GUADIANA RIVER ESTUARY

Investigating the past, present and future

Edited by
Delminda Moura, Ana Gomes, Isabel Mendes & Jaime Aníbal

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Forward

The Centre for Marine and Environmental Research (CIMA) is a multidisciplinary research centre of the University of Algarve. In addition to the scientific research and technological innovation, CIMA is involved in service delivery, graduate training and knowledge transference to the society.

The scientific dissemination to the society is the main goal of this book. The CIMA researchers develop their scientific activity using a multidisciplinary approach, which contributes to produce an integrate knowledge of the ecosystems' behaviour and to understand the evolution resulting from global changes and anthropogenic impacts. These activities are developed in several territorial foci, of which the Guadiana River and in particular its estuary is one of the most intensely studied by the CIMA researchers.

This book synthesizes part of the scientific knowledge undertaken by various researchers allowing an integrated view of the Guadiana River estuary. The authors had a high degree of freedom to write their chapters. It could not have been otherwise given the diversity of matters. However, there was a common point: transform the scientific writing, frequently hermetic, into easy comprehensive manuscripts for the general public without neglecting scientific rigor. Other scientists named in this book, to whom the editors and authors are grateful, have reviewed all the chapters and illustrated some annexes.

It is our hope that this book may contribute to the dissemination of the scientific knowledge, which is a common objective of the University of Algarve and the Centre for Marine and Environmental Research (CIMA: http://www.cima.ualg.pt/)

Editors

7. Chemical stressors in the Guadiana River

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7.1. What is this Chapter about?

The Guadiana River, the fourth major river of the Iberian Peninsula, represents an important aquatic system from a socio, geo and ecological point of view for Portugal and Spain. Important economic activities such as agriculture, tourism and aquaculture are present along with several economic facilities such as harbour (commercial and fishing), marina and small shipyards for construction and repair of small vessels. All these activities generate wastes some of them toxic to the aquatic environment. That is why in the river there are several aquatic species some of them endemic, rare and even threatened. Recently, the water regime of the river changed due to the construction of the Alqueva Dam (the largest artificial lake in Europe) with the capacity to store 4 150 hm^3 of water, which reduced the river flow and the sediment transport to the coastal area. This flow reduction might have an impact in the levels of the stressors present in the river.
The above referred anthropogenic activities and their technological development imply the use of a lot of materials, especially metals, which are generally obtained as a result of mining exploration. The exploration of these metals give origin to the production of acid mining waste containing high amounts of metals some of which are toxic to the aquatic species and to humans. For these reasons, metals are considered traditional contaminants to the aquatic systems. Furthermore, estuaries are also targeted for several other economic services such as harbours and marinas for receiving commercial ships, ships maintenance and nautical activities, which are another source of pollutants. Indeed, all these activities if not properly managed can introduce chemical stressors such as petroleum hydrocarbons that are highly toxic to the aquatic environment. On the other hand, the enhancement in urban development, increasing the population that lives near the coast and mainly in the vicinity of the estuaries, results in the production of significant amounts of solid and liquid wastes containing several other chemical stressors. Moreover, the increase of human life expectancy is related to the increasing use of pharmaceutical compounds that are used in hospitals or at home. Therefore, these compounds were detected with significant concentrations in rivers and coastal areas around the world. However, the available technology to treat wastewater effluents is unable to eliminate most of them in the waste treatment process reason why they can easily reach the aquatic systems, inducing a serious threat to the aquatic and human health. For that reason, chemical stressors such as these pharmaceutical compounds are considered emerging contaminants to the aquatic environment.

7.2. Sources of Stressors in the Guadiana River

In the Guadiana River the majority of anthropogenic sources of chemical stressors are metals (among the most toxic Cd, Pb and Hg), persistent organic compounds (like polycyclic aromatic hydrocarbons-PAHs, biphenyl polychlorides-PCBs), pharmaceutical and personnel care products (like UV filters and fragrances). These traditional and emerging contaminants were detected in the water and are present in the sediments where they sink and become available for the aquatic organisms, in which they are then accumulated. Once accumulated in the aquatic organisms, they can induce biological changes in their metabolism resulting, most of the time, in a threat to these organisms' health. Because most of them are important as human food source they can also represent a threat to human health. In the Guadiana River, our studies revealed metal contamination, especially regarding lead, in water, sediments and fresh and marine organisms, indicating biological effects related to these stressors and revealing an impact of the acid mine drainage from the Minas of São Domingos located in the upper part of the river. Nevertheless, an additional source of metals was also detected as the result of the impact of sewage and tourism activity in the mouth of the river. In addition persistent organic pollutants (POPs), including PAHs, PCBs, and tributyltin (TBT) used in antifouling paints and herbicides, were also detected in the same samples. The presence of these compounds is responsible for endocrine disruptor effects detected in the aquatic bivalves present in the river. Direct human impact due to personal care was also detected in bivalves through the presence of UV filters coumpounds (2-ethyl-hexyl-4-trimethoxycinnamate - EHMC, octocrylene -OC and octyldimethyl p-amino benzoic acid - OD-PABA) that are used in sun tan lotions and through two types of musk (galaxolide and musk-ketone) present in fragrances, indicating that, besides bathing activities, wastewater discharges might also be a source of these compounds. Finally several pharmaceutical compounds, from different therapeutic classes, were detected in water namely analgesics, anti-asthmatics, lower lipid agent, anti-inflammatory, anxiolytics and antidepressants revealing the inefficiency of sewage treatment. The presence of diclofenac known as Voltaren in the Guadiana River is a cause of concern due to the effects that this compound can cause to aquatic organisms. These effects led to the inclusion of diclofenac in the list of toxic substances of concern of the EU Directive known as the Water Framework Directive (WFD), which main objective is that all European Waters reach a good ecological status by 2020. Therefore, diclofenac levels as well as those of the other stressors identified in the present chapter need to be followed in future studies in the Guadiana River.

7.3. Metals detected in the water of the Guadiana River

As already referred above, economic activities induce major anthropogenic sources of contaminants, some of them being considered major point sources. This is the case for industrial effluents, wastewater discharges and waste disposal sites including historic mining exploration from the Iberian pyrite belt. The other sources are considered diffuse sources like agriculture run off, road run off, accidental oil spills, etc …
In the Guadiana River, one of the major metal point sources is the acid mining waste from São Domingos Mines (Figure 7.1).

Figure 7.1.
Photography of acid mining water from S. Domingos, showing red-yellowish colour linked to iron and other high metal contents (photograph by Ana Gomes, 2007).

The exploration of iron (Fe) and cupper (Cu), along with lead (Pb) and zinc (Zn) in this mine dates back to prehistoric times (age of iron and bronze) but the largest quantities of these metals were extracted in the 19th and 20th centuries. Since then, the abandoned areas of the mine had a very weak intervention with regard to environmental remediation. Therefore, the areas of un-remediated mine waste and discharge of acid mine waters are the principal sources of metal pollution in the river; the metals are transported into the river flow and then dissolved or adsorbed to the suspended particulate matter. In fact, suspended particulate matter comprises iron-rich particles, with up to 12 % in weight of Fe, that also have high concentrations of Pb (20–80 ppm) and even higher concentrations of Cu and Zn during periods of moderate flow (i.e. winter). As for the dissolved phase, the information available for the presence of metals, besides for Pb, dissolved in water is scarce and only cadmium (Cd) and cupper (Cu) have been measured in waters one mile from the mouth of the river, with concentrations up to 0.36 nM and 11 nM, respectively.

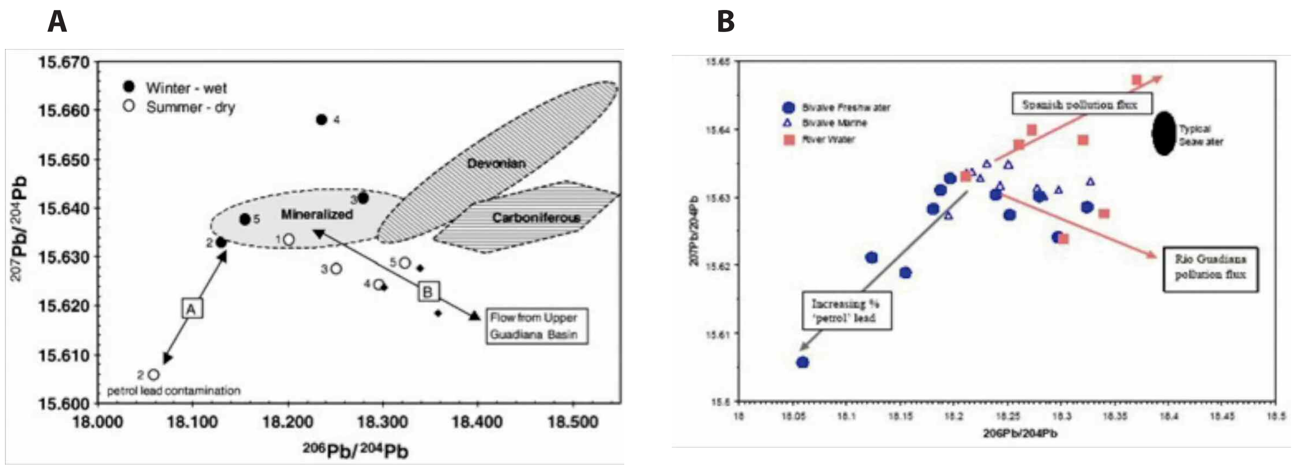


Figure 7.2.

A) Seasonal variation in the lead isotopic composition ($^{207}Pb/^{204}Pb$, $^{206}Pb/^{204}Pb$ ratios) of C. fluminea in the lower Guadiana River (sample sites as for Fig. 7.5.). Key: Summer values (○), winter (●) values. 'Devonian' defines lithogenic lead associated with volcanic and sedimentary rocks that host the Iberian Pyrite Belt (IPB) ore deposits. 'Mineralised' defines anthropogenic lead associated with mine contaminated soils. 'Carboniferous' defines lithogenic lead of unmineralised rocks south of the IPB. Small filled rhombuses (♦) are the isotopic composition of lower Guadiana River water sampled during the dry season (unpublished data provided courtesy of the Universities of Aveiro and Huelva: Surface and Groundwater Studies, UTPIA Project). B) Lead isotopic composition and anthropogenic (Company et al., 2008).

As Pb is a metal with no known biological function, it is considered as a priority substance of the Water Framework Directive (WFD). Therefore, a good environmental practice is needed to assess the impact of Pb in this aquatic system. The anthropogenic sources of Pb include burning of leaded fuels, metal smelters and mining activities. The toxic lead (Pb) effects, in aquatic organisms and mammals, are a result of Pb ability to displace other metals that are considered essential for biological functions, such as calcium (Ca), Fe and Zn.

In the Guadiana River, dissolved Pb concentrations during summer are lower than minimum detectable values by the existing analytical methods (<0.1 g l^{-1}) except in the Pomarão area where the levels are 0.2 g l^{-1}. However, in winter, levels of dissolved Pb are higher (ranging from 0.3 to 0.8 g l^{-1}) and attributed to the run-off contribution of acid mining waste and from land run-off. These Pb sources were assessed using high precision isotopic techniques to measure Pb isotopic ratios ($^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, $^{208}Pb/^{204}Pb$), which correspond to isotopic signatures of Pb sources (see results in Figure 7.2). In non-

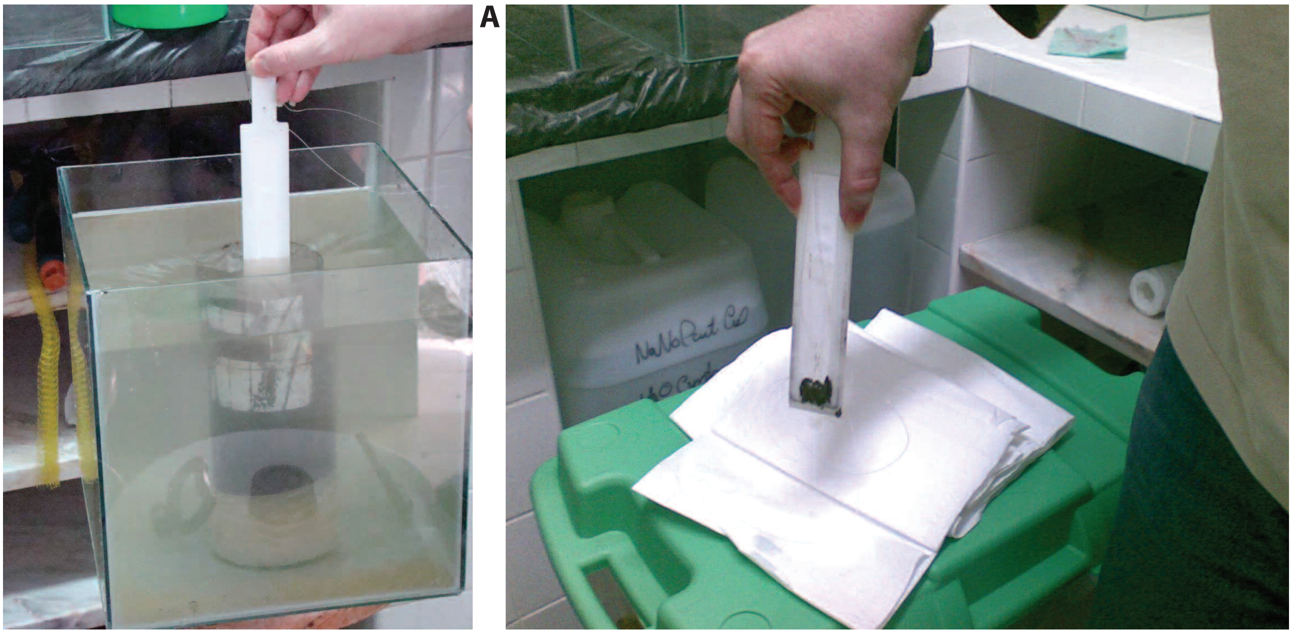
contaminated places, lead was not present and no isotopic signature could be measured. In the other sites, results revealed diverse Pb anthropogenic sources. The dominant one was from the impact of acid mine drainage, being also traced in the river until the open marine environment. In general, the Pb isotopic ratios fall within a field defined by the Devonian volcanic formation and sedimentary rocks that host the massive sulphide ore deposits of the Iberian Pyrite Belt. However, this technique also allows to identify a mixing in the Guadiana water between streams draining Devonian rocks and streams draining areas of the Carboniferous cover rocks. The same technique applied to fresh and marine bivalves suggest marked seasonal changes in the source of mine-related pollution. During the summer, most of the pollution is from the mining area, whereas in winter, it is from the Spanish mining sources. In addition to mining sources, results also revealed the presence of a petrol-lead additive component; especially near the marina and the major highway bridge between Spain and Portugal (Figure 7.3), even if it is forbidden in both countries since 1999.
Furthermore, petrol lead was also detected in freshwater bivalves downstream of the population centres of the River Guadiana confirming that besides mining wastes there are other Pb sources in the estuary. Finally, there might be still another Pb source to be confirmed in the Guadiana linked to hunting and respective shooting activity that is significant in the area.

Figure 7.3.
The international bridge over the Guadiana River, relating Spain and Portugal (photography by Maria Gonzalez-Rey).

7.4. Metals detected in sediments from the Guadiana River

Cadmium (Cd), cupper (Cu), manganese (Mn), mercury (Hg), nickel (Ni), lead (Pb) and zinc (Zn) levels are particularly high in Guadiana sediments since 1999, exhibiting a site and seasonal dependence. Cd, Ni, Pb and Zn concentrations were above the established Sediment Quality Guidelines (SQG) for Effects Range Low (ERL) in more than 50 % of the samples whereas Hg concentrations were above the Effects Range

Medium (ERM). This confirms that metal levels observed in the Guadiana estuary are from anthropogenic sources but not directly linked to oil usage since PAHs concentrations in sediments were always well below the ERL values.
However, these metal concentrations represent the total amount of metals present in the sediment and not only the quantity of metal available by the organisms, referred as the bioavailable metal concentrations. Accordingly, new methodologies based on new devices were developed to assess metal levels bioavailable in sediments, which also avoid the need for sediment sampling. These devices are known as Diffusive gradients in thin (DGT) films (see Figure 7.4) and were applied to document metal bioavailability and toxicity in estuarine sediments of the Guadiana.



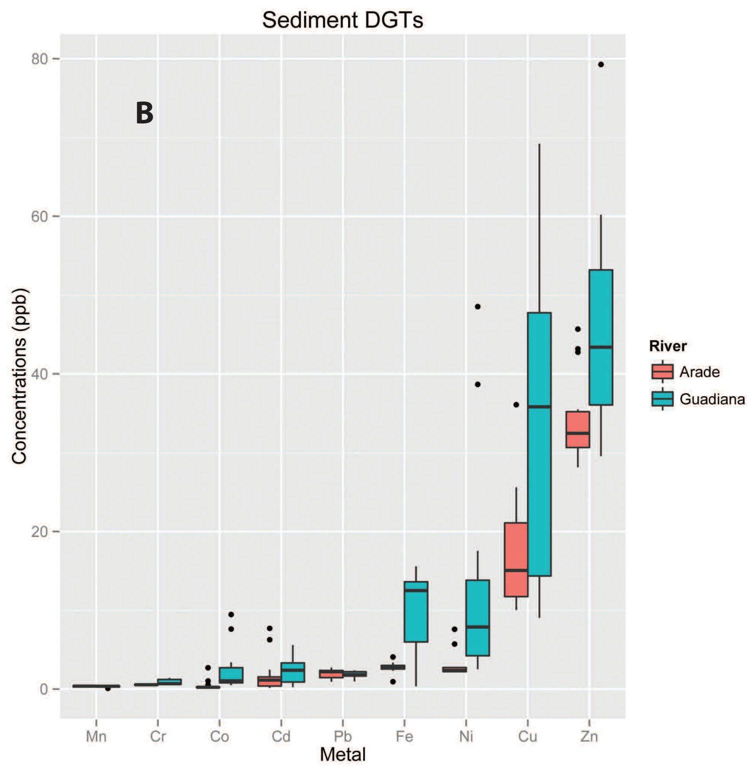


Figure 7.4.
(A) Photography of the apparatus mounted in the laboratory for using the DGTs in sediment cores (by Maria Gonzalez-Rey); (B) Concentrations of metal pollutants in sediments from Arade and Guadiana River obtained from DGTs.

For such this study, one sediment core was collected from the Guadiana estuary and another from the Arade estuary, for comparison purposes. Both cores were stored in laboratory, close-to-natural conditions, with one DGT probe placed in each of them for 15 days. The results showed the same tendency in both estuaries with metal concentrations ranging from 0.32 ppm for Mn to 46.11 ppm for Zn (Figure 7.4, Mn>Cr>Co>Cd>Pb>Fe>Ni>Cu>Zn), but with higher concentrations in the Guadiana than in the Arade, as well as higher ranges. The more important differences between the two sediments were found in the concentrations of Fe, Ni, Cu and Zn (Figure 7.4), which correspond to the main metals explored in the S. Domingos Mines exploration.

In parallel to these metal bioavailability evaluations, a sediment toxicity test was also carried out using a method known as Microtox solid phase test at two different sites from the Guadiana River. The results revealed half maximum effective concentrations (EC_{50}) of 6.9 and 21.8 mg ml^{-1} w.w. in the two sites, indicating that upstream sediments are more toxic than in the mouth of the estuary. These toxicity levels seem to be related to the levels of Cd, Hg, Pb and Ni present in the sediments that were higher than the ERL.

7.5. Metals detected in bivalve species from the Guadiana River

Freshwater clam *Corbicula fluminea* (an alien freshwater species recently introduced in the Guadiana River) and other marine species (the oyster *Crassostrea gigas*, the mussel *Mytilus galloprovincialis* and the clam *Scrobicularia plana*) are well-established indicators to assess the impact of stressors in the aquatic environment. Accordingly, these species were collected from several sites (Figure 7.5) in order to identify sources and effects of lead (Pb) in the Guadiana River.

The concentrations of Pb in the whole soft tissues of these bivalves are represented in Figure 7.6 and show that Pb concentrations in *C. fluminea* at the site adjacent to the abandoned mining area (Mina de São

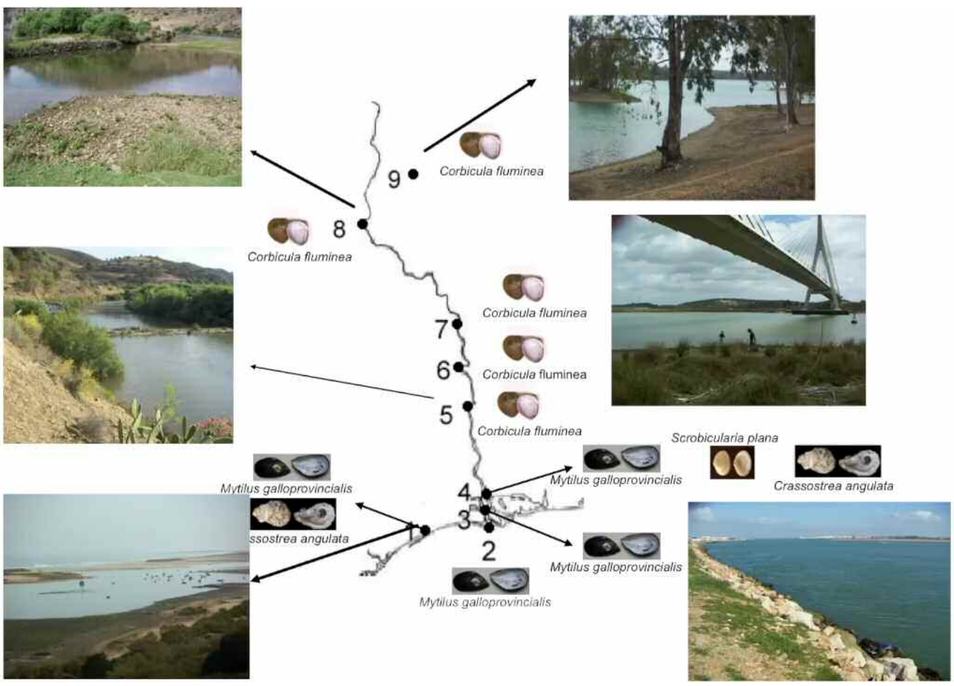


Figure 7.5.

Sampling sites of several bioindicators along a marine to freshwater gradient, from site 1 to site 9 respectively: oyster *Crassostrea gigas (*marine species), mussel *Mytilus galloprovincialis* (marine species), clam *Scrobicularia plana (*marine species) and clam *Corbicula fluminea* (alien freshwater species) (illustration by Rui Company).

Domingos) are 6-fold higher than at the main river sites (2.49 ppb compared to 0.2-0.5 ppb) (see Figure 7.5). For the marine species (mussels, oysters and clams), the highest Pb concentrations were in the deposit feeders *S. plana* (3.50 ppb) and *D. trunculus* (1.95 ppb) that are able to accumulate bioavailable chemical stressors both from water and sediments. High Pb concentrations, as well as high Cu concentrations, were also found in deposit feeder *Nereis diversicolor* (6.84 and 37.47 ppb, respectively), with levels higher than those obtained for the same species in the Southern Iberian coast. The lowest Pb levels were detected in the filter feeder species mussels (*M. galloprovincialis)* and oysters (*C. angulata)* (<0.38 ppb) showing a decreasing trend towards the mouth of the river. However, Pb concentrations in mussels (*M. galloprovincialis)* from the Guadiana estuary were the highest of the South Coast of Portugal. These results confirm the isotopic data, presented above, indicating that mining is an important anthropogenic Pb source to the Guadiana River. Besides Pb, other metals (Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb and Zn) as well as organic and organometallic compounds (polyaromatic hydrocarbons- PAHs, polychlorinated byphenyls – PCBs, trybutiltin -TBT) found in petrol, electric conductors and antifouling paints, respectively, were also detected in marine species from the Guadiana River. Metal concentrations in in the same bivalves species and sites as mentioned in Figure 7.5 decreased according to the following order: oysters *(Crassostrea angulata*), followed by clams (*S. plana)* and mussels (*M. galloprovincialis)*. However, cupper (Cu) and zinc (Zn) concentrations analysed in these species did not show any spatial or seasonal changes and their concentrations in mussels from the Guadiana River are comparable with the ones from other parts of the southern Portuguese coast (2.35 and 380±171 ppb for Cd and Zn respectively).

7.6. Biological effects in marine bivalves as a result of exposure to metallic chemical stressors

The exposure of marine bivalves to chemical stressors has different biological effects depending on their origin and chemistry, either metallic or organic, but also depending on their bioavailability both in time and in quantity. Some biological effects are so fast responding that they are considered as sentinel species for early pollution alert.

One of the early warning effects of the presence of lead (Pb) in biological species is the activity inhibition of three enzymes (aminolevulinic acid dehydratase - ALAD, coporphyrinogen oxidase, and ferrochelatase), the effects on ALAD activity being the more important. It is also why the degree of inhibition of ALAD activity on human erythrocytes is used to clinically estimate Pb poisoning in humans. ALAD levels in bivalves from Guadiana River are presented in Figure 7.6. Mean ALAD activity measured in the same bivalve species varies by an order of magnitude and is negatively related with Pb concentrations among the different species. Examples of this relationship are shown in Figure 7.6B for the fresh water species *C. fluminea* and the marine mussel *M. galloprovincialis,* confirming that this enzyme is inhibited in the presence of Pb in these bivalve species. Apart from ALAD inhibition, Pb also induces another early warning system that is the damage in cell membranes of aquatic organisms. This cell membrane damage, measured as lipid peroxidation (LPO), is negatively related with ALAD activity and directly related with some organic compounds (> 4 rings PAHs and total PAHs) concentrations along with high metal levels (Cd, Cr, Ni, Pb and Zn). In summer, LPO in *M. galloprovincialis* was higher than in winter, which suggests an additional environmental stress at this time of the year. Moreover, both summer and winter DNA damage measured in mussels haemocytes collected from the mouth of the estuary are low (10<% Tail DNA<25%) but still higher than when compared to mussels from other sites of the Southern Portuguese coast. This DNA damage is directly related to LPO, indicating that the stressors present in Guadiana promote cell membrane injuries and DNA damage in mussel's haemocytes.

A

B

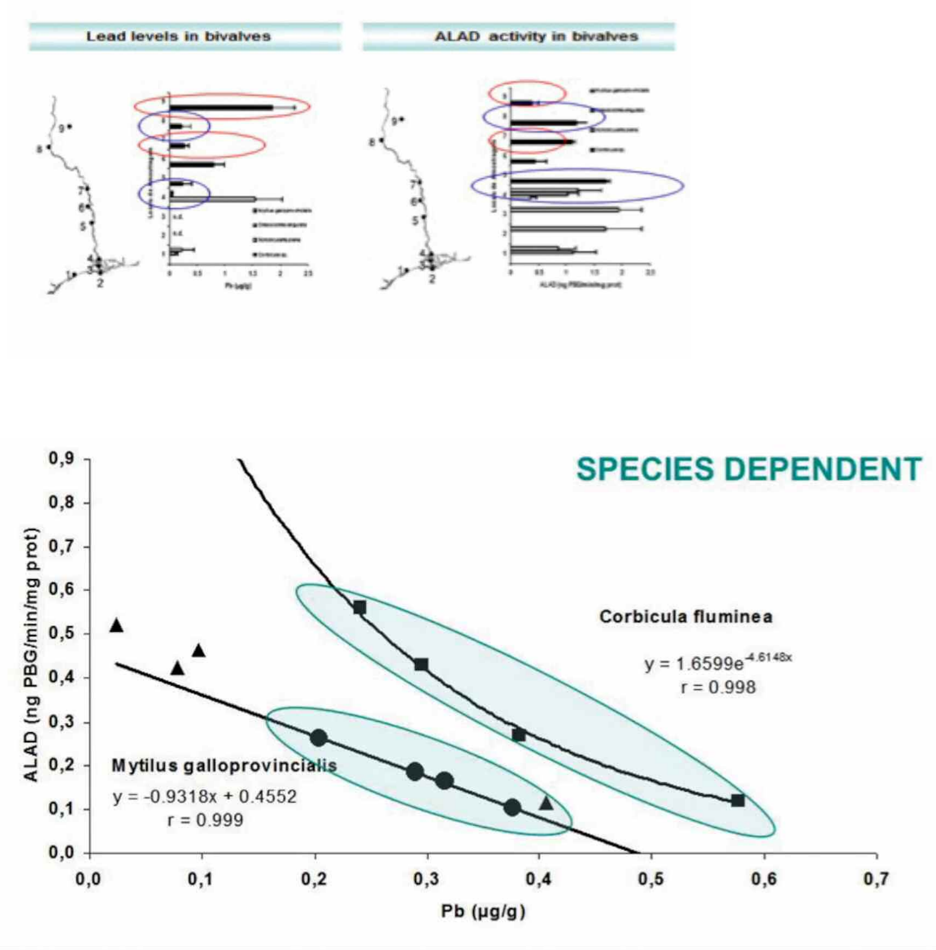


Figure 7.6.
Lead (Pb) concentration and ALAD activity along the salinity gradient (A) in *M. galloprovincialis* and *C. fluminea* (B), showing an inverse relationship between Pb concentrations and ALAD activity (see text for more informations).

Besides enzyme inhibition, there are other parameters that can assess and evaluate the biological effects of aquatic organisms to chemical stressors. For instance, histopathological parameters, a well-established general biomarker to assess the health of aquatic organisms, revealed seasonal differences and alterations in the form and volume of the hepatic cells of the mussels. The digestive gland of bivalves is an important target organ for storage of the presence of pollutants because it plays a central role in metabolizing and detoxifying stressors as well as in eliminating them. Metal levels were determined in the digestive gland of *S. plana* and revealed the presence of arsenic (As), cadmium (Cd), cupper (Cu), lead (Pb) and zinc (Zn).

Finally, nowadays, new technologies known as "omics" are presently used in order to assess the effects of the accumulation of stressors in bivalve tissues. One of these technologies is the proteomics that allows identifying protein changes in certain tissues due to the presence of stressors. Accordingly, a proteomic approach was also used to detect the effect of the metals mentioned above in the digestive gland of the marine clam *S. plana*.

In this study, twenty-one proteins were differentially expressed in the digestive gland of the clams retrieved from the Guadiana River, when compared to those of the same species from the Ria Formosa lagoon. Nine of these proteins were up-regulated, while twelve were down-regulated. These protein changes are related to toxicological mechanisms induced by some of the environmental stressors identified in the Guadiana River.

7.7. Persistent Organic Compounds (POPs)

As seen above, some anthropogenic activities are also directly or indirectly responsible for the release of organic compounds that are persistent and harmful in the aquatic environment and are thus considered as contaminants. This is the case of the persistent organic (PAHs and PCBs) and organometallic (TBT) compounds that are known to be present in tissues of several aquatic species in the Guadiana estuary. The variation of PAHs concentrations in the whole soft tissues of the mussels *(M. galloprovincialis)* are presented in Figure 7.7 and show a significant decreasing trend of PAHs levels in mussel tissues since 1997. It is important to explain here that PAHs are classified and differentiated according to their numbers of benzenic rings, an organic structure in the molecule, and that the persistent PAHs in the Guadiana River are mostly characterized by PAHs that have a high percentage of 5 benzenic rings (>79%) . Moreover, based on the values of the ratios between different PAHs, namely phenantrene/antracene and flourene/pyrene, it is clear that the origin of the PAHs accumulated in Guadiana mussels' tissues is from fuel source (see Figure 7.7)

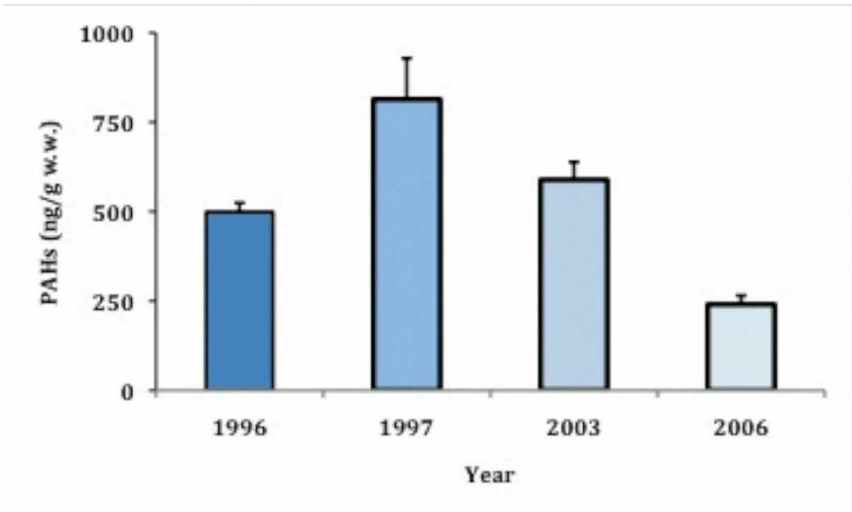


Figure 7.7.
Evolution of PAHs levels in the whole soft tissues of *M. galloprovincialis* for the last 20 years (units in nanograms of PAHs per gram of tissue in wet weight).

As already mentioned above, some chemical stressors accumulated in biological tissues are endocrine disruptors. One of these endocrine disruptors is the organometallic compound known as Trybutytin (TBT) that is responsible for the phenomenon of imposex, which is the superimposition of male characters onto the female of gasteropods, and also intersex, which is superimposition of female characters onto the male characters. This phenomenon was reported in the prosobranch gastropod *Ocenebra erinacea* present in the mouth of the Guadiana River, presenting higher levels of imposex in this species than in other places from the Southern Coast of Portugal. In addition, intersex with several degrees of intensity was also detected in the clam *S. plana* with oocites inside the male testis (ovotestis). The percentage of males affected were in the range between 6 to 71%, which can induce a decrease in the sex ratio of the future population of these species. Besides TBT, several other endocrine disruptor contaminants (EDCs) can be found in water and sediments, including already mentioned PAHs (phenantherene, pyrene, etc.), but also pesticides and their metabolites (atrazine, simazine, prometryn, among others), or herbicides (diuron and bisphenol A). These EDCs, although in small amounts, may also be directly linked with the levels of intersex and imposex detected in the clams or even with other examples of alterations of the endocrine system of marine invertebrates already detected in the Guadiana River.

7.8. New emerging contaminants

The new emerging contaminants, composed essential by personal care products (PCPs) and pharmaceutical compounds (PhACs) gained increasing attention due to their huge consumption and potentially harmful effects detected in the aquatic environment.

Levels of three UV filters used in personal care products such as sunscreens but also in food additives and two types of musk (galaxolide and musk-ketone) used in fragrances are recognized as important organic stressors in the aquatic environment due to their lipophilic properties and potential bioaccumulation. These compounds were detected in mussels *M. galloprovincialis* collected from the beach on the mouth of the Guadiana estuary. Levels of UV filters were higher than galaxolide musk while Musk-ketone, although detected in all samples, had concentrations close to the lower limit of analytical detection. It is important to highlight the fact that, once in the water, musk-ketone produces amino-musk that is another well-known endocrine disruptor compound. These results indicate that the sources of these compounds are not only from direct bathing activities but might also be from wastewater discharges.

On the other hand, other emergent contaminants, such as pharmaceutical products, are used for centuries in human health therapy and are ubiquitous in the environment. However, due to their bioactive action and presence in several types of water bodies they were classified as emerging environmental contaminants. One of the pivotal goals of the Water Framework Directive (WFD) is therefore the need to assess the concentration of these contaminants in water bodies. One of the means to detect the presence of these compounds in the aquatic environment is by using passive samplers known as Polar Organic Compound Integrative Sampler (POCIS, Figure 7.8). These passive samplers were designed to tackle the difficulty of biological data interpretation. Although designed to mimic biological uptake, they also provide a time-weighted average concentration of these pesticides and pharmaceutical compounds, which is a more holistic approach of the water quality status than spot sampling of a water body.

Figure 7.8.
Photography of three Polar Organic Compound Integrative Sampler (POCIS) within their metallic holder, retrieved after staying 30 days in water (photography by Maria Gonzalez-Rey).

With the help of these passive samplers (POCIS), the presence of eleven pharmaceutical compounds were detected in the Guadiana estuary (Figure 7.9), namely in decreasing order of concentrations: paracetamol (analgesic), theophylline and clenbuterol (antiasthmatic), carbamazepine (antiepileptic), gemfibrozil (Lower lipid agent), nordiazepam (anxyolitic), naproxen and diclofenac (anti-inflammatory), alprazolam

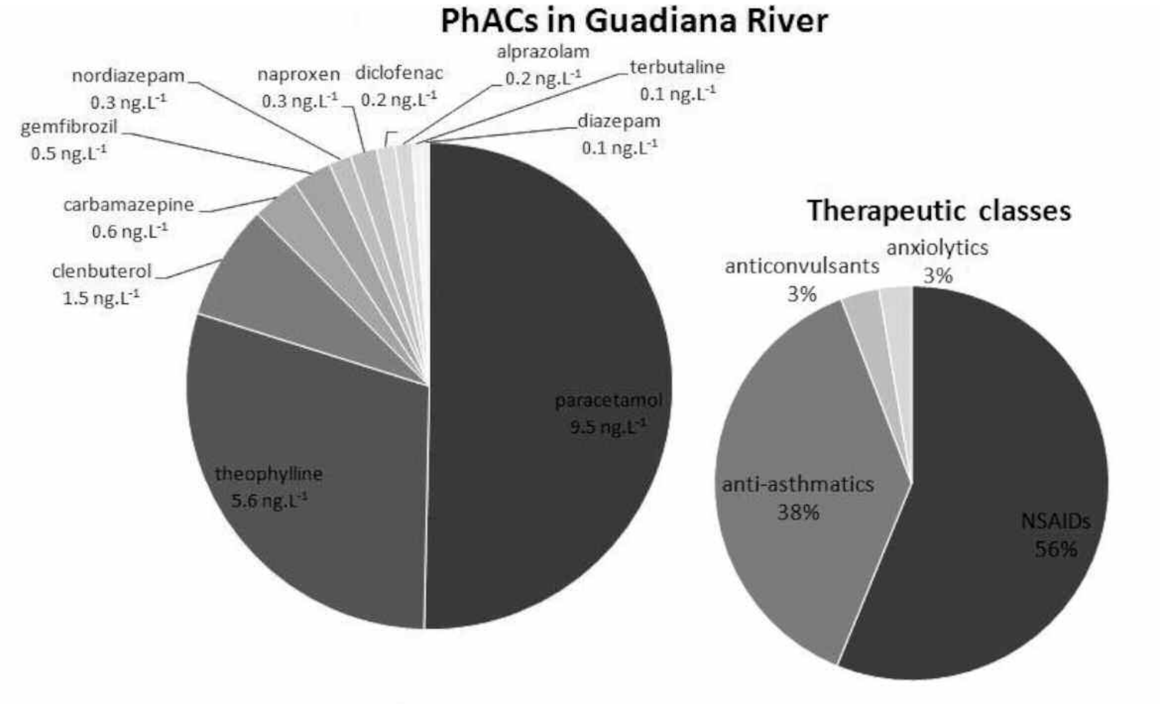


Figure 7.9.
Concentration and therapeutic classes of Pharmaceutical compounds (PhACs) in the Guadiana River.

(antidepressants), terbutaline (antiasthmatic) and diazepam (anxyolitic). Comparing the concentrations of pharmaceutical therapeutic classes obtained in the Guadiana revealed that the highest percentage represents analgesic compounds (51%), followed by the antiasthmatics (38%) and a similar percentage of antiepileptic, lower lipid agent and anti-inflammatory (3%) and lower and similar levels of anxyolitics and antidepressants (1%). Comparing these levels with those found in the same period in the Arade river, it appears that the concentrations of anti-inflammatory (naproxen and diclofenac) were 2-fold lower in the Guadiana River and that Ibuprofen, fluoxetine and bromozepam were present in the Arade and not detected in the Guadiana River. The presence of diclofenac anti-inflammatory in the Guadiana River is a cause of concern due to the known biological effects of this compound, reason why it was included , and by the European Union in the list of priority substances of WFD.

7.9. Conclusion

Although one of the major rivers of the Iberian Peninsula, the Guadiana River presents detectable, and some times high, levels of traditional contaminants (metals but also persistent organic compounds) as well as of emerging compounds (personal care products and pharmaceutical compounds), some of which are known to induce endocrine disruption contaminant (EDC) effects. In most of the cases, the detected levels are higher that in other parts of the Southern Portuguese Coast. These chemical stressor levels detected have already shown some effects in the aquatic species, which might be a cause of concern for the economy and the health of the Guadiana River.

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