become more fragile as a result of human activities and this led to the extreme compartmentalization of the biological units and a drastic reduction of the intertidal zones downstream (a loss of more than 100 km^2 between 1850 and the present). At the same time, the physico-chemical conditions of the estuarine milieu have inexorably declined for more than a century. By the 1980s, the estuary was highly contaminated; levels of metal contamination (e.g., Cd, Hg), hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs) were among the highest in the world and inadequate water treatment facilities created oxygen deficits downstream of Paris and Rouen.

In the marine estuary, abnormal biological functioning led to the collapse of the fisheries sector, particularly brown shrimp (*Crangon crangon*) fisheries, while in the fluvial estuary, professional fishing stopped entirely in the 1970s due to the near-total disappearance of migratory fish species. Today, the most significant danger to the long-term functioning of the estuary comes from chemical and microbiological sources such as endocrine-disrupting chemicals (EDCs), pharmaceutical products, and antibiotic-resistant bacteria in the water.

The recent Port 2000 extension in Le Havre (2000–2005) also seriously affected the morphological and sedimentary evolution of the downstream section of the estuary. The construction project and its compensatory actions contributed to both morpho-sedimentary changes and changes in habitats and biota. It will be several years before the estuarine system establishes some kind of equilibrium in its new dimensions. The geomorphological evolution of the downstream section of the estuary, including the silting of the waterways and the advance of the banks toward the Bay, remains one of the major preoccupations for the future. However, since the Port 2000 project ended, new estuary development projects intended to enhance the economic development of this highly prized zone have begun to emerge.

Nonetheless, despite the diverse environmental assaults, the Seine estuary is still a highly favourable milieu for juveniles of commercial fish species such as sole and European sea bass, and its ornithological richness is one of the major positive aspects of its natural heritage. The richness of this natural heritage can be judged by the overabundance of regulatory measures and inventories that have sprouted over the years. The resulting growth needs to be pruned and coordinated and the "over-protection" is more apparent than real. In fact, with the exceptions of the natural reserves and the *Boucles de la Seine Normande* regional nature park, only a very small number of zones, limited in area and totally separate from one another, are adequately protected. These include the territorial acquisitions of the Coastline and Lakeshore Conservancy (Conservatoire des Espaces Littoraux et des Rivages Lacustres or CELRL), the regional nature reserves, and a few prefecture-designated biotopes. Because this fragmentation of zones rich in natural heritage is incompatible with a concept of integrated management, finding a way to restore the estuary in its totality has become an urgent matter. It is a challenge for the future that SA hopes will be accomplished by 2025, give or take a couple of years. Nowadays, one of the objectives of the Groupement d'Intérêt Public Seine-Aval project is to participate in the Global Management Plan for the period 2007–2016, focusing on estuarine habitat restoration, and tackling the perceptions of the populations involved with regard to the health of the estuary.

1.5.2 Authie Estuary

The Authie estuary is located in the eastern part of the English Channel. The length of the River Authie is 103 km; its watershed covers 1305 km² and consists mainly of agricultural fields for breeding cattle; the area houses few industries apart from dairy operations and tourism. Agriculture began here in the 13th century, and plays an important role in the drying of the wetlands; a very dense network of small channels covers all parts of the river. About 75,200 inhabitants live in this territory, mainly in three towns including Berck sur Mer at the mouth of the estuary.

The Authie estuary covers an area of about 3000 ha, namely Authie Bay; it is a very small interface area characterized by a low freshwater input (annual mean at the mouth of estuary = 10.3 $m^3.s^{-1}$) and freshwater volume in comparison with the volume of seawater at each spring tide. The freshwater input varies weekly through the year from a minimum of 6 $m^3.s^{-1}$ at the end of the summer in September–October, to >30 $m^3.s^{-1}$ in the winter. The tide runs for a length of 14 km, and the tidal range is about 9 m at the mouth of the estuary on a spring tide.

Nevertheless, the freshwater input of the Authie contributes to the formation of a low salinity zone located along the French coast (about 3 nautical miles wide) from the Bay of Seine to the Belgium coast under the influence of freshwater input from the Scheldt. This low salinity water mass body called the Fleuve Côtier is more or less distinct, depending of the quantity of freshwater input of the two main rivers, the Seine and the Scheldt, but also of a lot of smaller rivers including the Authie.

The Authie is affected by only very weak anthropogenic activity and can be considered an estuarine reference zone of near-pristine state with very low contamination. The sediments are not polluted and are nontoxic, especially by metal contaminants (Billon, 2001). Some herbicide and pesticide sources have been identified (Billon, 2001), but they are in very low concentrations. The main source of pollution is the diffuse input of nitrates coming from agriculture practices and on some occasions high levels of suspended organic matter (SOM) are present. The total input of SOM is about 12,000 $t.y^{-1}$. Salmon and sea trout are common in the Authie, but dams in the upper part of the river stop their upward migration.

Two main characteristics illustrate the functioning of the Authie estuary: silting and high hydrodynamism (Chapter 2). As with other bays and estuaries along the French side of the Channel, the Authie estuary is affected by strong silting up resulting from transport of sediment of marine origin, mainly sand (dominating the flood tide) that accumulates in zones with low hydrodynamics (tide and swell protection due to a south–north natural dune and erosion in the north of the estuary mouth). The important polderisation of the estuary accelerated the process of silting associated with the progression of salt marshes during the 18th and 19th centuries. The hydrodynamism arising from the megatidal regime is reinforced by swells and winds.

The natural heritage has been mainly preserved by purchases by CELRL, which holds a total of 685 ha in five sites in the north and the south of Authie Bay. Natural habitats of Annexe II of the European Habitats Directive concern a large zone from the Somme to the Authie estuaries which is included in the same Natura 2000 area.

1.5.3 Comparison of the Seine and Authie Estuaries

Both sites are participants in the French Mussel Watch Programme (RNO 2006), and their levels of chemical contamination have been well documented for more than 30 years based on analyses of quarterly samples. Results of chemical analyses of mussels including metals (Cd, Cu, Hg, Pb, Zn, and more recently Ag, Cr, Ni, and V), ΣDDT (DDT + DDD + DDE), γHCH, αHCH, PCBs, and PAHs clearly contrast the pollution states of the two estuaries of interest. Contamination monitoring based on metal analysis in sediments revealed an important contribution of inputs from the Seine river into the coastal area (RNO 1995). Endocrine disruption based on the quantification of imposex in gastropod *Nucella lapillus* (Gibbs et al. 1987) has also been shown along the whole coastal area influenced by the Fleuve Côtier (see Section 1.5.2) and originating from the Seine (Huet in RNO 2004).

In the framework of the National Program of Ecotoxicology (PNETOX) under the jurisdiction of the French Ministry of Ecology and Sustainable Development, sediments as key compartments for the assessment of interactions of chemicals and biota in estuaries were studied comparatively in the multipolluted Seine estuary and the relatively clean Authie estuary (Amiard-Triquet et al. 2007).

In developed countries, pristine sites no longer exist and relatively clean sites are scarce—generally restricted to small estuaries and more likely to be spared from urbanization and industrialization. As a consequence, sites that are potentially available for use as controls have a number of natural characteristics that may differ from

TABLE 1.1
Characterization of Superficial Sediment (<1 cm deep) at Sampling Stations in the Seine and Authie Estuaries

	Parameter			
Station	**AN**	**AP**	**PN**	**HON**
Salinity:				
Mean (SD)	27 (2)	16 (5)	19 (4)	24 (3)
Fraction >250 µm				
Mean (SD)	0.9 (0.9)	0.6 (0.5)	0.3 (0.2)	1.5 (1.2)
Fraction <63 µm				
Mean (SD)	71 (14)	81 (4)	76 (13)	63 (17)
Organic matter (450°C):				
Mean (SD)	9 (2)	9 (2)	8 (4)	8 (6)

Notes: Quarterly samplings, 2002–2004. Means expressed as psu (salinity) or percentages (grain size and organic matter). SD = standard deviation. Acronyms of stations as in Figure 1.3.

those of bigger estuaries. Thus for the studies of interactions of sediment-bound chemicals and biota, particular attention has been paid to the selection of collection sites (Figure 1.3) as similar as possible in terms of sediment characteristics. Regarding superficial sediments (<1 cm deep), the relative importance of fine (<63 μm) and coarse (>250 μm) particles did not differ significantly nor did organic matter content (Table 1.1). In sediment cores collected from both sites, grain size was also very similar; silty particles were predominant (18 to 98 μm in the Seine estuary and 15 to 90 μm in the Authie estuary), while sand was present only occasionally. The total carbonates (20 to 50% in the Seine estuary and 28 to 40% in the Authie estuary) and the organic matter contents (13 to 15.5% in the Seine estuary and 12.5 to 19% in the Authie estuary) were also within the same range.

In both estuaries, salinity (measured in the field on each sampling occasion in water remaining at the mudflat surface at low tide) was of course higher at downstream sites than at upstream sites (Table 1.1). Stations AP in the Authie estuary and PN in the Seine estuary were the most directly comparable. However, the size of station AP was too restricted to endure frequent and significant sampling. Thus, for the studies dealing with the infaunal worm *Nereis diversicolor*—the biological model favoured for the sedimentary compartment—the main sampling stations were PN in the Seine and AN in the Authie. To assess the influence of salinity on the biological parameters of interest, a specific study was designed in September 2002. A complete set of samples was collected at three stations in the reference estuary along a salinity gradient (AP: 18.9 ± 2.0; AN: 29.5 ± 2.1; AS: 33.0 ± 1.0; Figure 1.3).

From an operational point of view, the purpose of this programme was to apply the findings of our research to (1) the development of analytical tools allowing the determination of bioavailable metals in porewater instead of total concentrations in sediment; (2) the validation of biological tools allowing us to distinguish between anthropogenic and natural fluctuations well before effects become evident at the level of population or community; and (3) the modelling of the impacts of bioturbating macroorganisms on the spatio-temporal dynamics of contaminants. The final aim is to provide a methodology allowing improved risk assessment, favouring a forward-looking approach, instead of a statement of environmental impairment at a stage when remediation is impossible or at best extremely difficult and expensive.

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2 Sedimentary Processes on Estuarine Mudflats

Examples of the Seine and Authie Estuaries

Julien Deloffre and Robert Lafite

CONTENTS

2.1 STUDY SITES

The macrotidal Seine estuary (maximum tidal range of 8.0 m at its mouth) is located in the northwestern part of France (Figure 2.1b). It is one of the largest estuaries on the Northwestern European continental shelf, with a catchment area of more than 79,000 km^2. The mean annual Seine river flow, computed for the last 50 years, is 450 m^3.s^{-1}. Marine sand has infilled the mouth of the estuary (Avoine et al. 1981; Lesourd et al. 2003). Over the past two centuries, the Seine estuary has been greatly altered by human activity (Avoine et al. 1981; Lafite and Romaña 2001; Lesourd et al. 2001).

Intensive engineering works have been undertaken between Rouen and Le Havre to improve navigation. As a result, the Seine estuary has changed from a primarily natural system to one that is anthropogenically controlled (Lesourd et al. 2001).

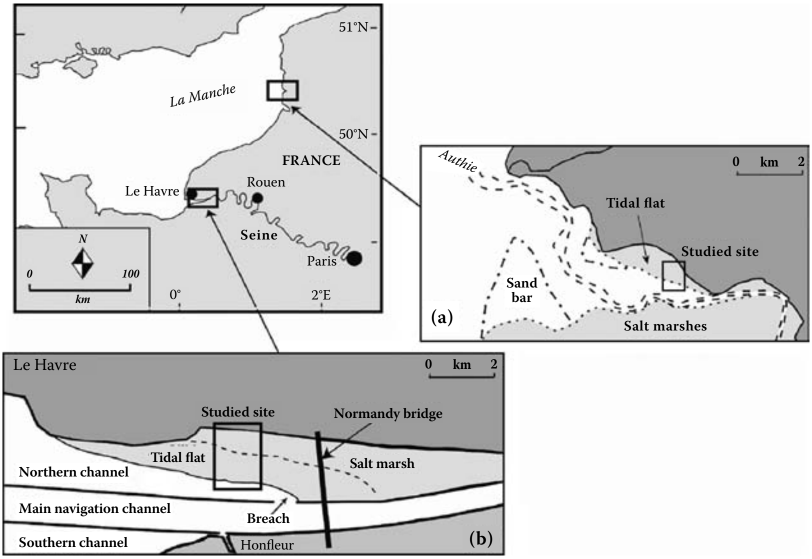


FIGURE 2.1 Locations of studied estuaries (modified from Deloffre et al. 2007). (a) Authie estuary. (b) Seine estuary.

Despite the highly dynamic nature of the system, tidal flats and salt marshes continue to develop in the lower estuary, but the intertidal surface area has drastically decreased during the past 30 years (Cuvilliez et al. 2008). The lower estuary is characterized by the presence of a distinct estuarine turbidity maximum (Avoine et al. 1981), which exerts pronounced control on the sedimentation patterns of intertidal mudflats at the estuary mouth (Deloffre et al. 2006). One of the principal hydrodynamic features in the Seine estuary is a 3-hour high-water slack period that can occur at the mouth. The funnel-shaped estuary is exposed to the prevailing SSW winds that make the intertidal regions at the mouth subject to erosion under the combined effect of waves and currents (Da Silva and Le Hir 2000; Verney et al. 2007).

The Authie estuary is also a macrotidal system (maximum tidal range of 8.5 m at the mouth) located in the northern part of France (Figure 2.1a). The mean annual discharge of the Authie River is 10 $m^3.s^{-1}$, and it has a 985 km^2 catchment area. This estuarine system is rapidly filling with silt, but a major feature is the penetration of a substantial sand fraction originating from the English Channel (Anthony and Dobroniak 2000). Morphologically, the Authie consists of a bay protected by a sand bar (located in subtidal to supratidal domains) at its mouth, which shelters the estuary from storm swells (Figure 2.1a). The principal hydrodynamic feature is the rapid filling of the bay by the tide: during low tide, most of the estuary, except the main channel, is emersed, and during the flood period significant resuspension of fine sediment occurs. From a morphological view, the Authie estuary is considered a relatively natural estuary, although some polders have been constructed, inducing a seaward progression of salt marsh and increased sedimentation (Anthony and Dobroniak 2000).

2.2 SAMPLING STRATEGY

2.2.1 Sediment Properties

In order to determine the relevant hydrodynamic processes and compare the evolution of the intertidal mudflats, superficial sediment properties were analysed. Surface sediments and short cores (length ~30 cm, diameter 10 cm) were sampled during each field work period (i.e., every 2 months). The physical characteristics of the sediment were determined using standard sedimentological procedures. The water content was measured using a wet–dry weight technique (water content = water weight × 100/dry weight). The grain size distribution (sand-to-clay fraction) was analysed using a Laser Beckman-Coulter LS 230. The organic matter content of the sediment was quantified by ignition loss at 525°C. Carbonate content was measured using a Bernard calcimeter.

The lithology of the cores was examined using the SCOPIX x-ray imagery method developed by the Bordeaux I University (Migeon et al. 1999). This high-resolution instrument permits the observation of millimetre-thick layers of sediment (Lofi and Weber 2001).

2.2.2 Hydrodynamic Measurements

The prevailing near-bed current velocities at the sites were measured during several spring semi-diurnal tidal cycles under low river flow conditions using a 6-MHz Nortek acoustic Doppler velocimeter (ADV) (Kim et al. 2000). The ADV measurement cell was located 15 cm from the transmitter, and was set to measure at a height of 7 cm above the sediment–water interface. This instrument measures three-dimensional current velocities near the bed at a 32-Hz frequency. These high-resolution measurements allow the calculation of bottom shear stress. The turbulent kinetic energy (TKE) method is judged to be the most suitable to estimate the turbulence generated by tidal currents and wind-induced waves on intertidal mudflats (Voulgaris and Townbridge 1998; Kim et al. 2000), but wave–current interactions are incorporated in the TKE shear stress calculations.

This study utilized the parametric Wave–Current Interaction (WCI) model proposed by Soulsby (1995). This model was applied to remove wave–current interactions in the shear stress calculations (Verney et al. 2007). The backscatter signal recorded by the ADV allowed estimation of the near-bed suspended solids concentration (SSC) (Kim et al. 2000). The relationship between ADV backscatter and SSC was derived at each site using surface sediment samples to minimize errors induced by grain-size variability (Voulgaris and Meyers 2004).

2.2.3 Altimetric Measurements

A similar sampling strategy was used for both mudflats. A Micrel ALTUS altimeter was placed at a similar elevation in each estuary (4 to 6.5 m above the lowest sea level, i.e., on the middle slikke). This instrument measures bed elevation at high frequency (1 acoustic pulse every 10 min), with high resolution (0.2 cm) and high accuracy (0.06 cm). The altimeter includes a 2-MHz acoustic transducer that measures the time required for an acoustic pulse to travel from the mudflat surface to the transducer that was fixed at a height of ~22 cm above the sediment surface. Pairs of poles were deployed along a cross-section on each mudflat. Data collected by the altimeter deployed in the middle of the cross-section are representative of the erosion–deposition processes along the section (Bassoulet et al. 2000; Deloffre et al. 2005).

2.3 RESULTS

2.3.1 Sediment Properties

The carbonate content in surface sediments ranged from 20 to 50% (Table 2.1). The organic matter content of these superficial sediments, however, was similar at each site, ranging from 12.5 to 19%. The estuaries showed little temporal variability in grain-size characteristics. The primary grain-size modes were 15, 40, and 90 μm at the Seine site and 40 and 90 μm on the Authie site (Table 2.1). The main granulometric difference between the sites was seen in the sand fraction: a 200-μm fraction over the Seine mudflat made up 5 to 15% of the sediment, while on the Authie mudflat the fine-grained sediment was usually associated with a sand fraction below 10% (modes: 200 μm and more rarely 800 μm).

The main parameter varying over an annual scale was water content. While this parameter was fairly constant over a 1-year monitoring period in the surface samples from the Authie estuary (65 to 90%), it varied widely on the Seine mudflat (75 to 250%) where fluid mud occurs during periods of sedimentation. Variations in water content in the superficial sediments of the Seine mudflat result from deposition of fluid mud (water content = 250%) on the mudflat and from dewatering processes resulting from consolidation and desiccation during neap tides. On the basis of laboratory experiments, Deloffre et al. (2006) estimated the impact of dewatering on the altimeter dataset; variations in bed elevation induced by dewatering have been removed from the raw altimeter dataset for the Seine estuary. The present altimeter dataset takes into account only erosion and sedimentation processes.

TABLE 2.1
Main Properties of Fine-Grained Sediment Sampled on the Studied Mudflats

	Seine Estuary	Authie Estuary
Carbonate content	20 to 50%	28 to 40%
Organic matter content	13 to 15.5%	12.5 to 19%
Grain-size modes	15, 40, 90	40, 90
Sand layer grain size	Recurrent (200 μm)	Rare (200 to 800 μm)
Water content	75 to 250%	65 to 90%

2.3.2 Hydrodynamics and Sedimentary Processes

An annual comparison of bed level measurements on the studied intertidal mudflats is shown in Figure 2.2. Mudflats in the Authie and Seine estuaries received net depositions of 15 to 18 cm.year^{-1} during the study. Although net sedimentation rates over an annual time scale were similar in the Authie and Seine estuaries, sedimentation rhythms were different (Figure 2.2).

On the Authie mudflat, topographical variations at a lower scale indicate that the sedimentation is controlled by the semi-lunar tidal cycle (Figure 2.3 and Figure 2.4a). Bed level increases during each spring tide and then decreases or is stabilized during neap tides when the water level is low on the mudflat or when the mudflat is emersed. The threshold between erosion and sedimentation phases corresponds to a water level of 110 cm on the mudflat, which in turn corresponds to a tidal range of 5.5 m. This pattern induces a lag of a few days between the end of deposition and

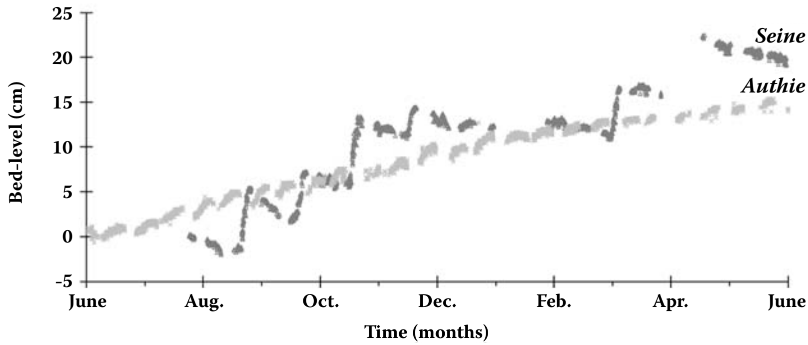


FIGURE 2.2 Topographic evolutions of Seine and Authie mudflats over one year (modified from Deloffre et al. 2007).

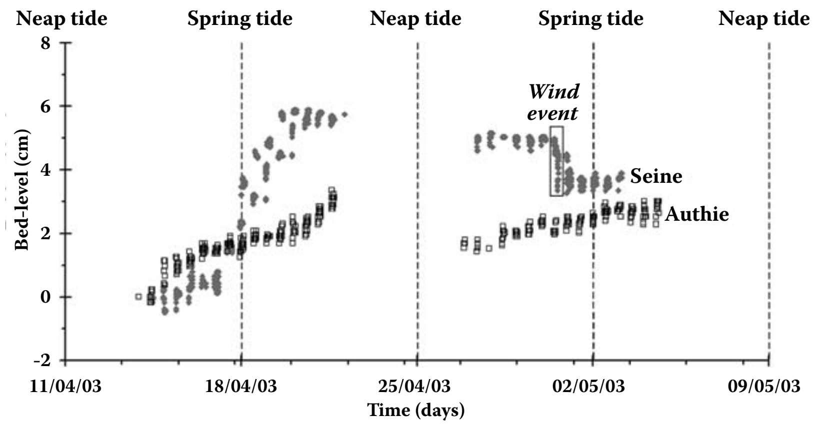


FIGURE 2.3 Topographic evolution of Seine and Authie mudflats over a lunar cycle.

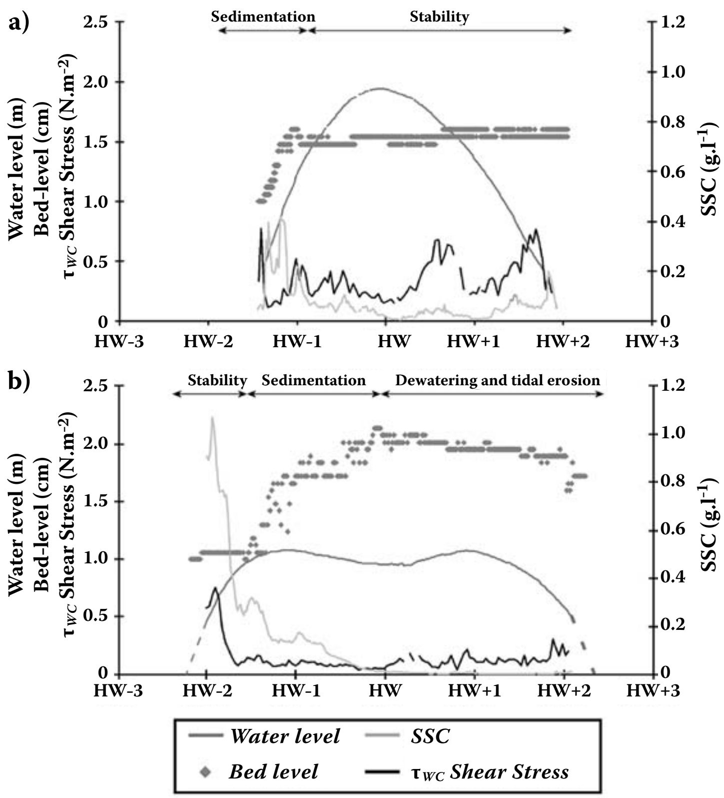


FIGURE 2.4 Sedimentary and hydrodynamic conditions on the studied mudflats during a semi-diurnal cycle (modified from Deloffre et al. 2007) (a) Authie estuary. (b) Seine estuary.

the maximum water level (Figures 2.4a and 2.4b). The sedimentation rates observed on the mudflat range from 0.1 to 0.6 cm per semi-diurnal tidal cycle, with more resuspension of fine particles in the main channel of the estuary during spring tides (when current velocities allow the reworking of fine-grained deposits), and a longer duration of immersion when a supply of fine particles was available (as opposed to during neap tides).

Processes observed at the semi-diurnal scale (Figure 2.4a) indicate that particles settle during flood periods, when the bed shear stress is low (~0.20 $N.m^{-2}$) and the SSC near the bed is high (~0.4 $g.l^{-1}$). As fine-grained sediments settle out of suspension, the SSC progressively decreases. After 1 hour of immersion, most of the sediment has settled out of suspension, resulting in a 0.6-cm-thick deposit. During the high tide slack water and ebb periods, the SSC and the bottom shear stress are low, with mean values of 0.05 $g.l^{-1}$ and 0.25 $N.m^{-2}$, respectively. Twice during the survey, bottom shear stresses reached a value of 0.8 $N.m^{-2}$ as a result of high energy events (Figure 2.4a). However, no impact on the surface of the mudflat was observed during these two events that each lasted 30 minutes. It is notable that during the second event, the water was lower on the mudflat and the SSC increased (Figure 2.4a).

This phenomenon might be linked to erosion of the upper part of the mudflat that resulted from the combined effect of waves and tidal currents. However, at the station studied, the recently settled sediment was not influenced by the waves. The Authie mudflat surface remained stable during these events. Apart from these events, all the sedimentary mechanisms recorded are related to the repetition of semi-diurnal cycles during spring tides (Figure 2.4a).

The annual sedimentation rate on the Seine estuary mudflat is 18 cm (Figure 2.3), but, in contrast to the Authie mudflat, the main deposition phase occurs during the highest spring tides, i.e., according to the lunar cycle, when the water level is >150 cm above the bed level at the station (corresponding to a tidal range of 7.1 m). During these periods, the turbidity maximum reaches high concentrations (>1.95 $g.l^{-1}$) and maximum volume (Le Hir et al. 2001; Lesourd et al. 2001) in both the main (navigation) channel and the northern channel, and the depositional rate on the mudflat is at a maximum (Deloffre et al. 2006). At these times, the sedimentation rate on the mudflat is high, from 0.3 to 0.8 cm per tide (Figure 2.4b).

As on the Authie mudflat, a lag between the depositional maximum and the water level maximum is observed (Figure 2.4b). During periods of lower water level (<150 cm water depth on the mudflat), the mudflat undergoes gradual erosion, with rates ranging from 0.02 to 0.085 cm during a semi-diurnal cycle. Over an annual time scale, the morphological evolution of the Seine mudflat corresponds to a few periods (6 to 10 per year) of high sedimentation, with increases in bed elevation of between 2 and 8 cm, followed by long periods of slow erosion caused by tidal currents (Figure 2.2). At the semi-diurnal scale, particle settling occurs during high water slack periods (Figure 2.4b). During flood tide when the Seine mudflat is covered, small wind waves occur, inducing a high bottom shear stress that reaches 0.8 to 1.0 $N.m^{-2}$. These small wind waves occur even outside storm periods. This bottom shear stress prevents deposition and the SSC in the water column remains high (up to 1 $g.l^{-1}$). During the early high water slack water, when the bottom shear stress decreases (~0.20 $N.m^{-2}$), the SSC also decreases as fine-grained material settles on the mudflat in a 1-cm thick layer (Figure 2.4b). After all the material has settled, the SSC in the water column is low. During the late slack and ebb periods, the topographic level decreases; this is interpreted to be the result of dewatering and erosion of the soft/fluid mud deposit by tidal currents. In the Seine estuary, the duration of high water slack is up to 3 hours during spring tides, with a well-developed double high tide that favours settling of fine particles and dewatering/consolidation processes just after deposition.

Altimeter measurements at a high resolution and high frequency were used to evaluate bed level changes at the tidal scale and determine the impacts of wind-generated waves on the mudflat. Compared to continuous slow tidal erosion, the wind-induced reworking of intertidal mudflats occurs rapidly.

The Authie mudflat shows no evidence of wind-generated erosion events (Figure 2.2 and Figure 2.3), consistent with the sheltered morphology of this estuary. In contrast, the Seine mudflat undergoes strong erosional phases induced by westerly to northwesterly swells and by local southerly to westerly waves in the Bay of the Seine (Lesourd et al. 2001). Such winds occur on the mudflat about 10 times per year, and are more common during the winters (Deloffre et al. 2006). At the study site, the amplitude of the wind-induced erosion was 0.2 to 2 cm, corresponding to wind speed intensities ranging from 12 to 20 $m.s^{-1}$ (Deloffre et al. 2006). A direct correlation between wind speed and erosion on the mudflat is difficult, however, as the consolidation state of the sediment must be taken into account. For example, for the same wind event, a fluid mud bottom (such as that found during a depositional period) will undergo more erosion than will a consolidated muddy bed (such as that found during tidal erosion periods).

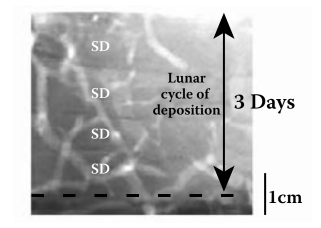
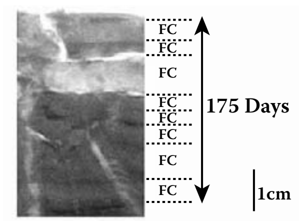
2.3.3 Coupling Altimetric Measurements and Core Images

The SCOPIX x-ray images of cores allow the identification of physical structures such as layers and surfaces and biological structures such as burrows, tracks, and shell remains that comprise the deposits. The images of the cores from the intertidal mudflats studied show that burrows always occur. As for physical features, the Seine and Authie mudflat deposits consist of thin layers. If only the data from the SCOPIX imagery are used, an interpretation of the sedimentary facies of the intertidal mudflats is difficult because single layers can be interpreted as the results of semi-diurnal, semi-lunar, or lunar depositional cycles. To resolve this problem for this study, we interpreted sedimentary core images in relation to the altimeter dataset. This approach allowed us to determine the duration of deposition for each layer and estimate deposition rates for each site on the basis of the number and thickness of layers.

In the Authie mudflat, a great deal of bioturbation is present, resulting primarily from the activities of polychaetes (*Nereis diversicolor*) at depth and of crustaceans (*Corophium* spp.) in the superficial subsurface. Physical facies, however, are also easily observed at this site as thin layers of fine sediment (Table 2.2). The occurrence of thin sediment layers is consistent with the observed bed level variations. At this site, where deposition is driven by the semi-lunar cycle, the depositional phases are recorded in the cores and correspond to centimetre-thick layers; however, not all the semi-lunar cycles are preserved in the cores (Table 2.2). This indicates that even in a protected setting, water current velocities are high enough to rework some deposits corresponding to fortnightly cycles and, as a result, gaps occur in the neap spring recording.

In the Seine estuary mudflat, freshly deposited sediments can clearly be identified in x-ray images of cores collected a few days after the highest spring tide period (Table 2.2). They are characterized by erosion surfaces at the bases of the elementary deposits that result from tidal- or wind-induced phases. Above these erosion surfaces, the fresh deposits are characterized by low consolidation state and low bulk density (water content of the order of 200%). The fresh deposits appear light grey in the positive x-ray images (Table 2.2). The layer thicknesses indicated by the altimeter dataset and the sedimentological variations in the cores are consistent. The lithological analysis of the uppermost part of the cores is more complicated, however, at sediment depths exceeding 10 cm, mainly because of strong mixing by bioturbation and the erosion of parts of the deposits by waves and/or tidal currents (Figures 2.2 and 2.3).

TABLE 2.2
Comparison of the Main Sedimentological Results on the Studied Mudflats

	Seine	**Authie**
Morphology at the mouth	Open estuary	Protected bay
Sediment supply	Turbidity maximum	Resuspended sediment inside the estuary
Forcing parameter(s)	• Strongest spring tides (TM development) • Wind (>15 m.s–1 westerlies)	Tidal cycles
Sedimentation rates at semi-diurnal scale (cm)	0.3–0.8	0.1–0.6
Main sedimentation cycles (deposit sequence)	Lunar	Fortnightly
Maximum sedimentation during one deposit episode (cm)	8	5
Number of sedimentation episodes/year	7–10	15–22
Annual sedimentation rates (cm)	18	15
Preservation rates (%)	50%	90%
Typical facies and estimated duration based on bed-level evolution		

Notes: Modified from Deloffre et al. 2007. SD = semi-diurnal cycle. FC = fortnightly cycle. LC = lunar cycle. TM = turbidity maximum.

2.4 DISCUSSION AND CONCLUSIONS

The sedimentation processes on the studied tidal mudflats examined here are strongly influenced by sediment supplies and by the morphologies of the estuaries at various time scales. On the Seine and Authie mudflats, although long-term sedimentation rates are similar, the rhythms of deposition are different (Figure 2.2 and

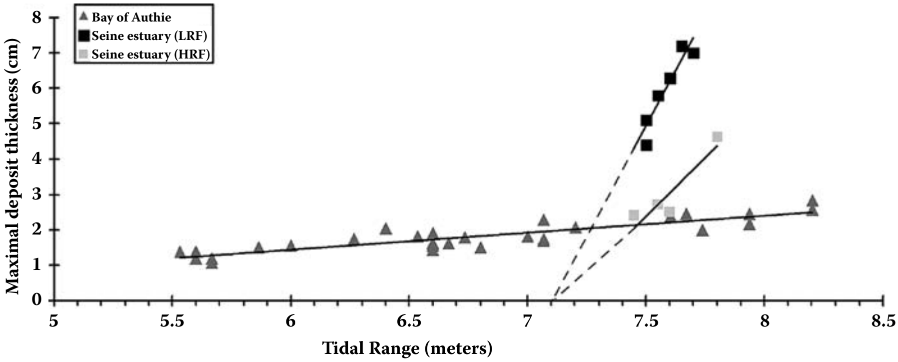


FIGURE 2.5 Relation between maximal deposit thickness and tidal range on the studied mudflats (modified from Deloffre et al. 2007). LRF = low river flow. HRF = high river flow.

Table 2.2). On the Authie mudflat, sedimentation is continuous, with rate controlled by the semi-lunar cycle. A linear relationship exists between the tidal ranges and the resulting deposit thickness, as determined from altimeter data (Figure 2.5). On the Seine estuary mudflat, no sedimentation occurs under neap to medium spring-tide conditions. Rather, sedimentation on this mudflat occurs when a tidal range threshold value of 7.1 m is reached (Deloffre et al. 2006; Figure 2.5). Sedimentation is thus discontinuous, occurring only during the higher spring tides and leading to only a few (<10) depositional episodes over the course of a year (Figure 2.2 and Table 2.2).

Sedimentation on the Authie mudflat corresponds to a semi-lunar rhythm typical of most modern sheltered mudflats. The lower Seine estuary mudflat, however, exhibits a distinct pattern of deposition–erosion. This unusual pattern is a result of the altitude of the study site; its elevation is the same as that of the Authie mudflat, and this pattern is recorded on other locations on the Seine mudflat, including at lower altitudes (Deloffre et al. 2006). The difference between the rhythms of sedimentation on the Authie and Seine mudflats is likely linked to sediment availability and sediment properties. On the Authie mudflat, the fine particles originate from the reworking of sediment from the lower parts of the slikke during the rapid filling of the estuary at flood tide. During each spring tide period, the fine material is resuspended and sedimentation occurs on the mudflat at the location studied on the middle slikke. In the Seine estuary, the delivery of sediment to the mudflat is related to the turbidity maximum (Deloffre et al. 2006). Because of the characteristics of the suspended particulates and the hydrodynamic conditions, development of the Seine estuary turbidity maximum is higher during tidal ranges that exceed 7.1 m (Avoine et al. 1981; Le Hir et al. 2001), which is the threshold value for deposition (Figure 2.5).

The control of sedimentation by the turbidity maximum also results in differences on an annual scale. Sedimentation rates are higher when river discharge is low, under which conditions the position of the turbidity maximum in the estuary is in the area of the mudflat (Le Hir et al. 2001; Lesourd et al. 2001). When river discharge is high, the turbidity maximum is expelled from the estuary into the Bay of the Seine.

During a lunar cycle (Figure 2.3), high sedimentation rates result from some specific characteristics of the Seine estuary. Because of high silt content (quartz, calcite) and low clay mineral content (Lesourd, personal communication), the settling velocities of particles in the lower Seine estuary are higher (~1 $mm.s^{-1}$) than in other estuarine settings (Delo and Ockenden 1992). These high settling velocities combined with the long high tide slack (up to 3 hours) in the Seine estuary lead to the high sedimentation rates observed on the mudflat during the highest spring tides. These conditions result in the settling of fluid mud, a phenomenon observed only in this estuary among the estuaries studied; thus on this mudflat, dewatering processes must be considered.

The properties of cohesive materials play an important role in controlling deposition (formation of laminae) and preservation of fine-grained sediments. Sediment properties such as grain size, water content, and settling velocities play a role in determining the thicknesses of deposits on intertidal mudflats. The depth of wind-induced erosion is related to the cohesion of surface sediments as well as to wave amplitude. As a result, erosion occurs on the open Seine mudflat where the mud is soft or even fluid (Figure 2.4b), whereas on the sheltered Authie mudflat, where the sediment is coarser-grained and less fluid, only a small amount of wave-related erosion is observed (Figure 2.4a).

Both macrotidal mudflats are highly dynamic. This implies that the mudflat surface changes during the year based on the age of the sediment (a few days to several months) and the sediment properties (especially mud state). On the other hand, the cores from both mudflats are laminated, one lamina corresponding to one deposit episode. These physical processes influence bio-geochemical processes.

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3 Quantification of Contaminants

Jean-Claude Amiard, Laurent Bodineau, Virginie Bragigand, Christophe Minier, and Hélène Budzinski

CONTENTS

3.1 INTRODUCTION

Both estuaries of interest, the Authie and the Seine, are participants in the French Mussel Watch Programme (RNO 1995; Claisse et al. 2006) and their levels of chemical contamination have been well documented through quarterly analysis of samples for more than 30 years. However, in order to link exposure to contaminants, incorporation into tissues of organisms, and responses of the biota, it was necessary to acquire chemical and biological data precisely at the same place and at the same moment, taking into account temporal changes within each year and between successive years. In addition, it was necessary to investigate the presence of emergent contaminants such as pharmaceuticals and brominated flame retardants as well as alkylphenol polyethoxylates for which no data were available for the Authie site.

Estuarine areas are characterized by the presence of huge quantities of sedimentary particles both deposited and in suspension (see Chapter 2). Sediments constitute the main sink for most organic and inorganic contaminants in the aquatic environment (Gagnon and Fisher 1997; Bernes 1998). Despite the fact that they live in close contact with these contaminated sediments, endobenthic species are not very widely used as filter feeders in biomonitoring programs. Previous reports provided evidence that accumulated contaminant concentrations in the endobenthic polychaete annelid *Nereis diversicolor* may be considered good biomonitoring measures of the local bioavailabilities of contaminants (Bryan and Langston 1992; Diez et al. 2000).

Thus in the present work, the quality of the environment was characterized by analyzing micropollutants in sediments and in *Nereis diversicolor* but also in water for contaminants whose persistence is limited or whose presence is mainly in the water column (dissolved phase: hydrophilic compounds).

3.2 CONTAMINANTS IN THE WATER COLUMN

For contaminants with limited persistence and/or are hydrophilic (pesticides, pharmaceuticals, alkylphenol polyethoxylates), analyses in water were conducted in the Authie estuary.

3.2.1 Pesticides

Pesticide concentrations determined in the Authie estuary were among the lowest that have been found in major French rivers and world systems (Le Calvez 2002) (Table 3.1).

For the Authie estuary, analyses of aqueous extracts revealed the presence of two nitrogen herbicide compounds (trifluraline and terbuthylazine), two phosphorus insecticide molecules (ethyl parathion), and a product of DDT degradation, 4,4′DDE. Cereal crops in the Authie's watershed explain the applications of trifluraline and terbuthylazine for treatment of undesirable vegetation. Due to their physical and chemical properties, the dissolved compartment served as the main reservoir of these hydrophilic compounds that were not found in particulate media such as deposited sediments and suspended particulate matter (SPM).

Lindane was quantified for each site in surface sediment and was found at very low levels (<0.1 $ng.g^{-1}$ dry weight). This indicates that lindane in the environment is decreasing since it was banned in Europe several decades ago, now attaining an approximate background level (still detectable but at very low concentration).

3.2.2 Pharmaceuticals

During the 1990s, pharmaceutical compounds such as analgesics, lipid-lowering drugs, antibiotics, and hormones were detected in waste waters across Europe (Heberer 2002; Ternes 2001) and the United States (Boyd et al. 2003; Kolpin et al. 2004). Several reviews dealing with the occurrence, fate, and effects of pharmaceuticals in the environment are available (Halling-Sorensen et al. 1998; Hernando et al. 2006) and show the main influence of sewage treatment plant discharges on the contamination of aquatic systems. These compounds are not completely degraded by