RIA FORMOSA

Challenges of a coastal lagoon in a changing environment

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

UAlg CIMA
UNIVERSIDADE DO ALGARVE
CENTRO DE INVESTIGAÇÃO MARINHA E AMBIENTAL

8. Human impact in the Ria Formosa lagoon

Maria João Bebianno, Patrícia Pedro, Ângela Serafim, Belisandra Lopes & Alice Newton

Centre for Marine and Environmental Research (CIMA), University of Algarve, Campus de Gambelas, 8000-139 Faro, Portugal

mbebian@ualg.pt; aserafim@ualg.pt; blopes@ualg.pt; anewton@ualg.pt

8.1. What is this chapter about?

The Ria Formosa lagoon is a complex, economic, social-ecological system that provides valuable ecosystem services and benefits for the region. Nevertheless, the presence of hazardous substances such as metals, persistent organic compounds (POPs), polycyclic aromatic hydrocarbons (PAHs) and emerging contaminants, including personal care products (PCPs) and pharmaceutical compounds, is a cause of concern for the sustainability of the lagoon. It can be concluded that the Ria Formosa lagoon is in danger, therefore management decisions need to be taken to reduce discharges and enable remediation. These will both protect and depollute, in order to decrease the impact of the mixtures of hazard substances and improve economic sustainability in the future.

8.2. Impacts of the Human activities in Ria Formosa

The Ria Formosa lagoon is a complex, economic, social-ecological system that provides valuable ecosystem services and benefits to the resident population and visitors (Newton et al., 2013; Newton et al., 2018). Nevertheless, some human activities in and around the Ria Formosa introduce contaminants (see Box 8.1) and hazardous substances (see Box 8.2) to the lagoon, degrading the environmental and ecological status of this important ecosystem.

In this chapter, we analyze the relationship between the causes and consequences of this degradation using a DPSIR approach (see Box 8.3). Looking first at the high-level DRIVERS, the Ria Formosa and catchment are important for food security. The area surrounding the lagoon, the 'Campina de Faro' is now increasingly urbanized, but there is still some agricultural activity. This is mainly production of citrus, corn, almonds and red fruits, including hydroponic production. There is some intensive agriculture in greenhouses, which are easily visible from satellite photographs (Figure 8.1). Animal rearing, both on land (poultry and pigs) and in the lagoon (fish) are also important. Food capture includes shellfish harvesting and fisheries. In particular, shellfish harvesting in the Ria Formosa represents 80-90% of total bivalve production of Portugal. The bivalves grow and breed in the intertidal areas of the lagoon that are directly influenced by the different pressures. Salt extraction remains an important industry as can be seen from satellite and aerial photographs (Figure 8.2). There are also large areas devoted to leisure, such as golf courses and swimming pools.

Box 8.1.

Contamination: Introducing any substance into water decreases its purity. So, putting lemon into a glass of water is a contamination, even if it is harmless.
Pollution: If the substance that is introduced into the water is harmful, such as a poison, then this is considered to be pollution and has recently be designed as hazardous substances.

Figure 8.1.
Satellite view showing greenhouses and salt pans between Faro and Olhão (Google Earth, 2018).

Figure 8.2.
Aerial photograph showing salt extraction (photograph by Tomasz Boski, 2009).

So, the main economic sectors and corresponding stakeholder groups around the lagoon include sand and salt extraction, agriculture, animal rearing, aquaculture, fisheries, food processing, golf, tourism, and real estate. The increase of waste production from these result in consequent pressures to the lagoon. Not all activities from these economic sectors result in the release of hazardous substances to the lagoon, but some do. The inputs of these various substances reach the lagoon by atmospheric deposition, river discharges, agriculture and road runoff, runoff from golf courses, sewage effluent, effluent from animal rearing and aquaculture industrial effluent, effluents and emissions from harbours marinas and boats. In addition, there is marine litter from fishing and tourism.

Box 8.2. Hazardous Substances and Priority Substances

What is the difference between Priority Substances, Hazardous Substances and Priority Hazardous Substances? Contaminants and pollutants are grouped in several categories as Hazardous Substances (https://www.ospar.org/work-areas/hasec/chemicals); Priority Substances and Priority Hazardous Substances (Directive 2008/105/EC).
Hazardous substances: Substances or groups of substances which are either (i) toxic, persistent and liable to bioaccumulate; or (ii) assessed by OSPAR as giving rise to an equivalent level of concern
Priority Substances: 33 substances or groups of substances for which environmental quality standards were set in Directive 2008/105/EC.
Priority Hazardous Substances: a subset of Priority Substances, of which they are the most dangerous. They are characterised by their persistence, bioaccumulation and toxicity, or by an equivalent level of concern.

What types of substances contaminate and pollute the Ria Formosa?

Nutrients and organic matter: these mainly come from fertilisers and animal wastes, including sewage, as well as food processing. They are not toxic but promote algal and bacterial blooms that can affect the water quality, especially clarity and oxygen.
Metals (Cd, Cr, Cu, Hg, Pb and Zn) occur naturally in the marine environment. Some like cadmium, mercury and lead are highly toxic and therefore are considered priority substances in the Water Framework Directive. Others like copper and zinc are essential to biota. In excessive amounts, they become toxic and even at lower levels they can affect the immune systems or the reproductive success of biota. Cadmium is used in batteries, paints, combustion plants, electroplating and incinerators. Mercury is applied in electrolysis chlor-alkali plants, combustion plants and gold exploitation. Lead and organic lead compounds were used in fuel for internal combustion engines, paint and as PVC (Polyvinyl chloride) stabilizer. For the essential metals, Cu is extracted from copper mining, and used in electric wiring, machinery, antifouling paints and in pesticides while zinc is used in combustion plants; surface treatment of sheet metal and cosmetics.
Tri-Butyl Tin (TBT): is an organotin compound found in the marine environment from different sources, but mainly from antifouling paint coatings of ship hulls and from agricultural runoff. Once released to the marine environment, TBT partitions between the dissolved phase or is adsorbed onto suspended particulates and settles in sediments, becoming bioavailable to biota through a combination of these compartments and from contaminated food. The effects include shell malformation in oysters, which reduces growth. TBT also causes imposex in neogastropod whelks, turning females into males by superimposition of male characters - a penis and a vas deferens- onto females of gonochoristic gastropods. This causes a population decline in the whelks.
Persistent organic pollutants (POPs): In contrast with metals, POPs are not natural compounds and are made by humans. They include in their composition carbon, hydrogen with halogens like chlorine or bromine or other halogens that resist to degradation. Some are used as biocides (insecticides, herbicides, etc.) while others are used in industrial processes. They are included in the Stockholm Convention on Persistent Organic Pollutants; a legal mechanism established to control the production and use of POPs. Among them 12 POPs should be banned or strictly controlled and further 10 POPs were subsequently included.
Polycyclic aromatic hydrocarbons (PAHs): PAHs are compounds consisting of benzene rings with carbon and hydrogen and, in some cases nitrogen, oxygen or sulphur. Unlike POPs, they occur naturally and can be created by imperfect combustion processes. Some of them are carcinogenic and/or can affect the reproductive system.
Contaminants of emerging concern: In this category Personal Care Products (PCPs), pharmaceutical compounds and micro and nanoparticles are included. PCPs include substances used for personal health or cosmetic reasons. Nanoparticles are particles whose size range from 1-100 nm. They can be metal, metal oxide or carbon based.
Endocrine disruptors: Endocrine disruptors are exogenous substances or mixture of substances that can alter the endocrine system and consequently causes adverse health effects in an organism.

Due to the restricted circulation within the inner part of the lagoon (only 70% of the water is daily exchanged with the Atlantic Ocean), many of the hazardous substances discharged from the land or from the atmosphere concentrate within the lagoon and the blind ends are particularly affected. Only the regions with direct access to the sea, such as the principal shipping channels (from Farol and Olhão channels) are routinely flushed, but these channels receive oil and other contaminants from shipping activities.

Box 8.3.

The analysis follows a Driver-Activity-Pressure-State-Impact on Human welfare approach, modified from the DPSIR (Driver-Pressure-State-Impact-Response) framework, (Gari et al., 2015) according to Elliott et al. (2017). The DPSIR framework has been chosen for this analysis because it was selected by many international institutions, such as the European Environment Agency (EEA), the Food and Agriculture Organisation (FAO) and recently by the United Nations (UN) as the basis for the second World Ocean Assessment.

8.3. What are contaminants and where are they coming from?

Contaminants include nutrients, especially from fertilisers containing Nitrogen and Phosphorus, which can result in eutrophication (Newton et al., 2003). Inputs of organic matter, for example from sewage, increase the Biochemical Oxygen Demand and can result hypoxia or anoxia.
The Ria Formosa lagoon receives the discharge of effluents from 28 domestic and industrial wastewater treatment plants (WWTPs), twelve of which release their effluents directly to the lagoon (Figure 8.3).

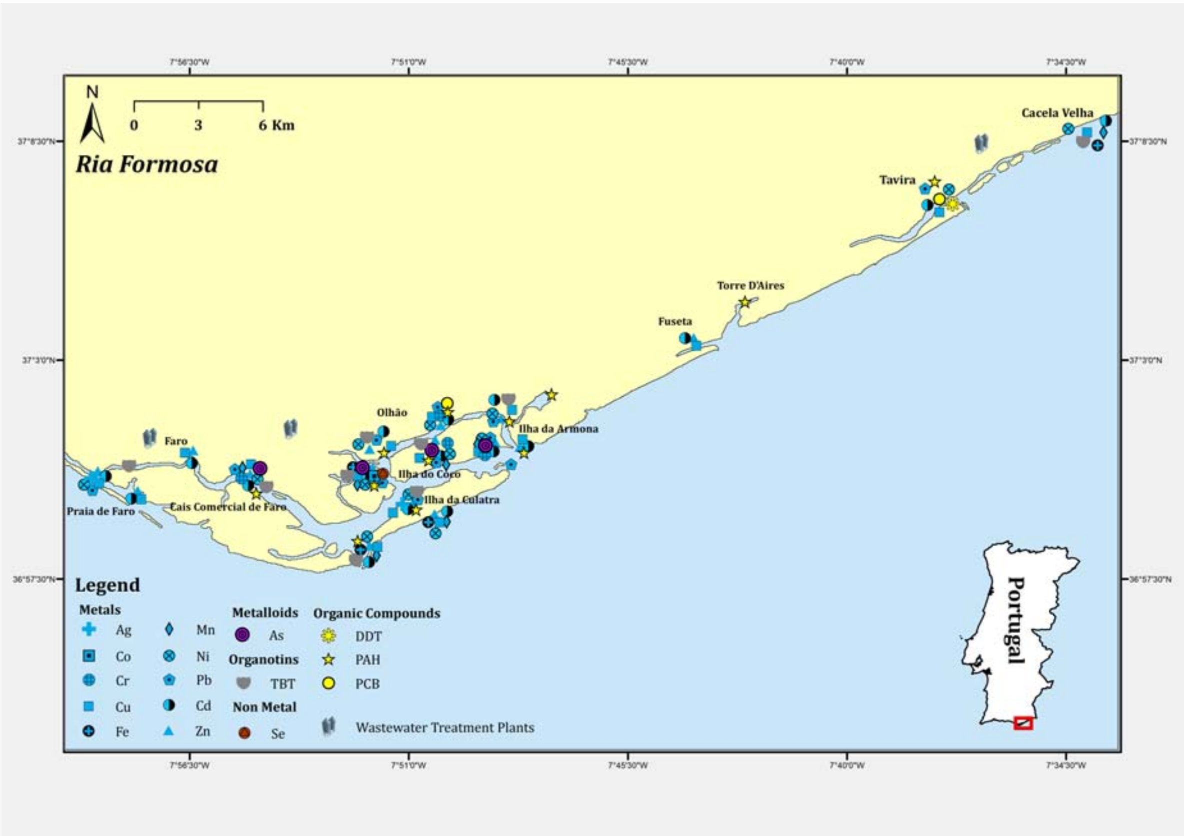

Figure 8.3.
The different hazardous substances detected in the lagoon.

Treatment of domestic sewage was insufficient until the middle 90s. However, sewage treatment has now improved so domestic sewage is treated in urban waste water treatment plants (UWWTP) using secondary treatment (activated sludge + UV and lagoon systems) serving a population equivalent of around 300 000 inhabitants. Sewage contamination in the lagoon has been monitored and detected including using lipid biomarkers such as cholesterol (Mudge et al., 1998). Pressures from nutrient and organic matter inputs can result in a change of environmental status, such as low oxygen, and ecological status, such as excessive algal blooms (Figure 8.4).

Figure 8.4.
Flushing of the Ria Formosa. The blue channel at the back is well flushed, whereas the water in the area at the forefront has been trapped for several days, time enough for an impressive algal bloom to develop (Photograph by Stephen Mudge, 2005).

8.4. What are hazardous substances and what are their impact on living resources?

Hazardous substances include metals and organometallic compounds, persistent organic compounds (pesticides), hydrocarbons, personal care products, pharmaceuticals and plastics. These have been detected in the Ria Formosa water, sediments and biota, posing serious risks to the biodiversity, to the economic development of the lagoon and to human health (see Box 8.2 for definitions). These adverse effects include acute toxicity, a threat to food safety and other impacts to human health such as an increase of cancer cases, weakness of the immune system, reproductive alterations and mutations in future generation.

Hazardous substances like metals (Cd, Cu, Cr, Ni, Pb and Zn) (Bebianno, 1995) and polycyclic aromatic hydrocarbons (PAHs) have been detected in water, sediments and bivalve species. The concentration of these hazardous substances is highly dependent on temperature, salinity, pH, tidal cycle, currents and seasonality. To assess the impact of these hazardous substances "canary species" known as sentinel or bioindicator species are used. Examples are the mussels *Mytilus galloprovincialis,* clams *Ruditapes decussatus* and oysters *Crassostrea gigas*, because they integrate the concentration of hazardous substances in space and time and the concentrations are a measure of their bioavailability. However, chemical analysis of concentrations of hazardous substances in bioindicator species does not give information on the biological effects that can affect health. Therefore, it is essential to also determine early warning systems, known as biomarkers, at molecular, cellular and tissue levels to assess the health of the species. In addition, hazardous substances are generally present as mixtures and the assessment of their cumulative impact is crucial to protect the environmental quality of the lagoon and human health. Figure 8.5 shows the different species in which contaminants have been detected.

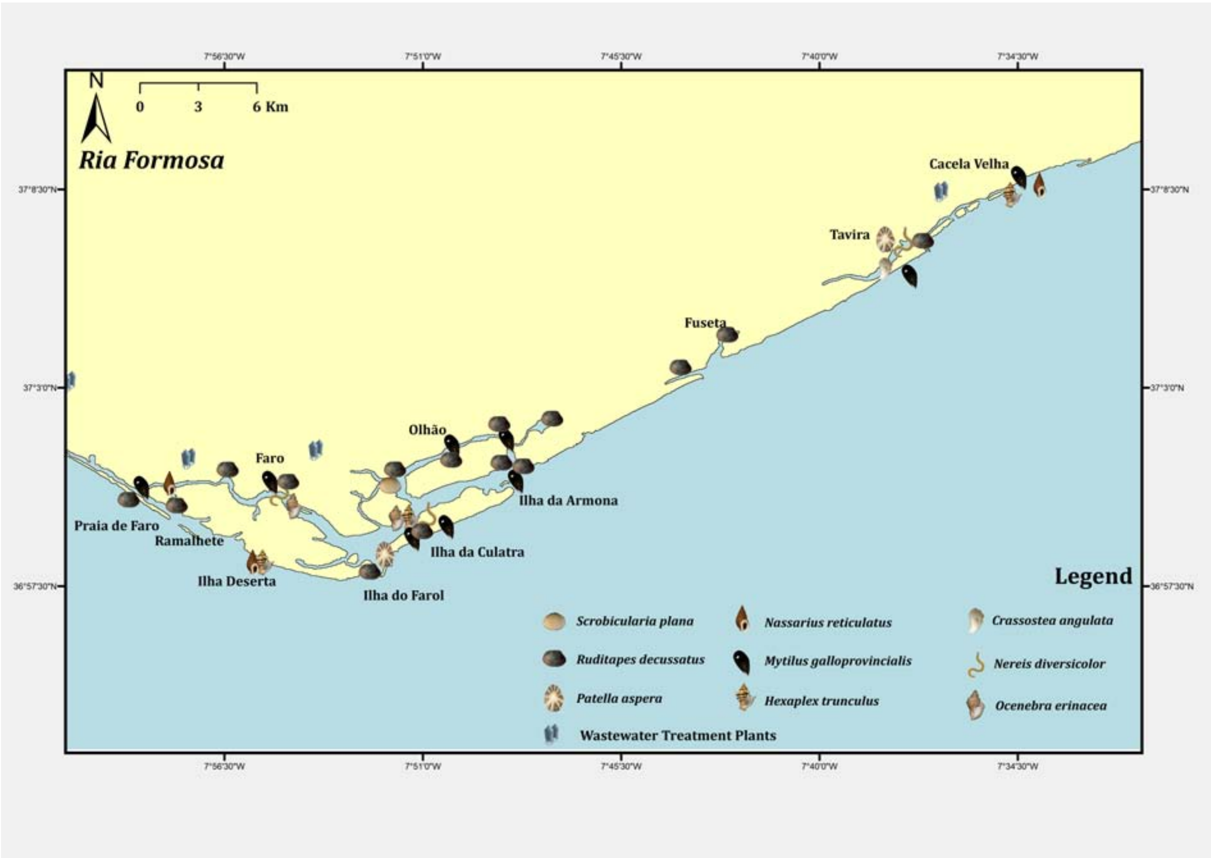

Figure 8.5.
The different species in which contaminants have been detected.

8.4.1. Metals and Tributyltin (TBT)

Among the metals, Cd, Cu, Hg, Pb and Zn are included in the priority list of the Water Framework Directive (additional information about Directive no76/464/CEE is available at_https://eur-lex.europa.eu/legal-content/FR/ALL/?uri=CELEX%3A31976L0464) due to their toxicity, persistence and bioaccumulation. Their presence in the lagoon was first detected in the 1970s, but metal levels were more regularly monitored after the 1990s. The trends for the various metals in the Ria Formosa (water, sediment and bivalves) are summarized in Table 8.1. This also shows the trend for TBT, Tri-Butyl Tin (see Box 8.2).

Table 8.1.
Summary of trends of metals in the Ria Formosa water, sediment and shellfish since the 1970s.

Metal	Water	Sediment	Shellfish	Hotspots
Cd-Cadmium	↘	↘		Near urban centres (Faro and Olhão)
Cu-Copper	↘	↘	↗	Olhão
Hg-Mercury	↔			
Pb-Lead	↔	↘	⌒	Inner parts of the channels
Zn-Zinc	↔	↘	⌒	Olhão, Tavira
TBT	↘	↘	↔	Olhão

8.4.2. Persistent Organic Pollutants (POPs)

This large group of organic substances are banned since 2001 by the Stockholm convention on persistent organic pollutants (POPs). They include many types of pesticides, such as fungicides, herbicides and insecticides, Polychlorinated Biphenyls (PCBs) and Polycyclic Aromatic Hydrocarbons (PAHs). The trends for the various POPs in the Ria Formosa (water, suspended particulate matter and bivalves) are summarized in Table 8.2.

Table 8.2.

Summary of trends of POPs in the Ria Formosa water, suspended particulate matter (SPM) and shellfish.

POPs	Water	SPM	Shellfish	Hotspots
Herbicides	↘	↘		
Fungicides	↘	↘		
General			↘	31% exceed 2008/105/ EC and 98/83/EC
DDT				Still detected although banned in 1970s
Dichlorvos				35 times higher than 2013/39/EU
Heptachlor				80 000 times higher than 2013/39/EU
PCBs	↗			Tavira, Armona
PAHs	↗	↗		Olhão

Pesticides

Organochlorine pesticides used in agriculture are known to induce hormonal disruption and cancer. In the Ria Formosa lagoon, fifty-six pesticides have been detected in water and, in suspended particulate matter. 31% of the pesticides detected exceeded the European directives levels (2008/105/EC and 98/83/EC) (additional information is available https://eur-lex.europa.eu/eli/dir/2008/105/oj and https://eur-lex.europa.eu/ legal-content /EN/TXT/?uri=CELEX%3A31998L0083). However, the data suggest that herbicide contamination is generally decreasing and there is a (2-fold) decrease in fungicides (Cruzeiro et al., 2015). The insecticide dichlorodiphenyltrichloroethane (DDT) has been used extensively worldwide in agriculture and for vector control since 1939 (Turusov et al., 2002). Nowadays, the use of DDT is restricted to disease vector control especially for malaria or as an intermediate in the production of dicofol (Stockholm Convention on Persistent Organic Pollutants, 2008). The major metabolite of DDT is pp'-dichlorodiphenyldichloroethylene (pp'DDE). Thus, despite the ban in the seventies of the last century, DDT/DDE are still marketed and used in many countries, and therefore still extensively widespread in the environment (Lopes et al., 2014). However, recently 4,4-DDT residues (both in dissolved phase and solid phase matter (SPM) detected were higher than its metabolites which indicates a continuous source to the lagoon. Therefore, DDT is still being used, despite of being banned from Europe in the 1970s. Cumulative levels of pesticides (3.1 g/L) were higher than the maximum established by the Portuguese law 236/98 and the 98/83/EC European Directive (water intended for human consumption) (additional information is available https://data.dre.pt/eli/dec-lei/236/1998/08/01/p/dre/pt/html and https://eur-lex.europa.eu/legal-content/EN/TXT/ ?uri=CELEX%3A31998L0083). When comparing the maximum levels (annual values for inland and surface waters) with those defined in the 2013/39/EU directive (additional information is available https://eur-lex.europa.eu/legal-content/EN/ALL/ ?uri=CELEX% 3A32013L0039), dichlorvos and heptachlor were 35- and 80,000-fold higher. The same pesticides were analysed in the whole soft tissues of the suspended feeder peppery furrow shell *Scrobicularia plana* and 83% of the data was above the legal limits set by the European Directive 2013/39/EU (additional information is available https://eur-lex.europa.eu/legal-content/EN/ALL/?uri=CELEX%3A32013L00 39). As for the other pesticides there was a decreasing trend (5-fold) between 2010 and 2012/2013 (Cruzeiro et al., 2016).

Polychlorinated Biphenyl (PCBs)

Organochlorine compounds comprise a heterogeneous category of highly toxic organic compounds designed for industrial applications. They have been banned or severely restricted since the 1970s and 1980s in North America and Europe due to their persistence and bioaccumulation in the environment, biomagnification in food chains, and capacity for long-range atmospheric transport (Negoita et al., 2003). The main PCBs source appears to be the Gilão river (Barreira et al., 2005; Ferreira & Vale, 1995). Total PCBs are higher in suspended matter than in the sediments, and concentrations are related to the organic matter content and the particle size. These also influence PCB distribution, so the major transport and redistribution are dependent upon the hydrodynamics of the lagoon. About 60% of the total PCBs detected are tri- and tetra-chlorinated biphenyls were the most abundant congeners, followed by the hexa (20%), penta (11%) and hepta+octachlorobiphenyls (9%) (Barreira et al., 2005) while previous data showed that tri- and tetra-biphenyls represented 27%, penta 11%, hexa 40% and hepta and octachlorobiphenyls 22% (specially at Tavira) (Ferreira & Vale, 1995) indicating a dechloronization of the PCBs. Historical data revealed that low concentrations were detected in the whole soft tissues of the oysters and clams. However, recently there is an increasing trend (3.6-fold) in the dissolved fraction of PCBs (Cruzeiro et al., 2015; 2016).

Polycyclic Aromatic Hydrocarbons (PAHs)

PAHs are considered priority organic substances, because they are human carcinogens and toxic to aquatic life. The main sources are urban runoff, atmospheric deposition as well as maritime traffic. PAHs concentrations are directly related to the organic matter content, like for PCBs. Hence, the organic carbon content has a strong influence on the PAH distribution in the lagoon (Barreira et al., 2007). Historically data revealed that the concentration of non-polar hydrocarbons in water varied between 0.5 and 0.6 mg/l, while in sediments, levels ranged from 4 g/g (in 1994) to 30 g/g (in 1998) (IH, 1998). These levels are lower than the ecotoxicological assessment criteria (EAC) set for sediments by OSPAR Commission (OSPAR, 2000) and therefore are considered slightly contaminated (PAHs< 250 ng/g) and have a marked petrogenic origin. In winter, PAH sources are mainly from pyrolytic origin, probably transported by urban runoff while in the summer it is from atmospheric deposition as well as from maritime traffic.
The highest concentration in mussels was from those collected at Olhão. PAH levels in mussels were of the same order of magnitude of those previously found in the south coast of Portugal, but lower than in mussels from areas affected by oil spills or tanker accidents (Cravo et al., 2012).
Like for the other hazardous substances, the consumption of PAH contaminated clams raises concern for human health. Most of the clams analysed are safe for human consumption, except from some particular clam beds with unusually high PAH concentrations, suggesting the need for a regular survey of PAHs levels in clam tissues.

8.4.3. Endocrine Disruptors

Endocrine disruptors include a group of "priority" substances linked to several endocrine disorders in humans. The industrial hazardous substances octyl- and nonylphenoland bisphenol (BPA) were banned in Europe in 2003 (Directive 2003/53/EC additional information is available https://eur-lex.europa.eu/LexUriServ/ LexUriServ.do?uri=OJ:L:2003:178:0024:0027:en:PDF) due to their estrogenic effects to wild fauna and humans. All these compounds are highly hydrophobic and so they adsorb to particulate matter and settle into sediments where their concentrations may be even higher, triggering endocrine disruptor effects to the biota and pose directly (bathing) or indirectly (contaminated seafood) risks for humans.

BPA is ubiquitous in the lagoon, with levels always higher than the maximum established in European legislation for surface waters (10 ng/L). On the other hand, some estrogens like EE2, also present in the lagoon can induce effects in bivalves and fish (Rocha et al., 2013). Feminization of the clam *S. plana* was already reported in the region and there is a cause of concern (Gomes et al., 2009), since this could have a negative impact on the economically important shellfish and the long-term sustainability of the lagoon. The main inputs of estrogens into the lagoon are from human and animal excretion transported by WWTPs effluents or from runoff. Levels are higher in the summer indicating that these compounds are linked to the increased population from visitors and touristic activities. The new WWTP that is being built might change the situation, so there is a need for a continuous monitoring programme.

8.4.4. Personal Care Products (PCPs)

Personal Care Products (PCPs) have been recognized as important organic contaminants of the aquatic environment due to their lipophilic properties and their potential for bioaccumulation (European Parliament, 2007). They have recently attracted attention due to their widespread use and the negative impact they have in the aquatic environment. PCPs include UV filters used in cosmetics and sunscreens to prevent chemical degradation and skin damage against sunlight irradiation. They also include synthetic musks used in fragrance ingredients and as washing and cleaning agents, which also have a potential endocrine disruption effects in marine organisms. Three UV filters (EHMC, OC and OD-PABA) and a musk (galaxolide) have been detected in mussel tissues from a beach outside the Ria Formosa lagoon (Picot Groz et al., 2014).

8.5. Impact on human health

Humans are exposed to multiple substances that can have hazardous effects on health. Numerous hazardous substances can be transported by the food chain and contaminate the food sources for human consumption. In this context, metals, PCBs, PAHs and organochlorine pesticides are among the most important contaminants to be considered. Although the levels of hazardous substances in Ria Formosa in both biotic and abiotic compartments have been identified, it is largely unknown the impact of these substances on the health of local human populations. Exposure to different pollutants is assessed by biomonitoring of blood serum, urine, adipose tissue, meconium, milk, placenta, hair and nails.

Over the past two decades numerous studies have linked the exposure of pregnant mothers to hazardous substances to several diseases in the newborn children. These hazardous substances can pass through the placenta, via the umbilical cord, and into the newborn children. The vulnerability of newborn children derives from both rapid development and incomplete defense systems. Children face amplified, lifelong risks from their body burden of these hazardous substances. The consequences can surface not only in childhood but also in adulthood.

8.5.1. Metals

The global increase of metals in the environment, their tendency to accumulate in humans, and their potential to be toxic even at low concentrations raise special concern about adverse effects on sensitive

segments of the population such as newborns. The health risks associated with in utero exposure to metals were studied extensively in the last few decades. In fact, there is increasing evidence regarding the threats posed on pregnancy outcomes and/or adverse developmental effects at levels lower than international guidelines, and therefore environmental exposures need to be as low as possible.
Toxic metals may act as mimics of essential metals, binding to physiological sites that normally are reserved for an essential element. Through mimicry, they may gain access to, and potentially disrupt, a variety of important or even critical metal-mediated cellular functions. Mimicry for and replacement of Zn is a mechanism of toxicity postulated for cadmium (Cd), cooper (Cu), and nickel (Ni) (Cousins et al., 2006). Another mechanism of metal toxicity is based on oxidative damage to important cellular components. Research studies in the IN-Health cohort (Project In-Health - Materno-Infant health related to environmental factors (PTDC/SAU-SAP/121684/2010)) with women living in south of Portugal, at the major cities of the Ria Formosa, identified non-essential metals with recognized toxicity (Cd, Hg and Pb) in all mother and umbilical cord samples, indicating that these metals have the capacity to circulate in the blood stream and/or transpose the placenta, reaching the fetus. Spatially, Cd levels were higher in women from Faro and Olhão relatively to Tavira. Contrarily, the highest Hg levels were detected in women from Tavira while Pb levels were elevated in women from Olhão. Although the south coast of Portugal is not a heavily industrialized area, metal levels found in these populations are at the same order of magnitude as those found by other authors in European countries (Serafim et al., 2012). The data are summarized in Table 8.3.

8.5.2. Persistent Organic Pollutants (POPs)

Pesticides

These compounds are highly persistent to degradation or metabolism. They are highly lipophilic so tend to accumulate in adipose tissues. Furthermore, they are suspected potent endocrine disrupters. Although banned, they continue to be manufactured by many other countries, and the presence of these hazardous substances in human serum, milk and adipose tissue have been reported (Cruz et al., 2003). For the general population, the greatest exposure to pesticides is from food intake. Since many of the chemicals are soluble in fat, the highest levels are found in meat, fish and dairy products. Little is known about the possible effects of pesticides in humans when exposed for long periods of time to small concentrations, but evidence of mother to child transfer has been reported. On the other hand, leukemia, non-Hodgkin's lymphoma and other cancers, neurologic pathologies, respiratory symptoms and hormonal and reproductive abnormalities have been associated with pesticide exposure, mostly in case-control and ecological studies. Human prenatal exposure to organochlorine pesticides has been associated to adverse developmental effects, including preterm birth and reduced birth weight, growth retardation, altered psychomotor and cognitive functions and effects on thyroid hormonal status (Asawasinsopon et al., 2006).
In Portugal, according with the legislation (Decreto-Lei nº 347/88 and Portaria nº 660/88) (additional information is available https://dre.tretas.org/dre/1709/decreto-lei-347-88-de-30-de-setembro#in_links and https://dre.tretas.org/dre/163955/portaria-660-88-de-30-de-setembro) most of the organochlorine pesticides were prohibited in 1980s, but they can be found in the environment even decades after being banned (Cruz et al., 2003). In the south of Portugal, they have been extensively used as pesticides in orange groves and greenhouses, and some authors have reported the presence of pesticides in the rivers and groundwaters of Portugal, primarily in association with the wide range of agricultural practices (Palma et al., 2014).

Levels of ***DDE***, the major metabolite of DDT was found in women living in the south of Portugal, whose main path of exposure and therefore accumulation is diet. Levels of DDE were highest in women living in Tavira (1.61 ng/ml mother/ 1.17 ng/ml newborn), followed by Olhão (1.06 ng/ml mother/ 0.79 ng/ml newborn) and Faro (0.98 ng/ml mother/ 0.76 ng/ml newborn) (Lopes et al., 2014).

Drines: Aldrin, dieldrin and endrin have been used as pesticides in agriculture. Although there are different routes of exposure for humans, it has been established that ingestion of food contributes more than 90% of total human exposure, and that the fatty fraction represents the main entrance to the human body. Aldrin is toxic to humans; the lethal dose of aldrin for an adult man has been estimated to be about 5g, equivalent to 83 mg/kg body weight (Hanley et al., 2002). Signs and symptoms of aldrin intoxication may include headache, dizziness, nausea, general malaise, and vomiting, followed by muscle twitchings, myoclonic jerks, and convulsions. Occupational exposure to aldrin, in conjunction with dieldrin and endrin, was associated with a significant increase in liver and biliary cancer (Taylor et al., 1996). Dieldrin is ubiquitous in breast milk and it is found in more than 99% of samples tested in most countries. Because dieldrin is attracted to fat, the level of dieldrin in a mother's milk is generally about six-fold higher than in the blood. WHO found, surprisingly, that the concentration of dieldrin in the blood and bodies of breastfeeding babies did not increase with age during their first six months of life.

In the IN-Health cohort aldrin, dieldrin and endrin were found in all mother and newborn babies. Aldrin presented the highest concentrations, representing about 62-73% of total –drins (-drins=aldrin+endrin+dieldrin), followed by endrin and dieldrin. Overall concentrations of –drins detected in mother and umbilical cord serum were higher in Olhão (9.56 ng/ml mother/ 9.12 ng/ml newborn; aldrin accounts for 62/62 % of total) and Faro (9.37 ng/ml mother/ 8.89 ng/ml newborn; aldrin accounts for 67/66 % of total), and minimum at Tavira (8.70 ng/ml mother/ 9.0 ng/ml newborn; aldrin accounts for 73/66 % of total) (data not published).

The ban of ***hexachlorobenzene*** (HCB**)** as a fungicide led to a significant decrease in its environmental concentration, but it is still being used in the chemical industry and is a by-product of chlorinated solvent production. Moreover, some of the HCB in the soil evaporates into the air, so it is likely that people will be exposed to this compound at levels similar to the current concentrations for some time. Although exposure to HCB in the general population decreased in recent years, there is some evidence of an association between exposure and fetal growth abnormalities and/or reduction in the length of gestation (Basterrechea et al., 2014). Levels of HCB found in people living in the south of Portugal were similar in Faro and Olhão (0.29 ng/ml mother/ 0.22ng/ml newborn and 0.29 ng/ml mother/ 0.20 ng/ml newborn, respectively, and lower in Tavira (0.11 ng/ml mother/ 0.10 ng/ml newborn) (not published).

Endosulfan **(**a dienic compound containing atoms) is still used in several industrialized countries, as it is indicated both in non-food crops, such as cotton and tobacco, timber, and ornamental cultures, and in food crops, such as vegetables, fruits, corn, cereals, oilseeds, potatoes, tea, coffee, cacao, and soy bean. They were also used to control termites and tsetse fly in the past (Cerrillo et al., 2005).

In the South of Portugal, levels of Endos (=alpha+beta+ether+lactone) where similar in Faro (12.50 ng/ml mother/ 11.62ng/ml newborn), Olhão (12.73 ng/ml mother/ 12.51 ng/ml newborn) and Tavira (12.88 ng/ml mother/ 13.17 ng/ml newborn). However, at all sites endosulfan alpha is the major metabolite both in mothers as in newborns, varying from 3.69 to 4.10 ng/ml and representing 29 and 32% of Endos, followed by endosulfan lactone, beta and ether, with minimum concentration varying from 0.68 to 0.92 ng/ml.

Vinclozolin, [3-(3,5-dichlorophenyl)-5-methyl-5-vinyl-oxazolidine 2,4-dione], is a widely used fungicide in fruits, vegetables and wines. It is one of several dicarboximide fungicides currently registered for use in the United States of America and in Europe (U.S. Environmental Protection Agency, 2003). Vinclozolin is a potent androgen antagonist and a cytotoxic compound with endocrine disruption capabilities. Whereas vinclozolin itself is not persistent, it's two metabolites display half-lives of more than 180 days and are

likely to be highly mobile in the water phase. There is little data available on human exposure to vinclozolin in and its possible effects on reproductive health. However, in an occupational study, where the morbidity of the personnel involved in the synthesis and formulation of this chemical was thoroughly investigated, an increase in testicular abnormalities was reported in the study group compared with controls (Zober et al., 1995).
Levels of vinclozolin of 2.02/1.75 ng/ml were found in women/newborn from the IN-Health cohort living in Faro; 2.0/1.61 ng/ml in women/newborn from Olhão and 1.50/1.89 ng/ml in women/newborn from Tavira. The data are summarized in Table 8.3.

Polychlorinated Biphenyl (PCBs)

Food intake is probably the most important source of PCB for the general population, and the consumption of fat rich foods (eggs, cheese, milk, butter, meat, fish and seafood) is one of the most commonly causes of PCB increase found in humans. Health effects associated with exposure to PCBs include skin conditions, liver diseases in adults and neurobehavioral and immunological changes in children, reduced birth weight and pre-term birth.
Three congeners of PCBs (138, 153 and 180) were found in the IN-Health cohort, in all samples of both mother and umbilical cord serum. Overall highest levels of PCBs found in these cohort (PCBs=PCB138+PCB153+PCB180) were found in women that live in Tavira (PCBs 1.78 ng/ml mother/ 1.54 ng/ml newborn) followed by those women that live in Olhão (PCBs1.58ng/ml mother/1.46 ng/ml newborn) and Faro (PCBs 1.50 ng/ml mother/1.33 ng/ml newborn). Strong relationships were found between maternal and umbilical serum PCBs concentrations, indicating equilibrium within the maternal-fetal unit. Residence and surrounding environment, diet and smoking habits appear to be the most significant factors contributing to both maternal and fetal exposures (Lopes et al., 2014). The data are summarized in Table 8.3.

Table 8.3.
Summary of concentrations of hazardous substances in mothers and new-borns around the Ria Formosa.

Hazardous Substances	Mothers	New-Borns	Hotspots
Cd (mg/l w.w.)	0.64	0.43	Faro-Olhão
Hg (mg/l w.w.)	0.56	0.48	Tavira
Pb (mg/l w.w.)	0.47	0.44	Olhão
DDE (ng/l w.w.)	1.61	1.17	Tavira
∑Drins (aldrin, dieldrin and endrin)	9.56	9.12	Olhão
HCB (ng/l w.w.)	0.29	0.22	Faro-Olhão
∑Endosulfan	12.88	13.17	Tavira
Vinclozolin (ng/ml w.w.)	2.02	1.75	Faro
PCBs (ng/l w.w.)	1.78	1.54	Tavira

8.6. Conclusions

From the data presented and the hydrodynamics of the Ria Formosa it can be concluded that lagoon is subject to multiple pressures from contaminants and hazardous substances, some of which have been banned for decades. Management measures and remediation steps need to be put in place to reduce discharges to protect and depollute, as well as to decrease the impact of mixtures of hazardous substances. This is necessary to protect food security and important natural resources such as the shellfish, and to protect the health of the population, especially pregnant mothers and children. These management measures should be complemented by a toxicological monitoring programme, as established by the descriptor 8 of the Marine Framework Strategy Directive.

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