

Chapter 2

Harmful Elements in Estuarine and Coastal Systems

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Abstract Estuaries and coastal zones are dynamic transitional systems which provide many economic and ecological benefits to humans, but also are an ideal habitat for other organisms as well. These areas are becoming contaminated by various anthropogenic activities due to a quick economic growth and urbanization. This chapter explores the sources, chemical speciation, sediment accumulation and removal mechanisms of the harmful elements in estuarine and coastal seawaters. It also describes the effects of toxic elements on aquatic flora and fauna. Finally, the toxic element pollution of the Venice Lagoon, a transitional water body located in the northeastern part of Italy, is discussed as a case study, by presenting the procedures adopted to measure the extent of the pollution, the impacts on organisms and the restoration activities.

Keywords Harmful elements • Coastal areas • Aquatic organisms • Health effects • Venice Lagoon

1 Introduction

Estuarine and coastal areas being the interaction zone between fresh and marine waters are highly complex due to tidal currents and waves (Morris et al. 1995). According to Ridgway and Shimmiel (2002), they are dynamic systems where various ecological and physicochemical functions occur. In many ways, estuaries are very important ecosystems (Legorburu et al. 2013) being a vital site for primary

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production (Bricker et al. 2008) and a suitable habitat for many species (Lotze 2010). In addition, they control exchange processes of elements between river and coastal areas (Das et al. 2010) and supply goods and services (Pinto et al. 2010). Recently, researchers throughout Europe have given priority to estuaries and coastal areas especially after the European Commission, in the European Water Framework Directive (WFD, 2000/60/EC), has emphasized the objective of achieving “Good Ecological and Chemical Status” in all European water bodies by 2015 (Borja et al. 2009; Tueros et al. 2009).

However, river banks and estuaries have always been a focus for human settlement and industrial development, recreation, tourism, development of port and boating facilities, agriculture, housing, mining and forestry. Estuaries are becoming polluted by various human activities due to a quick economic growth and urbanization (Xu et al. 2013). Estuarine and coastal areas act as a sink for trace metals and other pollutants incoming from adjacent catchments, up-watershed activities and nearby terrestrial areas, but also they are a source for the same materials to the adjoining coastal marine areas (Kennish and Fertig 2012). Moreover, estuaries have been frequently used as dumping grounds for sewages, rubbish and industrial wastes. All these activities are responsible for the pollution of estuaries and coastal marine areas. Waste discharges, accidental spills, urban and agricultural runoff and ground water flow carry a wide range of pollutants to the coastal marine areas (Water and River Commission 1997). Therefore, substantial amount of nutrients and trace metals are transported through riverine input and submarine groundwater discharges to coastal sea waters due to progressive anthropization in coastal areas (Moore 2006). Trace elements are taken by river and ultimately mixed into coastal marine areas after transportation and alteration in estuarine areas (Swarzenski et al. 2006).

The estuarine and coastal seas play a vital role in the biogeochemical cycles of various essential and non-essential elements, by favouring physico-chemical and biological processes such as variations in the chemical speciation, inorganic scavenging, sedimentation, bio-alteration, bio-accumulation and bio-magnification (Costa et al. 2012). Trace metals are natural elements of crustal materials which enter the aquatic environment via erosion process (Di Leonardo et al. 2009; Rocha et al. 2011; Weber et al. 2009). Although some metals are vital to biota, all are potentially toxic when concentrations exceed a certain limit. Metals are received in the estuaries through rivers, many of them are persistent, toxic and bioaccumulative in nature (Liang 2011). Trace metals enter the aquatic systems mostly from anthropogenic inputs such as leaching of impervious urban surfaces (roads, parking lots and roofs) and soil surfaces by runoff and to sewage overflow from sanitary sewer systems during high rainfall events, locally treated wastewater discharge and industrial effluents (Bay et al. 2003; Bothner et al. 2002; Nicolau et al. 2012). The entrance of trace elements from river to open ocean via estuaries depend on the partitioning of trace metals between dissolved and particulate phase, riverine and anthropogenic inputs, coastal and seafloor erosion, biological activities and also physical – chemical transport and biological interaction within these areas. Trace elements may be accumulated in sediments after recycling due to chemical and

biological processes and also may return back to the water column after resuspension (Förstner 1984; Tessier and Campbell 1987).

There are two processes controlling the partitioning of metallic species between the solution and suspended particulate matter (SPM) phase during estuarine mixing. Firstly, the removal of metals by flocculation of humic and fulvic acid-metal complexes and desorption of metals from river particles or from resuspended sediments (Roux et al. 1998). The features of a river or estuary's watershed such as climate (e.g., rain frequency and intensity), morphology, hydrology, geology and land use drive estuarine dynamics, particularly flushing times of waters and particle concentrations and residence times, which are among the most important factors controlling metal reactivity in estuaries (Elbaz-Poulichet 2005). Redox conditions (Zwolsman et al. 1997) and the presences of dissolved organic matter (DOM) also control the fate of metals in estuaries.

Keeping the above points in mind, the sources, chemistry, sediment accumulation and removal mechanisms of the harmful elements in estuarine and coastal seawater are described below. Elements are discussed in the following chapter in an order that reproduces a decreasing impact on the organisms and ecosystems. However, the chapter of the book first discussed metal, then non-metal (As) followed by organotin compounds (Tributyltin and Triphenyltin).

2 Harmful Elements in the Estuary and Coastal Areas

2.1 Mercury

Mercury is a widely distributed hazardous pollutant and has received great attention globally because of its persistence in environments, high toxicity to organisms, reactivity and tendency of forming more toxic organic mercury compounds and also biomagnifications capability along the food web (Jiang et al. 2006; Craig 1986; Beckvar et al. 1996). Although the use of Hg has declined considerably during the past several years, still now the metal has to be considered important in several sectors such as energy generation, incineration and mobilization from mining activities (Hines et al. 2012; Fitzgerald et al. 2007). Mining, industrial activities and urban expansion in estuarine and coastal zone are the main anthropogenic sources of Hg (Luo et al. 2012).

The coastal zone plays a vital role in the global mercury cycle (Mason et al. 1994) both as sink for terrestrial Hg and as source of methylated Hg to the ocean (Mason and Benoit 2003). Approximately 50–80 % of the total Hg coming from rivers is deposited within the estuarine zone (Cossa et al. 1996; Benoit et al. 1998). Input of Hg in the coastal zone is influenced by various natural and anthropogenic activities such as coastal and seafloor erosion, river and sewage/mining discharge, and atmospheric Hg deposition (Ci et al. 2011). Hg can exist in different forms which control its availability, complex distribution, and toxicity.

The most important forms of Hg are elemental Hg (Hg^0), inorganic Hg (Hg^{2+}), monomethylmercury (CH_3Hg^+) and dimethylmercury (CH_3HgCH_3) (Leermakers et al. 2001). All of these are influenced by various factors such as redox and pH conditions, and concentrations of inorganic and organic complexing agents (Horvat et al. 2003).

Approximately 10–30 % of the Hg exists as elemental Hg in ocean water (Mason and Fitzgerald 1993), where Hg^0 is mainly formed from the reduction of Hg (II) by aquatic microorganisms (Mason et al. 1995) and from photoreduction of Hg (II) (Amyot et al. 1997; Costa and Liss 2000) followed by geotectonic activity (Ferrara et al. 2003; Horvat et al. 2003). Abiotic methylation may take place in an environment loaded with humic organic matter (Weber 1993). Methylmercury (MeHg) is produced from inorganic mercury due to the activity of sulfate reducing bacteria (Mason et al. 1993; Morel et al. 1998; King et al. 1999). Although methylmercury is present in estuarine water at very low concentrations (Cossa and Coquery 2005), it is the most toxic form of Hg and may be accumulated in human body through the consumption of sea foods (Baldi 1997; Morel et al. 1998). Methyl mercury is a unique example of metal biomagnification in food chains due to its special characteristics such as (i) high lipid solubility and easy transfer through membranes and (ii) longer biological half-life. There are several factors controlling the production of MeHg such as temperature (35 °C is the optimum temperature in river), salinity (methylation rate decreases at increasing salinity due to the formation of chloride complexes), redox/sulphide levels (MeHg is higher in moderately anoxic sediments and increased proportionately with sulphide concentrations up to 1.8 mg S g⁻¹) (Callister and Winfrey 1986; Compeau and Bartha 1984; Breteler et al. 1981; Craig and Moreton 1983).

Dimethylmercury is an organic form of Hg found in seawater and mainly produced in oxygenated environments (Mason et al. 1995). There is little evidence of the production of dimethylmercury in surface water. However, it comes to the surface from deep water through deep water upwelling and deep thermocline mixing and degrades quickly due to its low stability with light and higher surface water temperature (Fitzgerald and Mason 1997). There is also evidence of the demethylation of the methylmercury (Marvin-DiPasquale et al. 2000; Barkay and Wagner-Dobler 2005) mediated by the bacteria through both reductive process (products: Hg^0 and CH_4) and also oxidative process (products: Hg^{2+} and CO_2) (Barkay et al. 2003).

The concentration of dissolved mercury ranged from 0.5–3 ng L⁻¹ to 2–15 ng L⁻¹ in ocean and coastal sea-water, respectively (WHO 1989), whereas its concentrations varied from 20 to 100 µg kg⁻¹ in ocean sediments. The concentration of methylmercury in UK estuarine sediments is less than 0.02 µg g⁻¹ (Langston 1982). Dissolved mercury has strong attraction for organic matter and suspended sediment and becomes accumulated in sediment after adsorption onto these particles. After deposited in sediment, inorganic Hg is transformed into methylmercury, which is bioavailable and toxic to aquatic organisms (Campbell et al. 1986). Methyl mercury can be accumulated at concentrations 10 (*Fucus vesiculosus*) and 100 (*Mytilus edulis*) times higher than sediment concentrations in estuarine algae

and invertebrates (Langston et al. 1996). The concentration of total mercury in the Isonzo River (northern Adriatic Sea) ranged from 1.72 to 31.4 ng L⁻¹, whereas the average value was 9.2 ± 7.9 ng L⁻¹. On the other hand, the concentration of methyl mercury ranged from 1.65 to 17.2 ng g⁻¹ in sediments. However, the concentration of methylmercury varied from 0.21 to 6.28 ng g⁻¹ which is 0.121 % of total Hg (Bratkič et al. 2013).

2.1.1 Effects of Mercury on Aquatic Organisms

The European Water Framework Directive – 2000/60/EC (2000) indicates mercury as a priority harmful substance. In addition, mercury is included in the first 20 compounds of the priority list of dangerous substances published by the Agency for Toxic Substances and Disease Registry (ATSDR 2007). This metal behaves as a resistant cation, which forms complexes and can interact with proteins, enzymes and cell membranes in biological systems. It is present under different oxidation states such as Hg²⁺, Hg⁺ or Hg⁰ in the methylated forms dimethylmercury (CH₃)₂Hg and methylmercury CH₃Hg⁺. These two derivatives are persistent and bioaccumulable. The methylmercury with its ionic form is hydrophilic and quite mobile in the environment, while the dimethylmercury is lipophilic and volatile. In mammals, depression and irritability indicate a low intoxication of mercury, whereas damages to the nervous system such as blindness, madness, paralysis, as well as effects on the DNA (Renzoni et al. 1998) can indicate a heavy intoxication of mercury. Elemental mercury is less dangerous because it is easily eliminated with the urine. As described by (Grieb et al. 1990), the methylmercury accumulates in muscle tissues, liver and kidney of fishes (Mackey et al. 1996) with a biological half life varying from 2 to 3 years (USEPA 1984 and references therein). Considering the trophic chain, the methylmercury contained in the benthos or the smaller fish tissues will deposit in different tissues of the predator (e.g. kidney, bile, muscle). As the level of intoxication in fish depends on its diet (Adams et al. 2010), age, weight and length, as well as on the physical-chemical parameters of the water body, no definitive intoxication parameters can be established, but a stress condition can be proved (Das et al. 1980), because a significant impairment of metabolic functions, and a modified morphology and behaviour can be detected (Alam and Manghan 1992; Scott and Sloman 2004). Adams et al. (2010) reported that at levels higher than 5 µg g⁻¹ of wet weight in fish muscles impairment in the reproduction can be observed. In the benthos, some difficulties were found in determining the toxicity of Hg, rather than of a mixture of metals (Suchanek et al. 2008). Brown and Ahsanullah (1971) and Arizzi Novelli et al. (2002b) demonstrated that Hg is the most toxic element compared to others such as Cu, Cd, Zn, Pb for larvae of *Ophryotrocha* and *Artemia* as well as for sperm cells and embryos of *Paracentrotus lividus*, respectively.

2.2 Cadmium

Great attention has been given to cadmium due to its toxic behavior in the environment (Steinnes 1989; Flyhammer 1995; Porter et al. 2004). The main dissolved forms of Cd are chloride complexes whereas the most available species is the free ion (Cd^{2+}), the proportion of which increases with decreasing salinity (Engel and Fowler 1979; Cross and Sunda 1985). Many scientists reported that there was a relationship between the Cd concentration in sediment and biota. A linear relationship was found between the concentration in the polychaete *Nereis diversicolor* and in surface sediment from estuaries in Devon and Cornwall (Bryan and Hummerstone 1973a).

The concentration of Cd in Ocean was found to range from 0.02 to 0.12 $\mu\text{g L}^{-1}$ (Bruland et al. 1979), whereas the concentration was 0.01–0.17 $\mu\text{g L}^{-1}$ in UK coastal waters. However, the concentration of Cd in estuary fluctuated from 1 to 50 $\mu\text{g L}^{-1}$ (Morris 1984; Bryan and Gibbs 1983). Although chlorinity is a vital parameter controlling Cd behavior in estuaries, other factors such as ionic strength (increase of Ca^{2+} and Mg^{2+} concentrations competing with Cd^{2+} for adsorption onto particles), pH, redox potential, microbial activity, organic matter degradation and the residence time of the particles in the mixing zone (type of estuary) can be involved.

Cd has higher affinity for the chloride ion rather than to organic ligands (Bilinski et al. 1991; Tipping et al. 1998). During the mixing of river water with sea water, mobilization processes occur from particulate matter by the formation of highly stable and soluble Cd-chloride complexes. The formation of chloride complexes increase with the increase of salinity which regulates the activity of the free ion (Paalman et al. 1994; Thouvenin et al. 1997; Lemaire et al. 2006). An organic complex is occurred at low salinity condition. There was also evidence of Cd desorption in the estuary (Boyle et al. 1982).

2.2.1 Effects of Cadmium on Organisms

This metal can be complexed by the seawater and form soluble forms such as CdCl^+ , $\text{CdCl}_2(\text{aq})$ and CdCl_3^- . Under these forms, Cd can be taken up from different organisms living in the aquatic environment, stored in liver, kidney and gills, and cause problems in the enzymatic regulation of the carbohydrate metabolism. Cd is one of the elements next to Mn and Ni which can disrupt the storage or mobilization of metabolic substrates like glucose, glycogen, lactate, lipids and proteins (Scott and Sloman 2004). As Cd and Zn have the same positive loading, it can substitute Zn in some enzymes causing an alteration of their structure, which compromises their activities. Moreover, Cd (in addition to Cu, As, Hg, Pb) influences reproduction processes of fishes (Das et al. 1980). Cd is accumulated in small amounts in the fishes' muscle but in higher amounts in other tissues and organs (USEPA 2001). In mammals, Cd can cause caught, nausea, thoracic diseases, but in

small quantities it is bound by proteins and eliminated easily with the urine. When exposed to high quantities, red blood cells can be destroyed and the kidney can be damaged. Therefore, Cd is considered a potentially toxic element (Mackey et al. 1996). In benthic organisms, Cd was linked to lysosomal damage and mortality of the organisms (Thompson et al. 2007).

2.3 Lead

Lead is one of the major anthropogenic pollutants and is now considered as ubiquitous (Chakraborty et al. 2012; Snape and Townsend 2008; Lobinski and Marczenko 1996). Nutritionally or physiologically lead is not an essential nutrient for either humans or other organisms. It is toxic, bioaccumulative and persistent. The contamination of lead from gasoline burning has declined in different environmental matrices, including aerosols (Migon et al. 1993; Grousset et al. 1994), seawater (Boutron et al. 1991; Wu and Boyle 1997) and rivers (Singh and Singh 2006).

Various uses of lead such as in storage batteries and as organic antiknocking additives (tetraalkyllead) to petrol, cables, solders, steel products, ammunition, shielding systems from radiation and x-rays, circuit boards in computers and electronics equipments, superconductor and optical technology, insecticides, pigments, paints, ceramics, enamels, glass, plastics and rubber products, coal-fired power stations, wastes from runoff and incineration and other industrial effluents have contributed significantly for the wide distribution of lead in the environment (Ritson et al. 1999; Hansmann and Köppel 2000). Although legislations have been implemented to enforce the use of alternative petroleum additives and recover lead from used batteries, the uses of lead are continuing in other areas of application.

Various forms of lead are available in the environment. Organometallic forms of lead are more lipophilic and can easily penetrate biological membranes. As a result, alkyllead species may be bioaccumulated in food chains. The main dissolved forms of Pb are PbCO_3 and PbOH (Nurnberg and Valenta 1983), whereas the most available inorganic form is the free ion Pb^{2+} (Freedman et al. 1980). Pb can be accumulated in the sediments by the deposit-feeding species. Pb levels in the polychaete *Nereis diversicolor* were correlated linearly to the Pb/organic matter ratio in the sediment (Bryan 1985). The availability of lead decreases with the increases of sediment organic matter concentration. This is due to the complexation of the free ion Pb^{2+} in the interstitial water, or possibly in the gut following sediment ingestion (Windom et al. 1982). Fe oxides have also effect on Pb concentration and its availability decrease with the increase of Fe oxides (Luoma and Bryan 1982). Inorganic lead may be a source for the contamination of birds. Tetramethyllead and tetraethyllead are the two main lead compounds introduced into the environmental. Both of these compounds are used as gasoline antiknock additives. However, tetramethyllead and derivatives of methylatedlead are the two main compounds found in the environment as organometallic compounds of lead.

Methyllead compounds are only found in the immediate vicinity of anthropogenic sources which are normally present at nanograms per gram level and decay occurs via R_3Pb^+ and R_2Pb^{2+} , with inorganic lead as the final products (Craig 1986). The principal factors governing the biological activity of lead in aquatic environment depend on its geochemical behavior. The physical and chemical properties of surface water and sediments such as pH, total hardness, porosity, Eh and organic matter affect the concentration of lead. Lead carbonates, lead sulfates and lead sulfides are predominant in sediments, whereas lower amount of lead were detected in surface water in dissolved form. Lower pH helps for the mobilization of inorganic lead.

Flegal and Patterson (1983) conducted an experiment and found the concentration of Pb in Ocean to be in the range 0.001–0.014 $\mu\text{g L}^{-1}$. The dissolved concentration of Pb ranged from 0.015 to 0.135 $\mu\text{g L}^{-1}$ along the east coast basin of Britain, whereas in the Humber estuary the concentration fluctuated from 0.010 to 0.055 $\mu\text{g L}^{-1}$ (Balls 1985). However, the highest portion of lead in coastal waters and estuaries is connected with particles. The concentration of inorganic Pb in UK estuarine sediments ranged from 25 $\mu\text{g g}^{-1}$ to more than 2,700 $\mu\text{g g}^{-1}$ of sediment (Bryan et al. 1985). Organolead compounds have also been detected in sediments such as the concentrations of tetraethyl, triethyl and diethyl Pb in Canada were 1.15, 0.19 and 0.022 $\mu\text{g g}^{-1}$, respectively (Chau et al. 1984). Riley and Towner (1984) conducted an experiment and found higher concentrations of tri and dialkyl Pb than those of dissolved inorganic Pb.

2.3.1 Effects of Lead on Organisms

When present in its ionic form Pb^{2+} , it becomes hazardous for the environment as it is easily taken up by organisms. Therefore, it is also included in the priority list of ATSDR (2007). In mammals, Pb is distributed firstly in the soft tissues, then in the bones, where it takes the place of Ca^{2+} . It may cause damage to liver and the reproductive system and to the DNA as well. In fish, the lead poisoning can cause permanent and severe damages in the reproductive system (Das et al. 1980) after long term exposure, depending on the species, size and age of the fish (Alam and Manghan 1992). Temperature, depth and movement of the water body influence the possibility for marine organisms to take up Pb, stored in liver, hepatopancreas and hard tissues and finally influence the metabolism of the organism (Prosi 1989). However, lead (Pb^{2+}) also influences the cytoskeleton, mitochondria, the nucleus in liver cells, causing the cell death, whereas in the kidney it inhibits only some enzymes (Rabitto et al. 2005).

2.4 Zinc

Zinc acts as metal cofactor for many enzymatic processes of both eukaryotic and prokaryotic organisms (Vallee and Auld 1993) and is used in nucleic acid transcription and repair protein (Anton et al. 2007). It also participates in nutrient uptake mechanisms especially for the uptake of CO₂ through the enzyme Carbonic Anhydrase (CA) (Morel et al. 1994) and also for the uptake of phosphate through the enzyme alkaline phosphatase (Shaked et al. 2006).

There are several forms of available Zn in the aquatic system. However, the most bioavailable and dissolved one is the free ion Zn²⁺ (O'Brien et al. 1990). The concentration of zinc in coastal areas and estuaries are much higher than in the ocean (less than 1 µg L⁻¹, Bruland et al. 1979). The concentration of zinc in a North Sea transect was 0.3–70 µg L⁻¹ (Duinker and Nolting 1982), whereas the concentration varied from 11 to 23 µg L⁻¹ in Bristol Channel-Seven Estuary (Morris 1984). The Zn concentration of sediment in Restronguet Creek, UK, ranged from less than 100 to around 3,000 µg g⁻¹. In interstitial waters, the concentration of Zn in Creek sediments varied from 262 to 396 µg g⁻¹, whereas it fluctuated from 67 to 216 µg g⁻¹ at a depth of 10 cm (Bryan and Gibbs 1983). The average Zn concentration in the western coast of Mauritius was 107 mg kg⁻¹ (Ramessur 2004).

Generally dissolved Zn is predominant in river water, whereas in estuaries a larger portion of the zinc is adsorbed to suspended particles where concentrations of suspended particles are higher (CCREM 1987). Zinc may be mobilized from sediments in low saline estuarine areas, due to the microbial degradation of organic matter and also displacement by calcium and magnesium. Zinc also can be deposited with flocculated particles during high turbidity and may accumulate in anaerobic sediments.

2.4.1 Effects of Zinc on Organisms

Zinc is a micronutrient for marine organisms, important in the enzymatic and metabolic regulation, but at high concentrations it becomes toxic and can cause different permanent and severe damages, e.g. in the reproduction processes (Das et al. 1980). Low concentrations of Zn were observed to stimulate the growth of the organisms in the marine environment. The water hardness (hardness <1 mg L⁻¹ as CaCO₃), when Zn is present only at low concentrations can influence the egg production and the fertilization process in fish (Sprague 1971 and references therein). An irregular development of some marine organisms has been detected when the concentration of Zn increases (Volpi Ghirardini et al. 2005). Further, it seems that diet borne Zn is not toxic, but it can influence the concentrations of Fe and Cu in the fish. However this feature is still depending on species, age, length and weight of the organism. However, in fish Zn is principally accumulated in the digestive tract after short-term and long-term exposure. Then, gills, liver, kidney,

spleen and skeletal tissues divide the second position in Zn accumulation (Clearwater et al. 2002).

2.5 Chromium

Chromium is an important component in industrial sectors and used for the production of ferrochrome, electroplating, pigment production and tanning. The major sources of Cr in the marine environment are the wastes of these industries, dumping of solid wastes and municipal wastes. Different forms of chromium are available in the aquatic environment, but the main biologically important forms are Cr (III) and Cr (VI). Trivalent species participates in glucose, lipid and protein metabolism (Eisler 1986), whereas hexavalent Cr is comparatively more toxic than the trivalent form due to its oxidizing potential, solubility and capability to cross cell membrane (Levy and Venitt 1986). The main forms of Cr (III) are CrOH^{2+} , Cr(OH)_3^0 and organic and inorganic complexes, whereas HCrO_4^- and CrO_4^{2-} are the main forms of Cr(VI) in aquatic system (Rai et al. 1987, 1986).

In offshore waters, the average concentration of Cr ranged from 0 to $234 \mu\text{g L}^{-1}$, while the concentration of Cr varied between 30 to over $200 \mu\text{g g}^{-1}$ in UK estuarine sediments (Murray et al. 1983). The total concentration of Cr in the upper 500 m water of the Sargasso Sea (Near to the Bermuda in the North Atlantic Ocean) ranged from 2.5 to 4.5 nM where the concentrations of Cr (III) and Cr (VI) were 1.2 and 2.4 nM, respectively (Connelly et al. 2006). The main way of the removal of Cr (III) from the sea water is adsorption to suspended particles such as oxides of Fe or by surfaces (Paternac and Legovic 1986; Mance et al. 1984). The adsorption of trivalent Cr increases with pH. However, adsorption process may decrease with the increases of competing cations. On the other hand, the adsorption of hexavalent Cr decreases with pH and the presence of dissolved anions. Chromium migrations are controlled by several processes such as competition between complexation, dissolution/precipitation, redox process and adsorption/desorption mechanisms. The migration of trivalent chromium occurs under acidic conditions and it occurs as dissolved organic complexes. On the contrary, Cr (VI) migrates rapidly but the process may slow down due to the presence of Fe (II) and high organic matter concentration (Richard and Bourg 1991). With the presence of dissolved oxygen, oxidation of Cr (III) to Cr (VI) is very low but increases with the presence of MnO_2 . On the other hand, the reduction of Cr (VI) to Cr (III) increases with the presences of organic matter-rich environment. Finally, after settling of the Cr in sediment, remobilization of Cr occurs either as chromate or as organic Cr (III) complexes (Fig. 2.1).

2.6 Nickel

Nickel is a ubiquitous and nutritionally essential nutrient for plants, animals and micro-organisms. Nickel is used for the production of stainless steel and nickel alloys which are ultimately used in vehicles, processing machinery, armaments, tools, electrical equipment, household appliances and coinage. Moreover, it is also used in catalysts, pigments and batteries. The main sources of nickel to the environment are the uses of coal and oil for power generation, incineration of wastes, nickel mining, steel manufacturing, electroplating, cement manufacturing. However, nickel from all of these activities finally reaches the marine environment due to dumping of wastes, surface-runoff of wastes and incineration (WHO 1991).

Nickel may exist in several forms in the aquatic system. However, Ni (II) is the prevalent oxidation state under normal environmental conditions. The other forms exist in oxidation of 1–, 1+, 3+ and 4+ (Young 1995; Clayton and Clayton 1994; Coogan et al. 1989). The concentration of Ni in fresh water ranged from 2 to 10 $\mu\text{g L}^{-1}$, whereas it ranged from 0.2 to 0.7 $\mu\text{g L}^{-1}$ (WHO 1991) in Ocean. In coastal, bay and estuary waters it varied from 0.20 to 5.3 $\mu\text{g L}^{-1}$ (Domínguez-Lledó et al. 2007). The concentration of nickel in sediment of Ria Ferrol (NW Spain) were in the range 11.3–67.2 $\mu\text{g g}^{-1}$, whereas the average concentration was 32 $\mu\text{g g}^{-1}$ (Barciela-Alonso et al. 2003).

Nickel exists in aquatic systems as soluble salts, absorbed on clay particles or together with organic materials such as humic and fulvic acids and proteins. However, sediments also act as a source of nickel through desorption (WHO 1991). The fate of nickel in sea water is controlled by several factors including pH, pE, ionic strength, type and concentration of organic and inorganic ligands, and the presence of solid surfaces for adsorption (Barciela-Alonso et al. 2003).

2.6.1 Effects of Nickel on Organisms

Ni is an essential element for all organisms, aquatic or not, which becomes toxic at high concentrations. In addition, it has been indicated as possible carcinogenic (Coogan et al. 1989; Denkhaus and Salnikow 2002). A long term exposure of marine organisms can modify their morphology and behavior (Alam and Manghan 1992) and disrupt the storage and/or mobilization of essential metabolic substrates (e.g. glucose, proteins) (Scott and Sloman 2004). However, there is no strong evidence about the relationship between the concentration of nickel and its toxicity in the organism (Griffitt et al. 2008).

2.7 Cobalt

Cobalt is an essential component for human and other organisms since it is an important component of Vitamin B-12. Cobalt has both natural and anthropogenic sources. The main human sources are coal and oil burning, industrial activities, vehicular exhausts and sewage sludge. Cobalt is used in steel and alloys, metallurgy, electroplating, nuclear technology, fertilizers, medicine, drier for paint, foam stabilizer in beer brewing (Tsalev and Zaprianov 1985; ATSDR 1999).

The main forms of cobalt in seawater are Co^{2+} and its sulfate-, chloro- and carbonate-complexes (Ahrland 1975) and is removed quickly from seawater with MnO_2 (Knauer et al. 1982). About 90 % of the cobalt can be found in the sediments and in suspended particulate matter in sea waters (Robertson et al. 1973). Sometimes cobalt acts as a limiting nutrient for marine phytoplankton when present at low concentration in the ocean waters (Knauer et al. 1982).

The mean concentration of cobalt detected in seawater was $0.3 \mu\text{g L}^{-1}$, whereas it varied from 0.1 to $10 \mu\text{g L}^{-1}$ in fresh water. The concentrations of cobalt in estuarine sediments ranged from 15 to 60 nM (Huynh-Ngoc et al. 1989), whereas Duchart et al. (1973) found the cobalt concentration 34 – 650 nM in estuarine sediments. The cobalt concentration in surface marine water is 18 – 300 pM , whereas it ranged from 20 to 50 pM at depth (Donat and Bruland 1995). The concentration of cobalt is comparatively higher in estuarine and coastal waters than in ocean. Achterberg et al. (1999) measured 140 – 310 pM cobalt in coastal water near Washed Humber Estuary.

The mobilization of cobalt in estuarine and coastal areas depends on the partitioning of the metal between dissolved and particulate phases (Martino et al. 2002). This is influenced by various factors such as types of metal ion, metal concentration, pH, salinity and dissolved oxygen (Stumm 1992). The primary ways of removal process of cobalt are particle scavenging and biological uptake. However, the metal is also released from the sediment to the dissolved phase due to desorption as a consequence of salinity changes (Kraepiel et al. 1997)

2.7.1 Effects of Cobalt on Organisms

Cobalt seems to be an essential element for certain blue-green algae, nitrogen-fixing bacteria and symbiotic systems as well as for animals. It can be found in two oxidation states, Co^{2+} and Co^{3+} . Co^{3+} is found rarely in organisms as it is thermodynamically unstable in natural waters and cannot be taken up easily. Co can also substitute other trace metals (e.g. Cu, Pb, Zn, Cd) in a wide variety of minerals due to its similar geochemical properties, to form complexes (EnvGovCa 2003). In addition, it can influence negatively the growth rate of, and the Ca-uptake in aquatic herbivores (De Schamphelaere et al. 2008)

2.8 Vanadium

Vanadium is a vital component for aquatic organisms such as marine phytoplankton (Moore et al. 1996), macroalgae (Patrick 1978; Nalewajko et al. 1995) and other organisms (Taylor et al. 1997). Vanadium is present in many enzymes such as haloperoxidases (Butler and Carter-Franklin 2004), nitrate reductases (Antipov et al. 1999) and nitrogenases (Rehder 2000) and also participates in metabolic activity of many components such as chlorophyll synthesis (Meisch et al. 1977; Wilhelm and Wild 1984), cell division (Meisch and Benzschawel 1978), phosphate uptake kinetics (Lee 1982), sulfoxidation (Andersson et al. 1997). Vanadium, on the other hand, is a very important metal for technology. Approximately 75–85 % of the vanadium is used in ferrous metallurgy (alloy additives in steel). The main inputs of vanadium into environment are the burning of fossil fuels, crude oil spillages and industrial activities (atomic energy industry, air craft construction and space technology, as catalyst for the production of sulfuric acid and plastics) (Kalogeropoulos et al. 1989; WHO 1988).

Vanadium in the aquatic environment exist in the form of many species, but the predominant stable oxidized forms are V(IV) and V(V). However, V(V) is more toxic than V(IV) (Pinto et al. 2013). El-Mosehy (2006), who collected sediment samples from the coastal area of the Egyptian seas (Mediterranean and Red Seas) found a mean concentration of $52.61 \mu\text{g g}^{-1}$ in the Red Sea sediments, whereas the mean value was $40.58 \mu\text{g g}^{-1}$ in the Mediterranean Sea. The concentrations of dissolved and particulate vanadium in the seawater of English Channel were in the ranges $15\text{--}28 \text{ nmol L}^{-1}$ and $2\text{--}32 \text{ nmol L}^{-1}$, respectively (Auger et al. 1999).

The speciation of vanadium is influenced by redox condition of the aquatic environment (Taylor and van Staden 1994; Pettersson et al. 2003). Various redox pairs such as $\text{NO}_3^-/\text{NH}_4^+$, $\text{Fe}^{3+}/\text{Fe}^{2+}$, $\text{MnO}_2/\text{Mn}^{2+}$, $\text{SO}_4^{2-}/\text{H}_2\text{S}$ play a significant role in vanadium speciation and cycling in coastal seawaters. The solubility of vanadium decreases with decreasing oxidation number. Most of the vanadium present in ocean waters has a conservative behavior, which turns into a non-conservative one in coastal water (Paulsen and List 1997). As most of the vanadium is accumulated in the sediment and only 10 % is present in a soluble form, it is evident that a continuous removal from the sea water occurs (WHO 1988).

2.8.1 Effects of Vanadium on Organisms

Vanadium is an essential element for mammals depending on its concentration and it is bioavailable in the environment. In marine mammals Vanadium was detected at concentrations around $0.2\text{--}1.2 \mu\text{g g}^{-1}$, wet weight, in liver tissues, where the concentration is proportional to the animal size and age. Furthermore, V shows a good correlation with the concentration of Hg in tissues of marine organisms and it forms complexes with phosphorus. These complexes cause the inhibition of

ATPase. It accumulates in bones, liver, kidney, muscles (Mackey et al. 1996). When V is present at low quantities, it stimulates the biosynthesis of chlorophyll in green algae in the presence of light (Meisch and Bielig 1975). Further, V^{3+} and V^{4+} show antimicrobial activities at low pH values. Therefore, a Vanadium accumulation in the tissues of an organism can be a defense against predators, bacterial infections and biofouling competitors (Odate and Pawlik 2007). At low concentrations (0.041 mg L^{-1}), Vanadium stimulates the growth and reproductive performance in fish, whereas high concentrations (11.2 mg L^{-1}) are toxic (Perez-Benito 2006).

2.9 Iron

Iron is one of the most important essential plant nutrients and plays an important role in various metabolic processes such as photosynthesis, respiration, nitrogen fixation and detoxification of reactive oxygen species (Sunda 2001; Crichton 2001). Iron enters the aquatic environment from weathering as well as from human activities such as burning of coke and coal, acid mine drainage, mineral processing, sewage, iron related industries and the corrosion of iron and steel (CCREM 1987).

Coastal waters receive iron from river water, groundwater inputs and terrestrial runoff. Generally iron exists in sea water in two oxidation states such as iron (II) and iron (III). These oxidation states play a significant role in the formation of soluble organic and inorganic complexes, colloids, insoluble ferric oxyhydroxides and particle phases (Bruland and Rue 2002; Achterberg et al. 2001). The iron (III) oxidation form is predominating in oxygenated waters, but it becomes insoluble after formation of oxyhydroxides.

The largest portion of dissolved iron (III) (80–99 %) occurs in the form of complexes with organic ligands probably produced by iron limited phytoplankton (Rue and Bruland 1995) or bacteria (Granger and Price 1999), whereas only a small portion is found in free hydrated (Fe^{3+}) or inorganically complexed form (Gledhill and Van den Berg 1994; Rue and Bruland 1995; Nolting et al. 1998). On the other hand, iron (II) is thermodynamically unstable in oxygenated water and is quickly oxidized to iron (III). The main sources of iron (II) in sea water are photoreduction of iron in surface water, atmospheric deposition and diffusion from sediments (Miller et al. 1995; Zhuang et al. 1992). This iron (II) contributes for about 50 % of the total dissolved iron in sea water (Gledhill and Van den Berg 1994; Hong and Kester 1986).

The concentration of iron in unpolluted oceanic seawater was found to range from $1.9\text{--}2.8 \text{ ng L}^{-1}$ to $224\text{--}1,228 \text{ ng L}^{-1}$ and higher concentrations could be found in estuarine water (Whitehouse et al. 1998). The mean concentration of iron was $20.8 \text{ } \mu\text{g g}^{-1}$, which was found in coastal salt marshes. Ergul et al. (2010) found an iron concentration of 0.033 ng g^{-1} and $25.1 \text{ } \mu\text{g g}^{-1}$ in sea water and sediment samples, respectively.

The greater part of the dissolved iron in river waters exists as small colloidal particles, whereas the estimated value of dissolved iron (Fe) input of rivers in the

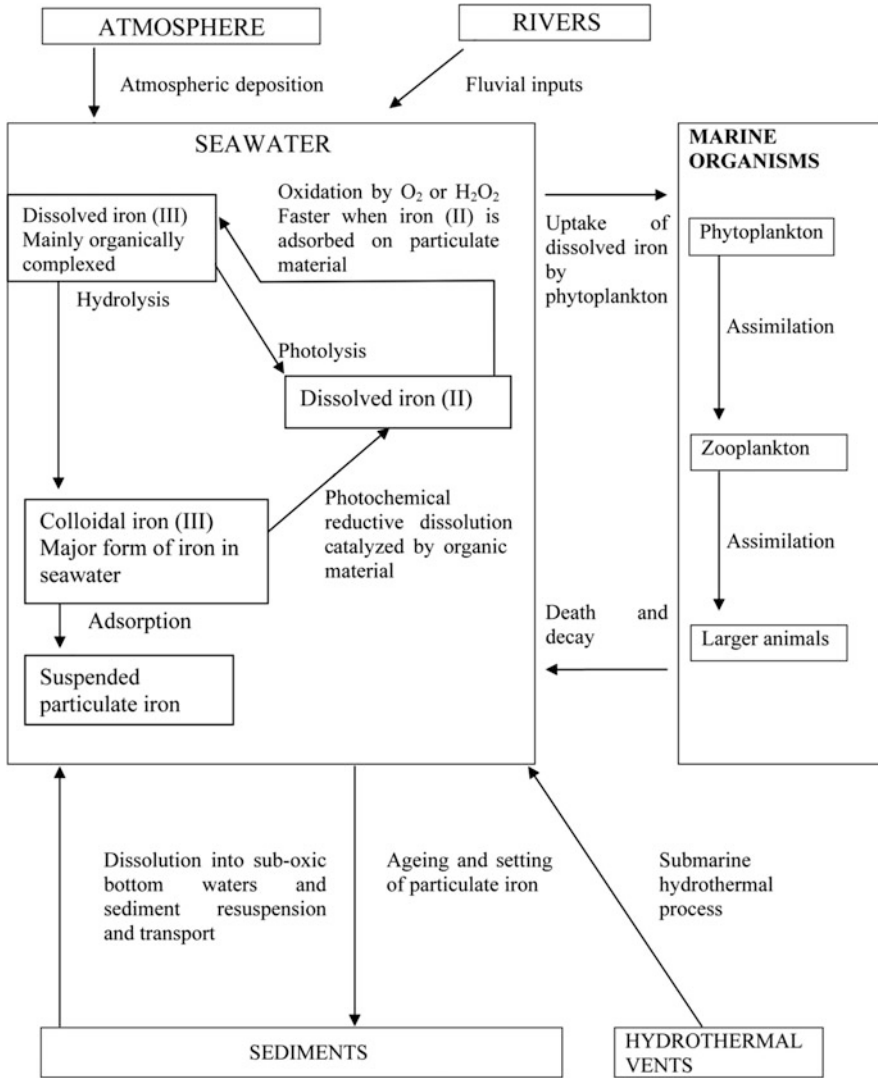


Fig. 2.2 Schematic diagram of biogeochemical iron cycling in the ocean (Adapted from Achterberg et al. 2001)

world oceans is 26×10^{19} mol year⁻¹ (de Baar and de Jong 2001). Removal of particulate Fe occurs through flocculation during the estuarine mixing of the river water with seawater (Sholkovitz 1978). The biogeochemical cycle of Fe in oceanic environment is given in Fig. 2.2. Organic complexation is one of the key factors of biogeochemistry of Fe in estuarine waters and keeps iron in dissolved phase at high salinities beyond the flocculation zone. This dissolved phase is being flushed from the estuary, whereas the non-organically complexed fraction becomes aggregate

and adsorb to particles, thus it remains within the internal cycle of estuary for a longer period of time (Morris et al. 1986). In anoxic marine waters, ferrous iron is mobilized from sediments and diffuses into the water column.

2.9.1 Effects of Iron on Organism

The bioessential element iron is not toxic itself, but it enhances the uptake of As(III) in some marine organisms, which causes adverse health effects for the organism, while it inhibits those of As(V) (Khang et al. 2012). Further, zero-valent iron has been tested by Gheju (2011) as a promoter of the reduction of the heavily toxic and mobile Cr(VI) into the less toxic Cr(III), a process which depends straightly of the environmental conditions of the aquatic system. The same effect was detected when marine organisms were exposed to Cd bound to ferric hydroxide which makes Cd less bioavailable for the organisms (Wu et al. 2012). Nevertheless, Fe is a fundamental element for many biological processes occurring in living organisms. One of them is the interference to the thyroid metabolism and to different enzymes in mammals and fish (Rejitha and Subhash Peter 2013).

2.10 Copper

Copper is a ubiquitous element existing in all natural waters and sediments. Copper is an essential plant nutrient and plays a vital role in the metabolic activities of the organisms. However, it may become toxic to aquatic organisms at concentrations 10–50 times higher than their normal recommended limit (Hall et al. 1997). Recently, the use of Cu as antifouling coating in ships has increased due to the ban of tributyltin and triphenyltin in antifouling coatings. Therefore, concerns are growing that copper has a detrimental effect on the aquatic environment and now it has become an issue in the European saltwater environment because of ecological risk from copper exposure (IMO 1997). Copper exists in various chemical forms such as free copper ions, or complexed with inorganic anions or organic ligands or as suspended particles when present as a precipitate or adsorbed onto organic matter (Mance et al. 1984). The free Cu^+ and Cu^{2+} ions are among the most toxic forms to marine life and toxicity decreases according to the order of Cu^+ and Cu^{2+} > inorganic copper and organic copper (Jones and Bolam 2007; Zamuda et al. 1985). Actually dissolved copper exists in aquatic environment in different forms such as free hydrated cations, organic or inorganic complexes (Achterberg and Braungardt 1999), whereas particulate copper is bound to various mineral phases (clays, quartz, carbonates), iron/manganese oxides and organics (Millward 1995). There are many factors that control the bioavailability and concentration of dissolved Cu such as the cupric ion concentration. These include salinity, the presence of organic ligands and pH (Bryan and Langston 1992).

Hall and Anderson (1999) conducted a research on seawater and found that the concentration of Cu ranged from 0.26 to 16 $\mu\text{g L}^{-1}$, 0.28 to 5.48 $\mu\text{g L}^{-1}$ and 0.069 to 5.56 $\mu\text{g L}^{-1}$ in marina/harbor, estuary and coastal/open sea, respectively. The average highest concentration was found in a harbor (geometric mean 1.53 $\mu\text{g L}^{-1}$), the slightly lower concentration was observed in an estuary (geometric mean value 1.49 $\mu\text{g L}^{-1}$) and the lowest concentration was found in the open sea (0.68 $\mu\text{g L}^{-1}$).

In estuarine systems copper may be removed from solution by adsorption onto suspended particles which are deposited and accumulate in sediments. The bio-availability of copper increases with decreasing salinity due to the reduced competition from Ca and Mg for uptake sites (Wright and Zamuda 1987). The sea weed *Fucus vesiculosus* has the capability of desorbing and accumulating Cu adsorbed onto particles of suspended sediment (Luoma and Bryan 1982). Estuarine sediments are thought to be the most important depositional sites for particulate copper transported from rivers, although re-mobilization may occur when sediment is disturbed. Copper is removed from oceans' over time through the formation of sediments by the help of several biological and physiological processes (Martin and Windom 1991) or by particulate settling.

2.10.1 Effects of Copper on Organisms

Cu at low concentrations is essential for living organisms as it maintains cellular functions and it plays an important role as a cofactor for different metabolic enzymes (Monteiro et al. 2009). However at higher concentrations free cupric ions have been indicated as the most toxic forms of Cu present in the aquatic environment for marine organisms (Nor 1987), as they are supposed to damage intracellular proteins which lead towards apoptotic cell death (Monteiro et al. 2009). Other studies (USEPA 1985; James et al. 2008; Jorge et al. 2013) revealed a strong correlation between the concentration of Cu in the water body and physiological changes such as a lag in growth in the organisms they studied. Further, Cu can influence negatively the reproduction process of different marine organisms (USEPA 1985; James et al. 2008) as well as the community structure of phyto – and zooplankton (Moore and Winner 1989). However, Jorge et al. (2013) have verified adaptive or compensatory mechanisms when organisms are exposed even to higher concentrations of Cu for longer terms. Furthermore, the toxicity of Cu can be mitigated by the presence of humic matter in the aqueous environment as it complexes Cu (Nor 1987).

2.11 Manganese

Manganese is a vital micronutrient for marine organisms and plays a significant role in photosynthesis (Horsburgh et al. 2002; Kernen et al. 2002). It is also associated with some proteins and enzymes which regulate physiological functions (Frausto da

Silva and Williams 1991). However, a higher concentration of dissolved Mn is helpful to reduce the toxicity of copper (Sunda and Huntsman 1983; Stauber and Florence 1985), cadmium and zinc (Sunda and Huntsman 1996).

The uses of manganese show an increasing trend and recent yearly data account for more than 1,5,000,000 ton (Zhang 2007). Various forms of manganese are present in water such as Mn(IV) oxides, Mn(III) oxyhydroxide and Mn(II) (Post 1999). In marine oxygenated environments, manganese (IV, III) oxides exist as insoluble forms, whereas Mn(II) is available in soluble or dissolved condition. Marine sediments have an aerobic surface enriched with Mn (III, IV) phases. When these oxides enter into deeper layers become reduced to soluble Mn (II) (Burdige 1993). Dissolved Mn (II) may move towards the oxidized zone and precipitate again as Mn (III, IV) (Sundby and Silverberg 1985). In anoxic sediments, Mn is primarily available as Mn(II) carbonates and in solid solution with CaCO_3 .

The sediment concentration of Mn in Galician rias (north-west Spain) was reported to vary from 93 to 500 mg kg^{-1} (Barreiro and Carballeira Real 1994; Belzunce-Segarra et al. 1997). Hartwell et al. (2000) conducted a research in Chesapeake Bay, USA and found that the total manganese level in sediment was from 940 to 2,400 mg kg^{-1} , dry weight. The total manganese level in the northern Adriatic Sea (Italy) ranged from 200 to 800 mg kg^{-1} dry weight, with an average value of 370 mg kg^{-1} dry weight (Fabbri et al. 2001). The average manganese concentrations in surface sediments of the Baltic Sea were 3,550 (Bothnian Sea), 5,070 (Gulf of Finland) and 8,960 (Bothnian Bay) mg kg^{-1} dry weight. The concentrations of dissolved Mn in sediment pore waters were in the range 0.2–24 mg L^{-1} (Eriksson and Baden 1998), whereas it fluctuated from 0.2 to 17 $\mu\text{g L}^{-1}$ (Hall et al. 1996) in bottom water. Bryan and Hummerstone (Bryan and Hummerstone 1973b) measured manganese concentrations in seaweeds from south-west England varying from 128 to 393 mg kg^{-1} (geometric mean), whereas manganese concentrations were 350 and 29 mg kg^{-1} in a seaweed of North Sea (*Fucus vesiculosus*) and mussels (*Mytilus edulis*), respectively (Struck et al. 1997). The concentration of manganese in lobsters living on sediments was 92 mg kg^{-1} of body weight (Eriksson 2000).

In anoxic conditions the concentration of manganese in Chesapeake Bay, USA, was 237 $\mu\text{g L}^{-1}$ (Eaton 1979), whereas it was approximately 700–800 $\mu\text{g L}^{-1}$ in anoxic bottom water in the Baltic Sea (Kremling 1983). Roitz et al. (2002) conducted a research on the distribution of dissolved manganese within the San Francisco Bay and found manganese concentrations in the range 12–210 nM at the freshwater interface, from 35 to 756 nM at intermediate salinities and from 86 to 435 nM at the oceanic interface. Tueros et al. (2008) determined concentration of dissolved Mn according to the ranges in salinity in estuary and coastal waters within the Basque Country (northern Spain). The median value of Mn within the polyhaline range (18–50 PSU) was 5.8 $\mu\text{g L}^{-1}$ while in the euhaline ranges (salinity ≤ 0.5 PSU) the value of Mn was 1 $\mu\text{g L}^{-1}$.

Dissolved manganese is particle reactive and may be removed from the water column by sorption onto inorganic and organic particles (Hunt 1983), bacteria

(Sunda and Huntsman 1990) and phytoplankton (Brand et al. 1983; Sunda and Huntsman 1996). However, there is also evidence of desorption of dissolved manganese from riverine suspended particles at the freshwater/seawater interface (Li et al. 1984; Yang and Sañudo-Wilhelmy 1998). The main sources of dissolved Mn in estuary are fluvial and atmospheric inputs, point and non-point source inputs and benthic fluxes from sediments.

Dissolved Mn shows a complex behavior in the estuarine mixing water zone where redox conditions play a vital role in the sedimentation, solubilization and dissolved-particulate partitioning processes. One of the main sources of dissolved Mn in the water column is the re-dissolution of Mn (II) ions (Laslett and Balls 1995). Desorption from suspended particulate matter (SPM) is favored in an environment with low dissolved oxygen and low medium salinity which also contributes for the formation of stably-dissolved Mn (III) chloride and sulphate complexes (Owens and Balls 1997). Mn (II) can be removed from the coastal areas through oxidative processes and the precipitation of Mn (IV) hydroxides (Laslett 1995; Nolting et al. 1999). However, the removal of Mn (II) has also occurred in estuarine reaches where dissolved oxygen increased. Changing of solubility of Mn ions due to the Fe (II)/Fe (III) solubilisation-precipitation processes affect the dissolution and co-precipitation of the other metals such as nickel and zinc (Laslett 1995; Audry et al. 2007). Generally the highest concentration was found in mesohaline-polyhaline ranges, whereas the concentration decreased gradually in the outer estuary and the coastal zone (Kraepiel et al. 1997; Nolting et al. 1999; Audry et al. 2007).

2.11.1 Effects of Manganese on Organisms

Manganese is an essential trace element which is involved in many metabolic processes in plants and animals, with the problem that an excess of the bioavailable ionic form Mn^{2+} can cause neurotoxic effects on marine organisms (Martin et al. 2008). Oweson and Hernoth (2009) detected immunotoxic effects of Mn in crustaceans. Mn was accumulated in the glands and the blood of the animals. This reduced the bactericidal capacity of the organisms, making them more susceptible to different infections. However, Mn was eliminated from the organism back into the water body when the Mn concentration of the latter decreased. Different aquatic organisms are widely used as bioindicators for the Mn concentrations prevailing in an aqueous environment (Steenkamp et al. 1994; Baden et al. 1999; Norwood et al. 2006). Mn-oxidizing bacteria also exist (Tyler 1970) in the aquatic environment. The resulting compounds can be faster taken up by organisms which use the oxidized Mn as energy source in their growth process (Kepkay and Nealson 1987).

2.12 Arsenic

Arsenic has received extensive attention during the last decades due to its relative mobility over a wide range of redox conditions, carcinogenic properties and also its occurrence in the aquatic environment (Wang et al. 2012). Arsenic is a ubiquitous element on earth with metalloid property and complex chemistry. In aquatic systems, arsenic can be originated from both natural and anthropogenic sources such as volcanism, weathering, as by-product of mining, metal refining process, burning of fossil fuels, wood preservation, herbicides, pesticides, fungicides, cement works, electronics industries, ammunition factories, chemistry (dyes and colors, wood preservatives, pesticides, pyrotechnics, drying agent for cotton, oil and dissolvent recycling), pharmaceutical works (medication) (Savory and Wills 1984; Pacyna 1987; Winter 1998; Cullen and Reimer 1989).

Arsenic is found in the atmosphere mainly in four oxidation states such as arsenate (As^{V}), arsenite (As^{III}), arsenic (As^0), and arsine ($\text{As}^{\text{III}-}$) (Sharma and Sohn 2009). In Earth, arsenic is commonly disseminated as the arsenides of copper, nickel, and iron, or as arsenic sulfide or oxide. Estuaries are zones between terrestrial and marine ecosystems and play important role in arsenic cycling (Maher 1984; Bone et al. 2006). The features of the estuaries change with the changes in salinity and redox potential (Wang et al. 2012).

However, arsenic (III) oxide is generated due to copper smelting, whereas methylated arsenic compounds are produced due to biological activity. The noxiousness of As in the aquatic system depends on its speciation and concentration. In water, arsenate and arsenite are more dominant than other forms of arsenic. Arsenate is predominant in oxygenated water, whereas arsenite is predominant in a reduced condition. Arsenic is transported from its sources to estuaries and marine system via atmospheric deposition and riverine input. Marine microorganisms are responsible for the transformation of inorganic arsenic into more complex organic compounds such as arsenobetaine, arsenocholine and arsoniumphospholipids.

Aquatic micro-organisms such as phytoplankton and bacteria keep a significant role in arsenic speciation, distribution and cycling in aquatic ecosystems (Howard et al. 1995; Hasegawa et al. 2001; Hellweger and Lall 2004; Sharma and Sohn 2009). Phytoplankton species are responsible for the conversion of inorganic arsenic into methylarsenicals and high order organic arsenic compounds such as arsenosugars, whereas bacteria play an important role for the mineralization of organic arsenic to methylarsenicals (Francesconi and Edmonds 1996; Hanaoka et al. 1995). Aquatic organisms keep and transform arsenic species inside their body after being exposed to arsenic from food or other sources such as water and sediments (Edmonds et al. 1997; Hasegawa et al. 2001). The ability of micro-organisms to accumulate, transform, detoxify, and modify the arsenic speciation depends on several parameters such as the phosphate concentration, pH, redox potential, salinity, temperature, and light intensity (Karadjova et al. 2008).

The average concentration of arsenic in marine water is less fluctuating than in freshwaters (Neff 1997; Smedley and Kinniburgh 2002). The mean concentration

of arsenic in marine water is 1.5 mg L^{-1} . The average concentrations of As in Pacific coast near Nakaminato (Ibaraki, Japan) and Onagawa (Miyagi, Japan) were $3.1 \text{ } \mu\text{g L}^{-1}$ and $0.6 \text{ } \mu\text{g L}^{-1}$, respectively (Ishikawa et al. 1987). In deep Pacific and Atlantic waters it ranges from 1.0 to 1.8 mg L^{-1} (Cullen and Reimer 1989). However, the concentrations of arsenic in estuaries are much more uniform than in open waters. Arsenic concentration in estuaries might be influenced by effluents from industry and mining activities, bioactivities of aquatic organisms and geothermic water (Smedley and Kinniburgh 2002). The distribution of arsenic is influenced by thermal stratification (Hasegawa 1996). Arsenic was detected uniformly distributed in the water column in Vestfjord estuary in Norway, where the value ranged from 0.75 to 1.05 mg L^{-1} (Abdullah et al. 1995).

Physical mixing of the fresh and seawater masses and salinity may influence the concentration of dissolved arsenic in estuaries and continental shelves. There is a linear relationship between arsenic concentration and salinity. For instance, Seyler and Martin (1991) reported a linear increase in total arsenic concentrations varying from 0.13 mg L^{-1} in freshwater to 1.8 mg L^{-1} in offshore waters, with the increase in salinity in Krka Estuary, Yugoslavia. Redox potential (Eh) and pH are the most important factors controlling arsenic speciation. Under oxidizing conditions, H_2AsO_4^- is dominant at low pH (less than about pH 6.9), whilst at higher pH, HAsO_4^{2-} becomes dominant. H_3AsO_4 and AsO_4^{3-} may be present in extremely acidic and alkaline conditions respectively. Under reducing conditions at pH less than about pH 9.2, the uncharged arsenite species H_3AsO_3^0 will predominate (Brookins 1988).

Arsenic can be removed from the estuary in several ways. Although As can be scavenged from the water column by the particulate matter, adsorption of As onto iron (and to a lesser extent Mn) oxyhydroxides may be a dominant way of removal (Crecelius et al. 1975; Langston 1983). There is a decreasing trend of arsenic from estuary to ocean due to flocculation of iron oxides with increased pH and salinity (Cullen and Reimer 1989).

2.12.1 Effects of Arsenic on Organisms

Arsenic is included in the priority list of dangerous substances established by ATSDR (2007) as it shows a high ability to accumulate in lipid tissues of organisms and can be transported easily upwards in the trophic chain. It can be found in water bodies as As(V), As(III), As(0), As(III-). Among these ionic forms, As(III) and As(V) are the most toxic ones. Those compounds derive from contaminated water and/or sediments and can be possibly biomagnified within the aquatic food web (Rahman et al. 2012 and references therein). In mammals, the poisoning can be acute (e.g. gastroenteritis) and chronic (e.g. effects on the reproductive – and the immune system) (Norwood et al. 2007). Also in fish, chronic poisoning of As can cause problems in the reproduction process as well as in the development of the young fish at concentrations as low as 1 ppb (Das et al. 1980). Major amounts (85–90 %) of arsenic compounds were found in edible portions of fish, whereas a

smaller amount (5–44 %) was detected in lipids of macroalgal species. The concentrations of arsenic differ significantly in phytoplankton and microalgae. Generally, brown algae contain higher amount of total arsenic (around 230 mg g⁻¹ d. w.) than green (approximately 23.3 mg g⁻¹ d. w.) and red algae (approximately 38 mg g⁻¹ d. w.) (Thomson et al. 2007). There are two different assumptions about the degradation of arsenic species: the first one is that As (V) is taken up mainly by phytoplankton and reduced to As (III), while the second one suggests that As(III), taken up by phytoplanktonic organisms, is converted to As(V) and to methylated forms of As which are further eliminated by excretion (Phillips 1990). Those methylated forms are in turn degraded by the action of bacteria, forming again the more bioavailable form As(V) (Rahman et al. 2012).

2.13 Tin and Organotin Compounds (Tributyltin and Triphenyltin)

The environmental significance of tin is mostly related to its organometallic derivatives, namely Organotin compounds (OTs) which are extensively used in the industrial sectors because of their special properties such as PVC stabilizers and catalysts, as biocides in agriculture and as antifouling agents in marine paints to limit the growth of aquatic organisms on ship hulls, fish cages, oil rig supports etc. Even though some natural methylated forms of tin are known, the impact of organotin compounds in marine ecosystems derives mainly from anthropogenic activities (Amouroux et al. 2011). Scientists are globally concerned about organotin due to their ubiquitous presence (at nanomolar concentration in water) and accumulation in aquatic organisms (Atanasov et al. 2005; Hu et al. 2006). Guruge et al. (1996) reported an annual use in 1992 of 50,000 tons, whereas in 1986 it was 35,000 tons. During the last 60 years, significant amounts of organotins have been added into various ecosystems (Hoch 2001). Thirty six organotin compounds are harmful to the natural resources out of 260 known compounds (Eisler 1989). Various factors control the solubility of organotin compounds such as oxidation/reduction potential, pH, temperature, ionic strength, and concentration and composition of the dissolved organic matter (USEPA 2003).

Organotin compounds are persistent in the aquatic environment because of their slow degradation rate and consistent flux (Michel and Averty 1999). Among the organotin compounds, tributyltin (TBT) and triphenyltin (TPT) are the most hazardous and largest discharged compounds into the marine environment. Although triphenyltin (TPT) is mainly used in agriculture such as fungicide and insecticide, it is also used in marine paint formulations. On the contrary, tributyltin (TBT) is widely used in antifouling agent in boat paints, in wood preservation, as an antifungal agent for textile and in industrial water systems (Donard et al. 2001). TBT is more hazardous than TPT and causes chronic and acute toxic effect to aquatic organisms such as zooplankton, algae, molluscs and fishes at larval stage

(Gibbs and Bryan 1996). However, OT compounds are recognized as priority substances in the EU directive on environmental quality standards in the area of the water framework policy (EU 2008). In 2008, the total ban on using harmful organotin in antifouling paints was introduced (EU 2003; IMO 2001).

Tributyltin and triphenyltin are ionizable and make complexes by reacting with different ligands present in the environment (Arnold et al. 1997; Buck et al. 2003). The fate and accumulation of the organotin compounds are determined by the speciation of organotin compounds. In water, tributyltin and triphenyltin exist as various states such as neutral, non-dissociated molecules (triorganotin hydroxide and triorganotin chloride) and/or as organotin cations. Speciation is normally regulated by the pH and salinity of the water. In seawater the hydroxyl-complexes (>93 %) are the dominant species, whereas under acidic medium (pH 6), the TBT-cation exists in addition to the neutral TBT-Cl and TBT-OH complexes (Arnold et al. 1997; Burton et al. 2005)

2.13.1 The Behavior and Distribution in the Environment

The biological effects of the TBT and TPT are mainly determined by the distribution of the compounds in the environment, timescale and environmental conditions where they exist. However, the environmental distributions depend on the physical, chemical and biological properties of these compounds and the myriad of the localized conditions.

TBT and TPT are hydrophobic in nature and quickly partition into water-borne particles and their aqueous solubility depend on salinity, pH and temperature (Hoch 2001). After partitioning in water, OTs are trapped in the sediments. These may undergo resuspension into the water column and OTs are returned back into the water. This accumulation acts as a temporary sink and sediments are also a long-term source of dissolved-phase contamination (Hoch 2001; Donard et al. 2001). Organotin compounds can be accumulated at the surface layer of air-water interface due to their hydrophobic characters and may be quickly lost due to volatilization and UV degradation (Adelman et al. 1990).

2.13.2 Bioaccumulation and Biotransformation

Organotin compounds are accumulated significantly by aquatic species while some species degrade or eliminate the effects of bioaccumulation because of having an efficient enzymatic mechanism (Laughlin 1996). Biomethylation is the main process of biotransformation of the organotin compounds, whereas chemical agents such as methylcobalamin (it transfers a methyl group to metals), methyl iodide (it is produced by microalgae and reacts with metals and metal sulfides), humic and fulvic acid (produced due to decomposition of vegetation) and other methyl metals can transmethylate OTs (Hamasaki et al. 1995). Although methylation or biomethylation can engage sediment-or estuary –containing microorganisms,

Table 2.1 Estimated half-lives of TBT in various environmental matrixes

Environmental matrixes	Half-life
Freshwater	6–26 days (light), 4 months (dark)
Estuarine water	1–2 weeks
Sea water	6–127 days
Water/sediment mixture	5 months–5 years
Estuarine sediment	3.8 years
Soil	4–5 months (TPhT)

Adapted from Cima et al. (2003)

sulfate-reducing bacteria and yeasts are predominant in methylating organotins. Organotin compounds are degraded through different processes such as photolysis, biological degradation and chemical cleavage. The degradation rates of organotin compounds can be evaluated from its half-life. Table 2.1 shows the half-life values of TBT at different environmental matrixes.

2.13.3 Effects of Tributyltin (TBT) and Triphenyltin (TPT) on Organisms

Tributyltin and Triphenyltin show adverse effects on the survival, growth and reproduction processes of different aquatic organisms (USEPA 2003; Arizzi Novelli et al. 2002a). Further, (Duft et al. 2003) tested the carcinogenicity of TBT on some organisms. They influence the reproduction process acting as endocrine disrupters causing imposex phenomena in many adult aquatic organisms, e.g. gastropods and daphnids (USEPA 2003 and references therein), sea- and mudsnails and mollusks (Duft et al. 2003; Arizzi Novelli et al. 2002b), *Nassarius nitidus* (Pavoni et al. 2007). The action of tin-compounds alone can introduce those adverse effects in aquatic organisms, but the presence of some other organic or inorganic compounds can improve the effects (Pavoni et al. 2007 and references therein). Further, Arizzi Novelli et al. (2002a, b) tested the toxicity of TBT and TPT on embryos of sea urchin and their sperm cells, with the results of high poisoning symptoms to phenyltin and butyltin, respectively. In fish, TBT inhibits the gonad development and it reduces the thymus as well as the number of lymphocytes. In mammals, the immune system is suffering from a poisoning in TBT and TPT as well as the reproductive one (Sekizawa et al. 2001 and references therein). As organisms of the higher trophic chain have appropriate detoxifying enzymes, TBT and TPT seem to be toxic only for lower organisms (Arizzi Novelli et al. 2002b). Nevertheless, it can have lethal effects on several aquatic organisms, such as crustaceans, algae, echinoderma and fish (Dimitriou et al. 2003 and references therein).

3 The Lagoon of Venice as a Case of Study of Metal Contamination

The international scientific literature offers a large number of studies focusing on the presence, dynamics and cycling of various polluting and harmful elements in both estuarine and coastal environments. Among these, the pollution of the Lagoon of Venice (Northeastern Italy) has received increasing attention from various scientific and socio-economical authorities in the past two decades. The reasons are principally due to its geomorphological complexity and the anthropogenic pressure. This includes the industrial impact and the intensive lagoon use for tourism and fishing purposes. Due to the international significance, Venice and its lagoon were included in the World Cultural Heritage list (UNESCO 1987) and, at present, it hosts 2.5 million tourists per year staying more than six million nights (Comune di Venezia 2012). Scientific studies, have focused on the physical, chemical, biological and ecological aspects of the Lagoon of Venice. Most studies evidenced that it suffers from numerous and worrying environmental and social problems arising from geological features, climate change, economical causes and many kinds of anthropogenic pressures. Among those, the increased frequency and intensity of flooding events, caused by the climate change related sea level rise and land subsidence, certainly represent the main threat for the future of Venice. The debate on this is still far from being conclusive (Fontini et al. 2010; Carbognin et al. 2010). Another controversial issue is related to the high density of anthropogenic pressures, which impacts seriously all the environmental compartments of the lagoon and its ecosystem and cause sediment, water and air pollution, eutrophication phenomena, exploitation of biological resources, degradation of biota, sediment erosion and the consequent salt marsh losses. Since the pollution of the Lagoon of Venice was largely studied in the last decades, it represents an ideal case of study for transitional environments. Various pollutants from different pathways and from both diffuse and point sources have polluted the lagoon. Solidoro et al. (2010) reported a comprehensive overview of the responses of the lagoon ecosystem to both natural and anthropogenic pressures over the last 50 years. Thereafter, some key findings of recent researches are reported and subdivided by pollution sources and environmental issues. This section provides a quick overview of the studies conducted on the lagoon and highlights the major issues addressed in the last 20 years.

3.1 Source of Contamination: Industrial Zone of Porto Marghera

The direct discharges from the industrial zone of Porto Marghera are largely recognized as the main source of the pollution for the Lagoon (e.g., (Pavoni et al. 1988; Frignani et al. 1997; Bernardello et al. 2006; Carrer and Leardi 2006;

Zonta et al. 2007)). Porto Marghera is one of the most important industrial districts of Italy and includes chemical and metallurgical activities, oil-refining and storage, shipbuilding, incineration and thermoelectric power plants burning coal, gas and refuse derived fuel, wastewater treatments, hazardous waste incineration and other factories. It was built on the border of the lagoon starting from 1917 with activities related to oil and coal and largely grew in the following 50 years, reaching a maximum of 31,000 employees and a surface area up to 20 km² in the early 1970s. Today, following the reduction of the industrial activity, the employees have decreased to ~12,000, but the area of Porto Marghera probably is still the main source of contamination for the lagoon. In addition to the main industrial zone, the island of Murano hosts small and mid-size glass-making factories having an impact on the lagoon and the atmosphere (Giusti and Polo 2002; Rampazzo et al. 2008). All these inputs resulted in this sediment pollution near the main industrial areas.

A large number of studies, including the older ones, indicated that the industrial zone of Porto Marghera was the main responsible of elevated concentrations of heavy metals in the Lagoon of Venice. For example, Donazzolo et al. (1984) studied the heavy metals pollution of sediments and attributed it to the industrial area. These findings were followed by a large number of more specific studies. For example, Bellucci et al. (2002) reported maximum values of As, Cd, Hg, Pb and Zn in channels of the oldest part of the industrial area. Bernardello et al. (2006) studied the distribution of various heavy metals in the superficial sediments and pointed out the industrial zone of Porto Marghera as the main source of contamination. They also reported maps of pollutant concentrations for the inner part of the lagoon. Coccioni et al. (2009) indicated that the lagoon is affected by trace element pollution (Cd, Cu, Ni, Pb, Zn and Hg) with the highest concentrations in its inner part, which corresponds to the Porto Marghera industrial area, and also revealed a strong relationship between trace elements (in particular Mn, Pb and Hg) and the occurrence of abnormalities in tests with foraminifera. In addition, a study by (Sommerfreund et al. 2010) showed that the current industrial discharges are the main cause of the pollution nearby the industrial area, but they also pointed out the role of tributary loadings as a source of contaminants to the lagoon. Apitz et al. (2009) used statistical methods to separate natural background and anthropogenic concentrations of trace elements in radio-chronologically selected surface sediments of the Venice Lagoon. Han et al. (2011) studied the relocation effects of dredged marine sediments on mercury geochemistry and found that organic matter play a key role in the control of methylation rates via the control of Hg solubility.

Also the role of glass-making factories on the Island of was assessed, but the extent of studies was largely lower. For example, Giusti and Zhang (2002) described the trace element distribution in sediments, marine water and mussels of the Venetian Lagoon around Murano. They found that sediments are contaminated with many elements (Zn, Cu, Ag, As and Pb) with the highest levels in the fine fraction (pelite, <63 µm), which was the main carrier of heavy metals in most sites.

Some studies have also reported on the cycling, transport and the accumulation of many elements in the finest sediments. For example, Martin et al. (1995)

highlighted the significance of colloids in the biogeochemical cycling of some trace metals, whereas Zonta et al. (1994) showed a strong correlation between heavy metals and finer particles content in the sediment ($d < 7.8 \mu\text{m}$) in a study conducted in a salt marsh. Perin et al. (1997) measured the bio-available and non-bio-available phases of some heavy metals in a channel near the industrial zone. They found that the inner canals were very polluted with heavy metals in the form of highly insoluble sulphides.

3.2 Sources: Urban Settlements

The urban agglomerations include the historical part of Venice on the main lagoon island, and the mainland urban settlement of Mestre (a total of 270,000 inhabitants) across the causeway, with the surrounding inland areas. The population dynamics of the historical center had a population peak during the 1950s, before declining to $\sim 112 \cdot 10^3$ in the early 1970s and to $66 \cdot 10^3$ in the 2000s. The sewer system is normally organized for the mainland, whereas for the islands it is not conventionally structured with some leaks of untreated domestic sewage into the lagoon. There are no more major industries and factories in Venice historical centre and the direct role of sewer systems discharges in heavy metals pollution of the lagoon can be of minor importance. However, a significant indirect effect on the bioavailability of many elements can be supposed.

3.3 Source: Drainage Basin

Rivers, streams and land runoff (Collavini et al. 2005) reach the lagoon. The lagoon has a drainage basin of $\sim 1,850 \text{ km}^2$, which provides a mean yearly freshwater input of $35.5 \text{ m}^3 \text{ s}^{-1}$ peaking up to $350\text{--}600 \text{ m}^3 \text{ s}^{-1}$ during significant adverse meteorological conditions. The main freshwater tributaries, contributing with more than 50 % of the total annual load (Zonta et al. 2001; Zuliani et al. 2005, 2001), are few small rivers mainly located in the northern lagoon; some of them are partially canalized. The sediment input associated with these river inflows was estimated to be $\sim 33 \times 10^3 \text{ tons year}^{-1}$ in the period 1999–2000. This hydrological pattern creates a typical brackish environment with a salinity gradient that ranges from 10 psu near the mainland border to 32–37 psu at the inlets (Molinaroli et al. 2007) with summer peaks over 40 psu in the most confined areas of the northern lagoon (Facca et al. 2011). Some studies were carried out to assess the role of drainage basin in the contamination of the lagoon. Among others, the DRAIN project (Collavini et al. 2005) studied the pollutant loads from the 12 major tributaries of the Venice Lagoon during 1998–2000.

3.4 *Source: Air Pollution*

The atmospheric wet and dry polluting depositions are principally linked to the industrial emission processes (e.g., Guerzoni et al. 2005; Rampazzo et al. 2008; Rossini et al. 2010). Rossini et al. (2010) and Bettiol et al. (2005) analyzed the atmospheric bulk deposition of Venice and estimated the metal fluxes to the lagoon. They indicate that industrial sources have a quasi-permanent effect in the composition of atmospheric depositions.

3.5 *Source: Engineering Works*

In addition, the continuous intervention of man with hydraulic works and the excavation of the lagoon canals resulted in continuous changes of geomorphology. Among those, the re-construction of stone jetties at the lagoon inlets (1860–1934), the dredging of deep and large canals for navigation purposes (1926 and 1970) and the mechanical and often illegal clam catching (1990s) had wide impacts on many lagoon areas (Guerzoni and Tagliapietra 2006). Starting from the second half of 2000s, the construction of mobile barriers to safeguard the lagoon from exceptionally high tides (MoSE project) has further altered the structure of the lagoon inlets with likely consequences in hydrodynamics, sediment exchanges with the open sea and the whole ecosystem (Ghezzi et al. 2010). A comprehensive chronology of the most relevant events that affected the lagoon morphology in the last century is summarized in Sarretta et al. (2010).

3.6 *Effects of Pollution on Organisms*

A number of studies were carried out in both animal and plant species to detect the bioaccumulation and the effects of many pollutants in the Lagoon of Venice. Some studies found high levels of metals in both sediments and target gastropods (Berto et al. 2012). Nesto et al. (2007) evaluate levels and effects of trace metals (Cd, Cr, Cu, Fe, Mn, Pb, Zn), PAHs and PCBs in mussels and fish native of the Lagoon of Venice.

Berto et al. (2006) analyzed the levels of mercury in both sediments and Gastropoda *Nassarius reticulatus* in the southern Venice Lagoon and stated that a main cause for mercury pollution might be attributed to the antifouling paints used in great quantity in the recent past near the town of Chioggia. Berto et al. (2007) analyzed the recent contamination of TBT and found high content of organotin compounds in the gastropods sampled near the dockyards, harbors, and marinas.

Among other species, the mollusc *Mytilus galloprovincialis* was used in most studies, probably for being edible and largely available in the lagoon. Zatta

et al. (1992) measured the content of heavy metals (Cd, Co, Cu, Cr, Hg, Fe, Mn, Ni, Pb, Zn) and As accumulated in the mollusc *Mytilus galloprovincialis* from the Venetian lagoon. Widdows et al. (1997) studied the effects of pollution on *Mytilus galloprovincialis* and demonstrated that the inhibitory effects of toxicants on the growth of organisms living in the more polluted inner sites. Da Ros et al. (2000) studied the cellular and biochemical response of mussels transplanted from a relatively pristine site to a polluted one and vice versa and evidenced a direct influence in the thinning of the digestive cells and in the increasing number of lysosomes in mussels from the more polluted site. Giusti and Zhang (2002) described the trace element distribution of the *Mytilus galloprovincialis* around the Island of Murano. Their results indicated that the highest trace element concentrations were in the soft tissue of mussels. However, the levels detected were within the recommended Italian and international guidelines for human shellfish consumption, except for arsenic. Irato et al. (2003) sampled a series of different bivalve mollusks: *Mytilus galloprovincialis*, ark clam (*Scapharca inaequivalvis*), and Japanese littleneck (*Tapes philippinarum*) in two sites and analyzed the concentrations of essential and nonessential metals in digestive gland and gills of each bivalve. Results indicated that all the three species accumulated metals to a considerable extent, and also evidenced the *M. galloprovincialis* and *S. inaequivalvis* as sentinel organisms to be used specifically for Zn pollution. Sfriso et al. (2008) investigated the concentration changes of elements (As, Hg, Cd, Cr, Co, Cu, Pb, Mn, Ni, V, Zn, Fe, and Hg) in the soft tissues of *Tapes philippinarum* during its growth. Arsenic was reported higher in clam tissues than in surface sediments and suspended particles, whereas other elements (Cr, Pb, Mn, Ni, and Fe) were found higher in suspended particles and sediments than in *Tapes*.

A large number of studies was also conducted in plant organisms, mainly algal species. Bragato et al. (2006) monitored growth dynamics, nutrient and heavy metal accumulation in the two dominating macrophytes *Phragmites australis* and *Bolboschoenus maritimus*, but they found that the heavy metal concentration in water and soil was not correlated to the plant content. Favero et al. (1996) investigated the metal accumulation of *Ulva rigida* and reported that this specie specifically accumulates Fe. Caliceti et al. (2002) measured the concentrations of heavy metals (Fe, Zn, Cu, Cd, Ni, Pb, Cr, As) in seven seaweeds of environmental and commercial relevance. They found high Pb levels in *Ulva* species and to a lesser extent in *Gracilaria*, whereas Brown seaweeds (*Cystoseira*) were highly contaminated by arsenic. Sfriso et al. (1995) reported that the dominant macroalgal species in the central lagoon, *Ulva rigida*, shows a preferential enrichment of Zn and Mn compared to other metals.

4 A Concluding Remark

After the period of the worst industrial impact and eutrophication, which caused anoxic events till the eighties, the lagoon appeared to enter a phase of progressive improvement of environmental conditions. In this process, in addition to a significant reduction of industrial activity and stricter limits to emissions enforced by law, an important role was played by the water exchange with the sea that ensured a water renewal and enabled a removal of the finest most polluted sediments from inside the lagoon out to the sea. However, as a consequence of the building of the MoSE barriers at the lagoon-sea channels, the water exchange is expected to be significantly limited. More research is in progress.

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