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PhD Student
Maria Bonsignore

Tutor

Prof. Paolo Censi

University of Palermo

Co-Tutor

Dott. Mario Sprovieri

IAMC- CNR Capo Granitola

Coordinator

Prof. Francesco Parello

University of Palermo

In collaboration with the Institute of Coastal Marine Environment, IAMC-CNR of Capo Granitola

Project: "***Dinamica dei processi di evasione, trasporto e deposizione del mercurio nell'area industrializzata della Rada di Augusta e definizione delle mappe di rischio sanitario per le popolazioni residenti"***

Reviewers

Dott. Stefano Covelli,
Dipartimento di Matematica & Geoscienze (DMG) Università degli Studi di Trieste

Prof. Pierpaolo Zuddas

Université Pierre et Marie Curie, Paris-Sorbonne Institut des Sciences de la Terre de Paris.

A Mattia

Una buona regola di vita è avere sempre il cuore

un po' più tenero della testa.

Alexander Graham Bell

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Bonsignore M. , Salvagio Manta D., Oliveri E., Sprovieri M., Basilone G., Bonanno A., Falco F.,Traina A., Mazzola S. (2013). *Mercury in fishes from Augusta Bay (southern Italy): Risk assessment and health implication*. Food and Chemical Toxicology 56 (2013) 184–194

Attachment II:

Bagnato E., Sproveri M., Barra M., Bitetto M., Bonsignore M., Calabrese S., Di Stefano V., Oliveri E., Parello F., Mazzola S. (2013). *The sea–air exchange of mercury (Hg) in the marine boundary layer of the Augusta basin (southern Italy): Concentrations and evasion flux.* Chemosphere 93, 2024‑2032.

Abstract

Mercurial, the metaphor for volatile unpredictable behavior, aptly reflects the complexities of one of the most insidiously interesting and scientifically challenging biogeochemical cycles at the Earth's surface. At the base of this toxic metal cycle there is the conversion between the different Hg chemical species, in which the balance between the reduced and oxidized forms depends primary on redox system conditions.

The potential risks of human exposure to Hg, especially in the form of monomethylmercury (MMHg), particularly prenatally, and the potential deleterious ecological consequences from localized to global scale Hg pollution, have given much impetus to mercury studies and regulatory activities at international level. Much of this advancement has come since the early 1970s, and the growth in mercury research continues at breakneck pace. The menace of this item for environment and human health deserves further information concerning the geochemistry of mercury, especially in coastal marine system.

The Augusta Bay is a semi-enclosed marine area, located in the SE of Sicily (southern Italy), well-known because of the high Hg pollution. The area indeed has experienced, since the early 60s, a significant industrialization phase that put in several chemical and petrochemical plants and oil refineries resulting in a severe pollution of the surrounding environment. In particular, the petrochemical district of Augusta Bay hosted one of the most important chlor-alkali plant in Italy, that produced chlorine and caustic soda by electrolysis of sodium chloride aqueous solution in electrolytic cells with a graphite anode and metallic mercury cathode. Uncontrolled chemical discharge of Hg occurred in the Augusta Bay until 1978, when restrictions were imposed by the Italian legislation. For this reason, in the last decade, several studies have provided detailed information on the pollution levels and risks for human health of resident populations of Augusta Bay. The effects of this indiscriminate Hg discharge include the alarming high concentrations of the

element recently measured in sediments of the basin, prompting the Italian government to include the Augusta basin in the National Remediation Plan. The “Augusta case“ menaces to not remain confined to a “local problem”, but to became a large-scale threat.

Indeed, the effects of meso-scale circulation of the Ionian Sea create a higher potential risk for HgT contamination of the basin, being affected by the transit and transformation of the major water masses, which regulate the general thermohaline circulation in the upper, intermediate and deep layers, respectively. Owing to the geographical location of the Augusta basin, its outflowing shelf waters are immediately intercepted by the surface Atlantic Ionian Stream (AIS) and mixed with the main gyres of the eastern Mediterranean Sea, thus representing a risk for the large-scale marine system. This complex water circulation system, together with the closeness with the steep continental slope (part of the Malta escarpment), make the area a potential point sources of mercury for the entire Mediterranean sea, as previously speculated by Sprovieri et al. (2011).

All this features make the Augusta Bay an ideal natural laboratory for deeper insights on the biogeochemical cycle of mercury in a coastal marine environment and the need to investigate the large-scale effect of Augusta Bay pollution has become imperative!

With the aim to fill this requirement, an integrated model on the biogeochemical cycle of Hg has been created.

Hg cycle is a very articulated topic. Once introduced in the aquatic system environment the fate of Hg in the marine system is affected by sorption/ desorption processes onto suspended particulate matter and, based on associated kinetics, it may be partially transferred from surface waters to bottom sediments. Microorganisms, at the water/sediments interface such as sulfate reducing bacteria (SRB), mediate the transformation of inorganic Hg to MMHg with high rates of methylation favored by the presence of high content of organic matter under reducing environmental conditions. Therefore, sediments are considered key contributors of MMHg to the marine ecosystem. Clearly, this analysis stresses the necessity for better knowledge of the specificity of the mercury biogeochemical cycle in this particular environment through the gathering of more data on the distribution and fluxes among the various compartments including the water column, sediment, atmosphere and biota.

This multidisciplinary approach offers a nice opportunity to explore the biogeochemical dynamic of mercury in highly complex coastal areas under important anthropic impact and the potential on larger scale diffusion.

Multiple oceanographic cruises, realized during 2011-2012 period, permitted to collect samples of sediments, seawaters and fishes inside and outside the Augusta Bay.

Furthermore in order to trace the entire chain, from sources (polluted sediments) to sink (man), analysis of Hg in fishes (the main route of Hg uptake for humans), and toxicological aspects have been addressed. Analysis of THg in muscles and liver of some pelagic, demersal and benthic species captured inside and outside the semi-enclosed area, has been analysed in order to explore the effects of HgT pollution on fish compartment and to assess the potential health risks associated with the consumption of contaminated fish. THg content of fishes shows a wide range of concentration (range: 0.02 - 2.71 µg g^{-1}and 0.03 -9.72 µg g^{-1} in muscles and in livers respectively), with highest values measured in benthic species and the lowest in pelagic ones. This increasing trend along the habitat depth suggests an active release mechanism of mercury from polluted sediments to the water column, with consequent effects of bioaccumulation in the trophic web. Anomalous THg content measured in pelagic species captured in the external zone of the bay confirms the role of the Augusta marine environment as pollutant source of Hg for the surrounding area and underscores the crucial risk associated with contaminant transfer from the basin to the open sea. Finally, values of hazard target quotient (THQ) and estimated weekly intake (EWI) demonstrate that consumption of fishes caught inside the bay represents a serious risk for human health and suggests caution in consuming demersal and benthic fishes from outside the Augusta Bay, definitively demanding for appropriate social actions.

Hg distribution in sediments (range: 1.77 - 55.34 mgKg^{-1}; mean: 13.78 ±10.72 mgKg^{-1}) clearly divides the area into three parts, with the lowest values recorded in the northern Augusta Bay, intermediate value in the center and the highest HgT concentrations recorded in the southern part of the Augusta basin (from the Pontile Cementeria down to the dam) with decreasing values from the coastline. Despite sequential extraction procedure (SEP) documented that the most part of HgT in sediments consists of strong complexes (~80% of HgT as strong complex, ~15% of Hg as less strong forms and ~ 2% of HgT as more soluble and bioavailable forms), some anaerobic microorganisms can manage these stable Hg trapped in minerals structures as substrate for their metabolism, making Hg more easily bioavailable for the environment. Analysis of THg and DHg content at different quote of the water column, provided significant information on Hg distribution along space and depth. The HgT distribution in seawaters (range: 0.45 - 129.27 ngL^{-1} and >0.01 - 21.3 ngL^{-1} for THg and

HgD respectively), putted in light an evident increasing trend of Hg content toward the southern and more contaminated part of the Augusta Bay, where waste spillage from chlor-alkali plant occurred. A clear trend was also observed on the vertical, with Hg concentration increasing near the bottom and reducing in surface water, strengthening the role of Augusta sediments as sources for the overlying water. Moreover the unexpected THg concentrations measured in seawater outside the bay (range: 2.62-11.95 ng L^{-1}; mean: 6.46±2.95 ngL^{-1}), confirmed the hypothesis of transport of Hg from Augusta harbor to the open sea representing a vehicle of contamination for the entire Mediterranean basin through the complex circulating currents affecting the western Ionian.

In this scenario, fluxes assessment at the interface sediments-seawater-air became crucial in order to create a mass balance of Hg in the study area and to determine the net outflow for the Mediterranean sea. Detailed information on the mobilization processes from sediment to seawater and consequent escape to the atmosphere has been investigated. For this reason, for the first time in this area, a benthic chamber and a dynamic accumulation chamber, have been employed in order to evaluate fluxes at the interfaces sediments/seawater and seawater/air and to recognize equilibrium of exchanges among phases. Using in situ accumulation chamber Bagnato et al., 2013 reported an estimated sea–air Hg evasion for the entire Augusta basin (~23.5 km^2) of about 9.7 ± 0.1 g d^{-1} (~0.004 t yr^{-1}), accounting for ~0.0002% of the global Hg oceanic evasion (2000 t yr^{-1}).

Simultaneously using in situ benthic chamber, a total flow from sediment to seawater for the whole Augusta Bay has been estimated in 0.22 kmol y^{-1} in 2011 (0.05 ty^{-1}) and 0.38 kmol y^{-1} in 2012 (0.11 ty^{-1}). The mass balance calculation permitted to estimate a HgT output from the Augusta basin to Ionian surface waters (O) corresponding to an average of 1.29 kmol y^{-1}.

Analysis of Hg isotopes in sediments and fishes of the Augusta Bay, provided unique information on Hg sources in the environment and processes influencing Hg cycling. The success of such an approach strongly depends on two factors. First, different natural and anthropogenic Hg sources must have analytically discernible Hg isotope signatures. Second, the processes that transport and transform emitted or discharged Hg into the environment must not obscure the original Hg source isotope signatures. This requires that fractionation of Hg isotopes after release is either small relative to source differences or is predictable enough to be corrected for, allowing estimation of the source isotopic composition. The magnitude of

mass-dependent (MDF) and mass-independent fractionation (MIF) has been described primarily as δ^{202}Hg and Δ^{201}Hg. The positive MIF fractionation in fishes, especially in pelagic one, demonstrated photochemical reaction of Hg(II) prior of the intake in the marine food web. Sediments isotopes fractionation demonstrated reaction of methylmercury production biological mediated. A geographic pattern in δ^{202}Hg and Δ^{199}Hg values suggests that the sources of Hg to the sediment are locally controlled. Hairs exhibit positive MIF fractionation, suggesting reaction of photochemical reduction of MeHg in presence of organic matter. The overlapping δ^{202}Hg values of both sediments and fishes suggested sediments represent the source of Hg for fish. The positive relationship obtained by plotting Δ^{201}Hg *vs.* Δ^{199}Hg of both hairs and sediments demonstrate fish consumption represents the first pathway of exposure for human. Difference of 2‰ between δ^{202}Hg in fishes and values, could be due to could suggest that substantial MDF takes place during MMHg human metabolism

Rare Earth Elements (REEs) are important because their geochemical properties enable them to be powerful tracers of chemical processes. Their distribution has been investigated in seawater of the Augusta Bay in order to verify if anthropogenic sign can also transpire through the investigation of REE. The REEs distribution along the water column suggests that the high dissolved organic matter created ideal condition for an increasing of REE in dissolved phases, much to hide the negative Ce anomaly usually recorded in the oligothropic water. Gd anomaly, expressed as Gd/Gd*>1, suggests significant contributions of the petrochemical industries, using gadolinium, in the form of gadolinium oxide, as petroleum cracking catalyst.

A common thread, started from the evaluation of Hg in the key component of the cycle, the study of fluxes at the interfaces, the evaluation of Hg isotopic fractioning and the REE distribution in water column, permitted to evaluate the fate of Hg in the Augusta Bay and the main processes rule the Hg biogeochemical cycle.

Chapter I:
Introduction

1 Preface

The knowledge of the Hg complex biogeochemical cycle improves at the beginning of the twenty-first century, when the potential risks of human exposure to mercury (Hg), especially in the form of monomethylmercury (MMHg) and the potential deleterious ecological consequences from mercury pollution have given much impetus to mercury studies and regulatory activities. Nowadays the growth in mercury research continues at breakneck pace.

Studies of the mercury behavior in strongly impacted sites, especially in coastal marine environment, result crucial in order to a deeper understanding on the biogeochemical cycle of this dangerous element. In this view the Augusta Bay, due to the careless discharge of Hg from industrial and petrochemical plants, and the complex water system involving the Sicilian coast, represents an ideal natural laboratory for advancement on Hg geochemistry.

In particular, the southernmost part of the Augusta basin hosted one of the most important chlor-alkali plants of Italy (Syndial Priolo Gargallo), which made up over 20% of total Italian emissions in 2001 (Le Donne and Ciafani, 2008). In order to supply helpful data on the Hg behavior in a polluted and complex coastal marine system, an integrated model on the biogeochemical cycle of Hg in the Augusta Bay will be detailed.

The aims of this thesis are specified below.

1.1 Goals of the thesis

1.1.1 General goal

✓ The main aim of this PhD thesis is the generation of integrated biogeochemical models of mercury in the Augusta Bay by the analysis of processes at the sediment-seawater-atmosphere interfaces and the transfer in the trophic web

1.1.2 Specific goals

✓ Study of Hg bioaccumulation processes in the biotic compartment and risk analysis for human health;

- ✓ Analysis of Hg fluxes at the interfaces (sediment-water, water-atmosphere);
- ✓ Analysis of the metal speciation in sediments;
- ✓ Mass balance calculation;
- ✓ Study on Hg isotopes finalized to the assessment of sources and pathways of mercury contamination;
- ✓ Study of REEs distribution in the water column as tracers pollution.

1.2 Mercury element

Mercury is a natural element of the earth, a lucid liquid metal, present in a variety of chemical forms in rocks, soil, water, air, plants and animals. It is found usually combined with both inorganic (e.g., the mineral cinnabar, a combination of mercury and sulfur) or organic (e.g., MeHg) compounds (EPA, 1980; Clarkson et al., 1984), although occasionally Hg occurs in its elemental form, as (Hg^0) in liquid or vapor forms.

Hg has not known biological function and it is potentially hazardous for human health. Biological processes can convert forms of mercury with relatively low toxicity, in the most toxic form, methylmercury (MeHg) present in fish and seafood products, while in other foods, mercury is in inorganic and not toxic form (WHO, 1991b).

Moreover mercury can bioconcentrate in organisms and undergoes biomagnified processes through the food chains (e.g., Westöö, 1966; Fitzgerald and Watras, 1989; Wiener et al., 1990; Gilmour and Henry 1991; Watras and Bloom, 1994; Watras et al., 1994; Rolfhus and Fitzgerald, 1995; Hall et al., 1998; Benoit et al., 2003).

Increasing of Hg in environmental compartment has been demonstrated to have increased up to 5X pre-cultural levels, primarily as a result of man's activities, sometimes with dramatic consequences on environment and human health (Bakir et al., 1973; Smith, 1975; George, 2001).

1.3 Chemical properties

Mercury element (Hg, from the Latin hydrargyrum or “watery silver”; Fitzgerald and Clarkson, 1991) is readily familiar as a silvery liquid at room temperature and its highly volatility.

Mercury is the metal with the lowest melting point and with a vapor pressure lower than liquids. Due to its high reduction potential, mercury behaves in similar way to a noble metal at room temperature, resulting not attacked by non-oxidizing acids, alkali, oxygen, nitrogen, phosphorus, carbon, ammonia, hydrofluoric acid and hydrochloric acid, while it is rather sensitive to nitric acid, bromide and iodide, halogens and ozone. At room temperature mercury oxidizes very slowly, but its oxidation proceeds with a useful speed to 300-350 °C.

Mercury easily forms alloys, or amalgams, with almost all of the most common metals, including gold and silver. Chemical speciation is probably the most important variable influencing ecotoxicology of Hg (Boudou and Ribeyre, 1983). Mercury can exist in three oxidation states: elemental mercury (Hg^{o}), mercurous ion (Hg^{I}), and mercuric ion (Hg^{II}). The oxidation state +1 is presented in the form Hg_2^{2+}, in which the two atoms of mercury are linked together with covalent bonds.

Mercury compounds in an aqueous solution are chemically complex and influenced by a variety of factors: pH, alkalinity, redox, organic matter and other variables. A wide variety of chemical species are liable to be formed, having different electrical charges and solubility. For example, $HgCl_2$ in solution can speciate into $Hg(OH)_2$, Hg^{2+}, $HgCl^{+}$, $Hg(OH)^{-}$, $HgCl^{3-}$, and $HgCl_4^{2-}$, anionic forms predominate in saline environments (Boudou and Ribeyre, 1983).

In solution mercurous ion is stable only in excess of metallic mercury, otherwise shift in the metallic mercury and mercuric ion. The chemical forms of mercury of interest in biological and environmental samples are listed in Table 1:

Table 1: Mercury compounds in environmental and biological samples.

Elemental mercury		Hg (0)
Inorganic Hg forms	mercuric ion	Hg^{2+}
Mercurous ion		Hg^{+}
Mercuric sulfide (o cinnabar)		HgS
Organic Hg forms	Methilmercury	CH_3Hg^{+}
Ethylmercury		$C_2H_5Hg^{+}$
Phenylmercury		$C_6H_5Hg^{+}$
Dimethylmercury		$(CH_3)_2Hg$

1.4 Sources and application

The remarkable Hg properties and its major mineralized form (cinnabar, HgS) have been well known (Goldwater, 1972; Fitzgerald and Clarkson, 1991). It was initially used in decorations, cosmetics and religious rites, but the introduction of mercury in science occurred in 1643 with the invention of Torricelli's barometer, for atmospheric pressure measures, and in 1720 with the Fahrenheit mercury thermometer.

Other employs include the use of Hg as “spring tonics,” as a “cure” for syphilis, and as panacea for other afflictions (Fitzgerald and Clarkson, 1991). Mercury can reach the environment through both natural and anthropogenic source (Turekian and Wedepohl, 1961; Mason et al., 1994;). The first one includes volcanoes, both volcanoes aerial and sub-marine activities (Patterson and Settle, 1987; Fitzgerald, 1981, 1996; Mason et al., 1994), weathering inputs from mineralized mercury deposits (Koski et al., 1994; Ozerova, 1996; Stoffers et al.,1999), low-temperature volatilization (Xiao et al., 1991; Carpi and Lindberg, 1998; Gustin et al., 1999; Boudala et al., 2000) and volatilization from the ocean (Fitzgerald and Clarkson, 1991). Various and widespread are the human-related sources of mercury to the environment, and contribute to ~2/3 of the mercury emitted from land-based sources each year (Pacyna and Pacyna, 2002).

In particular, inputs of mercury to the environment via the atmosphere, particularly high temperature processes due to coal and municipal waste burning, are of the greatest concern (NAS, 1978; Wang et al., 2000; Long and Kelly, 2002; Pacyna and Pacyna, 2002; Wilhelm, 2001; Fitzgerald and Clarkson, 1991). A short summary on global anthropogenic emissions of Hg calculated by Pacyna et al., (2006) is reported in Table 1.

Table 2: Global anthropogenic emissions of Hg in 2000 (in ton) (Pacyna et al., 2006)

Continent	**Stationary combustion**	**Cement prod.**	**Non-ferrous metal prod.**	**Pig iron & steel prod.**	**Caustic soda prod.**	**Mercury prod.**	**Gold prod.**	**Waste disposal**	**Other**	**Total**
Africa	205.2	5.3	7.9	0.4	0.3	0.1	177.8		1.4	398.4
Asia (Excl. Russia)	878.7	89.9	87.6	11.6	30.7	0.1	47.2	32.6	0.9	1179.3
Australasia	112.6	0.8	4.4	0.3	0.7		7.7	0.1		126.6
Europe (Excl. Russia)	88.8	26.5	10	10.6	12.4			11.5	15.3	171.1
Russia	26.5	3.7	6.9	2.7	8		3.1	3.5	18.2	72.6
South America	31	6.5	25.4	1.4	5	22.8				92.1
North America	79.6	7.7	6.4	4.3	8	0.1	12.2	18.7	8.8	145.8
Total	1422.4	140.4	148.6	31.3	65.1	23.1	248	66.4	44.6	2189.9

The category defined as ‘‘other sources’’ includes chlor-alkali production using the mercury cell process and production of battery, electrical lighting, wiring devices, switches and instruments (Pacyna et al., 2006). Although the use of the mercury cell to produce caustic soda in the chlor-alkali industry has decreased significantly over the past 10–15 years worldwide (www.eurochlor.org), the global consumption of mercury in this industry was still of ~800 ton in the year 2003 (Maxon, 2005).

Five chlor-alkali plant are still working in Italy: Tessenderlo of Pieve Vergonte (VCO); Caffaro of Torviscosa (Ud); Syndial of Porto Marghera (Ve); Solvay of Rosignano (Li); Solvay of Bussi sul Tirino (Pe). The sixth one, Syndial of Priolo Gargallo (Sr), located in the Augusta bay, is closed since 2005 (Le Donne and Ciafani, 2008).

Although some industries have established programs aiming at the reduction of mercury releases to the environment, as the chlor-alkali industry (EuroChlor, www.eurochlor.org), the phaseout of the mercury process in the chlor-alkali industry will be prolonged after 2020 (Pacyna et al., 2006).

1.5 The biogeochemical cycle of mercury in the environment

In marine environments, Hg undergoes a complex environmental cycle occurring between sediments, water column and atmosphere, and that implies the involvement of biotic compartment.

The balance between the reduced and oxidized Hg form depends essentially on the redox reactions of these media. In this view sediments can represent source of sink for Hg.

Inorganic mercury, present in environmental compartments, is mainly in oxidation state +2. Due to its nature of sulfur loving (i.e., chalcophilic) (Fitzgerald and Clarkson, 1991), the tendency of Hg^{2+} to bind with the sulfur-groups is notable, especially where the concentration of HS^- and S^{2-} is high, as in anoxic waters and sediments, where mercury sulfide, solid and slightly soluble in water, tends to accumulate into the sediments (Langer et al., 2001; Gilmour and Henry, 1991).

Methylation of inorganic mercury is the most important transformation affecting the behavior and fate of mercury in aquatic systems (Fitzgerald and Clarkson, 1991).

Indeed MMHg production represents the main vehicle of transport from sediment to seawater and fishes. In situ methylation of "reactive" or bioavailable mercury in aquatic systems appears to be predominately biotic (Benoit et al., 2003, Gårdfeldt et al., 2003) and causes MMHg accumulation in freshwater foodwebs (e.g., Westöö, 1966; Wiener et al., 1990; Gilmour and Henry 1991; Watras and Bloom, 1994; Watras et al., 1994; Hall et al., 1998).

Benoit et al. (1999 a, b, 2001 a, b) proposed that sulfide-oxidizing bacteria (SOB), being chemolithotrophs, are able to use sulfide as a source of energy and reducing power.

The mechanism for uptake of inorganic mercury by methylating bacteria is not known, Benoit et al., (2003) propose the mechanism of diffusion of HgS^0 through the cellular membrane as the key factor. Bacterial mediation enhances the rates at which mercury, a “soft acid,” can form alkylated species in aquatic environments.

Microbial production of MMHg in sediment is influenced the activity of methylating organisms (i.e., SRB) and by the availability of inorganic mercury for methylation. Maximum mercury methylation occurs in sediments where organic matter and sulfate are sufficiently high as to stimulate SRB metabolism, but not so high as to cause accumulation of sulfide, reducing the availability of mercury for methylation (Gilmour and Henry, 1991).

Other variables, such as dissolved organic carbon (DOC) and pH strongly affect the ultimate fate of mercury in an ecosystem. An increasing water acidity (decreasing pH) and/or DOC content, usually result in higher mercury levels in fishes and in higher methylation rate.

Methylation amplifies the insidiousness of historic mercury pollution and health risks to wildlife and humans. As well as inorganic mercury, MMHg, has a high affinity towards the ions Cl^-, Br^-, HS and OH and, therefore, in environmental compartments is present in associated form in different species depending on the ions concentration.

In natural waters MMHg levels are generally much lower than those of inorganic Hg, due to the difficulty with which the methylation reactions occur in aqueous phase and because of partial decomposition of mercury due to sunlight. On the contrary in sediment and biota (especially in fish) methylmercury concentration is much greater due to bioaccumulation phenomena.

Although MMHg represents the dominant chemical form in most of the organisms of the upper food pyramid, it constitutes only a small fraction of the total mercury present in an aquatic ecosystem (Lindqvist et al., 1984). Indeed once in the water column, in addition to the methylation process, Hg^{2+} can undergo reduction processes leading to the formation of volatile chemical species (Hg^0) and return to the atmosphere though

(Fig. 1) through which the ocean prolongs the residence of mercury at the Earth's surface.

The volatile chemical species of dissolved mercury are indicated by the acronym DGM (Dissolved Gaseous Mercury) of which the elemental mercury represents more than 90% (~1.25 yr; Hudson et al., 1995, Fitzgerald and Gill, 1979; Bloom N. S. and Fitzgerald, 1988; Iverfeldt, 1991a), although some chemical forms of Hg^{2+} also exist in the gas phase (the so-called "reactive gaseous mercury" or RGM; Stratton W. J. and Lindberg, 1995; Sheu and Mason, 2001; Landis et al., 2002).

The reduction mechanisms of Hg^{2+} are due to photo-chemical reactions (abiotic processes) and to the intervention of prokaryotic and eukaryotic organisms (biotic processes) (Fig. 1).

Atmospheric oxidation of elemental mercury in atmosphere goes back to the water column through dry and wet deposition (Lindqvist et al., 1991) (Fig. 1). Mason, Fitzgerald, and Morel in 1994 ("MFM") provided a Hg biogeochemical model, suggested that about half of the modern pollution-related emissions (20 Mmol yr^{-1}) enter the global cycle. Pacyna and Pacyna (2002) reported comparable value, estimating for 1995 an amount of ~9.6 Mmol yr^{-1}.

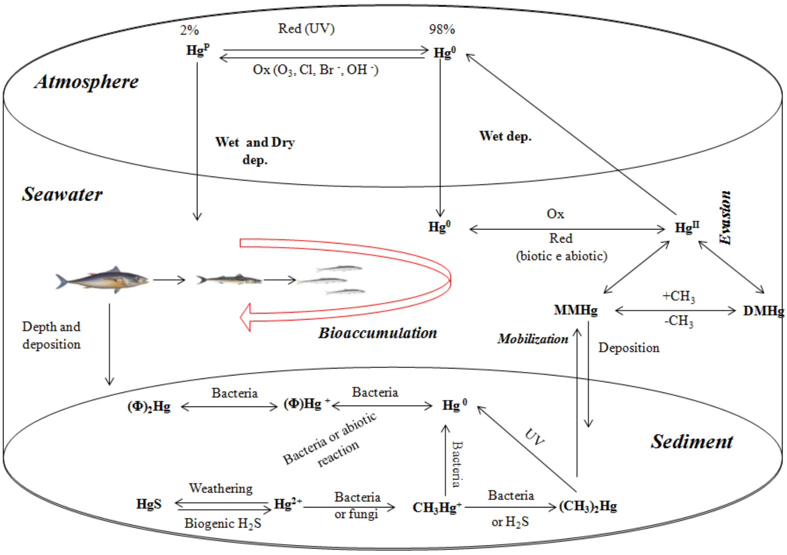


Figure 1: *Scheme of the biogeochemical cycle of Hg in marine environmental system (Fitzgerald and Clarkson, 1991 modified)*

1.5.1 How does mercury enter the food chain?

The exact mechanisms by which mercury enters the food chain remain largely unknown. As discussed above, certainly bacteria that process sulfate (SO_4^{2-}) in the environment take up mercury in its inorganic form and convert it into MMHg through metabolic processes.

The MMHg creation is important not only because its toxicity is greater but also because organisms require times considerably longer to eliminate it. Because animals accumulate methylmercury faster than they eliminate it, animals consume higher concentrations of mercury at each successive level of the food chain. Numerous biological and abiotic factors modify the toxicity of Hg compounds, sometimes by an order of magnitude or more.

Bellante et al., (2011) documented the existence of different mechanisms of bioaccumulation, through different diet patterns and/or uniqueness in physiological and/or biological control of Hg incorporation for *S. coeruleoalba* and *T. truncates* of the Mediterranean sea. Different studies demonstrated the MMHg accumulation in fish not only poses a threat to human health (Grandjean et al., 1997; Davidson et al., 2000), but also can reduce the reproductive success of piscivorous wildlife (e.g., Scheuhammer, 1991) and of fish themselves (Wiener et al., 1990b; Wiener and Spry, 1996; Hammerschmidt et al., 2002).

The evidences of the Hg effects were assorted and demonstrated by an extensive scientific literature, as well as news accounts of these tragedies. Particularly, the Japanese poisonings resulted from consumption of locally fish and seafood contaminated principally by MMHg abiotically synthesizing as a by-product during the acetaldehyde production.

In the Iraqi tragedy, bread was the contamination source, which had been made with flour, unknowingly milled from wheat treated with MMHg as a fungicide (Bakir et al., 1973). The following works on the Japanese poisonings provide an overview and useful starting point for a more in-depth examination: Smith (1975) Japan Public Health Association (2001), The Social Scientific Study Group on Minamata Disease (2001) and George (2001). The USEFDA and the JECFA, 2000 recommendation is equivalent to 0.5 mg kg^{-1} of body weight per day. The USEPA fix the reference dose in 0.1 μg Hg kg bw^{-1} d^{-1} (http://cfpub.epa.gov) while the acceptable daily intake determined by WHO (2003) is 0.23 μg Hg kg bw^{-1} d^{-1}).

1.6 Health concerns

The classification of mercury and its compounds, in accordance with 67/548/CEE Directive on the classification and labeling of hazardous substances, is "toxic" and "dangerous in environment". The toxicity to humans and other organisms depends on the chemical form, the amount, the pathway of exposure, and the vulnerability of the exposed person (US EPA, 1989).

Human exposure to mercury can result from a variety of pathways, including consumption of fish and fish products (primary pathway of exposure), occupational and household uses, dental amalgams, and mercury-containing vaccines. Mercury toxicity depends of the absence of homeostatic mechanism that regulates and limits its accumulation in the body. Mercury binds strongly with sulfhydryl groups, and has many potential target sites during embryogenesis; phenylmercury and methylmercury compounds (mono and dimethylmercury MMHg, DMHg) are among the strongest known inhibitors of cell division. MMHg and other organomercury compounds, cross the placental barriers and can enter mammals by way of respiratory tract, gastrointestinal tract, skin, or mucous membranes (Elhassani, 1983).

The toxicological properties of mercury for environment and human health strongly depend on physical and chemical form in which it occurs. Hg vapors for example, are very dangerous if inhaled, reach the lungs causing, pulmonary edema, pain and peeling of the respiratory epithelium of the bronchi.

Acute intoxication by organic mercury affects the central nervous system causing tremors, memory problems and neurodegenerative diseases such as Alzheimer's and Parkinson's. However only 10% of inorganic mercury is ingested it is absorbed as salt of Hg^2 and Hg^+, reach the human body through the skin and the oral cavity, causing diseases related to the digestive system and kidneys and renal toxicity in which cause apoptosis increment (type of cell death, different from necrosis) for inactivation of nuclear factor-kB (NF-kB), a thiol-dependent transcriptional system. Thiol groups (R-SH), which compete with Hg for protein binding sites, are the most important antagonists of inorganic mercury salts (Das et al., 1982). Mercury-antagonistic drugs include 2,3-dimercaptopropanol, polythiol resins, selenium salts, vitamin E, and sulfhydral agents (Nriagu et al., 1979;

Magos and Webb, 1979; Elhassani,1983). The protective action of selenium (Se) against adverse or lethal effects has been reported for algae, aquatic invertebrates, fish, and mammals (Bellante et al., 2011; Magos and Webb, 1979; Heisinger, 1979; Chang et al., 1981; Lawrence and Holoka, 1981; Das et al., 1982; Gotsis, 1982; Eisler, 1985; Satoh et al., 1985).

1.7 Mercury in Mediterranean Sea

1.7.1 The Mediterranean geochemical anomaly

The Mediterranean basin is characterized of relevant Hg sources of both natural and anthropogenic origin (Bacci, 1989). Table 3 reports range or mean mercury concentrations in intermediate and deep waters at different stations of the Mediterranean sea and of the world ocean. The dispute on what is the primary source that determines the so-called "Mediterranean geochemical anomaly" is still active. The simultaneous presence of cinnabar deposits, volcanoes and anthropogenic influences are the main causes. On the one hand about 60% of the mercury deposits around the world is located in the Mediterranean basin (Ferrara et al., 2000) (e.g. Almadén (Spain), Idrjia (Slovenia) and Monte Amiata (Italy)), from where mercury has been released by both natural and anthropogenic activities (Fig. 2).

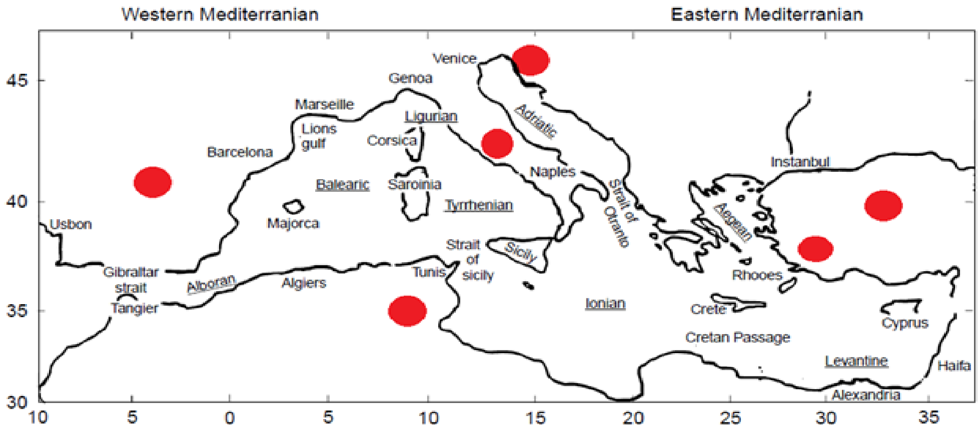


Figure 2: *Map of the main cinnabar deposits in Mediterranean basin (Ferrara et al., 2000 modified);*

On the other hand mercury emissions into the atmosphere by the Stromboli, Vulcano and Etna volcanoes, indicate volcanoes are a major source of mercury in the Mediterranean (Bagnato et al., 2007, 2011). Using *in situ* chambers, Covelli et al., 1999 determined mercury benthic fluxes of HgT and MMHg in the Gulf of Trieste (Northern Adriatic), and reported a mercury flux from exoreic runoff to the open Mediterranean of around 10 kmol yr^{-1}, ascribing to the shelf sediment a significant methylmercury source for the ecosystems.

Moreover, the specific geological and hydrogeological features (poor water exchange), together with the high solar radiation intensity and temperatures that characterize the Mediterranean for many months of the year, promote the biological, photo-chemical and physicists mechanisms responsible of the formation and emission from soils and waters of elemental mercury (Ferrara et al., 1986).

Particularly Bacci (1989) suggested that the higher temperature of the deep Mediterranean waters might promote the bacterial methylmercury formation in the water and/or sediments, with resulting higher mercury bioaccumulation in fish tissues. Research conducted in recent years, have estimated the total mercury emission from the water surface of the Mediterranean Sea amounts to 60 tons $year^{-1}$, representing the primary natural source of this metal to the atmosphere (Ferrara et al., 2000), higher than that of volcanoes sources (0.6-1.3 tons $year^{-1}$, Ferrara et al., 2000).

In conclusion, while the Mediterranean mercury “anomaly” or specificity was purported to be of a geochemical origin, the anomaly has probably biochemical or ecological reasons, including the high methylating potential.

The Ionian Sea is one of the most oligotrophic zones of the Mediterrenean sea and of the whole World Ocean. In summer 2000, the HgT concentrations measured in water between the surface and 2500m varied widely between 1.0 and 2.6 pM, and the methylated species were abundant throughout the water column (10–26% of the HgT) (Horvat et al., 2003).

Table 3: Range or mean mercury concentrations in intermediate and deep waters at different stations of the world ocean. HgT: total mercury; MeHg: methylated mercury including MMHg and DMHg

	HgT (pM)	**MeHg (fM)**	**MeHg/HgT (%)**	**Reference**
South and Equatorial Atlantic	0.8-2.4	25.200	~7.5	a
North Atlantic	2.4±1.6	29-160	~6.6	b
North Pacific	1.2±0.9	<50	<4	c
Equatorial Pacific	-	35-670	-	d
	0.5-4.0	20-290	1-35	e
Mediterranean	0.5-2.1	190-390	17-33	f
	0.5-3.2	100-460	-	g
NW Mediterranean	0.8-1.2	Up to 210	Up to18	h

a) Mason and Sullivan, 1999; b) Mason et al., 1998; c) Laurier et. al., 2004; d) Mason and Fitzgerald, 1993; e) Cossa et al., 1997; f) Horvat et al., 2003; g) Tessier et. al., 2004; h) Cossa and Coquery, 2005.

1.7.2 The Mediterranean global circulation

From the circulation point of view, the Mediterranean Sea is a semi-enclose basin, connected with the Atlantic Ocean through the Gibraltar Strait and with the Black Sea trough the Dardanelles Strait (Robinson and Golnaraghi, 1994). The surface evaporation rate is not in equilibrium with precipitation and the balance is achieved by flux of water entering through the Gibraltar Strait. On the Sicilian cost, surface waters, called Modified Atlantic Waters (MAW), enter from the Atlantic Ocean, while the Levantine Intermediate Waters (LIW) formed in the eastern basin as a process of surface cooling of water masses which undergoes a severe salt enrichment (Ovchinnikov, 1984; Malanotte- Rizzoli and Hecht, 1988). The northern part of the Sicily Channel is crossed by MAW (Raffa F. and Hopkins T. S., 2004) which flows eastward in the upper part of the water column, led by the Atlantic Ionian Stream (AIS). These surface waters meander, induced mesoscale cyclonic and anticyclonic gyres (Lermusiaux and Robinson, 2001; Béranger et al., 2004). The lower part of the water column, between about 250 and 400 m, is occupied by LIW which enters from the Ionian Sea through the passage south of Malta and flows westward, forming, in meeting the MAW, the anticyclone gyre in the Ionian coast.

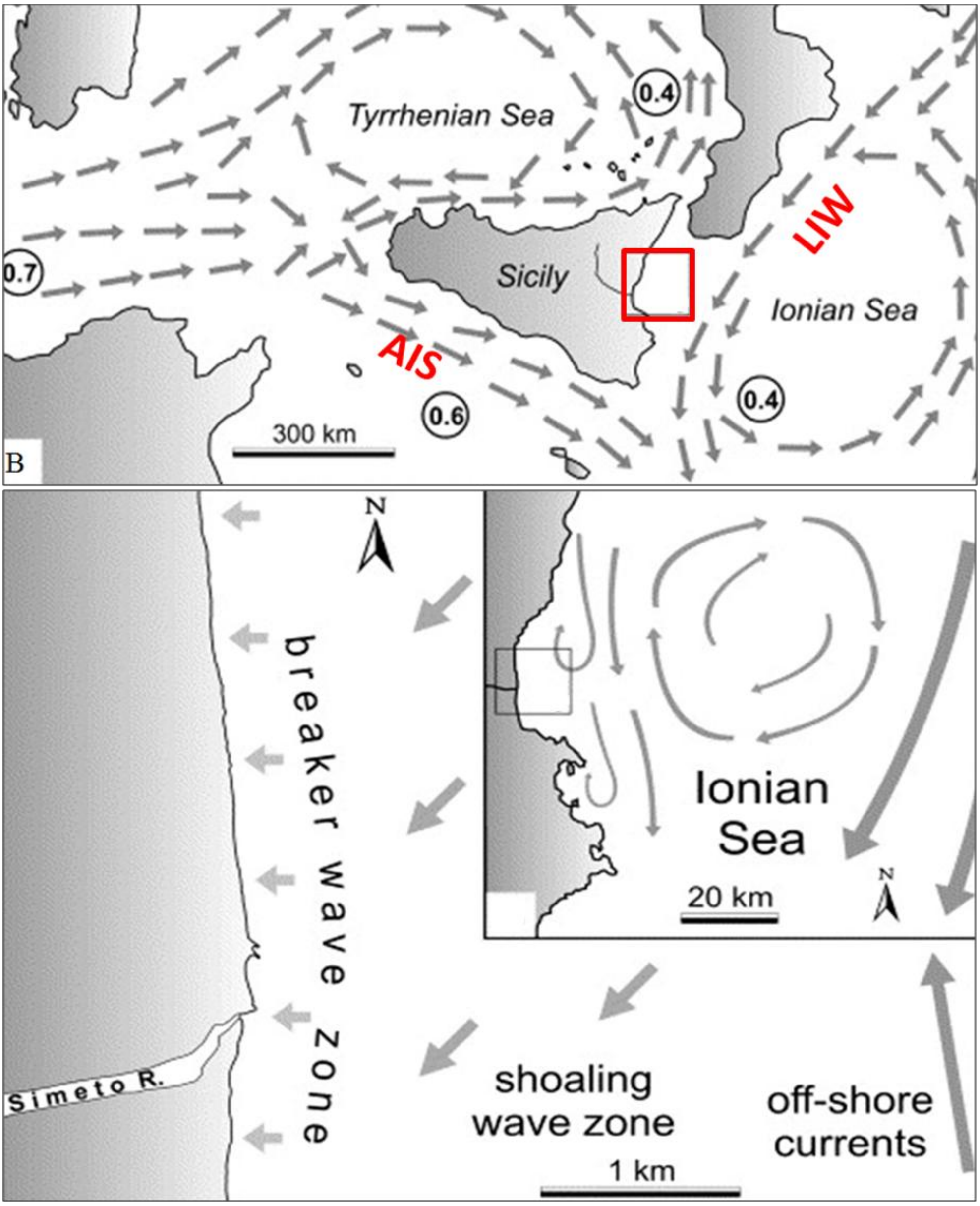


Figure 3: *Sub-basin scale and mesoscale circulation features in the eastern Mediterranean.*

Chapter II:

The study area

2 The study area

2.1 The Augusta Bay

Due to the crucial geographical position, the Augusta Bay (Sicily, Italy) hosts one of the most important European port in terms of good traffic. This features have promoted, since the early 60th, the born of one of the largest and most complex petrochemical district in Europe (Sprovieri et al., 2011). Nowadays the Augusta Bay is a high environmental risk area due to the uncontrolled chemical discharges that occurred before the Water Pollution Control Law (Merli law, 1978) and frequent industrial accidents (Ausili et al., 2008).

These features make the Augusta Bay an ideal natural lab for the study on the biogeochemical cycle of mercury in a coastal marine environment.

Moreover the complex water circulations system and the closeness with the steep continental slope (part of the Malta escarpment), make the area a potential point source of mercury for the entire Mediterranean Sea, with a consequent large scale effect of Hg pollution.

2.1.1 Geographical feature

The area, situated between Capo Santa Croce and Punta Magnisi (Lat. 37,21°N - Long. 15,23° E) is a wide natural bay which covers ~ 30 Km of the eastern Sicilian coast (Azzaro, 1993) (Fig. 4).

In the past years, part of the bay has been walled up with breakwaters forming a vast harbor basin communicating with the sea through two narrow inlets: the Scirocco inlet, 300 m wide and 13 m deep, and the Levante inlet, 400 m wide and 40 m deep (Sprovieri et al., 2011). The bay, ~ 8 Km long and 4 km wide, covers a surface area of 23.5 km^2 with a mean depth of 14.9 m.

The area can be divided into three main zones: the Xifonio harbor (north area, outside the bay), the Augusta harbor (internal area) and the Priolo sine (southern area, outside the Bay).

For “Augusta Bay” is intended the internal part of the harbor, within the northern, central and southern breakwaters. The basin is characterized by three different circulation systems. Water circulation in the Levante inlet is dominated by a northward flowing, with different mean speed at the surface

(18 cm s^{-1}) and at the bottom (7 cm s^{-1}) (ICRAM, 2005), while the southern current at the Scirocco inlet flows parallel to the coast with moderate speeds (8 and 4 cm s^{-1} at the surface and the bottom, respectively) and the northern portion of the basin is scarcely affected by active currents (ICRAM, 2005).

A very narrow shelf divided the Bay to the slope, part of the Malta escarpment (Scandone et al., 1981; Sprovieri et al., 2011). Owing to the low water turnover, the intense human activities and industrialization, the Augusta Bay is a complex area with a high state of degradation (Sciacca and Fallico, 1978; De Domenico et al., 1994).

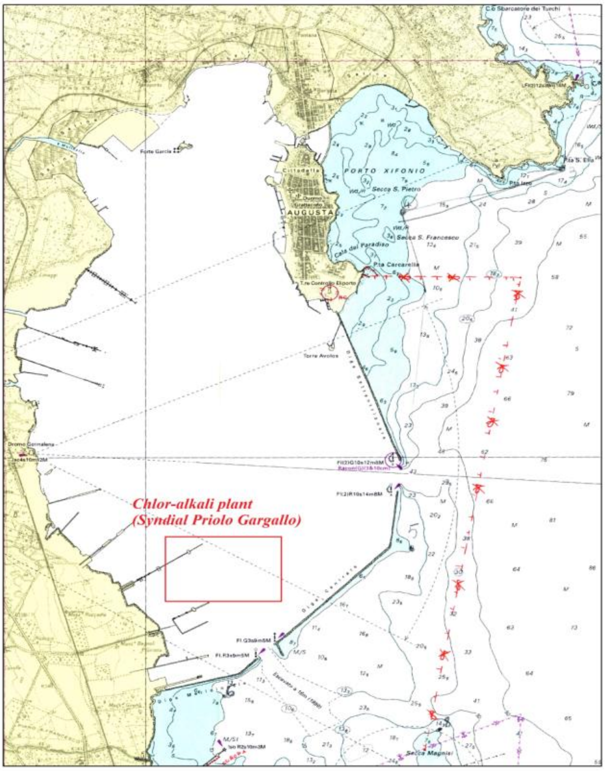


Figure 4: *The Augusta Bay, eastern Sicily (ICRAM, 2008, modified).*

2.1.2 Geological feature

From a geological point of view, the site is characterized by sedimentary land of different origins from Cretaceous to Quaternary ages, interspersed with volcanic rocks flows. The area corresponds to a graben formed between the end of the Pliocene and the early Pleistocene, limited by host of limestone and calcarenite stones. Sediments filled the graben are the products of the weathering of cliffs, volcanic rocks and limestone.

The water body is made up of coarse sands and organogenic calcarenite stones, while the substrate consists mainly of clays of variable thickness. Sands and calcarenite stones are present along the entire gulf. There are no "geological" reason for a local nature background of Hg in the area.

2.1.3 The Augusta harbor

Due to the strategic geographical position, the amplitude (more than 300.000 m^3) and the optimal meteorological condition, the Augusta Bay, homes one the most important harbor of the entire Mediterranean sea, with a global ability of about one million of tons, of which 30 millions of liquid good and 500.000 tons of cements (Fig. 5) (http://www.portoaugusta.it/1/il_porto_industriale_2176574.html) .

The commercial harbor (~5 km from the city center) is located at NW to the bay and is characterized by intensive activities of loading / unloading of dry bulk goods including, chemicals, fertilizers, iron, sulfur pills, concrete, marble, wood, mechanical parts and fittings (wind towers), clinker, basalt, and containers storage. Together with a commercial function, the Augusta harbor, since 1934, has been played an important military role because it houses a military base of the Italian Navy.

Figure 5: *The Augusta harbor.*

2.1.4 Industrialization history

The importance of the port and its functions, as well as strategic location, aroused interest in the creation of the industrial center. At the end of the Second World War (since 1949) the process of industrialization has begun in Italy.

The south-eastern part of Sicily reveals the most suitable in the national project of the industrial revival in the post-war period upon the De Gasperi government. In few decades, in the triangle of land including the municipalities of Augusta, Priolo and Melilli, on a coastline of about 15 km, it was planted the largest petrochemical complex in Europe, consisting of oil, petrochemical and chemical industries (Fig. 6).

The beginning of the industrialization process can be dated back to 1948 when Angelo Moratti, a young industrialist better known as the Inter football club president, decided to build in Augusta a refinery, the RA.SI.OM (Refinery Sicilian Mineral Oils) subsequently sold to the Esso management.

The choice of Augusta was determined by some features: primarily the flat nature and the strategic geographical position, on the Suez-Gibraltar rout, were fulfilled by the highest traffic of crude oil from the Middle East and Russia, in second time by the wide availability of low cost manpower, the presence of a natural port and the ability to use the underground tanks and the pier of the Navy, used during the Second World War.

The refinery began to produce in 1950, giving rise to the so-called "Economic Miracle", consisting of an oil hub, a cement plant and a petrochemical plant with a chlor-alkali plant doted of mercury cell. Today arise on the bay several major companies (ENEL Augusta, Esso Italiana S.r.l., Sasol Italy S.p.A, Maxcom Petroli S.p.A, Polimeri Europa S.p.A., Dow Italia S.r.l, Syndial S.p.A, Buzzi Unicem) (Fig. 6), a production system that consisted of a "integrated-cycle” which produces aromatic compounds, polymers and intermediates for plastics production, synthetic lubricants, rubber, paints, detergents, pharmaceutical products.

The process of industrialization changed dramatically a territory that from agriculture was forcibly converted to industrial, causing a radical shift in environmental, social and economic terms.

The lush natural backdrop of the Augusta bay changed radically; olive trees, almond and citrus trees, and the salt marshes along the coast, gave way to sheds, steel columns and chimneys.

Esso docks

SASOL docks

ISAB docks

“Cementaria docks”

Figure 6: *Photo gallery of plants and piers in the Augusta Bay (photos of F. Bulfamante).*

2.1.5 The chlor-alkali plant in Augusta Bay

The plant, owned by Montedison from 1958 to 1991, passed first to EniChem, then to Syndial and putted out of service in 2003. The chlor-alkali plant produced chlorine and caustic soda by means of the electrolysis of a sodium chloride aqueous solution in a cell with graphite anode and metallic mercury cathode (Castner-Keller method, or “Solvay method”) (Fig. 7).

About 1 mm of liquid Hg flows on an inclined plan of iron which constitutes the cathode, above which, at about half a centimeter, are suspended the anode, constituted of graphite horizontal plates.

The sodium chloride electrolysis with the Hg cathode gives rise to a “sodium amalgam” that, for subsequent oxidation with water, forms a solution of sodium hydroxide. The flow of current develops chlorine gas at the anode, while at the cathode occurs the reduction of sodium, which melts in forming mercury amalgam.

It was obtained caustic soda, hydrogen and mercury, than recycled. The electrolysis of 1.5 t of NaCl with the Castner-Keller method consumes about 2 kg of graphite and about 0.2 Kg of Hg cathode, producing 1 ton of NaOH and 0.87 t of Cl_2.

$$Na^+ + xHg + e^- \rightarrow Na(Hg)x \quad \text{(Mercury amalgam)}$$

Electrode processes of the stack:

$$\text{(pole -)} \quad 2Na(Hg)x \rightarrow 2Na^+ + 2xHg + 2e^-$$

$$\text{(pole +)} \quad 2H_2O + 2\,e^- \rightarrow H_2 + 2OH^-$$

$$\text{global process:} \quad 2Na(Hg)x + 2H_2O \rightarrow 2(Na^+OH^-) + H_2 + 2xHg$$

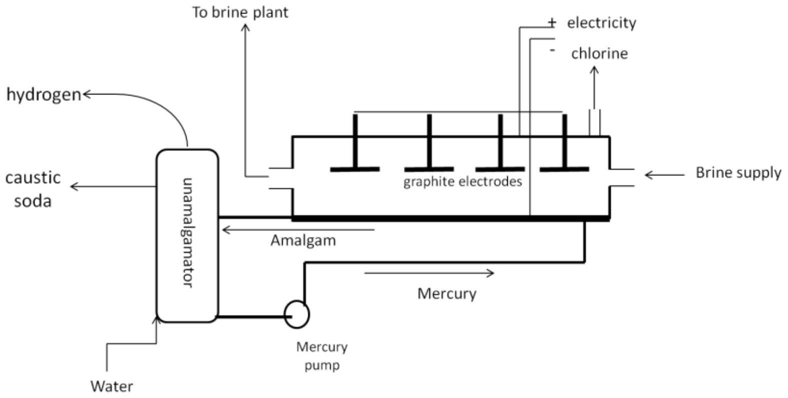


Figure 7: *Hg cell of the chlor-alkali plant.*

During the process, therefore, each ton of soda leads to losses of mercury in the air (in small quantities) and in the processed waters (in a more massive) of the order of 200g. This Hg lost, in absence of efficient recovery systems, can produce serious pollution (Bacci, 1989).

Treatment with the sulphides is an excellent method to remove the ionic species of mercury; this method, however, is ineffective for the dominant forms of Hg in the discharges of chlorine-soda (Hg^0 and calomel). This limit may be overcome by coupling the use of sulphides with the use of polysulfides (Na_2Sn) that allows, at pH> 9, the removal of 93% of Hg^0. By coupling both methods at a pH ranging between 9 and 11, it is possible to obtain the removal of 99% of total Hg.

Increasingly restrictive regulations on the environment have led, in most advanced countries, to the complete replacement of mercury cells with a "membrane cell".

In Priolo replacement never happened, but the graphite anode of the chlor-alkali plant was replaced in 1979 and steel electrodes were introduced and the chlor-alkali was equipped with of a special system through which the waste water is first treated with thiourea, able to precipitate mercury in the very low solubility form of mercuric sulphide, than clarificated and filtratered on sand and activated carbon.

The chlor-alkali plant discharged through the “Vallone della neve” (southern Augusta bay), in amount variable in time. Mercury that causes contamination of sediments of the Augusta Bay derives from untreated wastewater of the chlor-alkali plant (1958-1979).

About 500 tons of mercury were spilled to the sea without treatment between 1958 and 1979; negligible is the next quantity.

2.2 Human health and environmental concerns in Augusta Bay

The first evidences of pollution effects on environment appeared in the early 80th, when the Muscatello hospital (Syracuse) denounced an increase of malformed born and the entire area was included into the I.P.I.M.C monitoring program on congenital malformations.

The main evidence regards defects birth, heart and circulation, digestive system, uro-genital system (hypospadias) cancer and rates abortion double respect of the rest of the province and four times higher respect of national reference (ASMAC, 1990; Madeddu, 2006; WHO, 2001, ENEA, 2001 ASL 8 of Syracuse, Epidemiological Observatory of the Health of Sicily, 2005).

In November 1990 the industrial area between Syracuse and Augusta was declared to "high risk of environmental crisis”.

2.3 Environmental Hg pollution in Augusta Bay

Together with data on human health, environmental degradation of Augusta Bay was well documented. Indeed in the last decade, several studies provided detailed information on the pollution levels and risks for human health of resident populations of Augusta Bay (ICRAM, 2005; Ausili et al., 2008; Di Leonardo et al., 2007, 2008; ENVIRON International Team, 2008; Ficco et al., 2009; Sprovieri et al., 2011).

Data recently collected by ICRAM (2008), ENVIRON International Team (2008) Ausili et al. (2008), demonstrated HgT transfer from the abiotic system (sediments and seawater) to fishes (top predators and filter-feeders) and documented significant health risks associated with the consumption of fish caught in the area.

Toxicological Hg effects were also evaluated on mussels and red mullet by micronuclei (MN) studies, documenting DNA damages (Ausili et al., 2008 and ICRAM, 2008), in agreement with Tomasello et al. (2012) reported on DNA genotoxic and oxidative damages in *Coris julis* specimens from Augusta Bay. Fantozzi et al., (2012) found high Hg content in seawater collected close to Augusta.

Sprovieri et al., in 2011 speculated on the key role played by the Augusta bay as Hg point source for the surrounding marina environment and reported high-resolution maps of HgT distribution from superficial sediments collected in 2005, highlighting the extremely high concentrations of Hg in sediments (Fig. 8).

With the exception of Sprovieri, ICRAM and ENVIRON investigations, no more data are available on Hg distribution inside the bay.

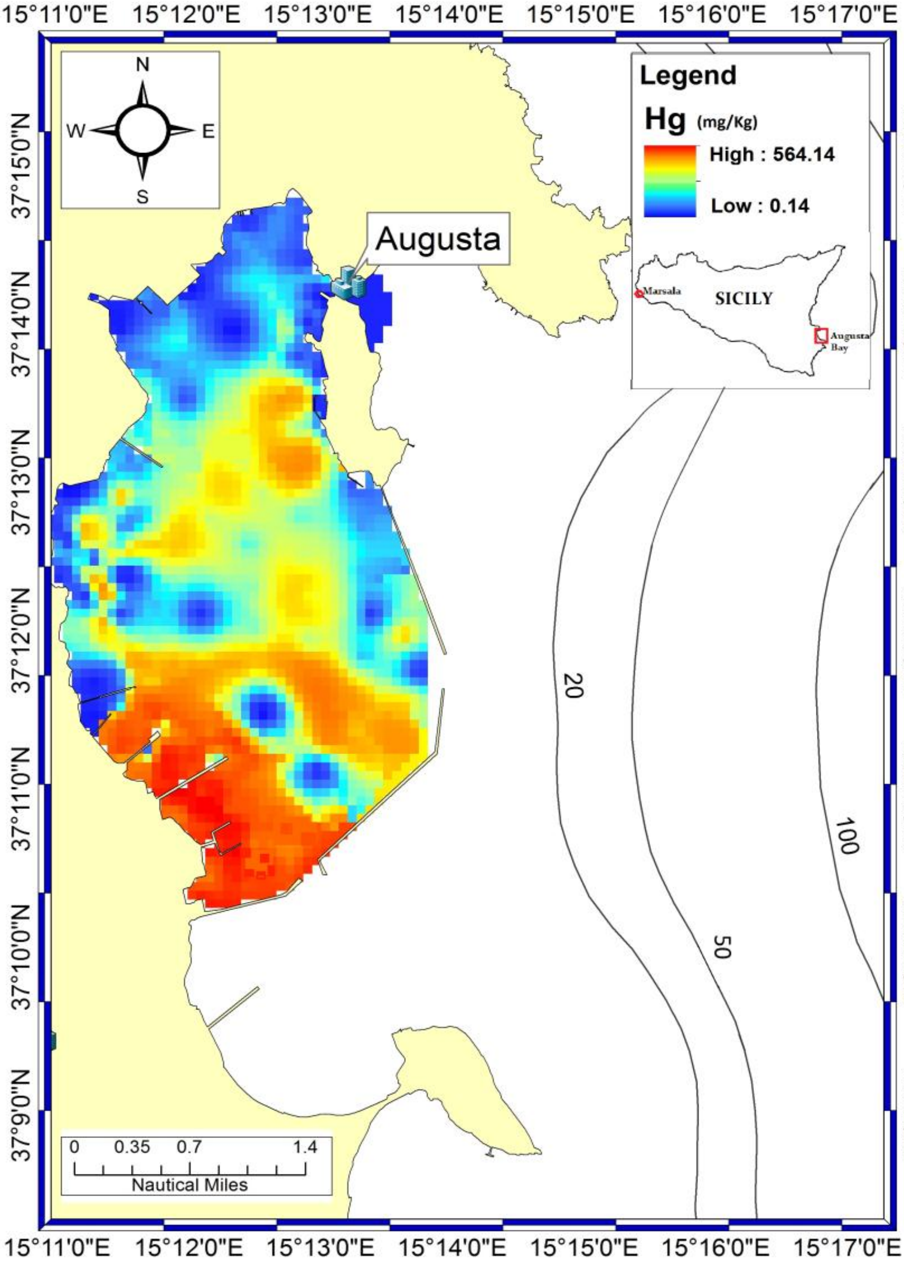


Figure 8: *High resolution map of Hg distribution in sediments reported (from Sprovieri et al., 2011).*

Chapter III:
Methodology

3 Methodology

This chapter details on the sampling strategy, treatment and analyses finalized to Hg analyses in sediments, fishes, seawater and atmosphere. The methodology used for flux assessing Hg at the interface between the exchange surface (sediments-seawater and air-seawater) was also reported. Analyses of REEs in seawater and of Hg isotopic analyses in sediments, fishes and human hairs are also detailed.

Temperature data were acquired from the continuous acquisition by a weather station (DAVIS – Vantage Pro 2Wi-Fi) installed on the roof of the Augusta port authorities office.

3.1 Sampling strategy

Sampling activity has been carried out during different seasons and periods of the years 2011-2012.

Details about sampling periods, kind and number of samples, relative station sites and collection methods are reported in Tab. 4 and 5 and in Fig.s 9, 12 and 13. The sampling plan has been planned in function of the mercury distribution in the Augusta Bay previously reported by Sprovieri et al. (2011) (Fig. 8).

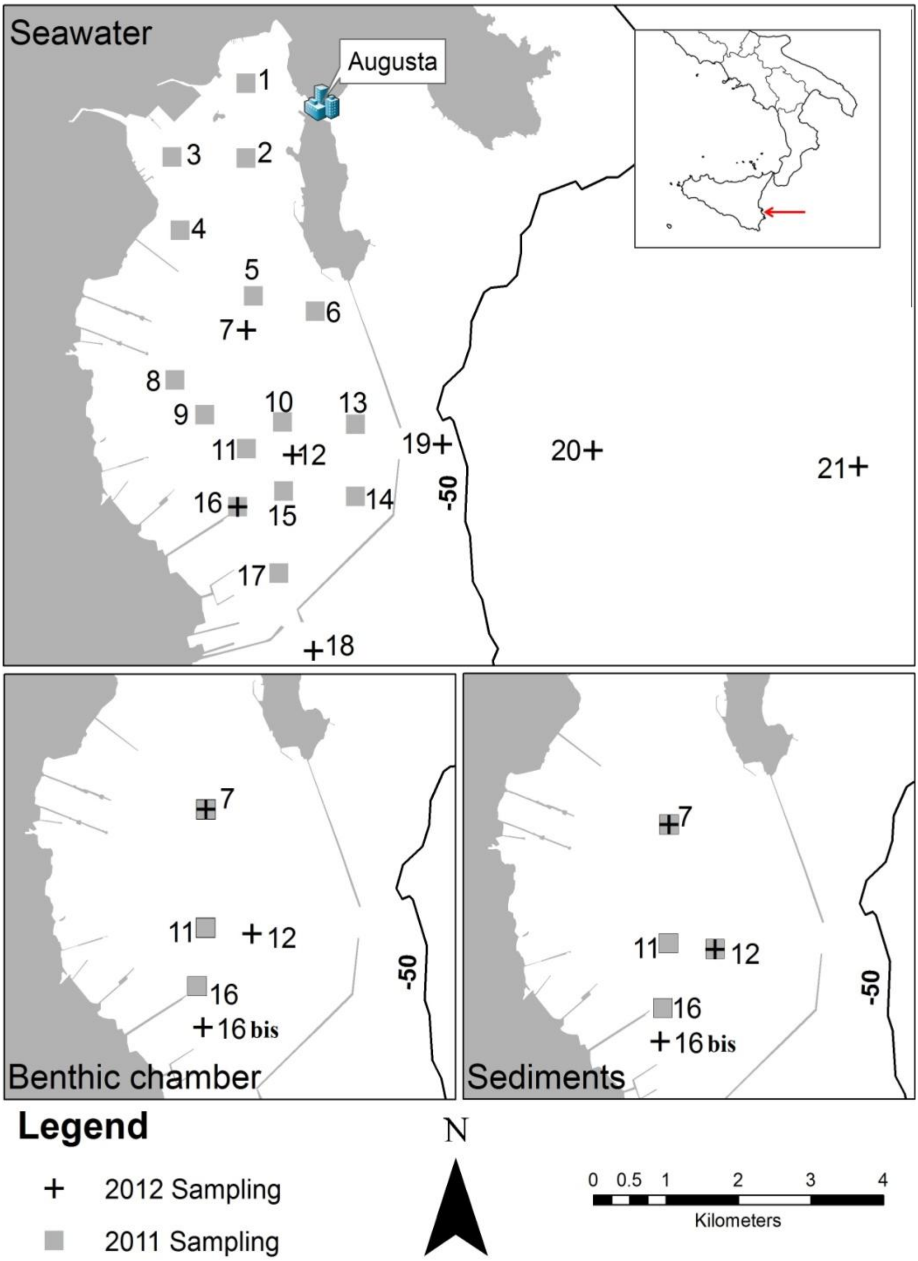


Figure 9: *Sampling location of seawaters, sediments and benthic chambers station planned in Augusta Bay.*

3.1.1 Sediment sampling

In May 2011 sediments were collected in station 7, 11 and 16 by means of the research vessel "Dallaporta" in four station points of the Augusta Bay by means of a box-corer instrument (Fig. 10a). Sediment collection during the campaign of June 2012 (station 7, 12, 16bis) (Tab. 4; Fig. 10b), was carried out by scuba divers with Plexiglas tubes (30cm long and a diameter of 6cm) inserted into the sediments and carefully recovered and transported onboard. All sediments were immediately sub-sampled onboard using a pre cleaned (HNO_3 10%) acrylic tube, sealed in polyethylene flasks and stored at −20 °C until analysis.

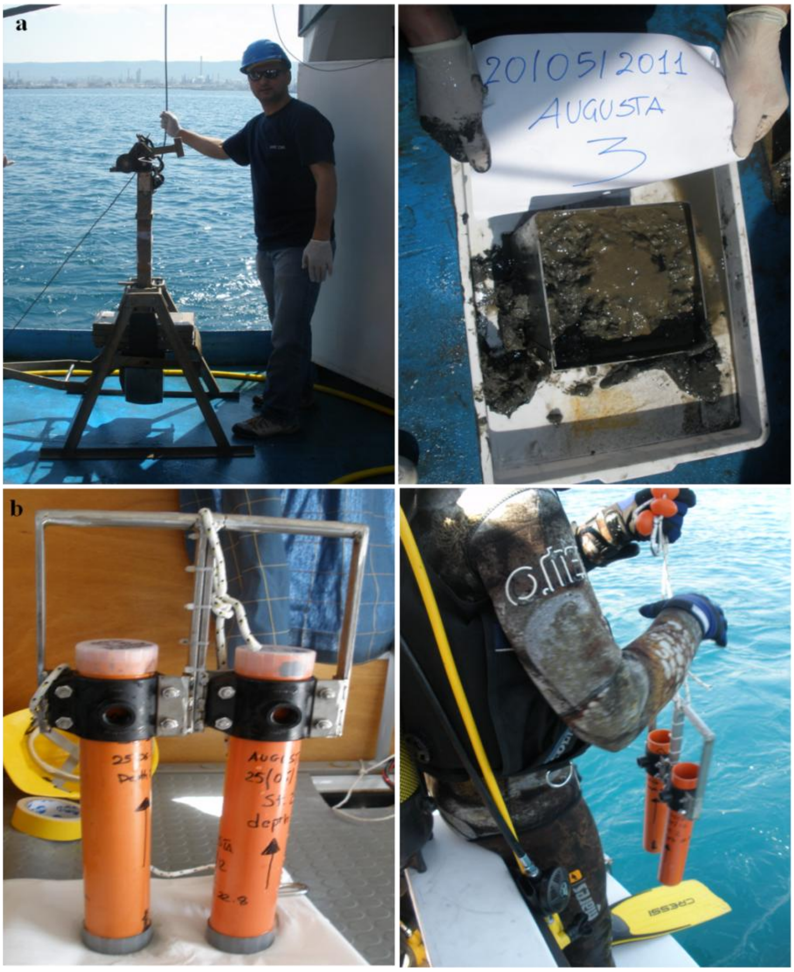


Figure 10: *Sampling sediment strategy; box-corer instrument (a) and manual sediment sampling (b).*

3.1.2 Seawater collection

Seawater samples are collected in May 2011 by means of the research vessel “Dallaporta” in 15 stations of the Augusta Bay (Tab 4; Fig. 9) by means of Niskin bottle rosette (Fig. 11a) at three different depth s (surface, mid-water, bottom) at variable shares depending on the total bottom depth. On February 2012 water samples has been collected in four points (Fig. 9, station 18-21) outside the Augusta Bay at three depths on board of the URANIA research vessel. Finally sample waters have been collected in June 2012 on board of the “Luigi Sanzo” vessel in three point (Fig. 9, station 7, 12 and 16) by means of a single bottle carried by a sub at the three depths of interest (Fig. 11b).

In order to avoid samples contamination, ultra-trace Hg handling techniques were employed during the collection and the analysis of water samples (US-EPA, 2004). All containers were cleaned prior to use with HNO_3 (10%) acid and rinsed three times with Milli-Q water (N18.2 MΩ cm^{-1}). Samples were stored in sterile bags at -20°C until the analysis were carried out (Covelli et al., 2008; Horvat et al., 2003).

The Niskin rosette has been doted of a multiparameter probe able to acquire environmental data (T, salinity, pH, eH).

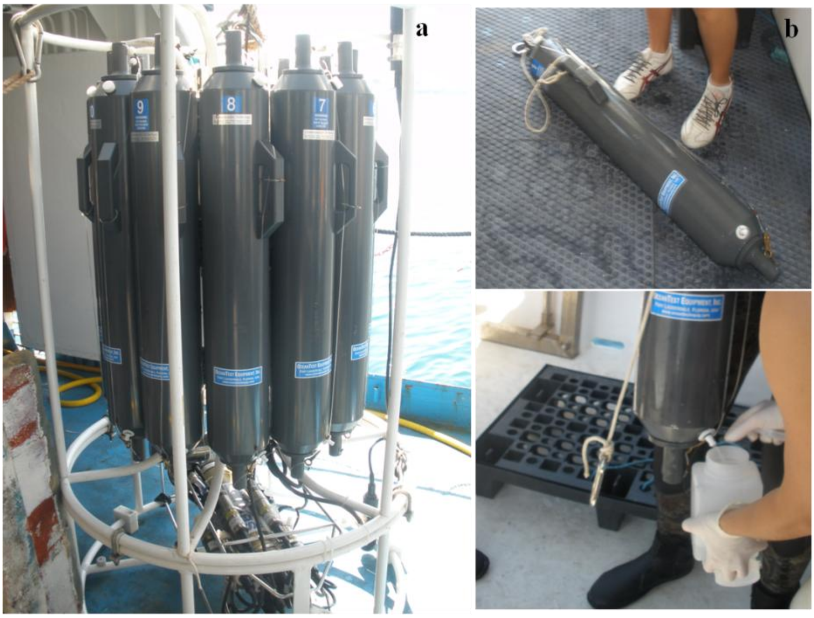


Figure 11: *Seawater sampling by means of a rosette Niskin bottles (a) and a single Niskin bottle used manually by a scuba diver (b).*

Table 4: Sampling details with kind of sampling, employed vessel, sampling period, real station positions and used instruments.

Sampling	Vessel	Sampling period	Station name	Station point		Instrument
				Lat.	Long.	
Seawaters	N/O G. Dallaporta	23-26/05/11	1	37°14.392N	15°12.537E	Niskin
			2	37°13.864N	15°12.519E	
			3	37°13.863N	15°11.845E	
			4	37°13.353N	15°11.902E	
			5	37°12.849N	15°12.595E	
			6	37°12.743N	15°13.176E	
			8	37°12.267N	15°11.863E	
			9	37°12.009N	15°12.161E	
			10	37°11.961N	15°12.855E	
			11	37°11.696N	15°12.512E	
			13	37°11.943N	15°13.536E	
			14	37°11.434N	15°13.536E	
			15	37°11.445N	15°12.865E	
			16	37°11.363N	15°12.434E	
			17	37°10.871N	15°12.833E	
	N/O Urania	2/02/12	18	37°10.310N	15° 13.148E	Niskin
			19	37°11.807N	15° 14.328E	
			20	37°11.742N	15° 15.767E	
			21	37°11.604N	15° 18.240E	
	M/N L. Sanzo	23-26/06/12	7	37°12.578N	15°12.583E	Single Niskin bottle
			12	37°11.697N	15°12.917E	
			16	37°11.288N	15°12.459E	
Sediments	N/O G. Dallaporta	23-26/05/11	7	37°12.618N	15°12.473E	Box-corer
			11	37°11.818N	15°12.540E	
			12	37°11.745N	15°12.985E	
			16	37°11.399N	15°12.375E	
	M/N L. Sanzo	23-26/06/12	7	37°12.578N	15°12.583E	Scuba diver
			12	37°11.697N	15°12.917E	
			16	37°11.288N	15°12.459E	
Sediments-seawaters	M/N L. Sanzo	19-21/09/11	7	37°12.618N	15°12.473E	Benthic chamber
			11	37°11.818N	15°12.540E	
			16	37°11.399N	15°12.375E	
	M/N L. Sanzo	23-26/06/12	7	37°12.578N	15°12.583E	
			12	37°11.697N	15°12.917E	
			16bis	37°11.288N	15°12.459E	

3.1.3 Fish sampling

Four different sampling sites were selected: two inside, and two outside the Augusta bay (Fig. 12). Sampling outside the bay was performed during May 2001, on board of the N/O "Dallaporta", by means of a mid-water trawl-net at 50-100 m of depth in two sampling areas, in front of the Scirocco inlet (300 m wide and 13 m deep), and of the Levante inlet (400 m wide and 40 m deep) (Fig.12, points C1, C2). Mainly pelagic fish specimens were caught (Tab. 5). Sampling inside the bay was performed during May 2012 by means of a fishing boat equipped with a gillnet wall, positioned at the bottom (mean depth = 20-25 m) (Fig 12, points C3, C4). Several specimens of benthic and demersal fishes were collected. From the two sampling activities, a total of 227 fish specimens were collected: 107 from mid-water sampling (outside the bay) and 120 from bottom-water sampling (inside the bay). Moreover, specimens of *Engraulis encrasicolus* (n = 38) were caught from the unpolluted marine area of Marsala (western Sicily), during July 2001, on board of a fishing boat equipped with a purse seine net. After collection, fishes were stored at T= -20°C until biological and chemical analyses.

Table 5: Number of specimens *per* species caught in the sampling sites.

Mid-water sampling (outside the bay)				**Bottom-water sampling (inside the bay)**			
Species	**C1 (n°)**	**C2 (n°)**	**Habitat**	**Species**	**C3 (n°)**	**C4 (n°)**	**Habitat**
Engraulis encrasicolus	20	20	Pelagic	*Diplodus annularis*	59	15	Demersal
Sardina pilchardus	8	20	Pelagic	*Diplodus vulgaris*	-	3	Demersal
Boops boops	-	20	Pelagic	*Pagellus erythrinus*	1	6	Demersal
Trachurus trachurus	-	6	Pelagic	*Pagellus acarne*	11	1	Demersal
Illex coindetii	6	-	Pelagic	*Sepia officinalis*	2	6	Demersal
Loligo forbesi	3	-	Pelagic	*Serranus scriba*	2	-	Demersal
Pagellus erythrinus	1	-	Demersal	*Caranx rhonchus*	1	-	Pelagic
Pagellus bogaraveo	2		Demersal	*Sphyraena sphyraena*	1		Pelagic
Mullus barbatus	1	-	Benthic	*Scorpaena notata*	-	5	Benthic
				Scorpaena scrofa	3	1	Benthic
				Mullus barbatus	-	3	Benthic
				Mullus surmuletus	1	1	Benthic
				Murena helena	1	-	Benthic
				Octopus vulgaris	-	1	Benthic

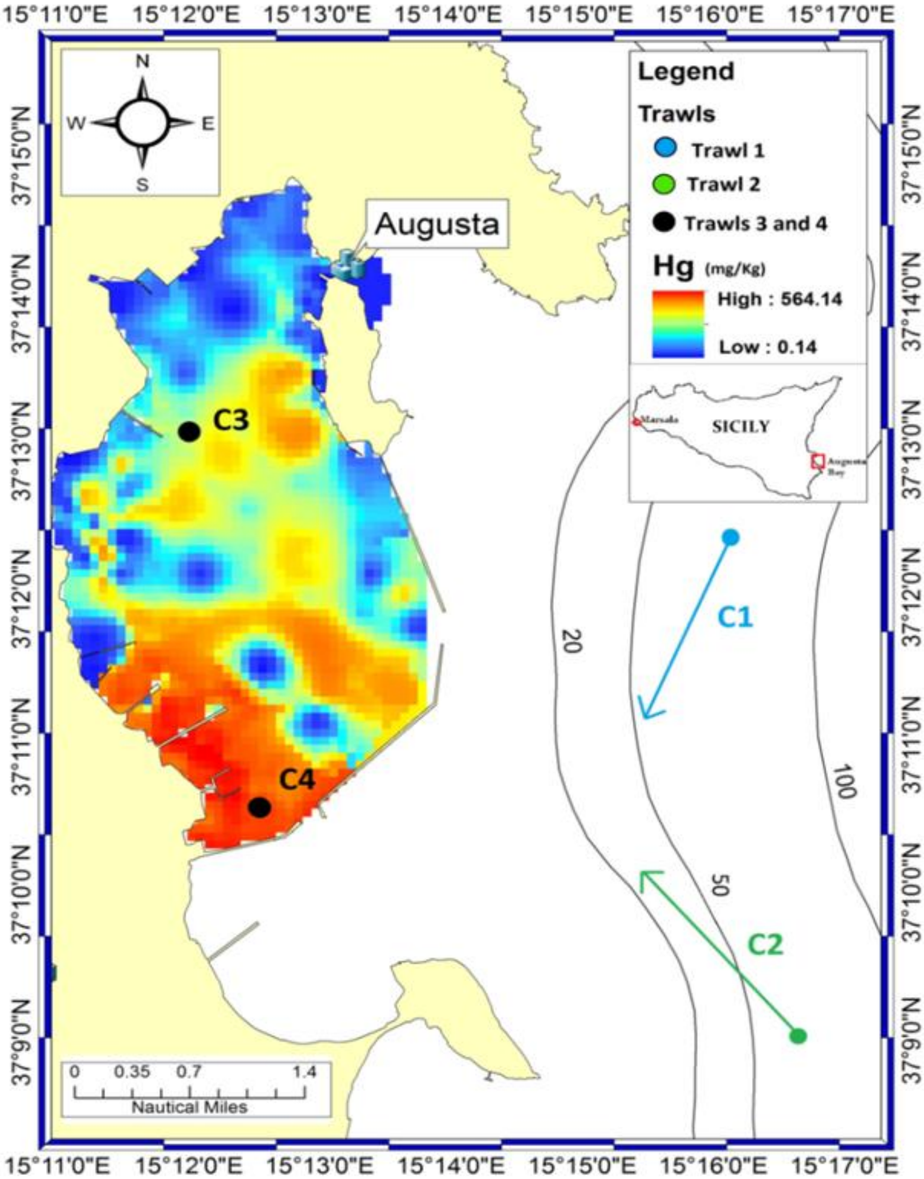


Figure 12: *Sampling sites of fishes in the Augusta bay. The map reports also the distribution of total mercury (HgT) in bottom sediments (Sprovieri et al., 2011 modified).*

3.1.4 Atmospheric GEM assessment

In order to assess how elemental gaseous mercury GEM concentrates and distributes in the Marine Boundary Layer (MBL) above the Augusta basin, measurements of GEM were performed across the Augusta basin on-board the Italian CNR research vessel Luigi Sanzo, during three main oceanographic cruises carried out along the same route in the winter (November 2011) and summer (July 2011-June 2012).

The cruise paths of the campaigns to date are shown in Fig. 13a. The atmospheric investigation was finalized to assess the GEM content over the land and the marine boundary layer (MBL).

The analysis of atmospheric GEM was performed using an automated real-time atomic absorption spectrometer (Lumex-RA 915+). Wet and dry deposition collection were been collected in the area. Details on atmospheric GEM measurement and deposition collection were reported in Bagnato et al., 2013.

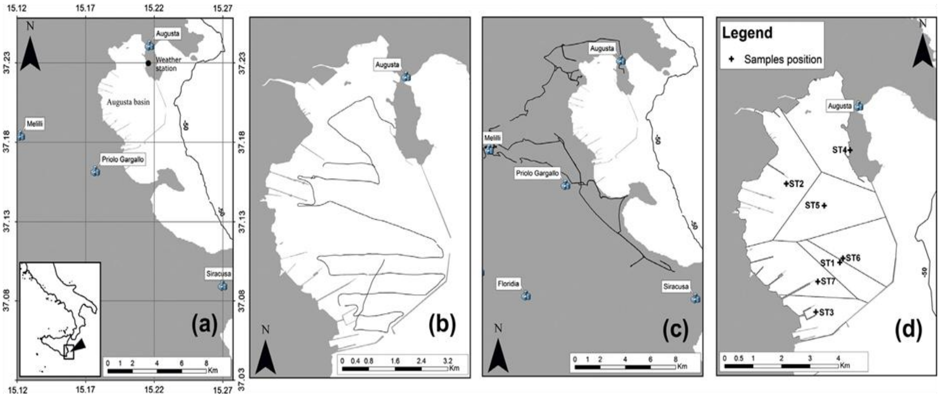


Figure 13: *Maps showing the (a) route of the cruises performed to measure GEM concentrations in the MBL over the Augusta basin, (b) the land trajectories to detect GEM contents in the atmosphere over the coastal internal area, (c) stations of measurements of Hg evasion flux by accumulation chamber technique. Map (c) Voronoi polygons, each relative to one station of measurement. (Bagnato et al., 2031)*

3.2 Flux at the interfaces

3.2.1 Fluxes at the sediment-seawater interface

In order to assess Hg fluxes at the interfaces among sediments, seawater and atmosphere, an in situ benthic chamber and a dynamic accumulation chamber were employed simultaneously in Augusta bay. The adopted strategy to study fluxes of Hg through the interfaces is summarized in Fig. 14. The used in situ benthic chambers allowed to determine benthic fluxes of dissolved mercury at the water–sediment interface throughout the time. The benthic chamber was built by the technical staff working in the laboratories of electronic at IAMC-CNR (Capo Granitola), according to the different schemes proposed in literature (Covelli et al., 1999, 2008; Point et al., 2007). The box-shape chamber (50x50x30cm), open at the bottom side, was constructed from Plexiglas and equipped with a stirring mechanism which consisted of a rotating bar (30 cm long; 5 rpm speed) inside the chamber connected through a magnet to an electromotor, coupled with 12 V batteries and located in a separate housing on the top of the chamber. A plastic skirt, fitted to the outside of the chamber, controlled its penetration into sediment to a depth of about 7.5 cm (Fig. 15).

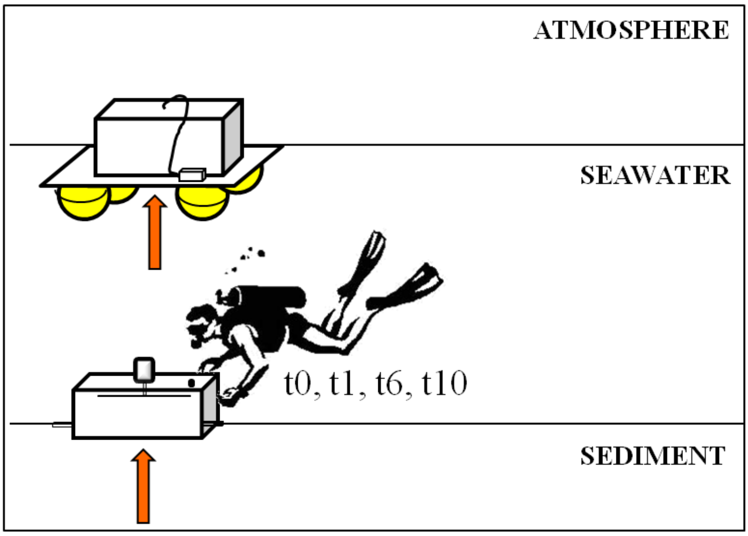


Figure 14: *Working scheme adopted in order to study fluxes at the interfaces.*

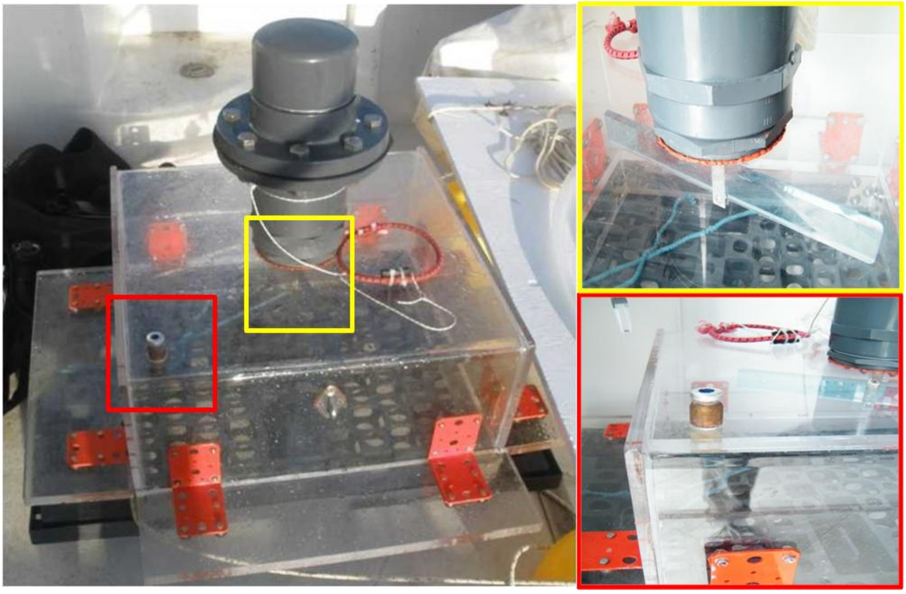


Figure 15: *Benthic chamber built at the IAMC-CNR laboratories (Capo Granitola) implied for the sediment-water sampling.*

Benthic fluxes were assessed by deploying the *in situ* benthic chamber on the sea-floor, isolating an area of sediment surface and overlying water. Sampling at the sediment-water interface were carried out in Augusta Bay on September 2011 (Station 7, 11, 16; Tab. 4) and June 2012 (Station 7, 12, 16bis; Tab. 4). The chamber was gently placed on the sea bottom by a scuba diver and water samples from the benthic chamber were periodically collected, at t=0, t= 1, t=4, t=6, t=10 and t=12 h, by scuba by means of a 50 ml syringes, inserted in a cap equipped with rubber septum pierceable (Fig. 16). Water was immediately transferred to the acid-pre-cleaned containers and stored frozen.The sampling strategy adopted by sub has been detailed by Patti et al., 2013 technical report.

Benthic fluxes of Hg dissolved species (DHg) were calculated from the difference in concentrations, ΔC = Cf - C0, over the experiment time, Δt = (tf - t0), following the Eq. (1):

$$\Phi Hg = \left(\frac{(\Delta C) \times (V / A)}{\Delta t} \right) \tag{1}$$

where tf and t0 are the final and starting times, respectively, V is the benthic chamber volume (57.5 L) and A is the sea-bottom area covered (0.25 m^2) (Santschi et al., 1990).

Figure 16: *Sub aerial and submarine imagines of benthic chamber setting in the bottom sediment by scuba diver (photo of V. Di Stefano and C. Patti).*

3.2.2 Fluxes at the air-seawater interface

The open-bottom (50×50×50cm) dynamic flux chamber (made up of plexiglass) used to estimate the flux during the cruises, was built by the technical staff working in the laboratories of electronic at IAMC-CNR (Capo Granitola), according to the schemes proposed in literature by Kim and Lindberg, 1995 and Carpi and Lindberg, 1998.

The transparent plexiglas was chosen in order to permit solar radiation penetration. The 125 liters flux chamber was used in conjunction with a RA-915+ Lumex Hg vapor analyzer connected to the inlet and outlet of the flux chamber situated about 20 cm above the water surface (Fig. 17). Details on accumulation chamber experiments were reported by Bagnato et al., 2013 (Attachment II).

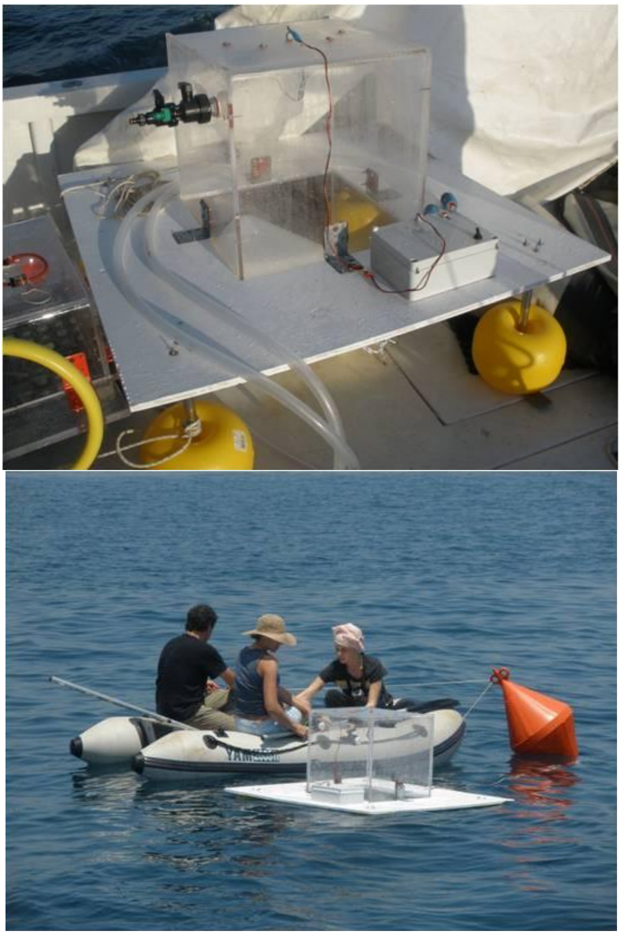


Fig. 17: *Positioning and in real-time measurements of sea–air GEM evasion flux by using the accumulation chamber technique*.

Mercury flux from the water surface exposed in the chamber was then calculated to the Eq. (2) (Lindberg and Price, 1999; Zhang et al., 2001)

$$\Phi_{\mathrm{GEM}} = Q\,(C_0 - C_i)/A \qquad (2)$$

where Φ_{GEM} is the GEM total emission rate per area and unit time (ng m^{-2} sec^{-1}); (C_o-C_i) is the difference in GEM concentrations in air exiting (C_{o}) and entering (C_{i}) the chamber (ΔC) (in ng m^{-3}); A is the basal area of the chamber in m^2; and Q is the flow rate of ambient air flowing through the chamber in m^3 sec^{-1}.

3.3 Samples preparation and analysis

3.3.1 Sediment treatment for THg analyses

Sediment samples were treated at sedimentology laboratory of IAMC-CNR (Capo Granitola) (Fig. 18). Each core was defrost, extruded by liner and, after macroscopic description, sectioned in cut at 1-3 cm intervals with a stainless steel bandsaw. Aliquot of ~3.5 gr was used for grain size composition, the remainder sediment slices were dried at 40 °C (Di Leonardo et al., 2006) in order to remove water content.

Dry sediments were powdered manually in an agate mortar for analyses of THg. Grain size analyses were performed following the procedure reported by ICRAM, 2008.

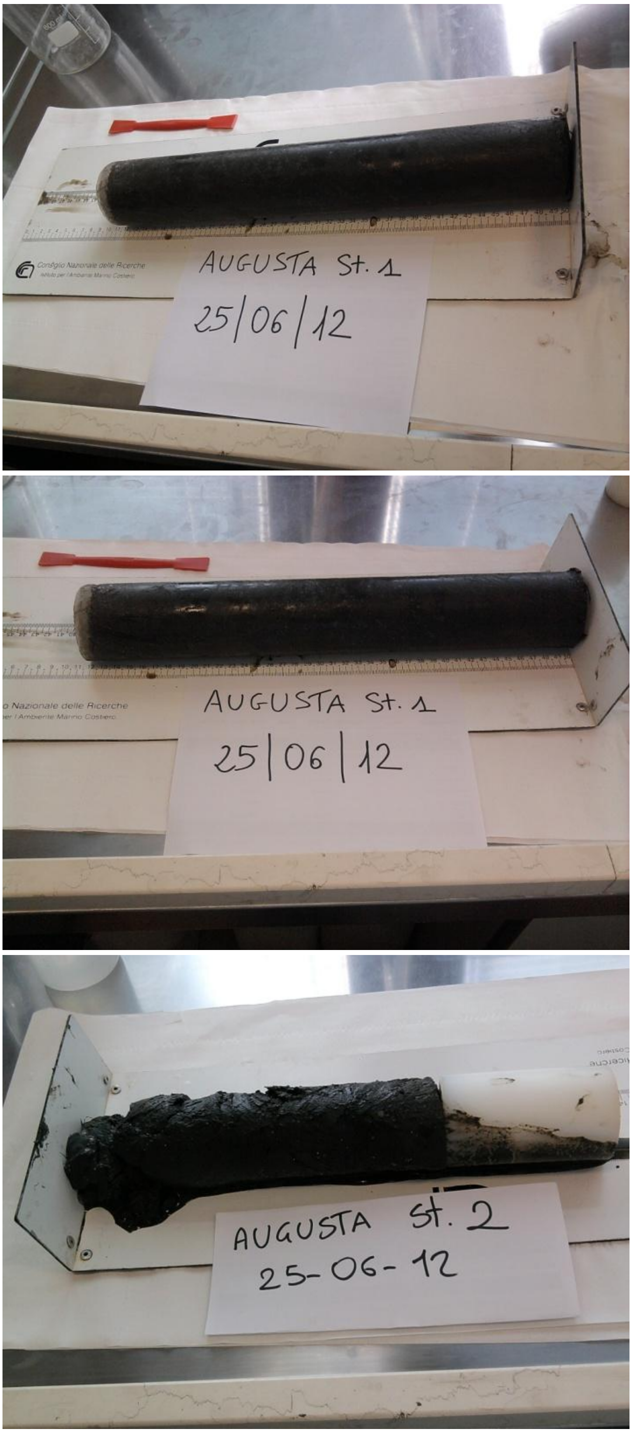


Figure 18: *Sediments treatment at sedimentology laboratory of IAMC-CNR (Capo Granitola).*

3.3.2 Sequential extraction procedure (Bloom et al., 2000)

Speciation is critical to understanding and modeling Hg contaminated soils because the particular distribution of compounds and their interaction with soil under aqueous conditions determine their environmental mobility and bioavailability (Davis, et. al, 1997). To address this need, the robust solid phase analytical scheme based upon sequential selective extractions of Bloom, et al., 2000 was applied. This method does provide precise and accurate data regarding the biogeochemically relevant fractionation of Hg in sediments and soils. The method differentiates Hg into behavioral classes including water soluble, ‘stomach acid’ soluble, organochelated, elemental, and mercuric sulfide. Inorganic Hg speciation was determined by sequential selective extractions of separate 2 gram aliquots of the homogenized solids (Bloom, et. al., 2000).

The extraction was performed using a 100:1 liquid-to-solids ratio in 40 mL vials. Sequential extraction procedure has been applied to May 2011 collected core sediments.

Each extraction step was conducted for 18±3 hours, with constant agitation, at 18-22 °C. At the end of each step, the samples were centrifuged, and the supernatant liquid was filtered through a 0.2 μm filter (Fig. 19). The solid pellets were then re-suspended in the same extractant, re-centrifuged, and re-filtered.

The two filtrates were combined in a 125 mL bottle, oxidized by the addition of BrCl, and diluted to 125 mL prior to analysis for total Hg by EPA Method 1631. After the rinse step, the sample pellet in the centrifuge tube was resuspended in the next extractant, and the entire process was repeated, according to the step specified in Table 6.

Table 6: Sequential Extraction Method Summary

Step	*Extractant*	*Description*	*Typical compounds*
F1	DI water	water soluble	$HgCl_2$, $HgSO_4$
F2	pH 2 HCl/HOAc	“stomach acid”	HgO
F3	1N KOH	organo complexed	humics, Hg_2Cl_2
F4	12N HNO_3	strong complexed	mineral lattice, Hg_2Cl_2, Hg^o
F5	aqua regia	cinnabar	HgS, m-HgS, HgSe, HgAu

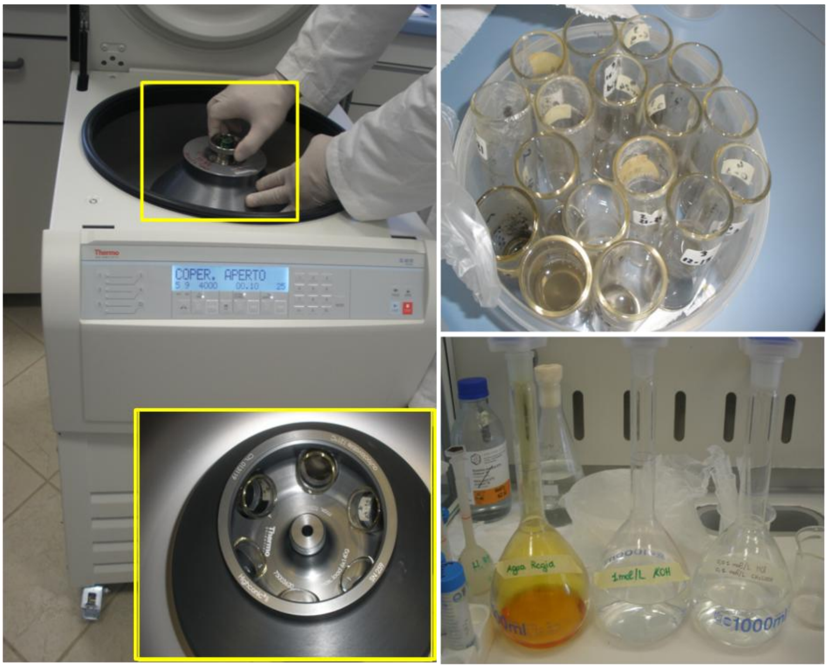


Figure 19: *Centrifuge, extractant and other tools used for SEP procedure.*

3.3.3 Fishes treatment for THg analyses

The total length (TL) of each specimen was measured (Fig. 20). Muscle and liver tissues were collected using plastic materials, cleaned with HNO_3 (10%) and MillQ water, in order to avoid Hg contaminations. Tissues were stored at -20°C until THg analysis.

Otoliths were extracted from anchovy and sardine specimens for age determination. Readings and interpretations of otolith increment growths were carried out according to the procedure adopted for European anchovy age determination follow Uriarte et al. (2007) and La Mesa and Donato (2009).

Figure 20: *Fish treatment for THg analyses*

3.3.4 Seawater treatment for THg and DHg analysis

After the whole liter of water was defrost and shaking, aliquot of 50 ml was treated with a BrCl solution (250 µl) for HgT analysis according to the EPA 7473 method. The remained part was filtered with polycarbonate filters (Fig. 20) and treated with BrCl for HgD analysis. Samples were stored at room temperature and analysed after 24h. KBr and $KBrO_3$ are Hg free. 0.27 gr of KBr were dissolved in 25 ml of HCl and shaken for ~ ½ h, finally 0.38 gr of $KBrO_3$ were added to solution that assumed yellow color. Chemical reagents were suitable for ultra-trace Hg analysis. The THg and DHg analysis in seawater, performed by means of the DMA-80 instrument.

3.3.5 THg analyses and data quality

Hg analyses in all the collected samples were performed using a direct mercury analyzer (DMA80, atomic absorption spectrophotometer, Milestone, Wesleyan University, Middletown, CT, USA) with optical path spectrophotometer, achieving a detection limit of 0,0015 ng of mercury (Fig. 21).

The DMA-80 is fully compliant with US EPA method 7473 (“Mercury in solids and solutions by thermal decomposition, amalgamation, and atomic absorption spectrophotometry”) and with ASTM method D-6722-01 (“Standard test method for total mercury in coal and coal combustion residues by direct combustion analysis”). DMA-80 instrument uses the principle of thermal decomposition, amalgamation and atomic absorption at 253,65 nm.

A total amount of 787 samples have been analysed by means of DMA-80 instrument, divided into: 462 fish tissues (231 muscles and 231 livers), 132 seawaters (66 for THg and 66 for DHg), 139 portion of sediments (85 for THg and 54 for SEP procedure), 54 seawaters at the interface with sediment (27 for THg and 27 for DHg).

Each sample has been analysed in duplicate or triplicate for a total number of ~2000 analyses. In order to taste precision and accuracy in solid samples, reference standard materials were measured each 10 measures.

Analyses of liquid (seawater, porewater) ~400µl of samples were placed into quartz boats and analysed using a calibration range of 0-0.05 ng (Fig. 21). Hg liquid standard solution (Std 100 ngL^{-1}) was analysed in order to assess analytical accuracy. The detection limit, (Ld) and the critical value, (Lc) for liquid solutions have been calculated following the "Water Research Centre" (Cheeseman and Wilson 1979) procedure.

The critical value, Lc, ant the detection limit, Ld, (Tab. 7) were calculated using the following equations:

$$Lc = 2.33\sigma_{wb} \qquad Ld = 4.65\sigma_{wb}$$

where σ_{wb} is the within batch standard deviation of the blank (the term "within-batch" signifies analyses made under the same experimental conditions at essentially the same time).

For the instrument detection limits calculation, replied of blank sample has been performed long time (n=10), resulting a instrumental detection limits of 10.03, 20.02, 43.06 ngL^{-1} for Lc, Ld and Lq respectively. Results of the blank measures were subtracted for the value calculation.

For HgT measurement in sediment samples, an aliquot of ~0.05 g was loaded in nickel boats and transferred into the DMA-80 system (calibration range: 5-500 ng).

Different standard materials were chosen and analysed, depending on the sample Hg enrichment (Reference Standard Materials PACS-2 or MESS-3), in order to test accuracy and precision (~7 and 6% respectively).

For HgT measurement in fish tissues, a wet aliquot of ~0.1 g was loaded in nickel boats and transferred into the DMA-80 system (calibration range: 1-200 ng).

A Reference Standard Material (TORT-2) was analysed to assess analytical accuracy precision (4 and 7% respectively). Finally, duplicated samples (about 20% of the total number of samples) were measured to estimate reproducibility (~7%). Table 7 detailed reports data used for quality control data and limits of detection.

Particularly, the precision, or variation coefficient, has been calculated by standard deviation (σ) and mean value (Gini, 1912):

$$\Pr ecision(\%) = \frac{\sigma}{mean} * 100$$

The accuracy (%), or relative error (%) has been calculating following the ISO GUM (*International Organization for Standardization*, Guide Uncertainty Measurement):

$$A(\%) = \left[\left(\frac{x-Y}{Y}\right)\right] * 100$$

Where X represent the measured value and Y the reference value.

Table 7: Quality data

	Reference material	**N° replies**	**Mean THg Measured**	**S.D.**	**Accuracy (%)**	**Precision (%)**
Sediments	Mess-3 (0.091±0.009 mg/Kg)	22	0.085	0.005	6	6
	Pacs-2 (3.04±0.20 mg/Kg)	19	2.77	0.19	9	6
Fishes	Tort-2 (0.27±0.006 mg/Kg)	22	0.280	0.002	4	7
Seawaters	Std (100 ng/L)	10	95.66	5.79	4	6
***Limits** (calculated on the Blank)(ngL^{-1})*	Lc=10.03			Ld= 20.02		

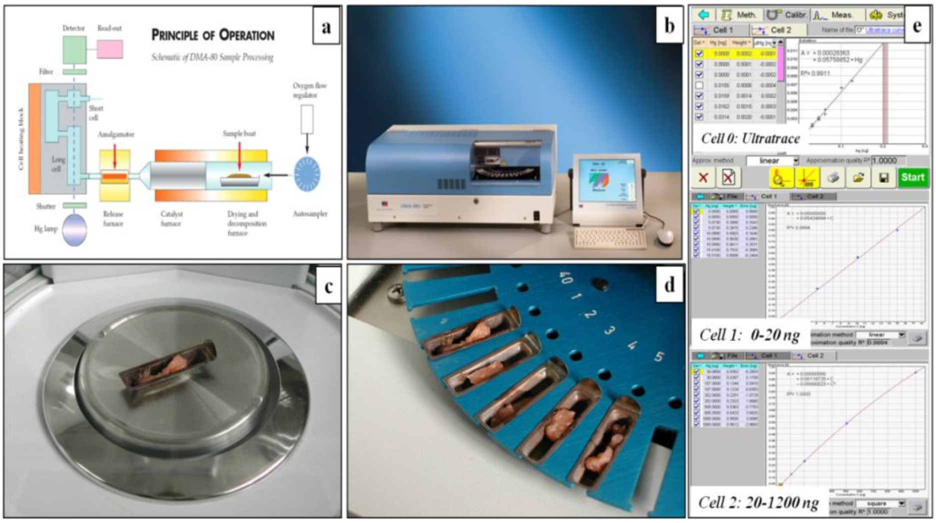


Figure 21: *Direct Mercury Analyzer (DMA-80 Tricell). a) Principle of operation; b) Related software; c) sample weight in a nikel boat; d) typical calibration.*

3.3.6 REEs treatment and analyses in seawater

Sample for REEs analyses were collected during June 2012 sampling (Fig. 9) in stations point 7, 12 and 16. Treatments and analyses were performed at the University of Palermo following the pre-concentration technique detailed by Raso et al. (2013). The typical features of the distribution of shale-normalised REE concentrations, $[REE_i]_n$, calculated according to the expressions:

$$[REE_i]_n = \frac{[REE_i]_{sample}}{[REE_i]_{reference}} \tag{3}$$

with respect to Post Archean Australian Shales (PAAS; Censi et al., 2007), By studying enrichments or depletions of single elements along the series, usually named "anomalies", the evaluation of "geochemical behaviour" of REE is carried out. These anomalies can be assessed according to the equation:

$$\frac{[REE]_i}{[REE]_i^*} = \frac{2[REE]_i}{\{[REE]_{i+1} + [REE]_{i-1}\}} \tag{4}$$

where the subscript "i" indicates every element along the REE series whereas "(i-1)" and "(i+1)" are its immediate neighbour before and after within the series (Alibo and Nozaki, 1999a). Only Gd anomaly can be expressed according a different equation (Moller et al., 2007):

$$\frac{Gd}{Gd^*} = \frac{Gd_n\sqrt{Ho_n}}{\sqrt{Tb_n^3}} \tag{5}$$

where the subscript "n" is referred to normalised concentrations. Features of normalised-REE patterns can also be evaluated considering enrichments or depletions of groups of REE subdivided into light REE, from La to Sm (LREE), middle REE, from Eu to Dy or Ho (MREE) and heavier REE, from Ho or Er and Lu (HREE) according to their atomic weight. These features allow to define the geochemical behaviour of these elements during natural processes.

3.3.7 Hg isotopes analyses

Sediments, fishes and hair samples chosen for Hg isotopes analyses are listened in table 8.

Table 8: List of fish, sediment and hair samples, with relative THg content (*mg Kg*$^{-1}$) selected for Hg isotopes

Fish				**Sediments**			**Hairs**	
	Inside/ outside		**THg** (*mgKg*$^{-1}$)	**St.**	**Depth**	**THg** (*mgKg*$^{-1}$)	**Age**	**THg** (*mgKg*$^{-1}$)
Sardina pilchardus	O	**Pelagic Fishes**	0.04	**Station 7**	0-1	8.34	20	1.71
Sardina pilchardus	O		0.04		2-3	6.79	30	1.34
Sardina pilchardus	O		0.09		4-5	6.42	30	1.46
Sardina pilchardus	O		0.11		13-14	8.66	35	0.45
Engraulis encrasicolus	O		0.04		14-16	6.84	35	0.72
Engraulis encrasicolus	O		0.04		18-20	7.23	35	0.72
Boops boops	O		0.13		24-26	5.74	35	3.06
Boops boops	O		0.16		26-28	4.12	40	1.37
Trachurus trachurus	O		0.31		30-32	5.59	40	3.43
Trachurus trachurus	O		0.33		36-37	5.64	40	3.42
Sphyraena sphyraena	I		2.27	**Station 12**	0-2	15.96	40	2.32
Diplodus annularis	I	**Demersal Fishes**	1.42		2-4	13.36	40	1.49
Pagellus acarne	I		0.26		6-8	12.16	40	1.47
Pagellus acarne	I		0.70		8-10	16.83	40	1.83
Pagellus acarne	I		0.26		10-12	12.80	40	1.42
Pagellus acarne	I		0.26		14-16	9.33	40	5.07
Pagellus erythrinus	I		0.42		18-20	39.96	40	2.61
Pagellus erythrinus	I		0.47		20-22	8.01	40	1.97
Pagellus erythrinus	I		0.35		22-24	9.12	40	4.81
Mullus barbatus	I	**Benthic fish**	0.71	**on 16**	0-2	17.11	40	5.28
Mullus barbatus	I		0.71		4-6	18.99	40	2.74

Table 8 continued

Mullus surmuletus	I	0.60	10-12	28.13	40	1.28
Scorphaena notata	I	1.65	12-14	38.41		
			14-16	55.34		
			18-20	39.96		
			24-26	18.51		
			28-30	22.08		
			34-36	1.78		

Samples for Hg isotopes analyses were achieved after total digestion. ~50 mg of dry and homogenized sediment were treated with a strong acid mixture (9ml of HNO_3 + 3 ml of HCl) in a closed microwave system, while 6 ml of HNO_3 were added to ~20 mg of dry and homogenized fishes muscles prior the microwave digestion and hair samples were dissolved with 2 HNO_3 + 0,5 H_2O_2.

Isotopic analyses were performed at the UNIMORE Laboratory of Modena by cold vapor multi-collector inductively coupled plasma mass spectrometer MC-ICP-MS (Thermo-Fisher Neptune) (Fig. 22).

The standard bracketing technique (Fig. 23) has been used in order to compensate the effects of mass bias changes during the measures sequences. The technique consists of a specific acquisition sequence, in which two standard measures are placed before and after each sample analysis. The average standard values are used for δ calculation. Moreover each sample or standard measure is immediately preceded and followed by two white samples.

The two washing solution consisted of a solution of HNO3 4% in H_2O MilliQ® and of L- cysteine, able to form the complex $Hg(Cys)_2$.

The intensity of the detected signal are subtracted, cup for cup, to those of the respective standard or sample.

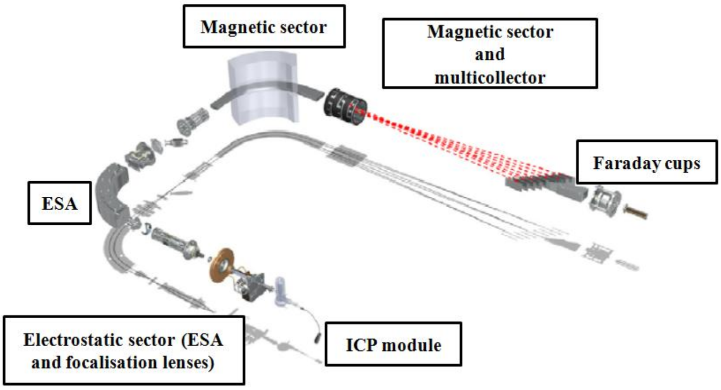


Figure 22*:* Scheme of the ICP multicollector spectrometer Neptune (Berni PhD Thesys).

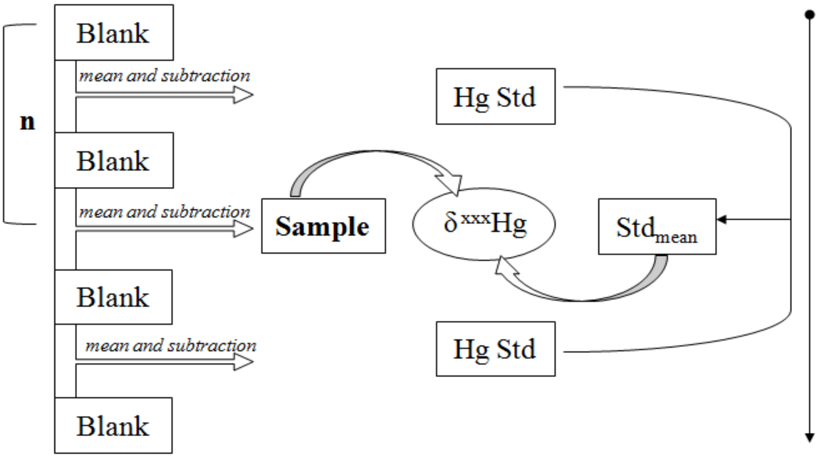


Figure 23: *Block diagram of the readings and calculations sequence for RI determination using the technique of bracketing standard. For n samples, must be repeated n times the part of the sequence between parentheses (Berni PhD Thesys, modified).*

Mercury has seven stable isotopes with the following approximate abundances for the National Institute of Standards and Technology (NIST) Standard Reference Material (SRM)-3133: ^{196}Hg = 0.155%, ^{198}Hg = 10.04%, ^{199}Hg = 16.94%, ^{200}Hg = 23.14%, ^{201}Hg = 13.17%, ^{202}Hg = 29.73%, ^{204}Hg = 6.83% (Blum and Bergquist 2007). These abundances are referenced to the certified ^{205}Tl/^{203}Tl ratio of 2.38714 for the NIST SRM-997.

The ^{202}Hg/^{198}Hg ratio will be used to describe mass-dependent stable isotope fractionation (MDF) relative to the NIST SRM-3133. Hg isotopic compositions relative to NIST SRM-3133 are reported as Eq. (6):

$$\delta xxx = \left\{ \frac{(^{xxx}Hg/^{198}Hg)_{sample}}{(^{xxx}Hg/^{198}Hg)_{SRM3133}} - 1 \right\} * 1000 \qquad (6)$$

Mass-independent isotope fractionation (MIF) has been observed for the odd isotopes of Hg and is reported as Δ^{199}Hg and Δ^{201}Hg. These values represent the differences between the measured δ^{199}Hg and δ^{201}Hg values and those predicted based on the measured δ^{202}Hg and the kinetic mass-dependent fractionation law derived from transition state theory.

For variations of less than ~10‰, these values were approximated by Blum and Bergquist (2007) to be:

$$\begin{gathered}
\Delta^{199}Hg = \delta^{199}Hg - (\delta^{202}Hg * 0.2520) \\
\Delta^{200}Hg = \delta^{200}Hg - (\delta^{202}Hg * 0.5024) \\
\Delta^{201}Hg = \delta^{210}Hg - (\delta^{202}Hg * 0.7520) \\
\Delta^{204}Hg = \delta^{204}Hg - (\delta^{202}Hg * 1.493)
\end{gathered} \qquad (7)$$

The magnitude of mass-dependent and mass independent fractionation will be described primarily with δ^{202}Hg and Δ^{201}Hg.

In addition to variations in the magnitude of these isotope ratios, trends in the ratios of the isotope ratios, in particular the Δ^{199}Hg/Δ^{201}Hg and Δ^{201}Hg/δ^{202}Hg have been shown to be diagnostic of some chemical transformation mechanisms (Bergquist and Blum 2007).

Chapter IV:
Results

4. Results

4.1 THg distribution in sediment and grain size composition

The HgT contents measured in the core sediments show a wide range of measures between 1.77 and 55.34 mgKg^{-1} (Tab. 9; Fig. 24). The lowest values of THg are recorded in sediments collected in the northern Augusta Bay (Fig. 9, station 7 replied in both sampling), ranging between 3.26 and 7.82 mgKg^{-1} (mean THg = 6.15±1.54 mgKg^{-1}) in May 2011 sampling and replied in June 2012 (range: 4.12- 8.66 mgKg^{-1}; mean THg = 6.33±0.90 mgKg^{-1}) (Tab. 9; Fig. 24).

THg in sediments collected in the centre Augusta Bay (Station 11 and 12 of 2011 sampling and station 12 of 2012 sampling; Fig.24;) have intermediate THg values, ranging between 13.79 and 17.98 mgKg^{-1} (mean THg = 16.23±1.46 mgKg^{-1}) and between 5.17 - 39.53 mgKg^{-1} (20.98±11.45 mgKg^{-1}) for core 11 and 12 of sampling 2011 respectively. THg content in core 12, (sampling May 2012) range between 8.01 and 16.83 mgKg^{-1} (mean THg = 12.47±2.69 mgKg^{-1}).

Finally THg content in sediment collected in the southern Augusta Bay (stations 16bis, sampling 2012; Fig. 24), has the highest THg values; range: 1.77 - 55.34 mgKg^{-1} (mean THg = 25.38±14.44 mgKg^{-1}). The HgT content measured in core collected in station 16 in May 2011 (mean THg: 7.81±1.66) appears lower than those expected, with respect to the geographical location (Fig. 24). The highest peaks of HgT contents were measured in the southern collected cores, in core 12 (May 2011) at 13.5 cm (39.53 mg Kg^{-1}) and in core 16bis (June 2012) at 15 cm (55.34 mg Kg^{-1}).

Sediments were texturally rather uniform at both sampling sites (Tab. 9; Fig.25). Sediment layers consisted mostly of silt (~50%), and clay (~30%), whereas the sandy fraction represents a small percentage (Tab. 9; Fig.25). The only exception is represented by core 16 of May 2011 sampling, mainly composed of sandy (~75%), thus justifying the minor THg content measured in this core sediments (Tab. 9; Fig.25).

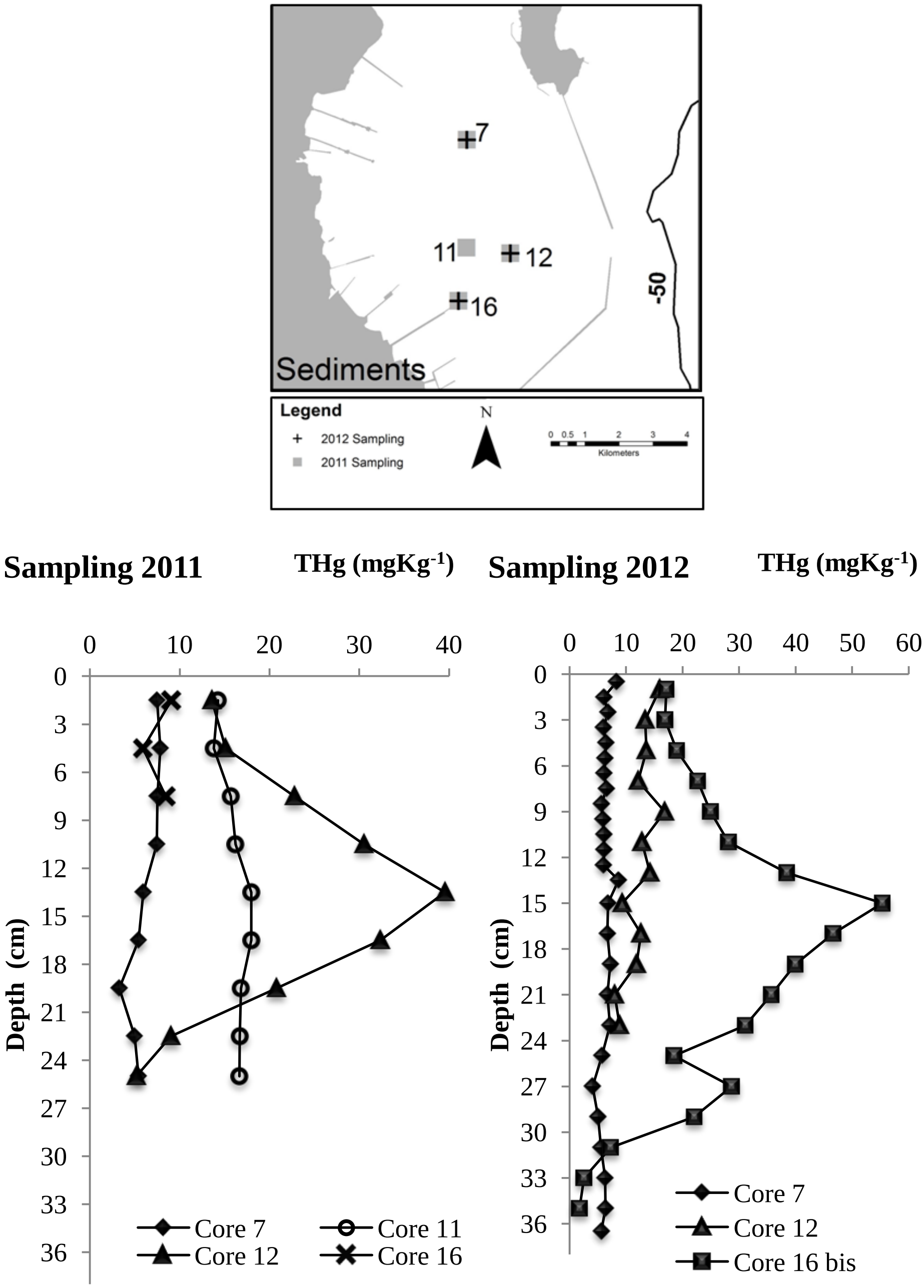
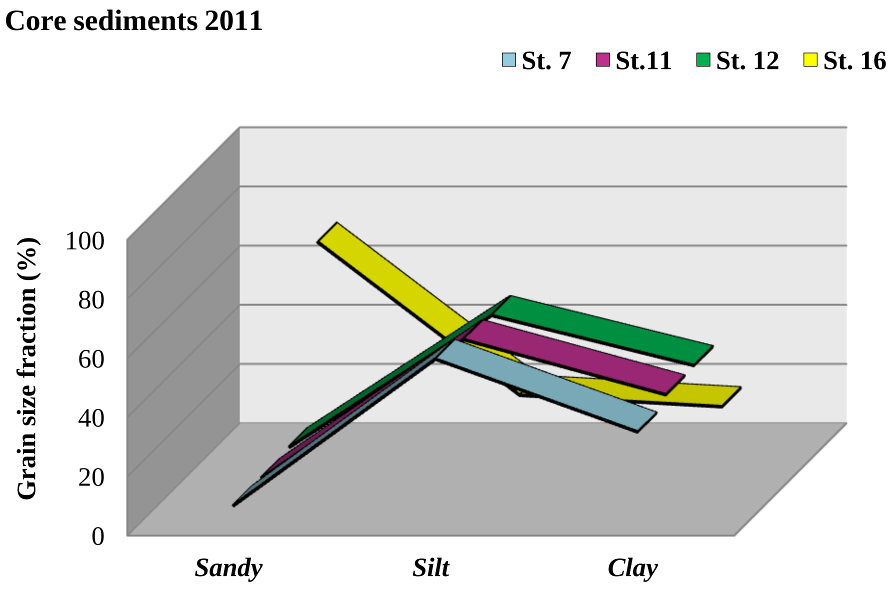


Figure 24: *Profile of THg content along all the collected cores in 2011 and 2012, with related sampling map.*



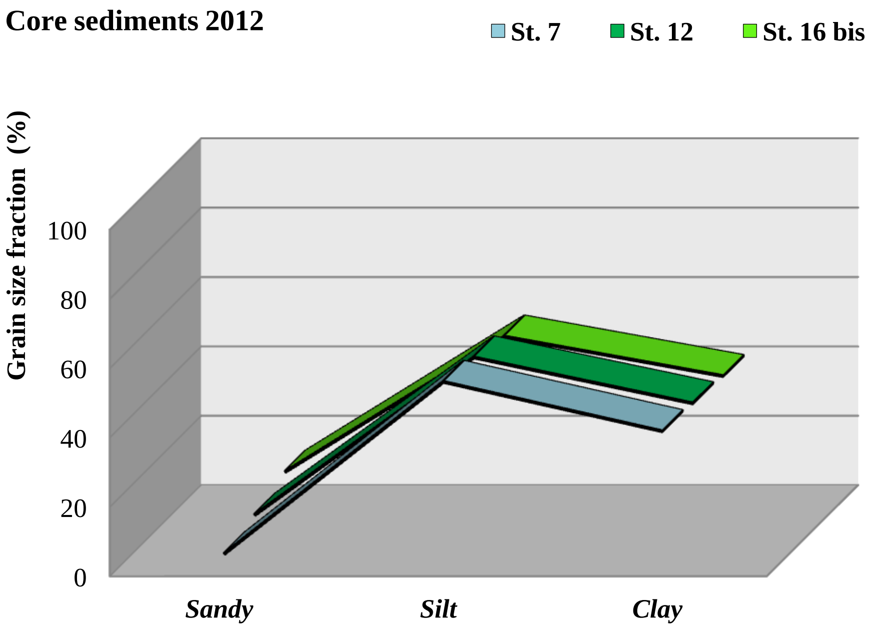


Figure 25: *Grain size composition in collected cores of sampling 2011 and 2012.*

Table 9: THg measures and grain size composition in all the collected sediments. THg DHg are also reported for porewater sediment collected in June 2012.

	Station	Depth	THg	Mean diameter	Sorting	Sandy	Silt	Clay
		(cm)	*(mgKg^{-1})*	*(µm)*	*(µm)*	*(%)*	*(%)*	*(%)*
Sampling May 2011	**7**	0- 3	7.48	9.11	5.02	8.14	59.91	31.95
		3- 6	7.82	8.91	5.44	9.71	57.10	33.19
		6 -9	7.53	8.72	5.23	8.69	58.03	33.28
		9 -12	7.44	8.12	5.03	6.74	58.92	34.34
		12 -15	5.96	8.72	5.34	8.61	57.37	34.02
		15 -18	5.43	9.16	5.28	8.81	58.36	32.83
		18 -21	3.26	8.25	5.43	8.70	56.95	34.35
		21- 24	4.97	8.73	5.19	8.13	58.17	33.70
		24 -26	5.41	9.04	5.22	8.77	57.90	33.33
	11	0- 3	14.26	8.127	5.66	8.52	55.78	35.70
		3-6	13.79	7.716	5.88	9.20	53.88	36.92
		6-9	15.68	7.604	5.75	8.73	54.45	36.82
		9-12	16.21	7.274	5.70	8.09	55.41	36.50
		12-15	17.98	8.711	5.62	10.33	55.59	34.08
		15-18	17.98	7.244	5.74	8.00	54.34	37.66
		18-21	16.82	6.661	5.06	5.54	56.18	38.28
		21-24	16.68	7.764	5.20	7.82	55.85	36.33
	12	0-3	13.59	8.161	5.73	9.89	53.93	36.18
		3-6	15.11	8.845	5.59	10.44	54.64	34.92
		6-9	22.77	9.099	5.67	11.71	53.59	34.70
		9-12	30.51	7.791	5.36	7.84	55.04	37.12
		12-15	39.53	7.095	4.76	5.71	56.27	38.02
		15-18	32.33	6.368	4.80	5.10	55.65	39.25
		18-21	20.77	6.202	6.81	8.69	52.39	38.92
		21- 24	9.02	8.875	6.00	11.96	52.35	35.69
		24 -26	5.17	8.367	6.19	12.08	50.52	37.40
	16	0-3	9.05	250.694	10.07	77.89	12.25	9.86
		3-6	5.92	160.762	12.20	68.41	17.54	14.05
		6-9	8.46	111.568	11.95	61.21	22.24	16.55
Sampling June 2012	**7**	0-1	8.34	4.24	6.64	3.27	52.65	44.08
		1-2	6.07	4.80	6.41	4.00	54.62	41.38
		2-3	6.79	4.45	6.61	3.46	53.86	42.68
		3-4	6.04	4.61	6.63	3.74	54.39	41.87
		4-5	6.42	4.43	7.26	4.67	52.62	42.71
		5-6	6.31	4.51	6.20	3.30	53.98	42.72
		6-7	6.16	4.52	6.54	2.01	55.66	42.33
		7-8	6.55	5.64	6.84	6.35	55.03	38.62
		8-9	5.66	7.27	7.26	10.27	55.20	34.53

Table 9 continued

		9-10	5.88	5.80	7.10	6.34	55.91	37.75
		10-11	6.09	5.16	7.04	4.96	55.61	39.43
		11-12	6.15	3.89	7.35	3.27	52.18	44.55
		12-13	5.99	4.56	6.42	2.74	54.67	42.59
		13-14	8.66	4.73	7.37	6.13	52.17	41.70
		14-16	6.84	5.00	6.36	2.47	56.54	40.99
		16-18	6.67	4.67	6.59	3.96	53.36	42.68
		18-20	7.23	5.93	6.16	5.48	56.25	38.27
		20-22	6.72	5.85	6.66	6.77	54.29	38.94
		22-24	7.15	6.28	6.21	6.68	55.25	38.07
		24-26	5.74	5.14	7.02	5.13	60.07	34.80
		26-28	4.12	4.77	7.10	4.18	54.69	41.13
		28-30	5.08	6.54	7.19	10.19	52.45	37.36
		30-32	5.59	5.84	6.96	6.53	55.37	38.10
		32-34	6.32	5.46	6.70	6.12	55.17	38.71
		34-36	6.35	4.56	7.11	5.16	52.47	42.37
		36-37	5.64	4.77	7.04	3.57	55.27	41.16
	12	0-2	15.96	7.37	5.98	8.79	53.71	37.50
		2-4	13.36	8.07	5.74	8.98	55.51	35.51
		4-6	13.61	4.95	7.93	8.22	49.84	41.94
		6-8	12.16	4.91	7.07	7.01	50.74	42.25
		8-10	16.83	6.53	5.96	6.53	54.61	38.86
		10-12	12.80	6.57	6.23	7.81	53.40	38.79
		12-14	14.24	6.13	6.50	7.38	53.04	39.58
		14-16	9.33	6.61	6.18	7.69	52.89	39.42
		16-18	12.63	4.57	6.92	5.30	51.60	43.10
		18-20	11.83	4.72	6.54	3.68	53.76	42.56
		20-22	8.01	8.10	5.91	9.11	55.68	35.21
		22-24	9.12	5.40	7.69	9.14	49.81	41.05
	16	0-2	17.11	8.10	7.09	12.72	51.20	36.08
		2-4	16.90	9.05	7.20	15.84	49.52	34.64
		4-6	18.99	5.45	7.87	10.57	47.13	42.30
		6-8	22.69	5.66	7.75	11.23	47.22	41.55
		8-10	24.94	6.63	6.56	9.55	50.03	40.42
		10-12	28.13	5.03	6.98	7.96	47.68	44.36
		12-14	38.41	5.82	7.40	9.80	48.90	41.30
		14-16	55.34	5.69	6.51	8.77	48.69	42.54
		16-18	46.67	6.42	6.84	9.97	49.17	40.86
		18-20	39.96	7.10	6.75	9.91	52.04	38.05
		20-22	35.71	6.05	6.82	7.93	51.97	40.10
		22-24	31.12	5.93	7.81	11.05	48.41	40.54
		24-26	18.51	6.95	7.28	11.21	51.43	37.36
		26-28	28.69	7.40	7.11	12.16	50.70	37.14

Table 9 continued

		28-30	22.08	6.81	7.01	10.32	51.71	37.97
		30-32	7.28	7.14	7.90	13.55	49.75	36.70
		32-34	2.57	10.61	6.72	15.84	52.26	31.90
		34-36	1.77	9.03	6.62	11.86	54.65	33.49

4.1.1 Sequential extraction procedure

More than 80% of HgT in the sediments were extracted in step 4 (Tab. 10; Fig. 26) thus documenting a highly stable phase of Hg, like Hg_2Cl_2 (calomel), or trapped in mineral lattice, or bound to humic substances (Bloom et al., 2000). Around a 15% of Hg was extracted at the step 5, possibly like insoluble Hg forms as cinnabar (HgS), m-HgS, HgSe and HgAu. Only ~2% of HgT were released in the first three steps, as more soluble, and bioavailable forms (Tab. 10; Fig. 26).

Table 10: THg extracted from each step applying the sequential extraction procedure on sediments collected in May 2011.

Station	**Depth** *(cm)*	**THg** *($mgKg^{-1}$)*	**STEP 1** *(%)*	**STEP 2** *(%)*	**STEP 3** *(%)*	**STEP 4** *(%)*	**STEP 5** *(%)*
7	6-9	7.53	0.206	0.059	1.472	84.832	13.431
	21-24	4.97	0.048	0.040	0.276	95.267	4.370
11	0-3	14.26	0.039	0.026	0.300	82.106	17.528
	3-6	13.79	0.031	0.031	1.001	89.804	9.1320
	6-9	15.68	0.004	0.024	0.465	86.328	13.179
	9-12	16.21	0.038	0.022	0.581	81.891	17.469
	12-15	17.98	0.031	0.018	0.569	83.953	15.429
	12-15 bis	17.98	0.021	0.119	0.813	93.190	5.857
	15-18	17.98	0.026	0.080	0.541	86.240	13.112
	18-21	16.82	0.039	0.024	0.641	80.037	19.259
	21-24	16.68	0.038	0.018	0.545	82.895	16.504
	24-26	16.66	0.042	0.017	0.559	87.156	12.225
12	0-3	13.59	0.042	0.025	1.037	81.293	17.603
	0-3 bis	13.59	0.025	0.017	0.817	82.557	16.583
	9-12	30.51	0.036	0.133	0.163	88.050	11.618
	15-18	32.33	0.009	0.019	0.151	85.141	14.679
	18-21	20.77	0.021	0.023	0.262	91.752	7.942
	24-25	5.17	0.045	0.044	0.504	94.765	4.642

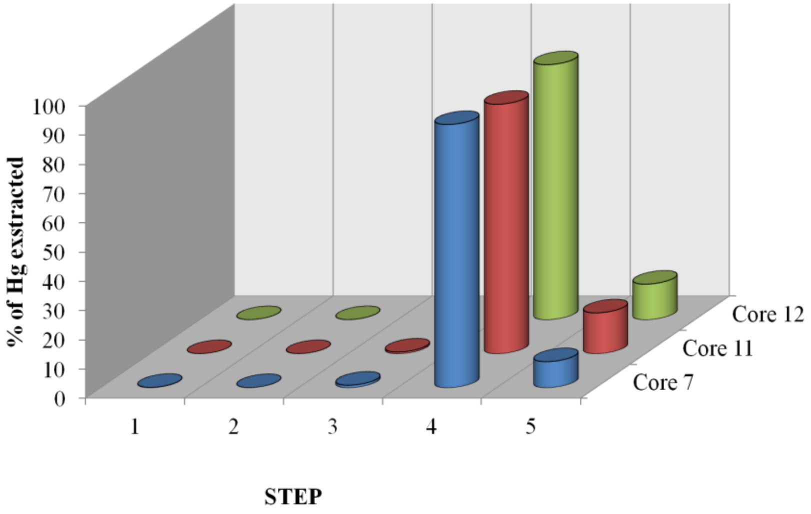


Figure 26: *Hg (%) extracted from each step using the sequential extraction procedure.*

4.2 Mercury in fishes

4.2.1 Total mercury concentrations in fishes

Hg analysis and bioaccumulation processes in fish compartment were reported in attachment I (Bonsignore et. al., 2013).

Total mercury concentrations measured in tissues from pelagic, demersal and benthic fishes, caught inside and outside of Augusta Bay, are graphically summarised in Figures 27 a and b.

Mercury mean values calculated for each species, together with available comparative data from the literature and HgT content measured in anchovies from Marsala, are presented in Table 11.

Mercury concentrations ranged between 0.021 and 2.709 μg g-1 in muscles (Fig. 27a) and between 0.029 and 9.720 μg g^{-1} in livers (Fig. 27b). The HgT content in liver is from 1.5 to 6 times higher than that measured in muscles from the same specimens (Table 11).

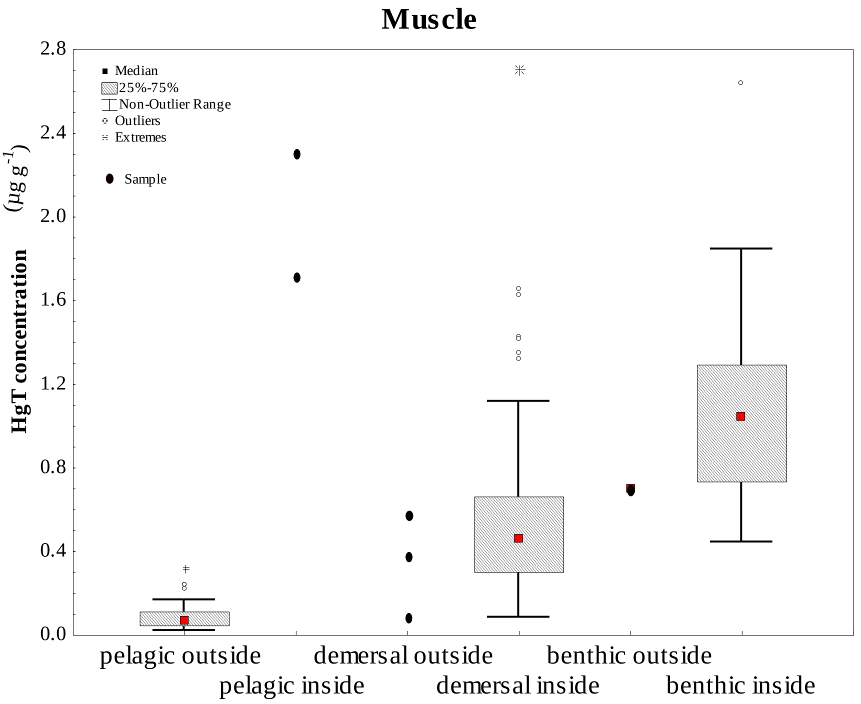
The highest HgT values were found in species caught inside the bay: 2 demersal specimens, a specimen of *Diplodus vulgaris* (HgT in liver = 4.979 μg g^{-1}) (extreme point in Fig. 27b) and a specimen of Serranus scriba (HgT in muscle = 2.709 μg g^{-1}) (extreme point in Fig. 27a), a large pelagic specimen of *Sphyraena sphyraena* (HgT = 9.720 and 2.269 μg g^{-1} in liver and muscle, respectively) (Table 11) and a benthic specimen of Murena helena (HgT = 2.638 μg g^{-1} in muscle) (Table 11).

However, these very high levels represent outliers of the whole dataset (Figs. 27 a, b).

The highest non-outlier values refer once again to specimens caught inside the bay and specifically to benthic species (Figs. 27 a, b). In particular, *Scorpanea scrofa* and *Scorpanea notata* show the highest HgT mean concentrations for both liver (1.638 and 2.339 μg g^{-1}, respectively) and muscle (1.082 and 1.341 μg g^{-1}, respectively) (Table 11).

The lowest non-outlier ranges were found in pelagic specimens caught outside the bay (0.021 - 0.167 μg g^{-1} for muscles and 0.029 - 0.5708 for livers) (Figs. 27 a, b), and the HgT mean values measured in the different studied species are substantially comparable (Table 11).

Finally, data for demersal species from the inner bay show the widest non-outlier ranges (0.084 - 1.116 μg g^{-1} for muscles, 0.109 - 2.747 μg g^{-1} for livers) and the most elevated number of outliers and extreme values (Figs. 27 a, b). In particular, the highest HgT mean values (2.165 μg g^{-1} in liver and 2.581 μg g^{-1} in muscle) were measured in the *Serranus scriba* species (Table 11).



(a)

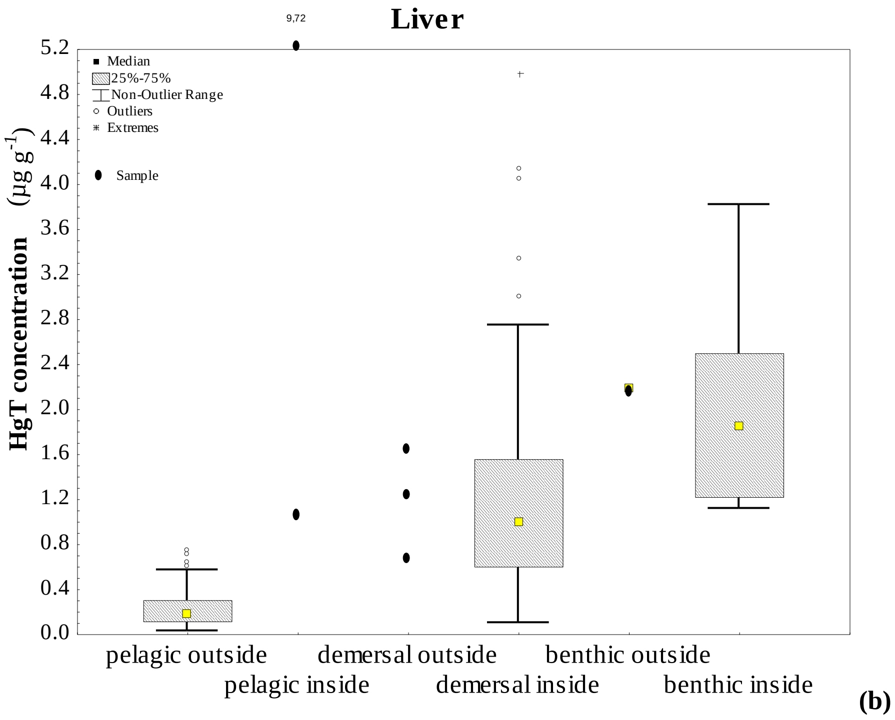


Figure 27: *Box-plots with HgT concentrations in the muscles (a) and livers (b) of pelagic, demersal and benthic fishes.*

Table 11: HgT means concentrations in muscle and liver of the analysed species and comparison with data for other areas.

Species	**N°**	**Range of total length** (mm)	**HgT Muscle** (µg g^{-1})	**S.D.**	**References**	**Site**	**HgT Liver** (µg g^{-1})	**S.D.**
Engraulis encrasicolus	40	109-138	0.052	0.019	*This work*	Augusta	0.204	0.147
	11	120-139	0.057	0.014	*This work*	Marsala	0.119	0.038
			0.040		*Bilandžić et al., 2011*	Adriatic sea		
	9	121-147	0.070	0.090	*Gibičar et al., 2009*	Adriatic sea*		
			0.030	0.030	*Copat et al., 2012*	Sicily (Catania)		
			0.060	0.030	*Copat et al., 2012*	Syracuse (Sicily)		

Table 11 continued

	18		0.060		*Pastor et al., 1994*	Mediterranean sea (Spain)*		
			0.070		*Martorell et al., 2011*	Mediterranean sea (Spain)		
	4		0.055	0.003	*Tuzen, 2009*	Black Sea (Turkey)*		
Sardina pilchardus	28	115-150	0.082	0.035	*This work*	Augusta	0.196	0.157
	10	168-178	0.090	0.040	*Gibičar et al., 2009*	Adriatic sea*		
			0.080	0.030	*Copat et al., 2012*	Catania (Sicily)		
			0.180		*Buzina et al., 1995*	Adriatic sea*		
			0.198		*Buzina et al., 1995*	Adriatic sea (Kastela Bay)*		
	14		0.052		*Wolfgang, 1983*	Adriatic sea*		
	35	190-260	0.066		*Wolfgang, 1983*	Biscay Bay		
	5	157-165	0.050		*Wolfgang, 1983*	Mediterranean sea		
	41		0.170		*Wolfgang, 1983*	Ligurian sea		
	28	120-150	0.030		*Wolfgang, 1983*	North Africa (Ceuta)*		
	20	160-210	0.040		*Wolfgang, 1983*	Western English Channel		
	38		0.105		*Pastor et al., 1994*	Mediterranean sea (Spain)*		
			0.019		*Martorell et al., 2011*	Mediterranean sea (Spain)		
	7	188-200	0.033	0.016	*Harakeh et al., 1985*	Lebanon		
Boops boops	20	95-150	0.120	0.049	*This work*	Augusta	0.236	0.191
	11	158-198	0.196	0.204	*Hornung et al.,1980*	Israel*		
	1		0.075		*Pastor et al., 1994*	Mediterranean sea (Spain)*		

Table 11 continued

	2	130-160	0.190		*Stoeppler-Nürnberg, 1979*	Med. Sea (Dubrovnik)		
			0.267		*Buzina et al., 1995*	Adriatic sea		
			0.312		*Buzina et al., 1995*	Adriatic sea (Kastela Bay)*		
	16	139-171	0.036	0.025	*Harakeh et al., 1985*	Lebanon		
Trachurus trachurus	6	56-222	0.131	0.147	*This work*	Augusta	0.344	0.176
	2	260-285	0.170		*Stoeppler-Nürnberg, 1979*	North sea (German Bight)		
		170	0.170		*Mikac et al., 1984*	Adriatic sea (Kastela Bay)*		
	37	130-236	0.122	0.101	*Hornung et al.,1980*	Israel*		
	16	159-203	0.045	0.019	*Harakeh et al., 1985*	Lebanon		
			0.053		*Martorell et al., 2011*	Mediterranean sea (Spain)		
	4		0.078	0.005	*Tuzen, 2009*	Black Sea (Turkey)*		
	5		0.053	0.012	*Keskin et al., 2007*	Marmara sea (Turkey)*		
Diplodus annularis	74	109-179	0.557	0.303	*This work*	Augusta	1.195	0.827
			0.653		*Buzina et al., 1995*	*Adriatic sea**		
			0.628		*Buzina et al., 1995*	*Adriatic sea (Kastela Bay)**		
Diplodus vulgaris	*3*	102-179	0.643	0.614	*This work*	Augusta	*2.035*	*2.554*
	5		0.378	0.017	*Keskin et al., 2007*	Marmara sea (Turkey)*		
Sphyraena sphyraena	1	1190	2.269		*This work*	Augusta	9.727	
	14	219-295	0.167	0.068	*Hornung et al.,1980*	Israel*		
Caranx rhonchus	1	264	1.701		*This work*	Augusta		

Table 11 continued

Pagellus acarne	12	149-161	0.254	0.028	*This work*	Augusta	0.618	0.178
	3	135-141	0.112		*Hornung et al.,1980*	Israel*		
	15	164-182	0.032	0.014	*Harakeh et al., 1985*	Lebanon		
Pagellus bogaraveo	2	178-179	0.266	0.227	*This work*	Augusta	1.230	0.700
Pagellus erythrinus	8	154-205	0.407	0.100	*This work*	Augusta	2.322	0.445
	5	110	0.341	0.025	*Papetti-Rossi, 2009*	Tyrrhenian sea (Lazio)		
	57	115-187	0.180	0.094	*Hornung et al.,1980*	Israel*		
	9	89-173	0.240	0.190	*Gibičar et al., 2009*	Adriatic sea*		
	28	140-152	0.042	0.023	*Harakeh et al., 1985*	Lebanon		
	5		0.168		*Pastor et al., 1994*	Mediterranean sea (Spain)*		
	5		0.290	0.044	*Keskin et al., 2007*	Marmara sea (Turkey)*		
Serranus scriba	2	122-140	2.165	0.768	*This work*	Augusta	2.581	0.592
	3		1.030	0.459	*Gibičar et al., 2009*	Tyrrhenian sea (Tuscany)*		
Mullus barbatus	4	155-202	0.815	0.777	*This work*	Augusta	1.518	0.582
		102-230	0.116	0.056	*Hornung et al.,1980*	Israel*		
			0.400	0.400	*Storelli et al., 2004*	Ionian sea		
			0.490	0.500	*Storelli et al., 2004*	Adriatic sea*		
	13	117-180	0.700	0.730	*Gibičar et al., 2009*	Adriatic sea*		
			0.370		*Buzina et al., 1995*	Adriatic sea		
			0.318		*Buzina et al.,*	Adriatic sea		

Table 11 continued

					1995	(Kastela Bay)*		
	59		0.139		*Pastor et al., 1994*	Mediterranean sea (Spain)		
			0.010		*Martorell et al., 2011*	Mediterranean sea (Spain)		
	30	128-166	0.054	0.025	*Harakeh et al., 1985*	Lebanon		
		130-200	0.233		*Stoeppler-Nürnberg, 1979*	Mediterranean Sea (Sardinia)		
	4		0.036	0.002	*Tuzen, 2009*	Black Sea (Turkey)*		
	5		0.434	0.012	*Keskin et al., 2007*	Marmara sea (Turkey)*		
Mullus surmuletus	2	200-209	0.662	0.089	*This work*	Augusta	1.112	
	9	120-160	0.086		*Hornung et al.,1980*	Israel*		
	59		0.139		*Pastor et al., 1994*	Mediterranean sea (Spain)*		
	2	185-203	0.250		*Stoeppler-Nürnberg, 1979*	North sea (German Bight)		
	37		0.060		*Bilandžič et al, 2011*	Adr.sea (Croatian coast)		
Scorpaena scrofa	4	93-112	1.082	0.285	*This work*	Augusta	1.637	0.380
			0.222		*Buzina et al., 1995*	Adriatic sea		
			0.390		*Buzina et al., 1995*	Adr. sea (Kastela Bay)*		
Scorpaena notata	5	114-133	1.340	0.380	*This work*	Augusta	2.339	0.529
	5		0.490	0.430	Gibičar et al., 2009	Tyrrhenian sea (Tuscany)*		
Illex coindetii	6	33-92	0.078	0.039	This work	Augusta		
	13	52-224	0.100	0.100	Gibičar et al., 2009	Adriatic sea*		
Loligo forbesi	3	45-	0.147	0.024	*This work*	Augusta	0.311	0.011

Table 11 continued

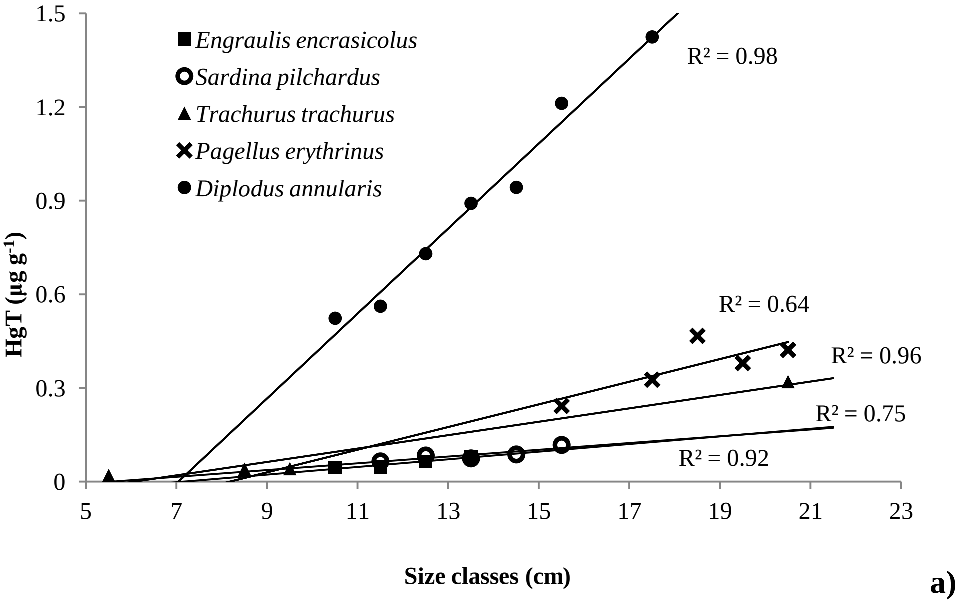
		170						
Sepia officinalis	8	108-148	0.766	0.288	*This work*	Augusta		
Octopus vulgaris	1	123	0.443		*This work*	Augusta		
Murena helena	1	800.5	2.638		*This work*	Augusta	3.817	

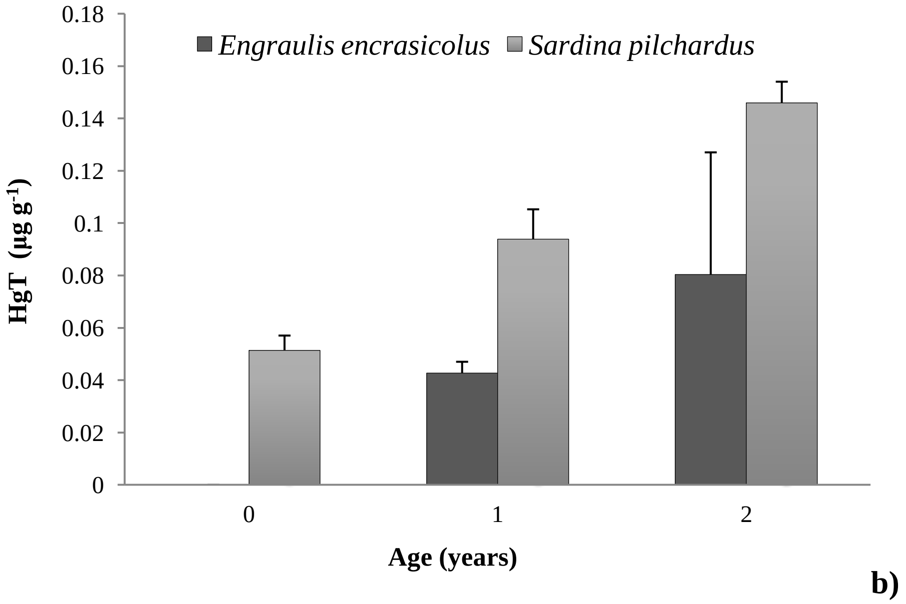
**Polluted site*

4.2.2 Biological features

The fish caught from bottom-water sampling (inside the bay) consisted of 2 pelagic, 106 demersal and 16 benthic specimens, while specimens from mid-water sampling (outside the bay), consisted of 103 pelagic, 3 demersal and 1 benthic. Almost all the caught species, in particular, *Engraulis encrasicolus, Sardina pilchardus, Boops boops, Mullus barbatus* and *Illex coindetii*, are typical of the Mediterranean Sea and are commercially relevant to Italian fishing (Irepa, 2010). Only one specimen was found to belong to a so-called alien species, specifically *Sphyraena sphyraena*. This is a typical species of the tropical seas, today present also in the Mediterranean Sea (Streftaris and Zenetos, 2006). Assuming the length of fishes as a reliable parameter for age estimates (Boening, 2000; Waldron and Kerstan, 2001; Scudder et al., 2009; Panfili et al., 2010; Basilone et al., 2011; Bacha et al., 2012) and, thus, reported HgT values *vs*. length to assess biomagnification of that contaminant with time (Fig. 28a). Statistically reliable and robust correlations were found between HgT mean values measured in muscles for size classes and length in *S. pilchardus* ($r^2 = 0.75$), *E. encrasicolus* ($r^2 = 0.92$), *T. trachurus* ($r^2 = 0.96$), *D. annularis* ($r^2 = 0.98$) and *P. erythrinus* ($r^2 = 0.64$) (Fig. 28a). Specifically, the calculated HgT accumulation rates for *S. pilchardus*, *E. encrasicolus*, *T. trachurus*, *P. erythrinus* and *D. annularis* are 0.011, 0.012, 0.022, 0.036 and 0.136 $\mu g\ g^{-1} cm^{-1}$, respectively, in good agreement with data reported by Hornung et al. (1980) for *P. erythrinus* and *T. trachurus* species. In our dataset an evident increasing trend was measured between HgT content and age in the two most abundant species, *E. encrasicolus* and *S. pilchardus* (Fig. 28b) with significant differences ($p<0.005$; ANOVA test) among age group, although, the restricted range of available age classes needs a larger data collection.

Additionally, contamination effects show a south-north gradient evident from HgT levels measured on the ubiquitous *Pagellus spp. and D. annularis specimens* (Fig. 28c). In particular, the highest HgT mean concentrations occur in fishes caught from southern Augusta Bay where bottom sediments show the highest concentrations of mercury.





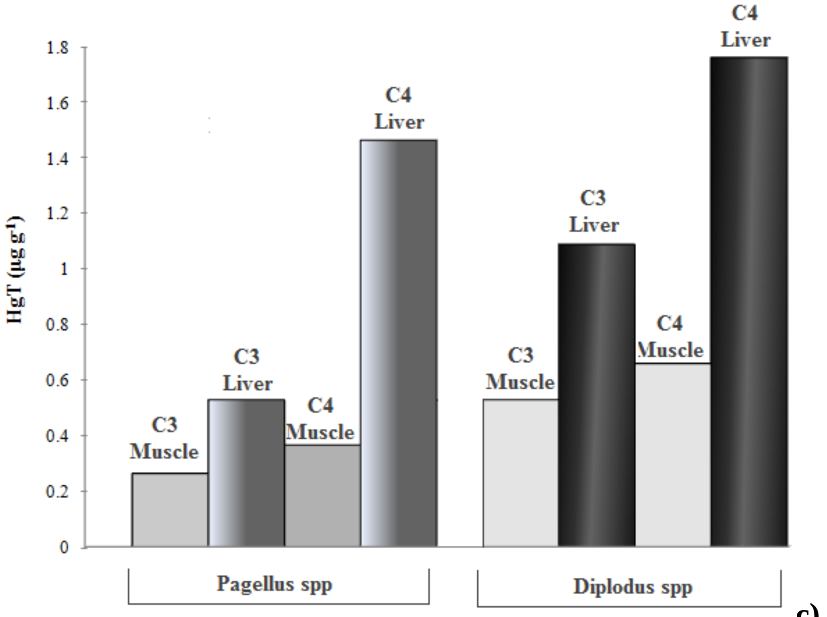
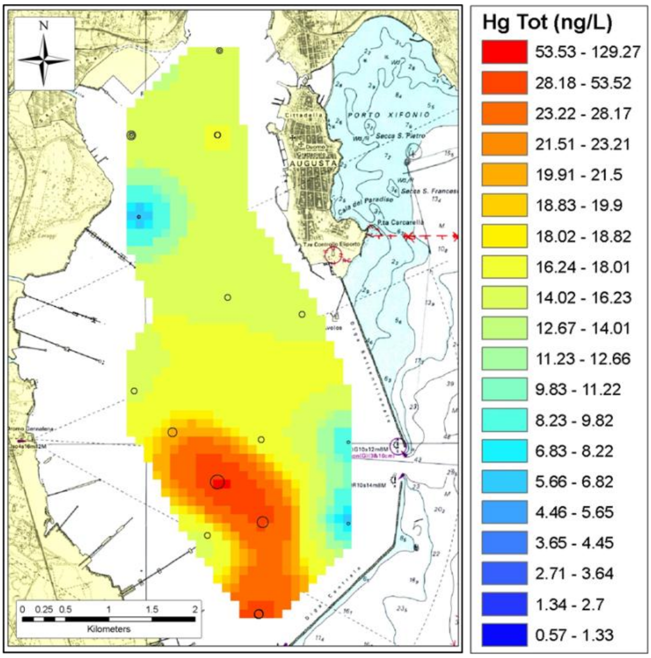


Figure 28: *Fish biological accumulation rate.* ***a)*** *Relationship between HgT concentrations and total body length for Sardina pilchardus, Engraulis encrasicolus, T. trachurus, D. annularis and P. erythrinus. Points represent the mean values for each size class; b) Relationship between total mercury concentration (median value of HgT) in fish muscles vs. age in E. encrasicolus and S. pilchardus. Black lines = confidence interval. c) Differences in muscle (M) and liver (L) HgT contents in Pagellus spp. and Diplodus annularis from the northern (C3) and the southern (C4) part of Augusta Bay.*

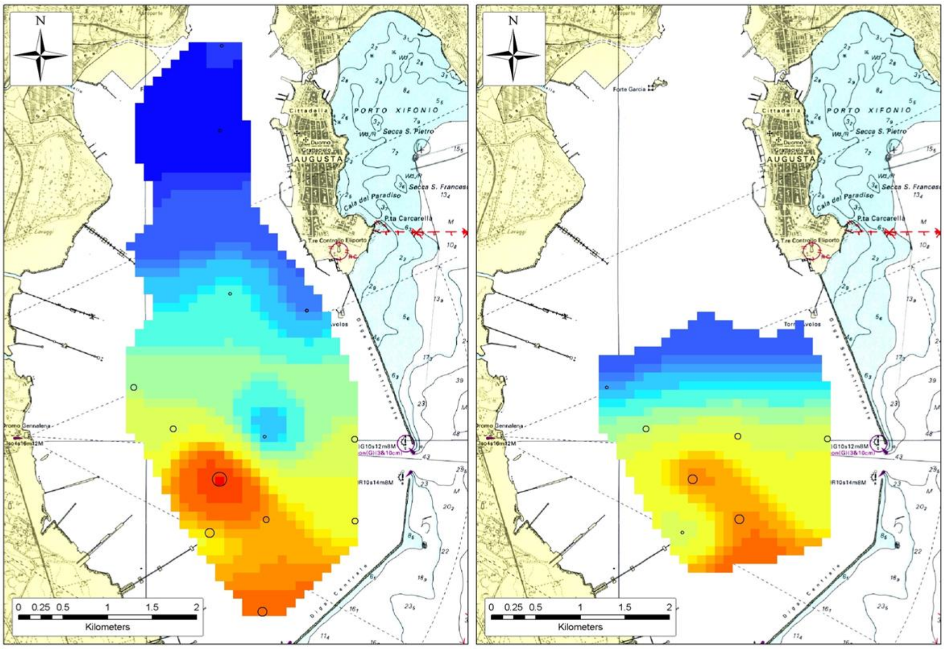
4.3 Mercury (THg and DHg) in seawater

Mercury in waters was analyzed as total Hg (THg) and dissolved Hg (DHg), the last one as filtered fraction, assuming that the difference between THg and DHg approximate the content of Hg in suspended particulate matter (PHg), as reported in other studies (e.g. Faganeli et al., 2003),

Reported THg and DHg values are calculated by difference with blank (10 ngL^{-}) and measures lower than detection limit of the blank (calculated as 2.33σ) are reported as >L.d.. Figure 29 reported all the made analyses, including values lower than the detection limits but close to the critical limits (calculated as 4.65σ). The HgT concentrations in seawaters collected during May 2011 (Tab. 12; Fig. 29) show a wide range of values, between >L.d. and 129.27 ngL^{-1} (mean HgT: 20.24±26.18 ngL^{-1}) while HgD, ranges between > L.d. and 21.3 ngL^{-1} with a mean value of 7.87±6.69 ngL^{-1} (excluding values < L.d.). An evident increasing trend of THg toward the southern and more contaminated part of the Augusta Bay (where waste spillage from chlor-alkali plant occurred) can be observed. In this zone very high THg content (129 ngL^{-1}) has been found. On the vertical, surface waters (20-30 m from the bottom, Fig. 29) show the lowest Hg content (mean THg of 13.64±8.93 ngL^{-1}), with the minimum THg value of 0.57 ngL^{-1}, middle waters (10-20 m from the bottom; Fig. 29) have intermediate concentration (mean THg of 24.36±30.9 ngL^{-1}) and deeper waters (10-20 m from the bottom; Fig. 29) the highest content (mean THg of 51.87±55.09 ngL^{-1}). Basically that testifies testify a key role played by the sediments as sources of mercury to the water column. THg in seawaters collected in June 2012 ranges between 0.45 and 14.85 ngL^{-1} (mean value: 7.43±5.19 ngL^{-1}) and HgD mean of 2.26±2.24 ngL^{-1} with a maximum of 6.35 ngL^{-1}). Mean THg results 4.48±4.65 ngL^{-1} in the northern Augusta Bay (station 7), 10.06±5.04 ngL^{-1} in the centre (station 12) and 11.31±9.07 ngL^{-1} in the south area (station 16), in agreement with data reported the year before. Concentrations of THg measured in seawater outside the Bay (Tab. 12; station 18-21) range between 2.62 and 11.95 ng L^{-1} (mean: 6.46±2.95 ngL^{-1}), with no evident systematic change with depth. The highest HgT values were measured closer to the bay (Fig. 9, station 19), with mean THg content of 7.80±5.60 ngL^{-1}), while values measured in station far from the Augusta Bay (Fig. 9; stations 19 and 20) are 5.15±0.83 and 6.44±2.37 respectively. Unexpected values were recovered in open sea (Fig. 9; station 21) with mean THg of 6.91±4.71 ngL^{-1} and DHg range between >L.d. and 5.55 ngL^{-1} (Tab. 12).



a) 10 m from the bottom



b) 10-20 m from the bottom c)20-30 m from the bottom

Fig. 29: *Map of HgT content distribution in the Augusta Bay seawater created from May 2011 samples at 0-10 m from the bottom, 10-20 m from the bottom and from 20m to surface water. Maps created by through3D block kriging and themed on the "natural breaks" method.*

Table 12: THg and DHg measurement in all the seawater samples collected inside (May 2011, June 2012) and outside the Augusta Bay (February 2012). Reported values are calculated by difference with blank (10 ngL^{-}); Lower measures are reported as >L.d.

	Station	**Bathymetry**	**Sampling depth**	**THg**	**DHg**
		(m)	*(m)*	*(ngL^{-1})*	*(ngL^{-1})*
Sampling May 2011	1	14.0	11.2	17.77	< L.d.
			6.2	9.17	6.70
			1.4	9.17	3.20
	2	16.0	10.7	17.67	< L.d.
			6.7	14.87	< L.d.
			2.2	0.57	0.30
	3	11.0	8.4	29.97	0.30
			4.6	11.97	1.30
			2.3	0.57	0.30
	4	8.0	3.1	6.27	3.20
			0.1	0.57	< L.d.
	5	20.0	15.9	17.67	0.30
			9.2	7.07	< L.d.
			1.0	9.17	< L.d.
	6	17.0	13.5	20.57	< L.d.
			6.7	3.37	< L.d.
			2.0	6.27	< L.d.
	8	22.0	19.2	14.87	7.30
			9.5	15.87	14.30
			1.0	4.27	3.20
	9	22.0	18.2	23.47	3.30
			10.2	14.87	< L.d.
			1.4	14.87	< L.d.
	10	27.0	23.4	19.27	11.80
			13.5	3.37	3.20
			1.6	17.67	3.20
	11	24.0	21.9	127.07	< L.d.
			11.5	129.27	19.80
			1.2	26.27	7.50
	13	32.0	29.3	3.37	< L.d.
			16.9	12.67	8.90
			2.4	17.67	3.20
	14	21.0	16.3	2.27	< L.d.
			9.4	18.67	8.90
			1.0	11.97	6.00
	15	26.0	20.6	57.77	20.30
			11.2	20.57	1.10
			2.4	23.37	21.30
	16	22.0	16.5	11.97	14.60

Table 12 continued

			11.3	23.47	14.60
			0.5	3.37	20.30
	17	16.0	12.7	34.87	3.20
			7.3	31.97	14.60
			1.6	22.57	6.00
Sampling February 2012	18	17.0	8.0	11.05	5.55
			2.0	4.55	< L.d.
	19	42.0	27.0	6.10	3.55
			16.0	4.80	< L.d.
			2.0	2.45	1.25
	20	85.0	81.3	9.15	3.55
			45.3	5.42	< L.d.
			6.1	4.75	0.55
	21	679.0	679.0	11.95	4.15
			375.0	6.15	5.55
			20.0	2.62	<L.d.
Sampling June 2012	7	22.8	1.0	1.85	0.95
			11.5	9.85	1.55
			21.0	1.75	2.55
	12	27.8	10.0	5.95	4.95
			13.5	8.55	2.35
			26.0	15.69	< L.d.
	16	22.8	1.0	1.02	6.35
			11.5	14.85	< L.d.
			22.0	18.09	0.95

4.4 Atmospheric GEM distribution

Results related to GEM atmospheric assessment and wet and dry Hg depositional flux were reported in (Tab. 12; Fig. 29) (Attachment II). Briefly GEM distribution in the MBL results to be 1.5 ± 0.4 (range 0.9-3.1) and 2.1 ± 0.98 (range 1.1-3.1) ng m^{-3} in the winter and summer, respectively. The collected data are, however, somewhat higher than the atmospheric background Hg level measured over the land at the downtown urban site of Augusta (averaged 0.9±0.5 ng m^{-3}). Results on wet deposition indicate Hg concentrations ranging from 21 to 32 ng l^{-1} (averaged: 26 ng L^{-1}).

Analysis carried out on dry deposition samples gave values ranging from 10.3 to 132.45 ng L^{-1} (averaged: 44 ng l^{-1}), indicating a variable amount of suspended particulate matter into the atmosphere during the period of surveying. The major input of Hg given by the particulate matter to the chemistry of bulk deposition has been observed in samples collected on April 2012, where we estimated a Hg contents of ~ 32 and 132.45 ng Hg L^{-1} in wet and dry deposition, respectively.

A total mercury depositional flux (wet + dry) indicates values of Hg bulk depositional flux ranging from 0.03 to 0.12 μg m^{-2} day^{-1} (which correspond to 11-44 μg m^{-2} yr^{-1}) (Bagnato et al., 2013) .

4.5 Hg fluxes at the interfaces

4.5.1 Meteorological pattern of the area

A meteorological data set, including air temperature, wind intensity and main direction, and precipitation amount, was developed using data from the continuous acquisition by a weather station (DAVIS – Vantage Pro 2Wi-Fi) installed on the roof of the Augusta port authorities office, sited in front of the site location.

Meteorological condition during the benthic chamber experiments varies during the 19-21 September 2011 (late summer-early autumn) and the 23-26 June 2012 sampling period (summer), with weather condition worst in the first period (T: 23.5 °C; wind: 2.35 NW; precipitation: 0.15 mm) and agreeable in summer (T: 26.4 °C; wind: 2.65 W-E; precipitation: 1.021 mm). Values do not represent monthly estimates, but are referred exclusively to the sampling periods.

The differences in meteorological pattern of the two sampling period (September 2011 and June 2012) allowed to consider seasonal variability in the marine environment and to extend the measured fluxes to a yearly estimation, although the last assessment may be overestimated because of the absence of winter Hg flux.

4.5.2 In situ benthic fluxes

Figure 30 shows DHg *vs.* time in water collected from the benthic chamber during the two experiments in September 2011 and June 2012 (Fig. 9). The in situ benthic flux in September 2011 in the northern part of the Bay (station 7) shows a linear rise with time (r^2= 0.53) ranging from 3.10 (t_0) to 23.00 ngL^{-1} (t_{10}) (Fig. 30a; Tab. 13).

On the contrary, trends of DHg content in the central Augusta Bay (station 11), (DHg range: 11.70 (t_0) - 26.30 ngL^{-1} (t_{10})), are not linear with time. Indeed the flux exhibits a rapid increase in the first hour (DHg= 35.40 ngL^{-1}), and a slow decrease with time (Fig. 30a; Tab. 13). A light, linear (r^2= 0.97) increment in DHg is observed in the southern station 16 (DHg range: 15.30 (t_0) – 31.31 ngL^{-1} (t_{10}).

In situ benthic flux in the northern Augusta Bay (St. 7) for June 2012 sampling, is comparable with the previous year, and increases linearly with time, from <d.l (t_0) to 6.34 ngL^{-1} at t_4 and 29.99 ngL^{-1} at t_{10} (r^2= 0.92; Fig. 30b; Tab. 13). DHg measured in station 12 (R^2=0.77) quickly rises from 29.68 at t_1 to 113.23 ngL^{-1} at t_{12}.

Also in chamber 16bis the growth is linear (r^2= 0.90) and range between 12.04 ngL^{-1} at t_1 to 55.58 ngL^{-1} at t_{12} (Fig. 30b; Tab. 13). The calculated Hg flux for the September 2011 sampling results 3, 8.1 and 8.4 µg m^{-2} day^{-1} for station 7, 11 and 16 respectively, while for June 2012 sampling Hg flux from each chamber results 8.1, 16.4 and 21.8 µg m^{-2} day^{-1} in station 7, 12 and 16 bis respectively.

The lower in situ benthic flux has been recorded in the north Augusta Bay (st.7) while the highest in central and southern Augusta Bay.

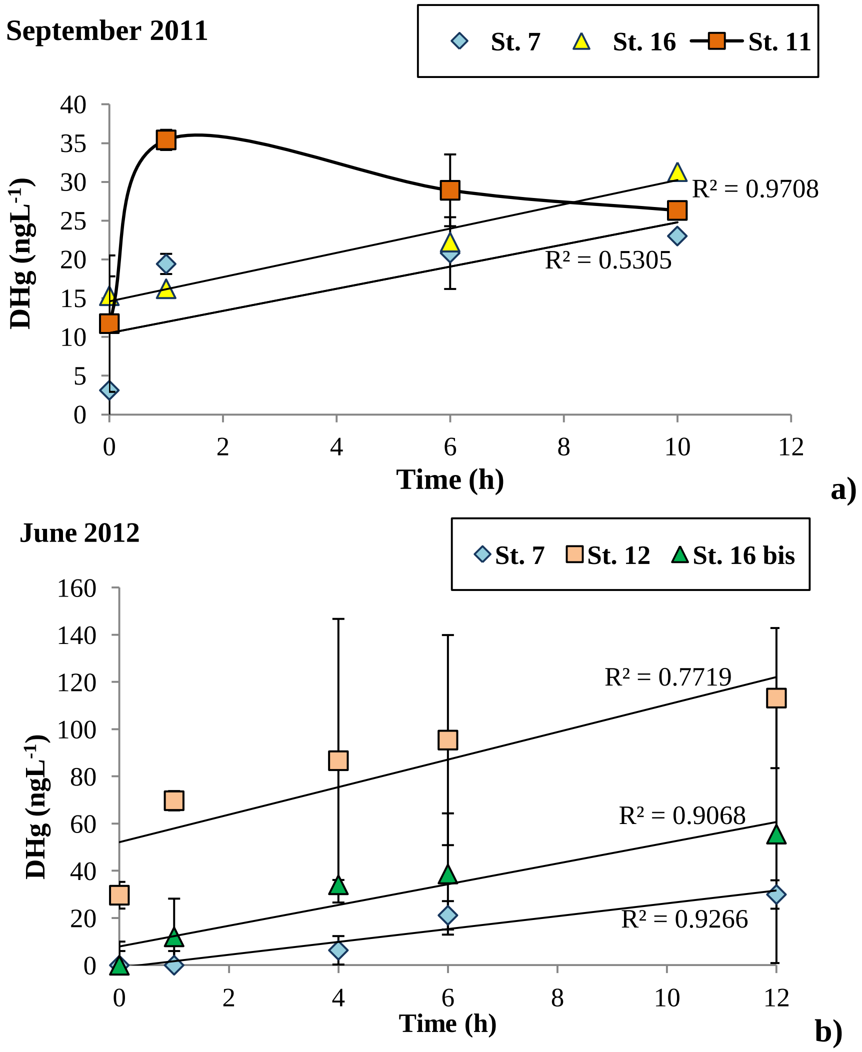


Figure 30: *Concentrations of HgD, vs. time during in situ flux chamber deployments in: a) September 2011 and b) June 2012.*

With the aim to estimate the total mercury flux from sediment to seawater over the entire surface of the Augusta basin (~23.5 km^2), we used the model of territorial distribution proposed by Aurenhammer (1991) (Voronoi Polygons method), calculating separate areas of the basin (in km^2) which were differently affected by Hg release from sediment.

Estimated fluxes from sediment to seawater for the whole Augusta Bay result to be 0.22 kmol y^{-1} in 2011 (0.045 ty^{-1}) and 0.53 kmol y^{-1} in (0.11 ty^{-1}) 2012, more than one order of magnitude than those estimated by Sprovieri et al. (2011) for the same study area. By mediating fluxes of the two years, a total amount of 0.38 Kmol y^{-1} (0.08 ty^{-1}) has been obtained.

Table 13: THg and DHg and standard deviation (3 replies) measured in water collected at the interface sediment-water over time.

	Sample	**Time** *(h)*	**HgT** *(ng L^{-1})*	**D.S.** *(n=3)*	**HgD** *(ng L^{-1})*	**S. D.** *(n=3)*	**Flux** *(µg m^{-2} day^{-1})*
Sampling September 2011	7	0	20.29	1.15	3.10		3.0
		1	29.02	2.97	19.40		
		6	24.02		20.80	7.30	
		10	43.67	9.69	23.00	5.15	
	11	0	28.28	8.81	11.70	8.80	8.1
		1	61.8	1.34	35.40	1.30	
		6	59.2	10.72	28.90	4.63	
		10	64.1	3.04	26.30		
	16	0	17.42	6.79	15.30	2.50	8.4
		1	21.52	8.27	16.20		
		6	25.52	5.66	22.22		
		10	36.52		31.32		
Sampling June 2012	7	0	15.96	19.07	0	10.03	8.1
		1	20.80	4.39	0	16.19	
		4	39.34	5.46	6.34	2.05	
		6	43.24	4.30	21.16	25.7	
		12	49.86	16.26	29.99	54.65	
	12	0	70.89	24.87	29.68	5.66	16.4
		1	95.50	0.05	69.73	4.10	
		4	137.06	1.84	86.70	60.10	
		6	145.66	14.00	95.43	44.53	
		12	152.78	14.40	113.23	29.69	
	16	0	19.16		0		21.8
		1	38.96	58.97	12.04	37.73	
		4	51.86	40.73	34.1	18.36	
		6	70.41	14.50	38.68	35.92	
		12	84.86		55.58	28.99	

Table 14: Calculated fluxes in Augusta Bay compared with those reported for other polluted site.

Period	**Site**	***Φ*** *μg* m^{-2} day^{-1}	**Ref.**
September 2011	7	3.0	This work
	11	8.1	
	16	8.4	
June 2012	7	8.1	
	12	16.4	
	16bis	21.8	
	Gulf of Trieste	5-6	Covelli et al., 1999
	Bellingham Bay	10	Bothner et la., 1980
	Arcachon Bay	5	Bouchet et al., 2011
	Grado Lagoon	37-77	Covelli et al., 2008

4.5.3 Air-sea GEM Flux

Flux assessment at the sea-air interface was reported by Bagnato et al., 2013 (Attachment II). The estimated mercury evasion fluxes range from 3.6 (unpolluted site) to 36 (most polluted sites) ng m^{-2} h^{-1}which correspond to an annually mercury evasion rate of ~ 31.5 and 315 mg m^{-2} yr^{-1}, respectively (Bagnato et al., 2013).

The sea-air evasion flux of Hg from the basin is not uniformly distributed but varies spatially, while any particular trend across the two seasons (November 2011-June 2012) has been observed.

The higher Hg evasion flux was estimated in the southern part of the basin, which corresponds to the most contaminated area of the basin in term of Hg contained in the bottom sediments.

The lowest Hg evasion flux has been estimated in the northern sector of the basin, close to the port, where the bottom sediments contain the lower Hg concentrations found.

4.6 REEs distribution in seawater

REE concentration in seawater collected in Augusta Bay ranges between 46.7 and 255.7 ngL^{-1}.

The highest REE contents were recorded for light REE (LREE) from La to Nd, with an unusual value for Ce. These values are maximum in the middle and deeper water column (between 11 and 25 m), and decrease in surface waters. A similar distribution has already been observed in the Mediterranean coastal areas and attributed to the leaching of REE from atmospheric particulate once in contact with the blade surface water (Censi et al., 2007; 2010).

As well as REE concentration differs in bottom water, also the PAAS-normalized distribution has the same trend (Fig. 31). Surface samples (Fig. 31a) have a generically increasing trend along the series, with a light enrichment of intermediate REE (MREE). In bottom water REE concentrations and their trend seem to be similar in station 12 and 16, while differ in station 7, in which REE concentration is lower. Gd anomaly (Gd/Gd*>1) was recorded in all the station for the entire water column, with the highest anomaly recorded in middle and deeper water.

Contrary to those expected in a marine water, in which Ce/Ce* values are generally <1 (de Baar et al., 1983), no Ce negative anomaly has been recorded.

Positive relationship was found by plotting Gd *vs.* Ce anomalies in the analysed samples (r^2=0.88) (Fig. 32), testified common anthropic process and consequent liquid waste discharge into the water column of the Augusta Bay. The Y/Ho ratio is commonly used as proxy of terrestrial contribution to sediments, because Y behaves in accord with Ho and no fractionation between the two elements occurs terrestrially, while Y fractionates from Ho in marine reaction systems. In the considered dataset, the Y/Ho molar ratio ranges between 55.2 and 95.0, with the higher values in surface water and lower in depth. Y/Ho value in station 7 are the closest to chondrites signature (molar ratio: 52), while ratio in station 12 is higher, especially in surface waters. This clearly indicates the leaching of element by lithogenic particulates, that justifies the crustal signature of station 7. This indication is less strong in station 16 and absent in station 12. In this station the Y/ho ratio suggests a preferential Ho removal, respect to Y, a quite common process in marine environment (Bau & Dulski, 1996; Bau et al., 1996; Alibo & Nozaki, 1999b).

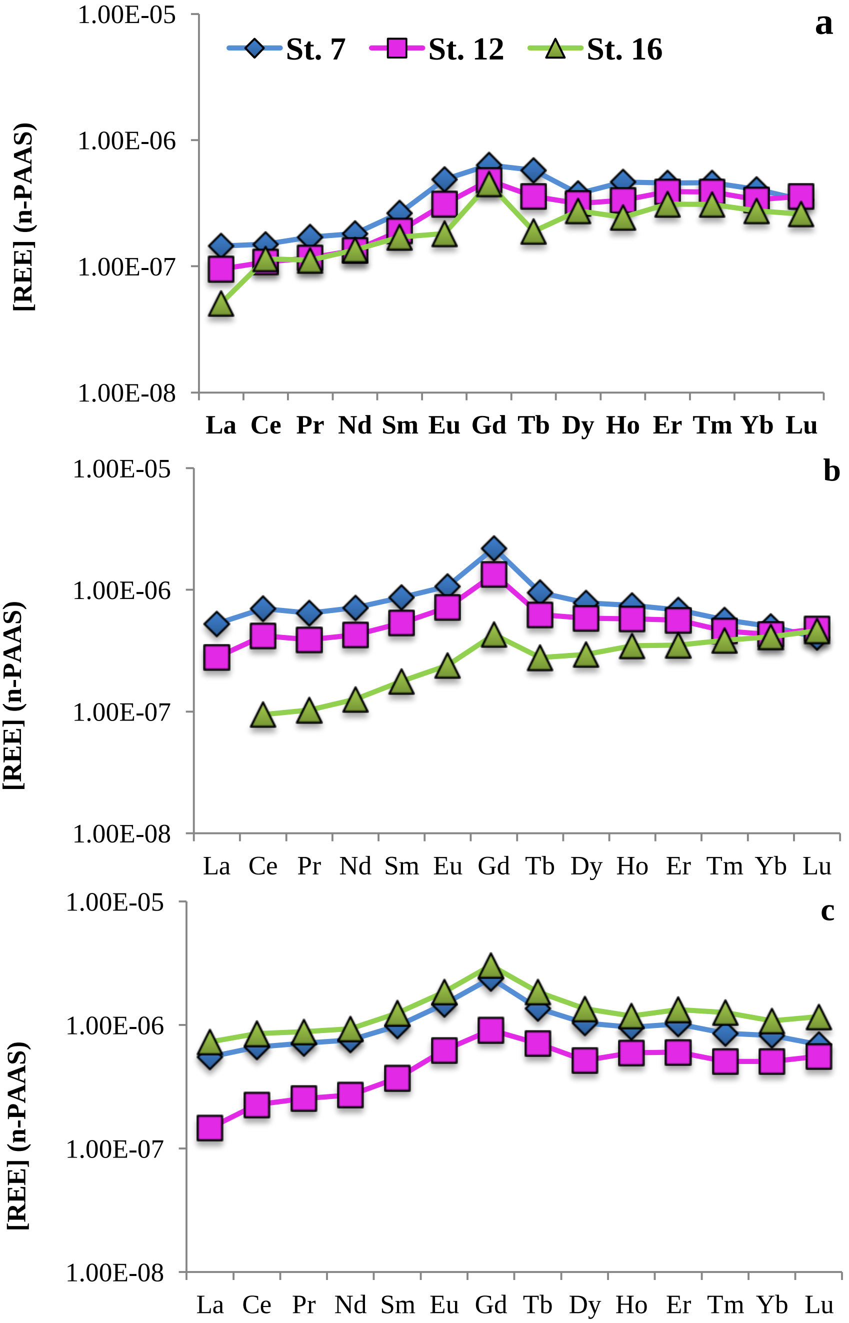


Figure 31: Shale-normalised (PAAS) REE patterns of the analysed seawater samples at different depths. a) surface water; b) middle water; c) bottom water.

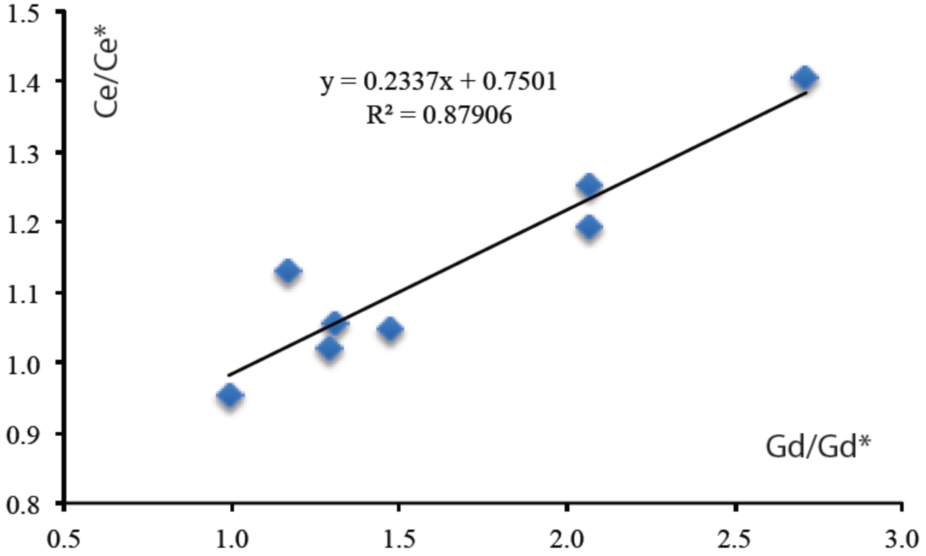


Figure 32: Relationship between Ce/Ce* and Gd/Gd* anomalies.

4.7 Hg isotopes analyses

4.7.1 Hg isotopic composition of fishes

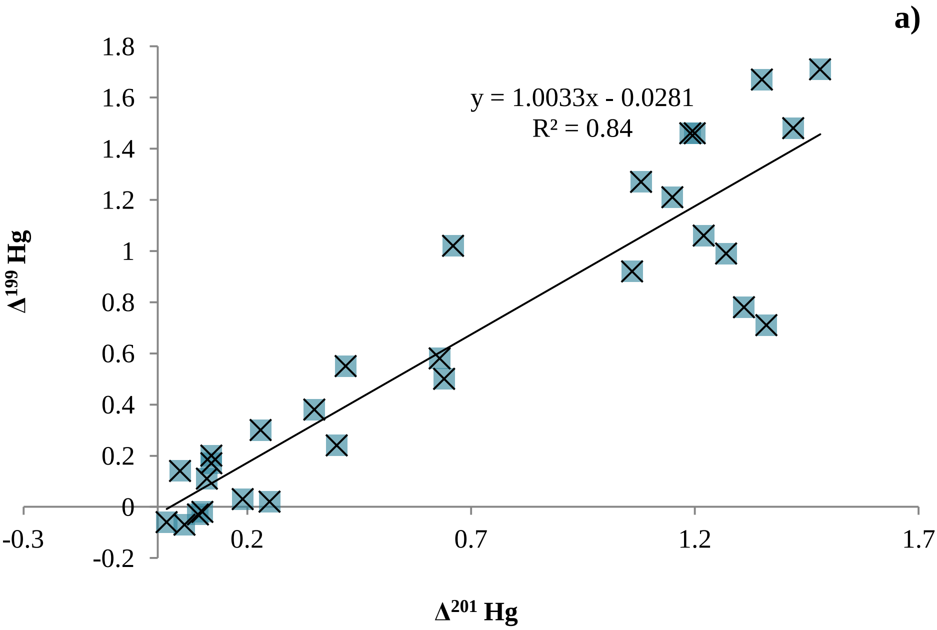
Mass dependent fractioning in fishes, expressed as δ^{202}Hg values, exhibits a wide range of measures (-1.52 to 0.37 ‰) with a negative mean δ^{202}Hg value of -0.36 ‰ (Tab.15).

Negative MDF fractioning are recorded especially in demersal and benthic species (*Pagellus spp, and Mullus barbatus*), with a unique exception for a specimen of *Sardina pilchardus*, considered as outlier.

Position of fishes in the water column appears to be the major driver of the range in δ^{202}Hg. Mass independent fractioning in fishes exhibits values positive or close to zero (range: -0.07 to 1.71 ‰ for Δ^{199}Hg and 0.02 to 1.48 ‰ for Δ^{201}Hg) (Tab. 15). Because the fish tissues display MIF, it is instructive to also plot the data as Δ^{199}Hg *vs.* Δ^{201}Hg. The Δ^{199}Hg vs Δ^{201}Hg ratio is diagnostic of the reduction of Hg (II) vs. MeHg. A good correlation was obtained by plotting Δ^{199} *vs.* Δ^{201} (r^2=0.84), and the slope ~1, indicating Hg(II) photoreduction (Fig. 33 a). Difference among species emerged when the fish dataset was divided according to the habitat depth that fish occupy (Fig. 33 b).

Contrary to benthic fishes, where Δ^{199}Hg and Δ^{201}Hg are close to zero (0.09 ‰ and 0.11 ‰ respectively), MIF increases in demersal (0.23 ‰ for Δ^{199}Hg and 0.29 ‰ for Δ^{201}Hg) and displays the maximum fractionation in pelagic fishes (1.2 ‰ for both Δ^{199}Hg and Δ^{201}Hg) (Fig. 33 b).

MeHg displays more MIF compared to Hg (II) and the ratio Δ^{201}Hg vs δ^{202}Hg is predictive of photos or demethylation reduction. The calculated ratio Δ^{201}Hg/δ^{202}Hg for fishes results to be 1.7.



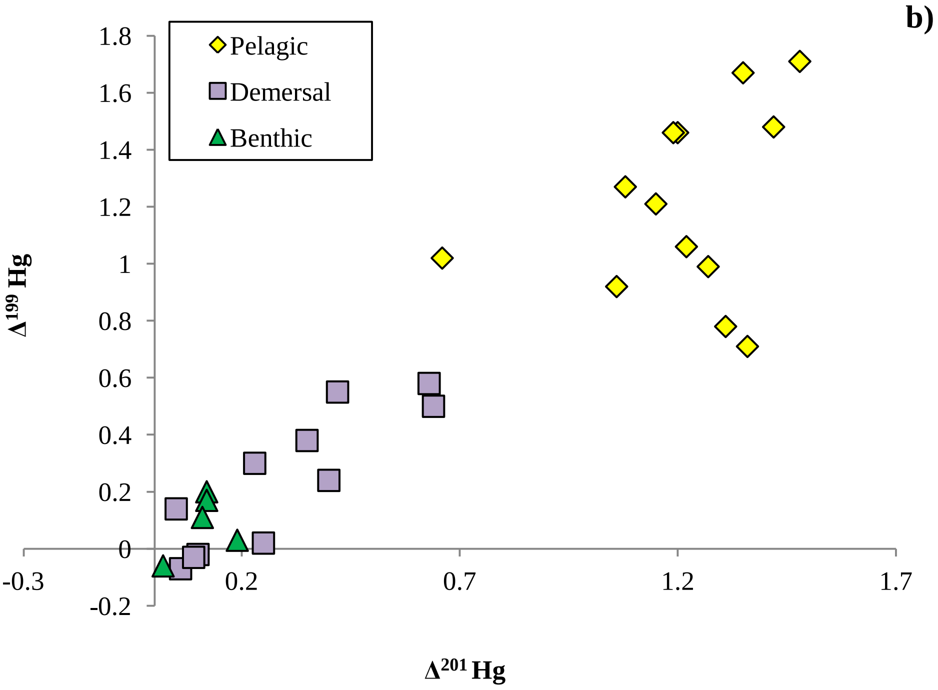


Fig. 33: *Linear correlations between Δ^{199}Hg and Δ^{201}Hg (‰) for the entire fish dataset (a) and divided into pelagic, demersal and benthic fishes (b).*

4.7.2 Sediment Hg isotopic fractionation

Mercury isotopes were first measured in marine sediments by Gehrke et al. (2009) in a study of mid- Pleistocene (955 kyr) Mediterranean sediment cores and reported the Hg isotopic composition of sediments of δ^{202}Hg = -0.91‰ and Δ^{201}Hg = 0.04‰, providing the first estimate of a preanthropogenic marine Hg isotope composition. The Augusta Bay sediment cores display negative δ^{202}Hg values, ranging between -0.91 and -0.03‰ (Tab. 15). As shown in Fig. 34a, MDF intensity varies in core collected in the tree station points; in core 7 (northern Augusta bay) the mean δ^{202}Hg results -0.26±0.12 ‰, while decreases in core 12 (middle station) (mean δ^{202}Hg: -0.36±0.17 ‰) and reaches the minimum value in core 16, collected in the southern part of the Bay (δ^{202}Hg: -0.52±0.25 ‰). On the other hand, MIF fractionation displays the opposite trend (Fig. 34 b), with higher values in the southern part (station 16) (Δ^{199}Hg: -0.004±0.02‰), intermediate in the middle (Δ^{199}Hg: -0.02±0.02‰) and the lowest values in the northern station 7 (Δ^{199}Hg: -0.04±0.02‰). The Δ^{201}Hg mean value for all the analyzed sediments results to be 0.02±0.03 ‰. By plotting δ^{202}Hg vs Δ^{201}Hg for the entire sediment core dataset, on obtain a peculiar trend (Fig. 35), corresponding, according to the scheme proposed by Blum (2011) and Rodriguez-Gonzales et al., (2009), to biological mediated MeHg production.

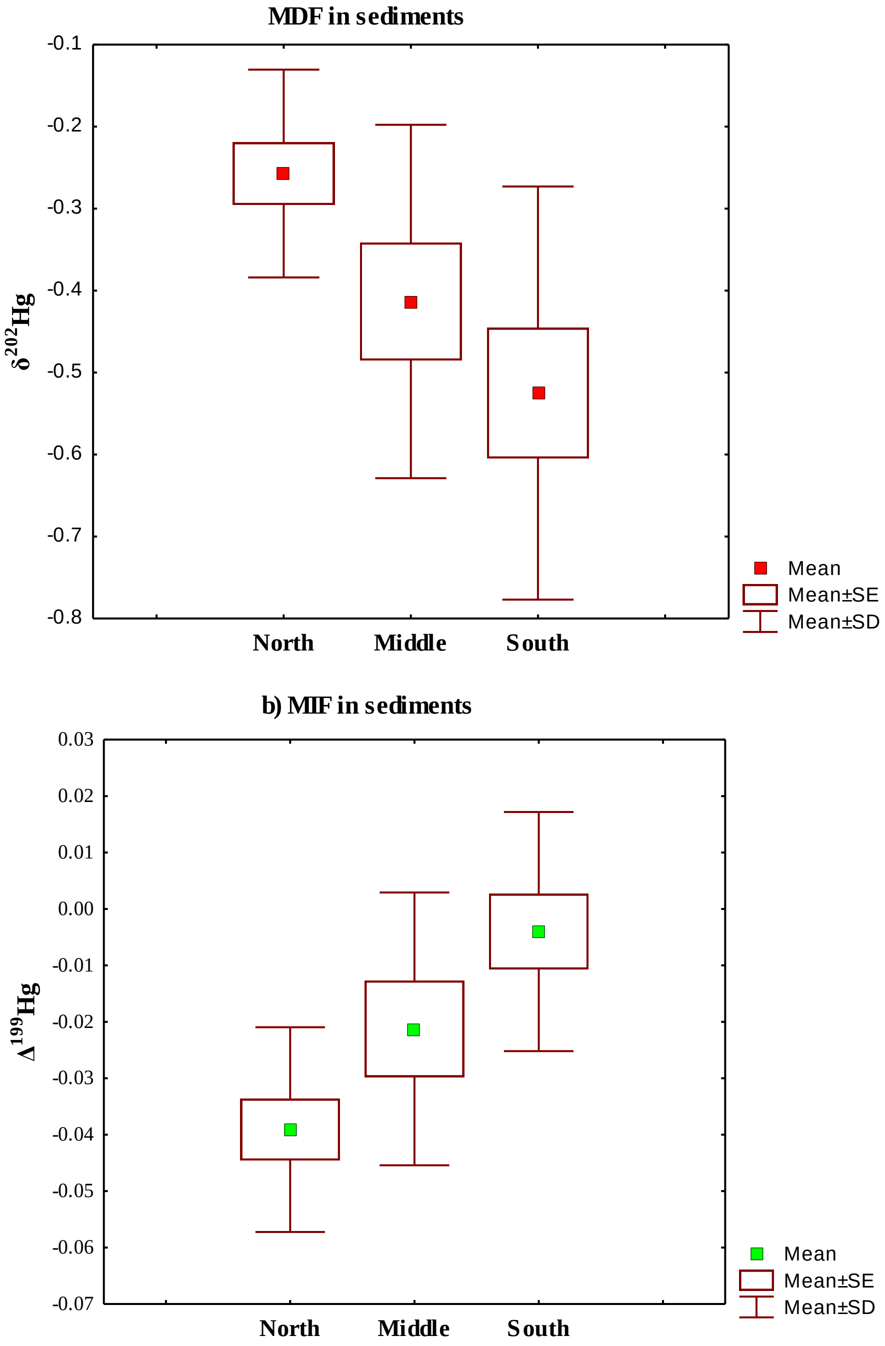


Figure 34: *Box plots of Hg isotopes fractionation in sediment core collected in north, middle and south Augusta Bay.*
a) MDF fractionation, expressed as $\delta^{202}Hg$*; b) MIF fractionation, expressed as* $\Delta^{199}Hg$*.*

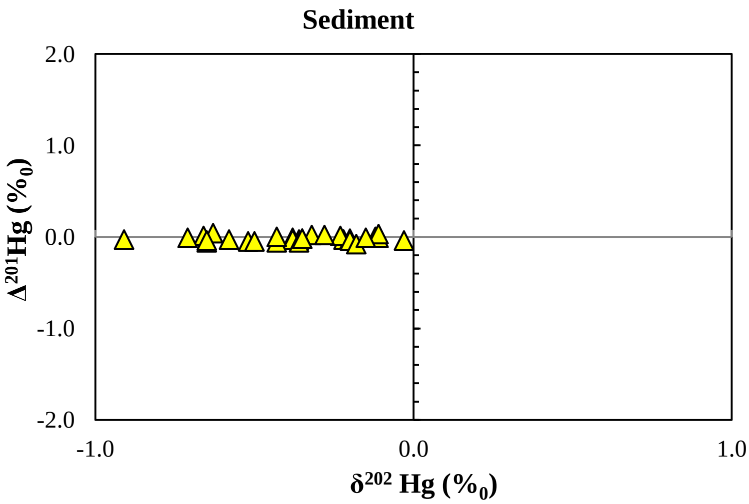


Figure 35: *Relationship between Δ^{201}Hg and δ^{202}Hg in sediments.*

4.7.3 Hair Hg isotopic composition

MDF values in hair samples range between 1.15 and 3.36 ‰ (mean δ^{202}Hg= 1.17±0.48‰) (Tab.15) with no evident shift with age. Also MIF values are positive (range: 0.73-1.51‰, mean 1.18±0.17‰ for Δ^{199}Hg; range: 0.80 - 1.33; mean 0.97±0.16‰ for Δ^{201}Hg). The Δ^{201}Hg trend shows a slight enrichment with increasing age, with Δ^{201}Hg of 0.83 ‰ at 20 year (n=1), 0.88 ‰ at 30 years (n=2), 0.93 ‰ at 35 year (n=4) and 1.01 at 40 years.

A positive correlation has been obtained by plotting Δ^{201}Hg vs Δ^{199}Hg (r^2=0.87), with a slope of 1.2 compatible, according to the scheme proposed by Bergquist and Blum (2007), with photochemical reaction (Fig. 36).

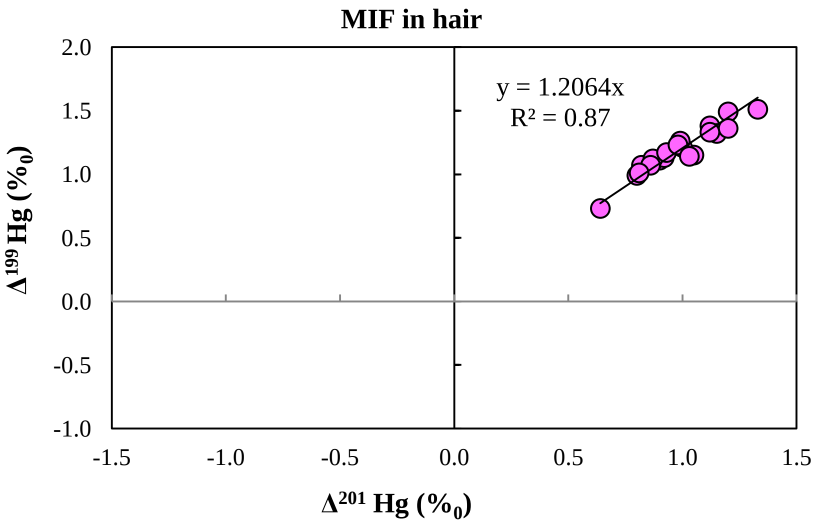


Figure 36: *Relationship between Δ^{201}Hg vs Δ^{199} Hg (r^2= 0.87; slope: 1.2) in human hair living in Augusta Bay.*

Table 15: Details on Analysed fish and sediment samples, THg content and Hg isotopic fractioning (‰)

	Range δ^{202}Hg	***Mean δ^{202}Hg***	***Range Δ^{199}Hg***	***Mean Δ^{199}Hg***	***Range Δ^{201} Hg***	***Mean Δ^{201} Hg***
FISH (Pelagic)	-1.52 to 0.07	-0.36	0.71 to1.71	1.21	0.66 to 1.48	1.21
FISH (Demersal)	-1.27 to 0.1	-0.51	-0.02 to 0.58	0.23	0.05 to 0.42	0.29
FISH (Benthic)	-0.75 to 0.37	-0.13	-0.02 to 0.55	0.09	0.05 to 0.64	0.11
ALL FISHES	-1.52 to 0.37	-0.39	-0.07 to 1.71	0.65	0.02 to 1.48	0.67
SEDIMENT	-0.91 to -0.03	-0.38	-0.11 to -0.02	-0.02	-0.37 to 0.04	-0.032
HAIR	1.15 to 3.36	1.71	0.73 to 1.51	1.18	0.80 to 1.33	0.97

Chapter V:

Discussions

5. Discussion

5.1 Pattern of Hg distribution in the Augusta Bay

In the last decade, several studies (ICRAM, 2005; Ausili et al., 2008; Di Leonardo et al., 2007, 2008; ENVIRON International Team, 2008; Ficco et al., 2009; Sprovieri et al., 2011) have provided detailed information on the pollution levels and risks for human health of resident populations of Augusta Bay, an area, located in the eastern Sicilian coast, strongly contaminated due to the uncontrolled chemical discharges from the most complex petrochemical district in Europe.

Here the extremely high concentrations of Hg measured in the Augusta Bay sediments, more than one order of magnitude higher than background literature (Di Leonardo et al., 2006, Ogrinc et al., 2007) confirm the warning previously reported and call for more detailed study on the biogeochemical dynamics of Hg in the study area, in order to better understand the effect of this pollution on the surrounding environmental compartments.

5.1.1 Spatial Hg distribution of THg content in sediment

A sud-north gradient of Hg exposure is testified by the extremely high Hg content measured in core sediments collected in the southern area, closest to the “Vallone della neve” where discharge from the alkali-plant occurred in the recent past. As known (Devai et al., 2005; Vane et al., 2009; Feyte et al., 2010), anthropogenic mercury has often been reported to be associated with both organic matter and fine-grained particles of bottom sediments, because of the tendency of fine-grained particles to bind large amounts of trace metals due to their chemical composition and great surface to volume ratio (Förstner and Wittman, 1979; Ravichandran, 2004).

Sediments were texturally rather uniform at both sampling sites and is primary composed of silt and clay, whereas the sandy fraction represents a small percentage. The only exception is represented by core 16 of May 2011 sampling, mainly composed of sandy, thus justifying the minor THg content measured in this core, lower than expected respect of the geographical position.

Hg speciation in contaminated sediments is crucial in order to understand Hg mobility and bioavailability (Davis, et. al, 1997). For this reason, the sequential selective extractions procedure (SEP), validated from Bloom, et al, 2000, has been applied, in order to differentiates Hg into behavioral classes including water soluble, ‘stomach acid’ soluble, organochelated, elemental, and mercuric sulfide.

Although this method do not provide species-specific information, it does offer the opportunity to investigate on the biogeochemically relevant fractionation of Hg in sediments. Sequential extraction procedure demonstrate the most part of HgT in sediments (~80% of the total) consists of highly stable phase of Hg, like Hg_2Cl_2 (calomel), or trapped in mineral lattice, or bound to humic substances, while ~15% of Hg were like insoluble Hg forms (as cinnabar (HgS), m-HgS, HgSe and HgAu), and only ~2% of HgT is in more soluble, and bioavailable forms. This is due to the tendency of Hg^{2+} to bind with the sulfur-groups is notable, especially where the concentration of HS^- and S^{2-} is high, as in anoxic waters and sediments, where mercury sulfide, solid and slightly soluble in water, tends to accumulate into the sediments (Langer et al., 2001; Gilmour and Henry, 1991).

Some anaerobic microorganisms can manage these stable Hg forms ($HgCl_2$, $Hg(SH)_2$, HgS and Hg^0 trapped in minerals structures) as substrate for their metabolism, this making Hg more easily bioavailable for the environment (Benoit et al., 1999 a, b, 2001 a, b).

Further investigation, regarding the analysis of other useful parameters such as dissolved Fe and Mn and H_2S and MMHg, will permit to have a complete view of the biogeochemistry.

5.1.2 Spatial Hg distribution of THg content in seawater

A north-south gradient of Hg distribution was confirmed by THg and DHg analysis in seawater. The highest values were recorded in the southern and more contaminated part of the Augusta Bay, in good agreement with Hg distribution in sediments.

A clear gradient was also observer along the water column, with higher values in deeper water and lower in surface.

This vertical trend is clearly owing to the major remoteness to polluted sediments and to volatilization processes, occurring in surface water when water column is undersaturated in the most volatile and long-lived Hg form, Hg^0 (Fitzgerald and Clarkson, 1991). Moreover, the THg and DHg measured in seawater collected outside are anomalous compared to Mediterranean sea (0.2 e 0.4 ngL^{-1}) (Kotnik et al, 2007; Horvat et al, 2003;

Rajar et al., 2007; Cossa et al., 1997), and exhibit the maximum values close to the two narrow inlets: the Scirocco and the Levante ones.

5.1.3 Mercury bioaccumulation pattern in fishes

The HgT content measured in fish tissues from Augusta Bay show an increasing trend with habitat depth, specifically, with highest values measured in benthic species, intermediate in demersal fishes and lower in pelagic organisms. In particular, the highest HgT mean concentrations occur in fishes caught in the southern Augusta Bay where bottom sediments show the highest concentrations of mercury.

Additionally, contamination effects show a south-north gradient evident from HgT levels measured on the ubiquitous *Pagellus spp*. and *D. annularis* specimens. In particular, the highest HgT mean concentrations occur in fishes caught from southern Augusta Bay where bottom sediments show the highest concentrations of mercury.

The Hg accumulation in marine fish primarily depends on some important biokinetic parameters: assimilation from the ingested prey, uptake constants from the aqueous phase, de-toxification rate (Wang, 2012; Wang et al., 1997, 1998; Wang and Fisher, 1999; Dang and Wang, 2011) and environmental features (e.g., Hg concentration and speciation in seawater, dietary sources, etc.) (Wang and Wong, 2003).

However, physiological and geochemical species-specific influences on Hg bioaccumulation are still not fully understood (Baines et al., 2002; Xu and Wang, 2002; Wang and Wong, 2003; Dang and Wang, 2012). Several studies have demonstrated that Hg concentrations in the muscles of marine organisms proportionally increase with size and age (Lange et al., 1994; Burger et al., 2001; Green and Knutzen, 2003; Simonin et al., 2008). Moreover, Hg de-toxification rates appear negatively correlated with the fish size (Trudel and Rasmussen, 1997), supporting a potential correlation between Hg levels and size/age in the organisms.

However, detailed investigations on different groups of species and on a wide range of HgT concentrations are lacking and, when available, sometimes controversial (Stafford and Haines, 2001), especially for fishes with low mercury levels (average below 0.2 ppm) (Park and Curtis, 1997; Burger and Gochfeld, 2011). Strong correlations between size and Hg levels in fish are reported for Swordfish (Xiphias gladius) and Bluefin Tuna (Thunnus thynnus) from the Mediterranean Sea (Storelli and Marcotrigiano, 2001), for several pelagic fish species from the Adriatic Sea (Storelli, 2008) and for *S. pilchardus* specimens from Tunisia (Joiris et al., 1999).

Furthermore, Burger et al. (2007) found a positive correlation between size and Hg levels for 11 of 14 species of marine fishes collected in the western Aleutians (Bering Sea/North Pacific) and Luten et al. (1987) found the same positive correlation in Atlantic Cod. Moreover, Leonzio et al. (1981) report positive correlations between Hg content and weight in M. barbatus and a slight Hg increasing trend with size in *E. encrasicolus* from the northern Tyrrhenian Sea.

Finally, Gewurtz et al. (2011) show strong correlation between HgT concentration and length in most freshwater fishes from the Canadian Great Lakes and Ontario (Canada).

Here, the high number of specimens available from pelagic, benthic and demersal fish species associated with a wide range of length/age and HgT variability detected in tissues offer a challenging opportunity to explore in more depth the actual bioaccumulation processes of Hg in the studied organisms. In particular, we assumed the length of fishes as a reliable parameter for age estimates (Boening, 2000; Waldron and Kerstan, 2001; Scudder et al., 2009; Panfili et al., 2010; Basilone et al., 2011; Bacha et al., 2012) and, thus, reported HgT values vs. length to assess biomagnification of that contaminant with time.

Statistically reliable and robust correlations were found between HgT mean values measured in muscles for size classes and length in *S. pilchardus, E. encrasicolus, Trachurus trachurus, Diplodus annularis* and *P. erythrinus.* Specifically, the calculated HgT accumulation rates for *S. pilchardus, E. encrasicolus, T. trachurus, P. erythrinus* and *D. annularis* are 0.011, 0.012, 0.022, 0.036 and 0.136 μg g^{-1} cm^{-1}, respectively, in good agreement with data reported by Hornung et al. (1980) for *P. erythrinus* and *T. trachurus* species.

This definitively supports a significant linear HgT-length relationship for the studied fish species and a species-specific accumulation effect on the studied marine organisms. In our dataset an evident increasing trend was measured between HgT content and age in the two most abundant species, *E. encrasicolus* and *S. pilchardus* with significant differences ($p < 0.005$; ANOVA test) among age group, although, the restricted range of available age classes needs a larger data collection.

Muscles are the most commonly analysed tissues to monitor Hg levels in fishes because they represent the edible part of the organism associated with human health risk implications (Henry et al., 2004). Indeed, Hg accumulates over time more readily in liver than in muscle, but muscle appears to retain Hg for a much longer period (Boudou and Ribeyre, 1995). Thus, liver may provide information only on short-term exposure to Hg pollution or may bioaccumulate only when an organism is exposed to constant or increasing levels of dietary mercury (Atwell et al., 1998). This is clearly reflected in the studied dataset, where HgT concentration measured in liver is up to two orders of magnitude higher than in muscles.

A direct comparison of HgT content in benthic species from Augusta Bay and other Mediterranean areas affected by comparable Hg discharges by chlor-alkali plant and sewage sludge disposal, specifically Tuscany and Israel (Hornung et al., 1980; Gibičar et al., 2009), show 2–7 times higher values, thus, underlying the combined effects of high pollution levels and specific biogeochemical pathways driving mercury bioavailability in the studied system.

The mean HgT concentrations measured in pelagic species caught outside the bay, are similar to those reported for other sites affected by Hg pollution: the Adriatic Sea (Wolfgang, 1983; Storelli and Marcotrigiano, 2001; Storelli et al., 2002, 2004, 2007, 2010; Gibičar et al., 2009), Turkish areas (Tuzen, 2009), Spanish coastal areas (Pastor et al., 1994) and Israel area (Hornung et al., 1980). Particularly the HgT mean concentrations measured in the livers of *E. encrasicolus* specimens from Augusta Bay are about twice as high ($p = 0.044$) as those measured in fishes from the unpolluted area of Marsala, suggesting a direct, short-term effect of the bay pollution on the pelagic fishes.

5.2 Toxicological effect on fish compartment

Although estimation of the target hazard quotient (THQ) and weekly intake (EWI), do not provide a quantitative estimate on the dangerous health effects on exposed populations, many authors implies these methodologies as a preliminary information on the health risk level resulting from pollutant exposure (Storelli et al., 2005, 2010; Storelli, 2008; Martorell et al., 2011; Domingo et al., 2012) .

Target hazard quotient (THQ) and estimated weekly intake (EWI) were calculated for muscles of fishes caught inside and outside the bay. The

Target hazard quotient was calculated according to the US EPA (1989) method and it is described by the following equation:

$$THQ = \left(\frac{EF \times ED \times FIR \times C}{RFD \times WAB \times TA} \right) \times 10^{-3}$$

where EF is exposure frequency (365 days/year); ED is the exposure duration (70 years), equivalent to the average lifetime; FIR is the food ingestion rate (36 g/person/day) (FAO, 2005); C is the metal concentration in seafood (µg g^{-1}); RFD is the USEPA’s reference dose (0.1 µg Hg kg bw^{-1} d^{-1}) (http://cfpub.epa.gov) or acceptable daily intake determined by WHO, 2003 (0.23 µg Hg kg bw^{-1} d^{-1}) (http://apps.who.int); WAB is the average body weight (60 kg), and TA is the average exposure time for no carcinogens (365 days/year x ED). The THQ was calculated for all the studied species in the Augusta Bay using the US-EPA’s reference dose (THQa) and the acceptable daily intake determined by the WHO (THQb).

These two values are relative to MeHg, nevertheless, we used them basing on the assumption that the majority, if not all, of the Hg bioaccumulated through the food chain is MeHg (Winfrey and Rudd, 1990; Mason and Fitzgerald, 1990, 1991; Gilmour and Henry, 1991; Horvat et al., 1999; Carbonell et al., 2009).

The estimated weekly intake (EWI) was calculated by multiplying the HgT concentration (C) times by the weekly dietary intakes (FIR x 7) and reporting to the average body weight (WAB). Finally, mean THQ and EWI values were calculated for each studied species. Also, considering that fishing activity within the bay has been interdicted since 2007 (Order N° 73/07), data relative to fishes from inside and outside the bay were processed separately. Mean THQ and EWI values calculated for each caught species, inside and outside the bay, are reported in Bonsignore et al., 2013 (attachment I). In particular, for no carcinogenic effects, an HQ exceeding 1.0 indicates a potential health risk (US EPA, 1989). In our dataset, either using USEPA’s reference dose (TQa) that WHO acceptable daily intake (TQ_b), species inside the Bay exceeded the value 1 in all cases, while fishes outside the Bay only in demersal and benthic fishes (*P. bogaraveo, P. erythrinus, M. barbatus*).

International Agencies indicate a provisional tolerable weekly intake (PTWI) of Hg, representing safe values for human population over lifetime, ranging from 0.7 µg kg^{-1} body weight (b.w.) (US-EPA, 2004) to 1.6 µg kg^{-1} b.w. (FAO/WHO, 2006).

The calculated EWI index exceed the PTWI (US-EPA, 2004; FAO/WHO) in almost all the species collected inside the Bay and in demersal and benthic fishes from outside, thus advising that consumption of fish from inside the Augusta Bay represents a serious risk for human health of the local populations, while suggest caution in consuming demersal and benthic fishes from outside the Augusta Bay definitively demanding for appropriate social actions.

5.3 Sediments as primary source of Hg

The high THg concentrations measured in benthic species, together with the anomalous THg content measured in pelagic species living outside the Bay, suggested active Hg release mechanism from polluted sediments to the water column, with consequent effects of bioaccumulation in the trophic web.

Also the THg and DHg distribution in water column confirm the hypothesis of sediments as primary sources for the surrounding environment. Indeed the reported high resolution maps of THg distribution in column water demonstrate a direct relationship between THg and DHg contents in seawater and THg content in sediments thus suggesting the key role played by the highly polluted sediments as sources of Hg to the investigated marine environment, as speculated by Sprovieri et al., 2011.

The applied benthic chamber experiment offered the unique opportunity to measure the authentic release of Hg from Augusta Bay sediment to seawater over time. The calculated fluxes at the interface between sediment and seawater in Augusta Bay are higher than those reported for the Trieste Gulf (Covelli et al., 1999), the Bellingham Bay (Bothner et al., 1980), the Arcachon Bay (Bouchet et al., 2011).

Calculated fluxes are linearly correlated (R^2=0.68) with mean THg content in the first 5 cm of sediments (Fig. 37), thus suggesting an increasing of Hg content in sediments determine a major release flow. The north-south gradient before reported for fishes, seawater and sediments, is also reflected by the in situ benthic fluxes. Indeed, the lowest diffusive fluxes were recorded in the northern Augusta bay (St.7), intermediate fluxes in the middle zone (St. 11 and 12) and the highest in the southern part (St. 16bis), as measured for sediment (Fig. 37).

The only exception is represented by station 16 (sampling September 2011), reflecting the lower THg content in sediment, due to the sandy nature of this core.

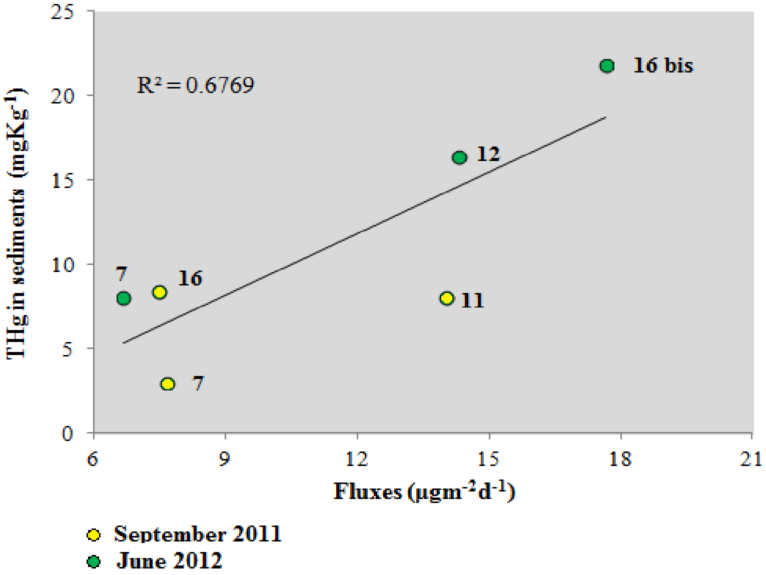


Figure 37: *Relationship THg content in sediments, calculated for the first 5 cm, vs. benthic fluxes in the same station point for the entire dataset(September 2011 sampling, yellow bubble and June 2012 sampling, green bubble).*

With the exception of station 16 (for the above evidence), higher Hg fluxes were connected to the higher temperature in warmer periods (June 2012) at both sites suggesting that temporal variations of these fluxes are temperature dependent (Fig. 37). Indeed during warmer period, the highest microbial activity, and bottom-water O_2 content enhance the importance of metal reductions in sedimentary biogeochemical processes (Covelli et al., 2008). Moreover higher temperatures enhancing microbial activity that, in turn, stimulate Hg methylation (Ullrich et al., 2001).

Moreover the here used dynamic flux chamber technique, coupled with a real-time atomic adsorption spectrometer, has represent an important step aimed to refine the estimation method to assess Hg fluxes from environmental surfaces (Wang et al., 2006).

Data of fluxes at the air-sea interface, result to be higher than Hg flux from background uncontaminated soils (Ericksen et al., 2006), while are comparable to those reported from volcanic/geothermal areas (Engle and

Gustin, 2002) and substrates associated with hydrothermal systems (Engle et al., 2006).

Calculated fluxes of Hg release from sediments result to be one order of magnitude higher than reported total sea-air mercury evasion flux, suggesting that the a good part of Hg released from sediments keep on recycle in the biogeochemical cycle involving sediment, seawater and biotic compartment. The total amount of each compartment remain unclear.

5.4 Mass-balance

Recently Sprovieri et al. (2011) and Fantozzi et al. (2013) have argued on a potential Hg export from Augusta Bay to the Eastern Mediterranean seawater, as a result of the measured 3D circulation system. Rajar et al., 2007 reported a total input of Hg from anthropogenic sources to the Mediterranean Sea of ~12.5 kmol y^{-1} excluding the Augusta Bay contribution.

Here, we extend the potential role of Augusta Bay as an Hg point source for the open ocean also considering the significant transfer of pollutants by pelagic fishes moving between the inner and external part of the bay. This implies potential effects on the food web of the surrounding area as already reported by several authors studying marine systems (Riisgard and Hansen, 1990; Futter, 1994; Jarman et al., 1996; Atwell et al., 1998). This hypothesis is supported by the high mean HgT concentrations measured in pelagic species caught outside the bay. Indeed, pelagic species prefer to inhabit warmer coastal seawaters during their first life stages (Basilone et al., 2011), but they generally move in deeper waters during the older stages (Wirszubski, 1953; Schneider, 1990; Whitehead, 1990), thus, representing a significant and potential vehicle of contaminants to the deep marine food web.

This evidence corroborates our hypothesis of a potential Hg export through the food web, from Augusta Bay to the surrounding area. Moreover the high Hg content measured in seawater collected outside the bay, confirmed the hypothesis of transport of Hg from Augusta harbor to the open sea representing a vehicle of contamination for the entire Mediterranean basin through the complex circulating currents affecting the western Ionian.

The above evidences definitively called for a more detailed information on the role played by the Augusta Bay on a large scale in order to assess the net outflow of Hg through the offshore waters.

A box model that calculates the budget of HgT in seawater and sediments of the Augusta area is here proposed. Sprovieri et al., 2011 considered the Augusta Bay as an 'environmental compartment with well-defined borders and constrained hydrodynamics" and reported an average output of water mass of ~2.34 x 10^{13} kg y^{-1}. The mass balance of HgT in the basin is calculated at the steady-state by the following equation:

$$\mathbf{I + A + AD + R = O + D + V}$$

Where:

I represents the total Hg influx from the surface Mediterranean seawater;
A represents the inputs of dissolved Hg from anthropogenic activities
AD corresponds to the atmospheric Hg deposition
R is the Hg re-suspension/release from sediments
O is the total Hg outflow from the basin
D corresponds to sedimentary deposition and burial
V is a term accounting for evasion of HgT to the atmosphere (Fig. 35).

All the budgets and parameters described below are summarised in Table 16. Values of I and A are calculated using the HgT concentrations reported by Kotnik et al., 2007 (1.46 ±0.62 and 1.21 ±0.32 pM in summer and spring, respectively), corresponding to an average input of Hg in the Augusta basin (I) of about 8.48 x10^{-7} kmol y^{-1} from the Ionian Sea (Fig. 38).

Values of anthropogenic HgT inputs to the basin (A) (0.018 t in water for the year 2005), are reported in the European pollutant emission register. Values of AD and V are those reported by Bagnato et al, 2013 performing a short-term (1 yr) monitoring study on Hg distribution and evasional flux in the atmospheric compartment of the Augusta Bay.

The calculated V (1.99 x10^{-2} kmol y^{-1}) result to be one order of magnitude higher respect of data used by Sprovieri et al., 2011, while the AD value (4.19x 10^{-3} kmol y^{-1}) results double. The applied benthic chamber experiment offered the unique opportunity to measure the authentic release of Hg from Augusta Bay sediment to seawater over time (R).

The R parameter was calculated by extending the in situ benthic flux to the whole Augusta area by the application of the Voronoi polygons methods, dividing space into a number of regions, represented by the investigate site.

The method define individual areas of influence around each of a set of points. Polygons are mathematically defined by the perpendicular bisectors of the lines between all points (Fig. 38).

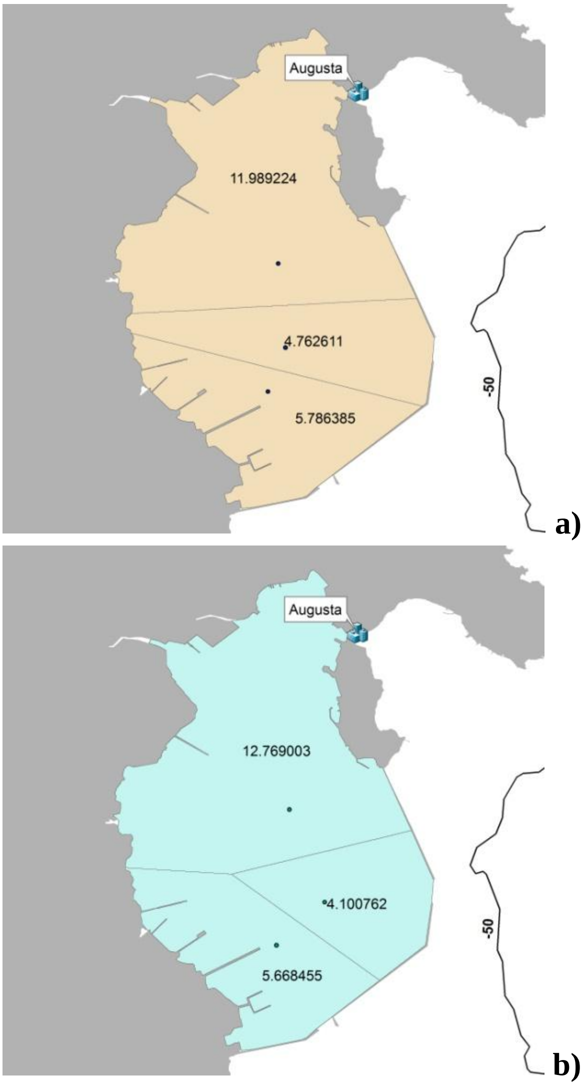


Figure 38: *Partition of the entire Augusta basin in Voronoi polygons,, each relative to one station of measurement for September 2011 (a) and June 2012(b)benthic chamber experiments.*

By extending the punctual fluxes to the entire Augusta area, a total amount of 0.38 Kmol y^{-1} has been estimated (Fig. 39). As Sprovieri et al., 2011, on consider null D parameter.

The calculated output of HgT from the Augusta basin to Ionian surface waters (O) corresponds to an average of 1.29 kmol y^{-1} (Fig. 39), more than one order of magnitude respect of those measure by indirect calculation reported by Sprovieri et al., 2011.

On the basis of the available hydrodynamic data, Sprovieri et al., 2011 calculate a residence time for the bottom water of the Augusta of ~10 months and therefore it is assumable that the HgT released from sediments to the bottom seawater of the basin is flushed on a yearly basis and outflows to the eastern coast of Sicily (Sprovieri et al., 2011).

Table 16: Parameters (sources and sinks) of HgT used to calculate the mass-balance of HgT in the Augusta basin.

Unit	**I**[a]	**A**[b]	**AD**[c]	**V**[c]	**R**[d]	**D**	**O**
Kmol y^{-1}	1.70 x 10^{-7}	1.80 x 10^{-2}	4.19x 10^{-3}	1.99 x10^{-2}	0.38	-	1.29

[a] Kotnik et al. (2007)

[b] From the EPER database

[c] Bagnato et al., 2013

[d] this work

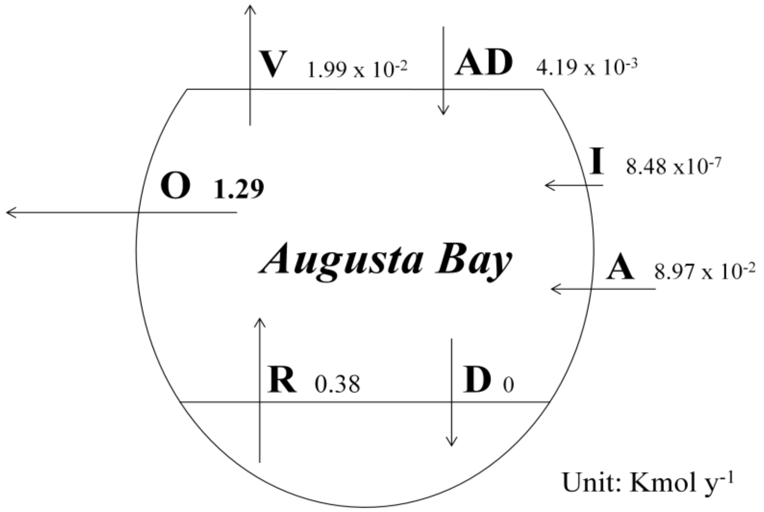


Figure 39: *Conceptual scheme for mass-balance calculation of HgT in the Augusta basin.*

The most critical point related to the role played by the Augusta Bay is the potential large scale effects associated to the outflow of waters intercepting surface meso-scale ocean circulation (Sprovieri et al., 2011). Indeed, water mass outflow from the Augusta Bay is immediately intercepted by the Atlantic Ionian Stream (AIS) flowing over the continental shelf off the southern Sicilian coast, due to the general thermohaline circulation in the upper, intermediate and deep layers, creating an anticyclone circulation.

Furthermore the narrow continental margin off the Augusta coast, associated to steep slope and several gullies (Sprovieri et al., 2011), creates preferential transfer routes for polluted sediments to the Mediterranean basin.

The recalculated input provided by the Augusta Bay (1.29 Kmol y^{-1}) have to be added as point sources to the previous mass balance estimate. By adding the estimated Hg input given by the Augusta basin to the total mercury input reported by Rajar et al., 2007 for the Mediterranean sea, the total output rises to 319.11 kmol y^{-1} (Fig. 40).

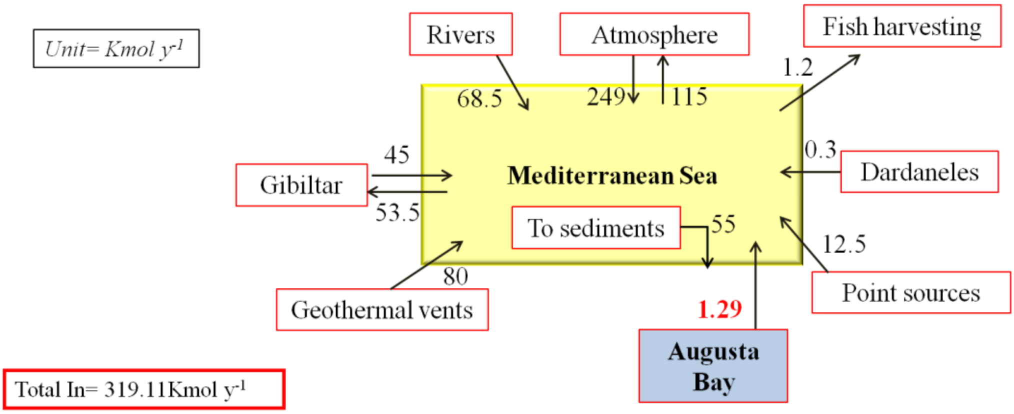


Figure 40: *HgT flows calculated for the Mediterranean Sea with the Augusta source point (Rajar et al., 2007 and Sprovieri et al., 2011 modified).*

5.5 REEs distribution in seawater

The use of REEs distribution as pollution tracer in environmental medium is due to the following evidences:

- Due to their unique chemical features, REE represents, in all likelihood, the best geochemical instrument for investigate processes realizing at the interface among different means, both of organic or inorganic origins (Bau & Dulski, 1996a; Bau, 1999; Takahashi et al., 2005; 2007; 2010).
- The activities related to oil refining industry produces a characteristic geochemical signature that REE distributions are able to record as positive anomalies of light REE (LREE), both in dissolved and in particulate phases suspended in atmosphere and hydrosphere (Olmez et al., 1991; Kulkarni et al., 2007; Moreno et al., 2008; Censi et al., 2011).
- The geochemical behavior of REE and their speciation in the dissolved phase are strongly influenced by the organic matter content. This evidence has also been recently demonstrated in coastal marine environment and constitutes a tracer of anthropic pressure in coastal water (Censi et al., 2010).

Various work has addressed the use of REEs in investigating the environmental impact of human activity and demonstrated that the REE natural distribution in water, soil, and sediment from densely industrialized and populated regions can be altered by anthropogenic influences (i.e. Bau and Dulski, 1996). This is a very important topic in the study of coastal areas, where strong anthropogenic pressure occurs such in as the Mediterranean Sea (Elbaz-Poulichet et al., 2002; Di Leonardo 2009; Censi et al., 2010). Particularly in the Augusta Bay the combination of industrial, agricultural and urban effluents, as well as dry and wet deposition, play a determining role on the evolutionary process of chemical characteristics in the Augusta marine system. Features of shale-normalised REE pattern in seawater are here used as proxy to recognize sources of these elements and processes involving them along the water column.

The main geochemical process highlighted by the REEs distribution in the examined samples, is the failure scavenging of Ce from the dissolved phase to the suspended particulate matter. Cerium anomaly in natural waters is related to the mechanism of oxidative scavenging of tetravalent cerium by iron and/or manganese oxides. Ce abatement, or its complete disappearance has been recovered in continental water of varies origins and results attributable to organic matter content (Dia et al., 2000). Pourret et al., 2008 showed that above pH 8.2, 8.6 or 8.7, Ce(III) is readily oxidized into Ce(IV), which is then preferentially adsorbed onto humic acids, resulting in the development of a negative Ce anomaly in the "truly" dissolved part of the solution, and a complementary positive anomaly occurs in the organic colloidal fraction.

In the reported dataset, the absence of Ce/Ce*<1 in dissolved phases is probably due to high concentration of dissolved organic. Ultra-filtration allows to physically separate inorganic to organic phases, permitting to discern the negative Ce anomaly (Pourret et al., 2008). Although this behavior has been detected only in laboratory studies (Davranche et al., 2004, Pourret et al., 2008) and confirmed for marine environment in a limited number of cases (Censi et al., 2010), data collected in Augusta Bay suggest this result could be due to the above described mechanism. The known anthropogenic pressure in the study area and the presence of petrochemical plant, the Gd anomaly can be ascribed to zeolites doped with REEs, which have been used as fluid-cracking catalysts in petroleum industry since the 1960s (Swift et al., 1979; Kulkarni et al., 2006).

The contemporary and correlated presence of positive Gd and Ce anomalies in seawater, let suppose a common origin. Data confirmed that Ce anomaly is sensible to dissolved organic matter, more than redox condition, in sample water submitted to simple filtration. The REE distribution along the water column suggests that the high dissolved organic matter increase the REE solubility from sediments in which they are concentrated because of industrial activities. Waste discharge of industrial wastewater, together with human non industrial wastewater, created ideal condition for an increasing of REE in dissolved phases.

5.6 Application of Stable Mercury Isotopes to biogeochemistry

The application of mercury (Hg) stable isotopes to problems in environmental chemistry is rapidly expanding field of investigation. The success of such approach strongly depends on two factors: first, different Hg sources must have analytically discernible Hg isotope signatures; second, some Hg geochemistry transformation have a known isotopic signature. The combination of mass-dependent (MDF) and mass-independent (MIF) fractionation provides a new isotopic fingerprint of mercury sources and processes into the environment. Here the Hg isotopic investigation on fishes, sediments and hairs permitted to define sources of Hg and the biogeochemical processes realized in Augusta Bay. A direct positive relationship (R^2= 0.92) has be found by plotting Δ^{201}Hg vs. Δ^{199} values of the entire dataset, included both fish, box-corer sediments and human hair of local population (Fig. 41). This clear reflect the crucial link between the main Hg source (sediment) and the last receptor, the man, assuming Hg primary by mean of fish consumption.

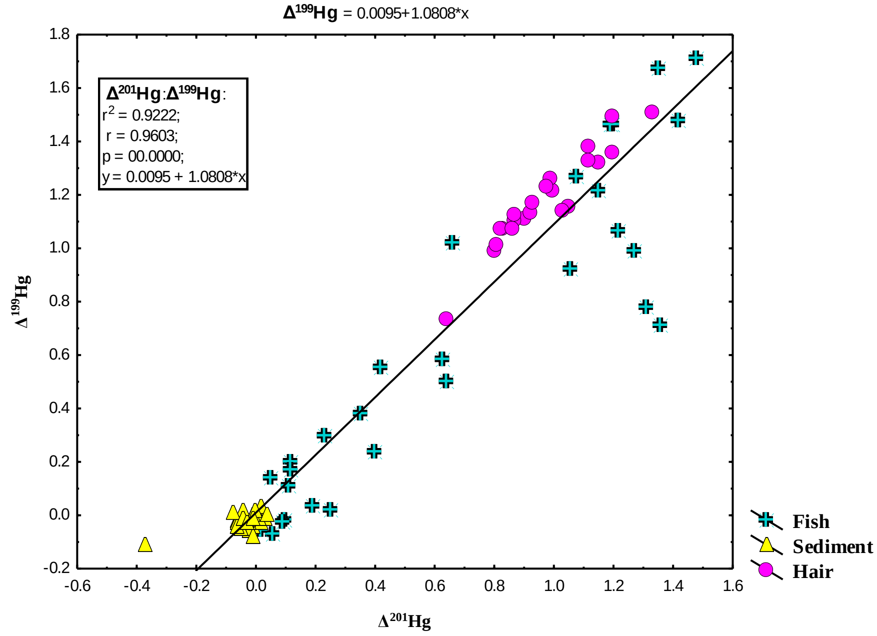


Fig. 41: *Plot of data for Δ^{201}Hg vs. Δ^{199}Hg of the Augusta Bay coastal sediments, fish muscle tissues and human hair of local population (r^2=0.92; slope: 1.08±0.009).*

5.6.1 Hg isotopes fractioning in fishes

Variations in Δ^{199}Hg and Δ^{201}Hg in fish tissues resulted from photochemical degradation of MeHg in the water column prior to its entry into aquatic food chain and the Δ^{199}Hg /Δ^{201}Hg ratio might be diagnostic of reduction of Hg (II) vs. MeHg. (Blum and Bergquist, 2007, Sherman and Blum, 2013). Indeed empirical observations of Δ^{199}Hg/Δ^{201}Hg slopes in natural materials show values of ~1.0 for processes that involve Hg(II) photoreduction (Biswas et al., 2008; Ghosh et al., 2008; Carignan et al., 2009; Sherman et al., 2010) whereas values in aquatic foodwebs, which uniquely involve MeHg, display slopes of ~1.2–1.3 (Bergquist and Blum 2007; Gantner et al., 2009; Laffont et al., 2010; Senn et al., 2010). Here the positive MIF trend, and the Δ^{199} *vs* Δ^{201} correlation (slope = 1 ± 0.03) clear testify Hg fractioning appended during photochemical reaction of Hg prior of the intake in the marine food web. MeHg display more MIF compared to Hg (II) and the ratio Δ^{201}Hg vs δ^{202}Hg is predictive of photos or demethylation reduction. The calculated Δ^{201}Hg / δ^{202}Hg for fishes results to be 1.7, confirming the most important reaction causes fractioning is the Hg(II) reduction prior of the intake in the aquatic food web.

Moreover MIF fractionate otherwise according to fish ecology. Senn et al. (2010) reported for coastal species in the Gulf of Mexico distinct and non-overlapping values of δ^{202}Hg and Δ^{201}Hg compared to oceanic specie. Difference in Δ^{201}Hg between sediments and fish results in enrichment of 0.7‰ in fishes, while for Δ^{199}Hg the difference result the 0.67 ‰.

The clear increase in MIF fractionation (both Δ^{199}Hg and Δ^{201}Hg) in pelagic fishes could be explained by their living habitat, more surface respect of demersal and benthic species, where penetrating sunlight promotes the processes of Hg photoreduction in the water column. On the other hand the higher positive δ^{202}Hg values measured in the benthic and demersal specimens could be due to microbial degradation of MeHg before entry into the food web.

The main pathway drive this fractioning can be summarizing as:

Hg (II) ☼⟶ Hg(0)

5.6.2 Hg isotopes fractioning in sediments

MDF fractionation occurs during biotical methylation processes in sediments. Studying fermentative methylation by sulphate reducing bacteria, Rodriguez-Gonzalez et al., 2009, demonstrate that the MeHg product had lower δ^{202}Hg than the Hg(II) starting material (-MDF) and also found no evidence for biotic MIF during methylation, contrary to Jackson et al. (2008) that argued that MIF of Hg occurred during microbial Hg methylation.

By plotting δ^{202}Hg vs Δ^{201}Hg for the entire sediment core dataset, on obtain a peculiar trend (Fig. 35), ascribable, according to the scheme proposed by Blum (2011) and Rodriguez-Gonzales et al., (2009), to biological mediated MeHg production. Moreover processes of Hg methylation in sediments could be drive the shift in δ^{202}Hg measured in the south and most contaminated Augusta Bay.

The highest Δ^{199}Hg and lower δ^{202}Hg recorded in the south area let hypothesize the higher microbial activity in the most contaminated area. This geographic pattern in δ^{202}Hg and Δ^{199}Hg values suggests that the sources of Hg to the sediment are locally controlled.

The gradually changing spatial pattern in sediment Hg isotopes is consistent with sediment Hg contamination derived from chlor-alkali plant, probably due to a stronger microbial activity in the southern Bay. The main pathway drive this fractioning can be summarizing as:

Hg(II) ○ ⟶ MeHg ○ = microorganism

5.6.3 Hair Hg isotopic composition

The importance of the Hg/DOC ratio and the effect of ligands on Hg isotope fractionation, has been tested by the exploration of photoreduction of Hg(II) in a series of laboratory experiments (Zheng and Hintelmann 2009, 2010b).
Laboratory experiment conducted by Bergquist and Blum, 2007, used natural sunlight to reduce Hg(II) and MeHg from aqueous solutions in the presence of DOC, demonstrated Δ^{199}Hg /Δ^{201}Hg ratio was 1.00 for Hg(II) reduction and 1.31 for MeHg reduction.
The authors suggested that this range represented differing behavior of Hg bonded predominantly to reduced sulfur groups at low Hg/DOC and to oxygen groups at higher Hg/DOC. The analysed hair samples display positive MIF with a slope Δ^{201}Hg *vs.* Δ^{199}Hg of 1.2 clearly indicated processes of MeHg-DOC reduction due to sunlight.
The main pathway drive this fractioning can be summarizing as:

MeHg-DOC ☼ $\longrightarrow$ Hg(0)

5.6.4 Sources of Hg for fishes

Several studies have explored the use of Hg isotopes to "fingerprint" point sources of Hg from historic Hg mines and trace them into the surrounding environment (Gehrke et al., 2011c) .
If Hg transformations do shift original source isotope signatures, then under certain conditions the shift may prove to be constant. Examples are the observed shifts in δ^{202}Hg by 0.6‰ between sediment Hg and fish Hg in San Francisco Bay reported by Gehrke et al., 2011c.
Here on report δ^{202}Hg values analogous for both fishes and sediment (mean δ^{202}Hg=-0.39 ‰), doubtless confirming the role of sediments as source of Hg for the marine biotic compartment.
The support at the hypothesis of sediments as sources of Hg for fishes, is also testimony by the high-quality relation (r^2=0.90) obtained by plotting δ^{202}Hg *vs.* Δ^{201}Hg of both fishes and sediments (Fig. 42).
The higher MIF displayed by fishes had been discussed above. MeHg photochemically demethylation in the coastal ecosystem, prior to being incorporated into the oceanic food web has been supported by experimental results reported Bergquist and Blum (2007), observing MIF in oceanic fish.

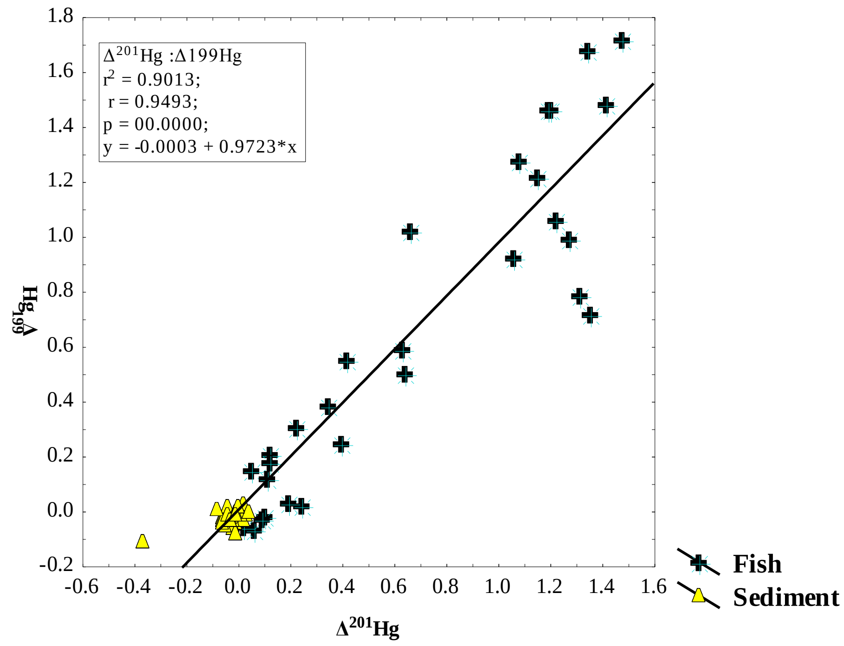


Fig. 42: Plot of data for Δ^{201}Hg vs. Δ^{199}Hg for the Augusta Bay coastal sediments and fish muscle tissues.

5.6.5 Sources of Hg for human

The most important pathway for human exposure to Hg is via the consumption of marine food (Sunderland 2007). Compared to blood and urine, hair, because of the stable Hg forms, is most suitable for monitoring study in polluted site (Gellein et al., 2008; Dongarrà et al., 2010). Here on investigate the Hg isotopic variations between fish tissue and human hair as a first step in evaluating Hg isotopes as a metabolic process and/or Hg exposure.

Here the meaningful relationship found by plotting Δ^{201}Hg *vs.* Δ^{199}Hg (R^2= 0.84; slope: 1.09, Fig. 43), demonstrate the familiarity between the Hg content in fishes and hairs.

Examples are the observed shift of 2‰ in δ^{202}Hg between fish and the scalp hair of human consumers of fish has been reported in San Francisco Bay (Laffont et al., 2010). For Augusta Bay compared to fish (mean δ^{202}Hg= -0.39), human hair (mean δ^{202}Hg= 1.71) shift for 2.1‰, while mean MIF difference are negligible (0.3‰ for Δ^{201}Hg e 0.5 ‰ for Δ^{199}Hg), suggesting that the anomalies act as conservative source tracers between upper trophic levels (men) of the tropical food chain (fishes), in good agreement with results reported by Laffont et al., (2010).

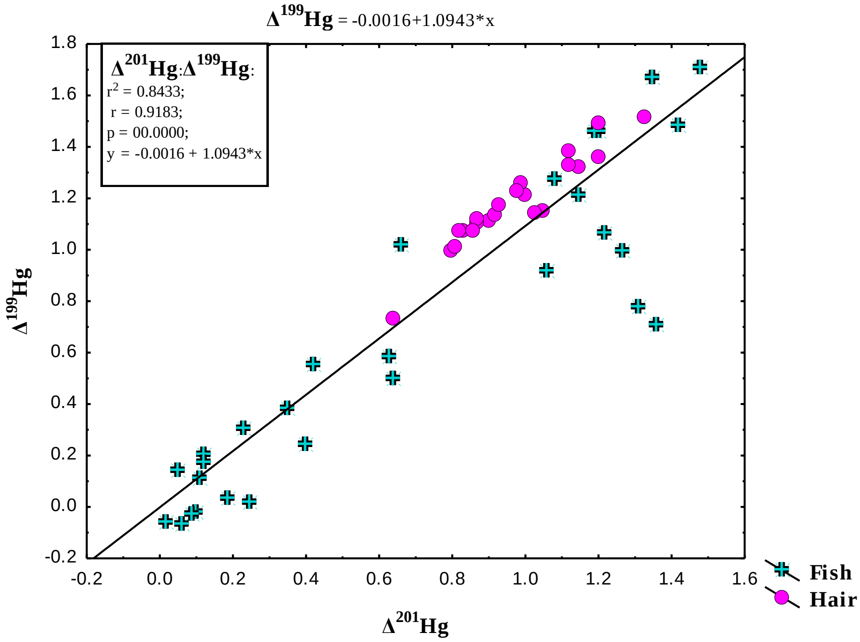


Fig. 43: *Plot of data for Δ^{201}Hg vs. Δ^{199}Hg for fishes and human hair samples.*

Although some MDF probably also occurs during trophic transfer of MeHg through the food web (Laffont et al., 2010, Das et al., 2009), trophic transfer could also push δ^{202}Hg values to higher values. Laffont et al., 2010 justified variation of ~ +2 ‰ to MMHg human metabolism, i.e. excretion in faeces of light isotopes of Hg or blood-hair transfer, that determine enrichment of heavier Hg isotopes (δ^{202} Hg).

Chapter VI:

Conclusions

6. CONCLUSIONS

Mercury has an extremely complex cycle in the Earth's ecosystems and the environmental bodies can be both active sink and source of Hg. The here reported multidisciplinary work permits to put a complete view on the biogeochemical behavior of Hg in a coastal marine environment. In this contest the Augusta Bay represent an ideal natural lab for study on the biogeochemical cycle of Hg in complex systems, because of relevant and uncontrolled discharges of Hg from the chlor-alkali plant. Analyses of Hg content in fishes, sediments, seawaters and atmosphere of the Augusta Bay allowed to investigate to the major actors of the cycle. Moreover fluxes studies at the interfaces sediment/seawater/air, performed by means of an in situ benthic chamber and of a dynamic accumulation chamber, allowed to accurately assess the fraction of Hg released from sediments and that escaped in atmosphere. Finally the creation of an integrated model on the biogeochemical cycle of mercury permitted to estimate the Hg contribution made by the Augusta Bay as point source for the Mediterranean basin, by means of the complex of water circulation involving the eastern Sicilian coast.

The main conclusion can be sensitized in the following sentences:

➢ Sediments of Augusta Bay played a key role as source of Hg for the surrounding environment. A still active Hg release mechanism from the polluted sediments to the marine environment is testified by several evidences:

¤ The highest Hg content, in both fishes, sediments and seawater samples, had been recorded in the southern Augusta Bay, where waste spillage from chlor-alkali plant occurred.

¤ The HgT content measured in fish tissues show an increasing trend along the habitat depth, with highest values measured in benthic species and the lowest in pelagic ones.

¤ THg and DHg content in seawater shows a clear trend on the vertical, with concentration increasing near the bottom and reducing in surface water.

¤ The total DHg content at the sediment/seawater interface increases with time.

¤ Fishes and sediments had the same isotopic signature, in terms of mass dependent fractionation (δ^{202}Hg).

- Active processes of Hg microbial methylation in sediments are testified by Δ^{201}Hg/ δ^{202}Hg ratio in sediments.

- The Augusta Bay represents a point sources for Hg to Mediterranean basin. The vehicle of contamination is favorite by the complex circulating currents affecting the western Ionian, by the closeness with the steep continental slope (part of the Malta escarpment) and by the presence of several gullies, dropping to the deep end of the Ionian basin. This conclusion is supported thought the following evidences:
  - High contamination of pelagic species measured in the external zone of the bay confirmed the role of the Augusta marine environment as a potential Hg source for the surrounding area and underscores the crucial risk associated with contaminant transfer from the semi-enclosed basin to the open sea by means of biotic transfer.
  - Unexpected THg concentrations have been measured in seawater outside the bay;
  - The mass balance calculation estimated a HgT output from the Augusta basin to Ionian surface waters (O) corresponding to an average of 1.29 kmol y^{-}.

- The REE distribution along the water column suggests that the high dissolved organic matter created ideal condition for an increasing of REE in dissolved phases, much to hide the negative Ce anomaly usually recorded in the oligothropic water. Gd anomaly, expressed as Gd/Gd*>1, let’s suppose significant contributions arising from the petrochemical plant.

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Attachment I

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Mercury in fishes from Augusta Bay (southern Italy): Risk assessment and health implication

M. Bonsignore [a], D. Salvagio Manta [b], E. Oliveri [a], M. Sprovieri [a,*], G. Basilone [a], A. Bonanno [a], F. Falco [a], A. Traina [a], S. Mazzola [a]

[a] Institute for Coastal and Marine Environment (IAMC) – CNR, Via del Mare, 3, 91021 Torretta Granitola, Campobello di Mazara (TP), Italy
[b] Institute for Coastal and Marine Environment (IAMC) – CNR, Calata Porta di Massa, 80100 Naples, Italy

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ABSTRACT

Our study reports on the total mercury (HgT) concentrations measured in the muscles and livers of several benthic, demersal and pelagic fish species caught inside and outside of Augusta Bay (southern Italy), a semi-enclosed marine area, highly contaminated by the uncontrolled (since the 1950s to 1978s) discharge of the largest European petrochemical plant. Mercury levels in fish tissues are discussed with regard to specific habitat, size and/or age of the specimens and HgT distribution in the bottom sediments. Results suggest a still active Hg release mechanism from the polluted sediments to the marine environment. Also, the high HgT concentrations measured in fishes caught in the external area of the bay imply a potential role of Augusta Bay as a pollutant source for the Mediterranean ecosystem. Finally, values of hazard target quotient (THQ) and estimated weekly intake (EWI) demonstrate that consumption of fishes caught inside the bay represents a serious risk for human health. Also, data indicate that intake of fishes caught from the external area of the bay, especially for that concern demersal and benthic species, could be represent a significant component of risk for the local population.

1. Introduction

The city of Augusta, located in the SE of Sicily (southern Italy), has experienced an important industrialisation phase since the early 60s. This has led to the creation of several chemical and petrochemical plants and oil refineries resulting in a severe pollution of the surrounding environment. In particular, the petrochemical industry in Augusta Bay is one of the largest in Europe with the most important chlor-alkali plant in Italy (Le Donne and Ciafani, 2008). Its activity started in 1958 and stopped in 2005, with production of chlorine and caustic soda by electrolysis of sodium chloride aqueous solution in electrolytic cells with a graphite anode and metallic mercury cathode. Uncontrolled chemical discharge of Hg occurred in the Augusta Bay until 1978, when restrictions were imposed by the Italian legislation.

In the last decade, several studies have provided detailed information on the pollution levels and risks for human health of resident populations of Augusta Bay (ICRAM, 2005; Ausili et al., 2008; Di Leonardo et al., 2007, 2008; ENVIRON International Team, 2008; Ficco et al., 2009; Sprovieri et al., 2011). Sprovieri et al. (2011) reported high-resolution maps of HgT distribution from superficial sediments collected in 2005, highlighting extremely high concentrations (ranging between 0.1 and 527.3 mg kg^{-1}) and speculating on the key role that Augusta Bay could play in exporting Hg to the Mediterranean Sea, as an effect of the outflow intercepted by the Levantine Intermediate Waters (LIWs). Also, data recently collected by ICRAM (2008), ENVIRON International Team (2008) and Ausili et al. (2008), demonstrated HgT transfer from the abiotic system (sediments and seawater) to fishes (top predators and filter-feeders) and documented significant health risks associated with the consumption of fish caught in the area. Toxicological Hg effects were also evaluated on mussels and red mullet by micronuclei (MN) studies, which documented DNA damage (Ausili et al., 2008 and ICRAM, 2008). Finally, Tomasello et al. (2012) report on DNA genotoxic and oxidative damages in *Coris julis* specimens from Augusta Bay.

Fish food seems to constitute the main route of Hg uptake for humans (Holsbeek et al., 1996; Nakagawa et al., 1997).

Renzoni et al. (1998) demonstrated that long-term and frequent intake of fish with high Hg levels is statistically associated with a toxic risk, especially in pregnant women. A sad, famous poisoning episode occurred in the 1950s among people living around Minamata Bay (Japan), showing the irreversible neurological damage and teratogenic effects due to consummation of Hg-contaminated fish (De Flora et al., 1994). Methylmercury (MeHg) is the most toxic form, able to interfere with thiol metabolism, causing inhibition or inactivation of proteins containing thiol ligands and ultimately

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* Corresponding author. Tel.: +39 092440670; fax: +39 092440445.
E-mail address: mario.sprovieri@iamc.cnr.it (M. Sprovieri).

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leading to mitotic disturbances (Das et al., 1982; Elhassani, 1983). Numerous recent studies indeed have concluded that the majority, if not all, of the Hg that is bioaccumulated through the food chain is as MeHg (Winfrey and Rudd, 1990; Mason and Fitzgerald, 1990, 1991; Gilmour and Henry, 1991; Horvat et al., 1999; Carbonell et al., 2009).

High mortality rates, statistical high frequency of neonatal malformations and cancerous diseases reported for resident populations around Augusta Bay (Martuzzi et al., 2006; Bianchi et al., 2004, 2006; Fano et al., 2005, 2006; Madeddu et al., 2006) definitively calls for more detailed exploration and definitive assessment of the role played by the intake of Hg-contaminated fish on the health of the consumers.

In this work, we aim to explore the effects of HgT pollution in Augusta Bay on the fish compartment, inside and outside the semi-enclosed area, and to assess the potential health risks associated with the consumption of contaminated fish.

2. Materials and methods

2.1. Sampling

Four different sampling sites were selected: two inside, and two outside of Augusta Bay (Fig. 1). Sampling outside the bay was performed during May 2001, on board of the N/O "Dallaporta", by means of a mid-water trawl-net at 50–100 m of depth in two sampling areas, in front of the Scirocco inlet (300-m wide and 13-m deep), and the Levante inlet (400-m wide and 40-m deep) (Fig. 1: C1, C2). Mainly pelagic fish specimens were caught (Table 1). Sampling inside the bay was performed during May 2012 by means of a fishing boat equipped with a gillnet wall, positioned at the bottom (mean depth = 20–25 m) (Fig. 1: C3, C4). Several specimens of benthic and demersal fishes were collected. From the two sampling activities, a total of 227 fish specimens were collected: 107 from mid-water sampling (outside the bay) and 120 from bottom-water sampling (inside the bay). Moreover, specimens of *Engraulis encrasicolus* ($n = 38$) were caught from the unpolluted marine area of Marsala (western Sicily) (Fig. 1), during July 2001, on board of a fishing boat equipped with a purse seine net. After collection, fishes were stored at -20 °C until biological and chemical analyses were performed in the laboratories of biology and biogeochemistry at the Institute for Coastal and Marine Environment (CNR) of Capo Granitola.

2.2. Biological data and tissue collection

The total length (TL) of each specimen was measured. Muscle and liver tissues were collected from each organism, using plastic materials cleaned with HNO_3 (10%) and MilliQ water, in order to avoid Hg contamination. Tissues were stored at -20 °C until analysis. Otoliths were extracted from anchovy and sardine specimens for age determination. Readings and interpretation of otolith increment growths were carried out by transmitted visible lights based on higher-resolution microscopy (20–25× magnification) (Campana et al., 1987; Nielsen, 1992). The procedure adopted for European anchovy age determination follow Uriarte et al. (2007) and La Mesa et al. (2009).

2.3. Chemical analyses

Total mercury concentrations (HgT) in tissues were measured using a direct mercury analyser (Milestone_DMA-80), atomic absorption spectrophotometer, according to analytical procedures reported in EPA 7473. Briefly, approximately 0.1 g of fresh tissue was loaded in nickel boats and transferred to the DMA-80 system. In order to minimise contamination risks, acid-cleaned laboratory materials were used during sample preparation and analyses. A Reference Standard Material (TORT-2; HgT certificate value = 0.27 ± 0.06 $\mu g\ g^{-1}$) was analysed to assess analytical accuracy (estimated to be ~3%) and precision (routinely better than 4%; RSD%, $n = 3$). Finally, duplicated samples (about 20% of the total number of samples) were measured to estimate reproducibility, which resulted in better than 7%.

2.4. THQ and EWI calculation

Target hazard quotient (THQ) and estimated weekly intake (EWI) were calculated for muscles of fishes caught inside and outside the bay.

The target hazard quotient was calculated according to the US EPA (1989) method and it is described by the following equation:

$$\mathrm{THQ} = \left(\frac{\mathrm{EF} \times \mathrm{ED} \times \mathrm{FIR} \times C}{\mathrm{RFD} \times \mathrm{WAB} \times \mathrm{TA}}\right) \times 10^{-3}$$

where EF is exposure frequency (365 days/year); ED is the exposure duration (70 years), equivalent to the average lifetime; FIR is the food ingestion rate (36 g/person/day) (FAO, 2005); C is the metal concentration in seafood ($\mu g\ g^{-1}$); RFD is the USEPA's reference dose (0.1 μg Hg kg $bw^{-1}\ d^{-1}$) (http://cfpub.epa.gov) or acceptable daily intake determined by WHO (0.23 μg Hg kg $bw^{-1}\ d^{-1}$) (http://apps.who.int); WAB is the average body weight (60 kg), and TA is the average exposure time for no carcinogens (365 days/year × ED).

The THQ was calculated for all the studied species in the Augusta Bay using the US-EPA's reference dose (THQa) and the acceptable daily intake determined by the WHO (THQb). In particular, we assumed that the measured mercury is integrally in its methylated form (Winfrey and Rudd, 1990; Mason and Fitzgerald, 1990, 1991; Gilmour and Henry, 1991; Horvat et al., 1999; Carbonell et al., 2009).

The estimated weekly intake (EWI) was calculated by multiplying the HgT concentration (C) times by the weekly dietary intakes (FIR × 7) and reporting to the average body weight (WAB).

Finally, mean THQ and EWI values were calculated for each studied species. Also, considering that fishing activity within the bay has been interdicted since 2007 (Order No. 73/07), data relative to fishes from inside and outside the bay were processed separately.

3. Results

3.1. Biological features

The fish caught from bottom-water sampling (inside the bay) consisted of 2 pelagic, 106 demersal and 16 benthic specimens, while specimens from mid-water sampling (outside the bay), consisted of 103 pelagic, 3 demersal and 1 benthic (Table 1). A total of 21 different species were recognised. The number of specimens per species and total length ranges are shown in Table 2. Almost all the caught species, in particular, *E. encrasicolus, Sardina pilchardus, Boops boops, Mullus barbatus* and *Illex coindetii*, are typical of the Mediterranean Sea and are commercially relevant to Italian fishing (Irepa, 2010). Only one specimen was found to belong to a so-called alien species, specifically *Sphyraena sphyraena*. This is a typical species of the tropical seas, today present also in the Mediterranean Sea (Streftaris and Zenetos, 2006).

3.2. Total mercury concentrations (HgT)

Total mercury concentrations measured in tissues from pelagic, demersal and benthic fishes, caught inside and outside of Augusta Bay, are graphically summarised in Fig. 2a and b. Mercury mean values calculated for each species, together with available comparative data from the literature and HgT content measured in anchovies from Marsala, are presented in Table 2.

Mercury concentrations ranged between 0.021 and 2.709 $\mu g\ g^{-1}$ in muscles (Fig. 2a) and between 0.029 and 9.720 $\mu g\ g^{-1}$ in livers (Fig. 2b). The HgT content in liver is from 1.5 to 6 times higher than that measured in muscles from the same specimens (Table 2). The highest HgT values were found in species caught inside the bay: 2 demersal specimens, a specimen of *Diplodus vulgaris* (HgT in liver = 4.979 $\mu g\ g^{-1}$) (extreme point in Fig. 2b) and a specimen of *Serranus scriba* (HgT in muscle = 2.709 $\mu g\ g^{-1}$) (extreme point in Fig. 2a), a large pelagic specimen of *S. sphyraena* (HgT = 9.720 and 2.269 $\mu g\ g^{-1}$ in liver and muscle, respectively) (Table 2) and a benthic specimen of *Murena helena* (HgT = 2.638 $\mu g\ g^{-1}$ in muscle) (Table 2). However, these very high levels represent outliers of the whole dataset (Fig. 2a and b). The highest non-outlier values refer once again to specimens caught inside the bay and specifically to benthic species (Fig. 2a and b). In particular, *Scorpanea scrofa* and *Scorpanea notata* show the highest HgT mean concentrations for both liver (1.638 and 2.339 $\mu g\ g^{-1}$, respectively) and muscle (1.082 and 1.341 $\mu g\ g^{-1}$, respectively) (Table 2). The lowest non-outlier ranges were found in pelagic specimens caught outside the bay (0.021–0.167 $\mu g\ g^{-1}$ for muscles and 0.029–0.5708 for livers) (Fig. 2a and b), and the HgT mean values measured in the different studied species are substantially comparable (Table 2). Finally, data for demersal species from the

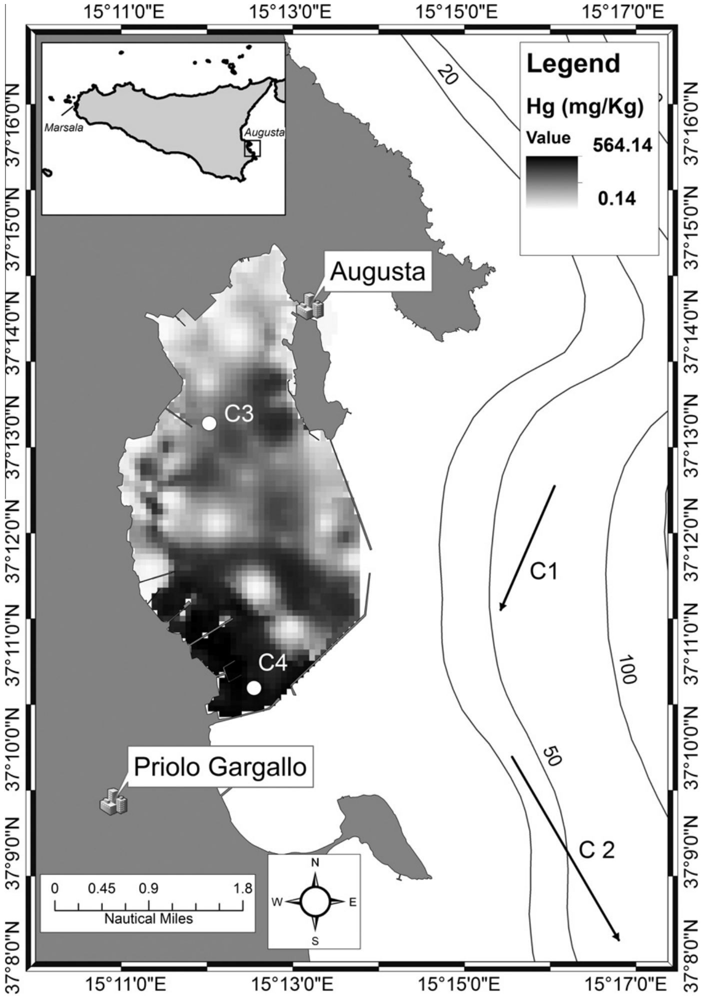

Fig. 1. Sampling sites in Augusta Bay and distribution of total mercury (HgT) in bottom sediments (data from Sprovieri et al. (2011)).

Table 1
Number of specimens *per* species caught in the sampling sites.

Mid-water sampling (outside the bay)				Bottom-water sampling (inside the bay)			
Species	C1 (no.)	C2 (no.)	Habitat	Species	C3 (no.)	C4 (no.)	Habitat
Engraulis encrasicolus	20	20	Pelagic	*Diplodus annularis*	59	15	Demersal
Sardina pilchardus	8	20	Pelagic	*Diplodus vulgaris*	–	3	Demersal
Boops boops	–	20	Pelagic	*Pagellus erythrinus*	1	6	Demersal
Trachurus trachurus	–	6	Pelagic	*Pagellus acarne*	11	1	Demersal
Illex coindetii	6	–	Pelagic	*Sepia officinalis*	2	6	Demersal
Loligo forbesi	3	–	Pelagic	*Serranus scriba*	2	–	Demersal
Pagellus erythrinus	1	–	Demersal	*Caranx rhonchus*	1	–	Pelagic
Pagellus bogaraveo	2		Demersal	*Sphyraena sphyraena*	1		Pelagic
Mullus barbatus	1	–	Benthic	*Scorpaena notata*	–	5	Benthic
				Scorpaena scrofa	3	1	Benthic
				Mullus barbatus	–	3	Benthic
				Mullus surmuletus	1	1	Benthic
				Murena helena	1	–	Benthic
				Octopus vulgaris	–	1	Benthic

Table 2
HgT means concentrations in muscle and liver of the analysed species and comparison with data for other areas.

Species	No.	Range of total length (mm)	HgT muscle (μg g^{-1})	S.D.	References	Site	HgT liver (μg g^{-1})	S.D.
Engraulis encrasicolus	40	109–138	0.052	0.019	This work	Augusta	0.204	0.147
	11	120–139	0.057	0.014	This work	Marsala	0.119	0.038
			0.040		Bilandžić et al. (2011)	Adriatic sea		
	9	121–147	0.070	0.090	Gibičar et al. (2009)	Adriatic sea[a]		
			0.030	0.030	Copat et al. (2012)	Sicily (Catania)		
			0.060	0.030	Copat et al. (2012)	Syracuse (Sicily)		
	18		0.060		Pastor et al. (1994)	Mediterranean sea (Spain)[a]		
			0.070		Martorell et al. (2011)	Mediterranean sea (Spain)		
	4		0.055	0.003	Tuzen (2009)	Black sea (Turkey)[a]		
Sardina pilchardus	28	115–150	0.082	0.035	This work	Augusta	0.196	0.157
	10	168–178	0.090	0.040	Gibičar et al. (2009)	Adriatic sea[a]		
			0.080	0.030	Copat et al. (2012)	Catania (Sicily)		
			0.180		Buzina et al. (1995)	Adriatic sea[a]		
			0.198		Buzina et al. (1995)	Adriatic sea (Kastela Bay)[a]		
	14		0.052		Wolfgang (1983)	Adriatic sea[a]		
	35	190–260	0.066		Wolfgang (1983)	Biscay Bay		
	5	157–165	0.050		Wolfgang (1983)	Mediterranean sea		
	41		0.170		Wolfgang (1983)	Ligurian sea		
	28	120–150	0.030		Wolfgang (1983)	North Africa (Ceuta)[a]		
	20	160–210	0.040		Wolfgang (1983)	Western english channel		
	38		0.105		Pastor et al. (1994)	Mediterranean sea (Spain)[a]		
			0.019		Martorell et al. (2011)	Mediterranean sea (Spain)		
	7	188–200	0.033	0.016	Harakeh et al. (1985)	Lebanon		
Boops boops	20	95–150	0.120	0.049	This work	Augusta	0.236	0.191
	11	158–198	0.196	0.204	Hornung et al. (1980)	Israel[a]		
	1		0.075		Pastor et al. (1994)	Mediterranean sea (Spain)[a]		
	2	130–160	0.190		Stoeppler and Nürnberg (1979)	Med. sea (Dubrovnik)		
			0.267		Buzina et al. (1995)	Adriatic sea		
			0.312		Buzina et al. (1995)	Adriatic sea (Kastela Bay)[a]		
	16	139–171	0.036	0.025	Harakeh et al. (1985)	Lebanon		
Trachurus trachurus	6	56–222	0.131	0.147	This work	Augusta	0.344	0.176
	2	260–285	0.170		Stoeppler and Nürnberg (1979)	North sea (German Bight)		
		170	0.170		Mikac et al. (1984)	Adriatic sea (Kastela Bay)[a]		
	37	130–236	0.122	0.101	Hornung et al. (1980)	Israel[a]		
	16	159–203	0.045	0.019	Harakeh et al. (1985)	Lebanon		
			0.053		Martorell et al. (2011)	Mediterranean sea (Spain)		
	4		0.078	0.005	Tuzen (2009)	Black Sea (Turkey)[a]		
	5		0.053	0.012	Keskin et al. (2007)	Marmara sea (Turkey)[a]		
Diplodus annularis	74	109–179	0.557	0.303	This work	Augusta	1.195	0.827
			0.653		Buzina et al. (1995)	Adriatic sea[a]		
			0.628		Buzina et al. (1995)	Adriatic sea (Kastela Bay)[a]		
Diplodus vulgaris	3	102–179	0.643	0.614	This work	Augusta	2.035	2.554
	5		0.378	0.017	Keskin et al. (2007)	Marmara sea (Turkey)[a]		
Sphyraena sphyraena	1	1190	2.269		This work	Augusta	9.727	
	14	219–295	0.167	0.068	Hornung et al. (1980)	Israel[a]		
Caranx rhonchus	1	264	1.701		This work	Augusta		
Pagellus acarne	12	149–161	0.254	0.028	This work	Augusta	0.618	0.178
	3	135–141	0.112		Hornung et al. (1980)	Israel[a]		
	15	164–182	0.032	0.014	Harakeh et al. (1985)	Lebanon		
Pagellus bogaraveo	2	178–179	0.266	0.227	This work	Augusta	1.230	0.700
Pagellus erythrinus	8	154–205	0.407	0.100	This work	Augusta	2.322	0.445
	5	110	0.341	0.025	Papetti and Rossi (2009)	Tyrrhenian sea (Lazio)		
	57	115–187	0.180	0.094	Hornung et al. (1980)	Israel[a]		
	9	89–173	0.240	0.190	Gibičar et al. (2009)	Adriatic sea[a]		

(continued on next page)

Table 2 (*continued*)

Species	No.	Range of total length (mm)	HgT muscle ($\mu g\ g^{-1}$)	S.D.	References	Site	HgT liver ($\mu g\ g^{-1}$)	S.D.
	28	140–152	0.042	0.023	Harakeh et al. (1985)	Lebanon		
	5		0.168		Pastor et al. (1994)	Mediterranean sea (Spain)[a]		
	5		0.290	0.044	Keskin et al. (2007)	Marmara sea (Turkey)[a]		
Serranus scriba	2	122–140	2.165	0.768	This work	Augusta	2.581	0.592
	3		1.030	0.459	Gibičar et al. (2009)	Tyrrhenian sea (Tuscany)[a]		
Mullus barbatus	4	155–202	0.815	0.777	This work	Augusta	1.518	0.582
		102–230	0.116	0.056	Hornung et al. (1980)	Israel[a]		
			0.400	0.400	Storelli et al. (2004)	Ionian sea		
			0.490	0.500	Storelli et al. (2004)	Adriatic sea[a]		
	13	117–180	0.700	0.730	Gibičar et al. (2009)	Adriatic sea[a]		
			0.370		Buzina et al. (1995)	Adriatic sea		
			0.318		Buzina et al. (1995)	Adriatic sea (Kastela Bay)[a]		
	59		0.139		Pastor et al. (1994)	Mediterranean sea (Spain)		
			0.010		Martorell et al. (2011)	Mediterranean sea (Spain)		
	30	128–166	0.054	0.025	Harakeh et al. (1985)	Lebanon		
		130–200	0.233		Stoeppler and Nürnberg (1979)	Mediterranean Sea (Sardinia)		
	4		0.036	0.002	Tuzen (2009)	Black Sea (Turkey)[a]		
	5		0.434	0.012	Keskin et al. (2007)	Marmara sea (Turkey)[a]		
Mullus surmuletus	2	200–209	0.662	0.089	This work	Augusta	1.112	
	9	120–160	0.086		Hornung et al. (1980)	Israel[a]		
	59		0.139		Pastor et al. (1994)	Mediterranean sea (Spain)[a]		
	2	185–203	0.250		Stoeppler and Nürnberg (1979)	North sea (German Bight)		
	37		0.060		Bilandžic et al. (2011)	Adr.sea (Croatian coast)		
Scorpaena scrofa	4	93–112	1.082	0.285	This work	Augusta	1.637	0.380
			0.222		Buzina et al. (1995)	Adriatic sea		
			0.390		Buzina et al. (1995)	Adr. sea (Kastela Bay)[a]		
Scorpaena notata	5	114–133	1.340	0.380	This work	Augusta	2.339	0.529
	5		0.490	0.430	Gibičar et al. (2009)	Tyrrhenian sea (Tuscany)[a]		
Illex coindetii	6	33–92	0.078	0.039	This work	Augusta		
	13	52–224	0.100	0.100	Gibičar et al. (2009)	Adriatic sea[a]		
Loligo forbesi	3	45–170	0.147	0.024	This work	Augusta	0.311	0.011
Sepia officinalis	8	108–148	0.766	0.288	This work	Augusta		
Octopus vulgaris	1	123	0.443		This work	Augusta		
Murena helena	1	800.5	2.638		This work	Augusta	3.817	

[a] Polluted site.

inner bay show the widest non-outlier ranges (0.084–1.116 $\mu g\ g^{-1}$ for muscles, 0.109–2.747 $\mu g\ g^{-1}$ for livers) and the most elevated number of outliers and extreme values (Fig. 2a and b). In particular, the highest HgT mean values (2.165 $\mu g\ g^{-1}$ in liver and 2.581 $\mu g\ g^{-1}$ in muscle) were measured in the *S. scriba* species (Table 2).

3.3. THQ and EWI values

Mean THQ and EWI values calculated for each caught species, inside and outside the bay, are reported in Table 3. Most of the fish species inside the bay show higher values (TQa = 1.53–15.8; TQb = 0.66–6.88; EWI = 1.06–11.0) than those outside the studied area (TQa = 0.31–4.20; TQb = 0.66–6.88; EWI = 0.22–2.91). In particular, the highest values were calculated for *M. helena* (TQa = 15.8; TQb = 6.88; EWI = 11.0), *S. scriba* (TQa = 13.0; TQb = 5.65; EWI = 9.02) and *Caranx rhonchus* (TQa = 10.2; TQb = 4.44; EWI = 7.09) caught inside the bay, while, the pelagic species outside the bay show the lowest values (TQa = 0.31–0.88; TQb = 0.14–0.38; EWI = 0.22–0.61). Finally, no significant differences were found between the same or similar species, collected inside (*Pagellus acarne, Pagellus erythrinus, M. barbatus, Mullus surmuletus*) and outside (*Pagellus bogaraveo, P. erythrinus* and *M. barbatus*) the bay.

4. Discussion

4.1. Mercury bioaccumulation effects: length/age vs. HgT content

The Hg accumulation in marine fish primarily depends on some important biokinetic parameters: assimilation from the ingested prey, uptake constants from the aqueous phase, de-toxification rate (Wang, 2012; Wang et al., 1997, 1998; Wang and Fisher, 1999; Dang and Wang, 2011) and environmental features (e.g., Hg concentration and speciation in seawater, dietary sources, etc.) (Wang and Wong, 2003). However, physiological and geochemical species-specific influences on Hg bioaccumulation are still not fully understood (Baines et al., 2002; Xu and Wang, 2002; Wang and Wong, 2003; Dang and Wang, 2012).

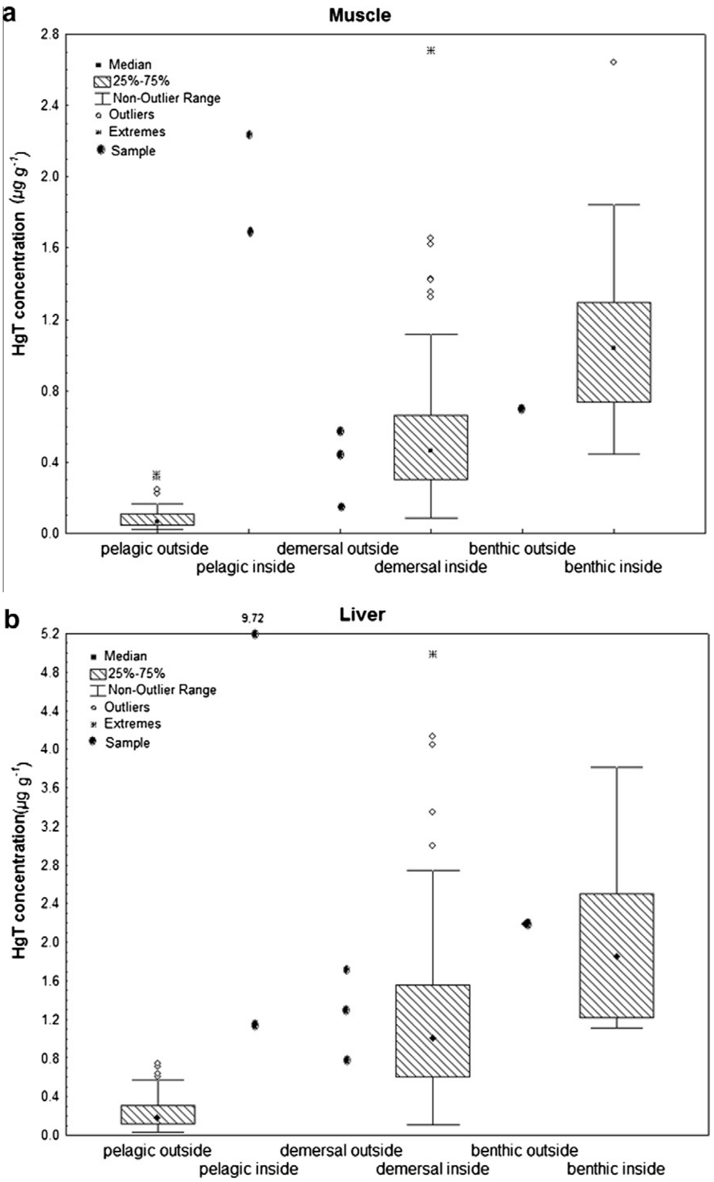

Fig. 2. Box-plots with HgT concentrations in the muscles and livers of pelagic, demersal and benthic fishes.

Several studies have demonstrated that Hg concentrations in the muscles of marine organisms proportionally increase with size and age (Lange et al., 1994; Burger et al., 2001; Green and Knutzen, 2003; Simonin et al., 2008). Moreover, Hg de-toxification rates appear negatively correlated with the fish size (Trudel and Rasmussen, 1997), supporting a potential correlation between Hg levels and size/age in the organisms. However, detailed investigations on different groups of species and on a wide range of HgT concentrations are lacking and, when available, sometimes controversial (Stafford and Haines, 2001), especially for fishes with low mercury levels (average below 0.2 ppm) (Park and Curtis, 1997; Burger and Gochfeld, 2011). Strong correlations between size and Hg levels in fish are reported for Swordfish (*Xiphias gladius*) and Bluefin Tuna (*Thunnus thynnus*) from the Mediterranean Sea (Storelli and Marcotrigiano, 2001), for several pelagic fish species from the Adriatic Sea (Storelli, 2008) and for *S. pilchardus* specimens from Tunisia (Joiris et al., 1999). Furthermore, Burger et al. (2007) found a positive correlation between size and Hg levels for 11 of 14 species of marine fishes collected in the western Aleutians (Bering Sea/North Pacific) and Luten et al. (1987) found the same positive correlation in Atlantic Cod. Moreover, Leonzio et al. (1981) report positive correlations between Hg content and weight in *M. barbatus* and a slight Hg increasing trend with size in *E. encrasicolus* from the northern Tyrrhenian Sea. Finally, Gewurtz et al. (2011) show strong

Table 3
THQ and EWI calculation for each caught species (inside and outside the Bay).

Inside				Outside			
Species	THQa	THQb	EWI	Species	THQa	THQb	EWI
Caranx rhonchus	10.2	4.44	7.09	*Engraulis encrasicolus*	0.31	0.14	0.22
Diplodus annlularis	3.34	1.45	2.32	*Sardina pilchardus*	0.49	0.21	0.34
Diplodus vulgaris	3.86	1.68	2.68	*Boops boops*	0.72	0.31	0.50
Pagellus acarne	1.53	0.66	1.06	*Trachurus trachurus*	0.79	0.34	0.55
Pagellus erythrinus	2.30	1.00	1.60	*Illex coindetti*	0.47	0.20	0.33
Scophaena scrofa	7.17	3.12	4.98	*Loligo forbesi*	0.88	0.38	0.61
Scorphaena notata	8.05	3.50	5.59	*Pagellus bogaraveo*	1.60	0.69	1.11
Mullus barbatus	5.59	2.43	3.88	*Pagellus erythrinus*	3.41	1.48	2.37
Mullus surmuletus	3.97	1.73	2.76	*Mullus barbatus*	4.20	1.82	2.91
Serranus scriba	13.0	5.65	9.02				
Murena helena	15.8	6.88	11.0				
Octopus vulgaris	2.66	1.16	1.85				
Sepia officinalis	4.60	2.00	3.19				

a: USEPA's reference dose (0.1 μg Hg kg bw^{-1} d^{-1}).
b: acceptable daily intake determined by WHO (0.23 μg Hg kg bw^{-1} d^{-1}).

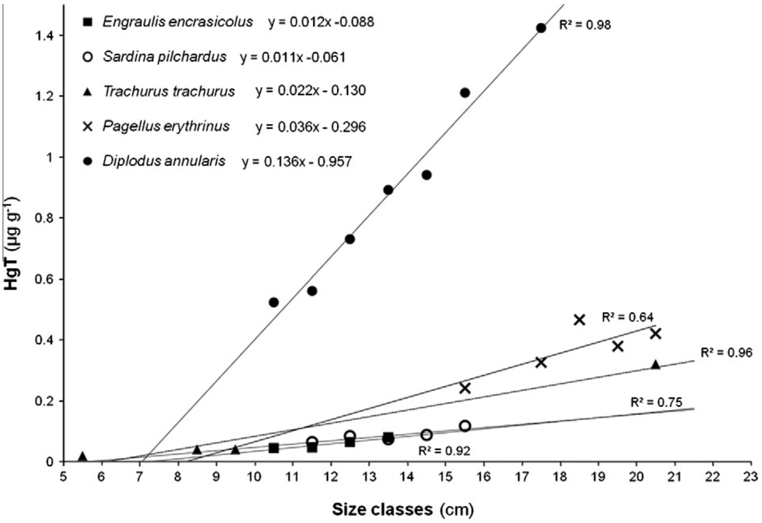

Fig. 3. Relationship between HgT concentrations and total body length for *Sardina pilchardus*, *Engraulis encrasicolus*, *T. trachurus*, *D. annularis* and *P. erythrinus*. Points represent the mean values for each size class.

correlation between HgT concentration and length in most freshwater fishes from the Canadian Great Lakes and Ontario (Canada).

Here, the high number of specimens available from pelagic, benthic and demersal fish species associated with a wide range of length/age and HgT variability detected in tissues offer a challenging opportunity to explore in more depth the actual bioaccumulation processes of Hg in the studied organisms. In particular, we assumed the length of fishes as a reliable parameter for age estimates (Boening, 2000; Waldron and Kerstan, 2001; Scudder et al., 2009; Panfili et al., 2010; Basilone et al., 2011; Bacha et al., 2012) and, thus, reported HgT values vs. length to assess biomagnification of that contaminant with time. Statistically reliable and robust correlations were found between HgT mean values measured in muscles for size classes and length in *S. pilchardus* ($r^2 = 0.75$), *E. encrasicolus* ($r^2 = 0.92$), *Trachurus trachurus* ($r^2 = 0.96$), *Diplodus annularis* ($r^2 = 0.98$) and *P. erythrinus* ($r^2 = 0.64$) (Fig. 3). Specifically, the calculated HgT accumulation rates for *S. pilchardus, E. encrasicolus, T. trachurus, P. erythrinus* and *D. annularis* are 0.011, 0.012, 0.022, 0.036 and 0.136 μg g^{-1} cm^{-1}, respectively, in good agreement with data reported by Hornung et al. (1980) for *P. erythrinus* and *T. trachurus* species. This definitively supports a significant linear HgT-length relationship for the studied fish species and a species-specific accumulation effect on the studied marine organisms.

In our dataset an evident increasing trend was measured between HgT content and age in the two most abundant species, *E. encrasicolus* and *S. pilchardus* (Fig. 4) with significant differences ($p < 0.005$; ANOVA test) among age group, although, the restricted range of available age classes needs a larger data collection.

4.2. Sources of HgT and fish contamination in Augusta Bay

Muscles are the most commonly analysed tissues to monitor Hg levels in fishes because they represent the edible part of the organism associated with human health risk implications (Henry et al., 2004). Indeed, Hg accumulates over time more readily in liver than in muscle, but muscle appears to retain Hg for a much longer period (Boudou and Ribeyre, 1995). Thus, liver may provide information only on short-term exposure to Hg pollution or may bioaccumulate only when an organism is exposed to constant or increasing levels of dietary mercury (Atwell et al., 1998). This is clearly reflected in the studied dataset, where HgT concentration

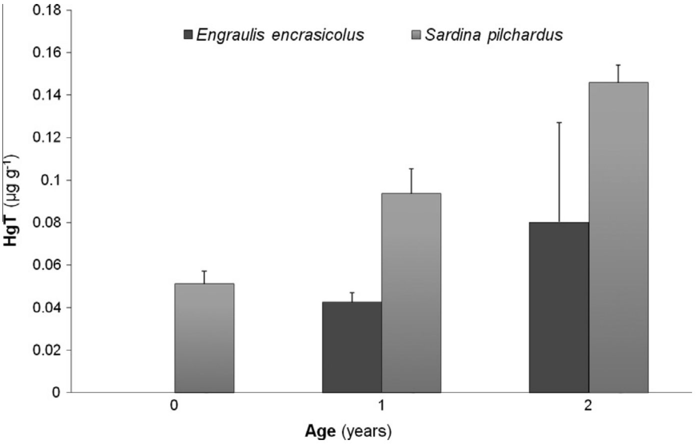

Fig. 4. Relationship between total mercury concentration (median value of HgT) in fish muscles vs. age in *E. encrasicolus* and *S. pilchardus*. Black lines = confidence interval.

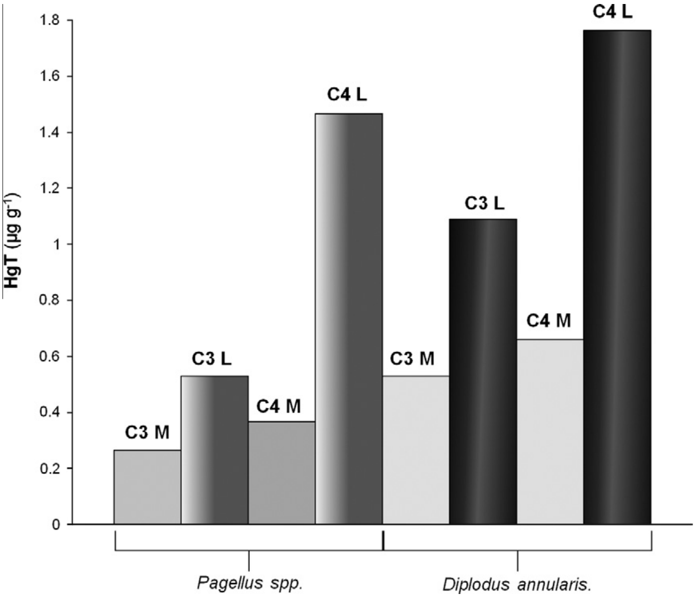

Fig. 5. Differences in muscle (M) and liver (L) HgT contents in *Pagellus* spp. *and Diplodus annularis* from the northern (C3) and the southern (C4) part of Augusta Bay.

measured in liver is up to two orders of magnitude higher than in muscles.

The HgT content measured in the tissues of fishes from Augusta Bay show an increasing trend with habitat depth, specifically, with highest values measured in benthic species with respect to the lowest levels detected in pelagic organisms (Table 2). Additionally, contamination effects show a south-north gradient evident from HgT levels measured on the ubiquitous *Pagellus* spp. and *D. annularis* specimens (Fig. 5). In particular, the highest HgT mean concentrations occur in fishes caught from southern Augusta Bay where bottom sediments show the highest concentrations of mercury (Sprovieri et al., 2011) (Fig. 1). This suggests a key role played by the highly polluted sediments as sources of Hg to the investigated marine environment. Also, measurements of HgT in seawater reported from the bottom, mid and surface waters by ENVIRON International Team (2008) with an average concentration of 0.25 nmol L^{-1} and range of 0.05–0.37 nmol L^{-1} show a crucial effect of Hg efflux from sediments of the bay to the water column with a potential direct impact on the bioaccumulation processes in the trophic web. A direct comparison of HgT content in benthic species from Augusta Bay and other Mediterranean areas affected by comparable Hg discharges by chlor-alkali plant and sewage sludge disposal, specifically Tuscany and Israel (Hornung et al., 1980; Gibičar et al., 2009), show 2–7 times higher values, thus, underlying the combined effects of high pollution levels and specific biogeochemical pathways driving mercury bioavailability in the studied system (Table 2).

Sprovieri et al. (2011) and Fantozzi et al. (2013) have argued on a potential Hg export from Augusta Bay to the Eastern Mediterranean seawater, as a result of the measured 3D circulation system.

Nonetheless, Hg contamination detected in sediments outside of Augusta Bay, by effects of dredged material from the inner bay (Di Leonardo et al., 2008; Tranchida et al., 2010), could also directly influence the state of pollution of the open sea.

Here, we extend the potential role of Augusta Bay as an Hg point source for the open ocean also considering the significant transfer of pollutants by pelagic fishes moving between the inner and external part of the bay. This implies potential effects on the food web of the surrounding area as already reported by several authors studying marine systems (Riisgard and Hansen, 1990; Futter, 1994; Jarman et al., 1996; Atwell et al., 1998). This hypothesis is supported by the high mean HgT concentrations measured in pelagic species caught outside the bay, which are similar to those reported for other sites affected by Hg pollution: the Adriatic Sea (Wolfgang, 1983; Storelli and Marcotrigiano, 2001; Storelli et al., 2002, 2004, 2007, 2010; Gibičar et al., 2009), Turkish areas (Tuzen, 2009), Spanish coastal areas (Pastor et al., 1994) and Israel area (Hornung et al., 1980) (Table 2).

The HgT mean concentrations measured in the livers of *E. encrasicolus* specimens from Augusta Bay are about twice as high ($p = 0.044$) as those measured in fishes from the unpolluted area of Marsala (Table 2), suggesting a direct, short-term effect of the bay pollution on the pelagic fishes. Moreover, the caught pelagic species prefer to inhabit warmer coastal seawaters during their first life stages (Basilone et al., 2011), but they generally move in deeper waters during the older stages (Wirszubski, 1953; Schneider, 1990; Whitehead, 1990), thus, representing a significant and potential vehicle of contaminants to the deep marine food web. This evidence definitively corroborates our hypothesis of a potential Hg export through the food web, from Augusta Bay to the surrounding area.

4.3. Target hazard quotient and weekly intake: a real health risk from fishery in the Augusta Bay?

Although estimation of the target hazard quotient (THQ) and weekly intake (EWI), do not provide a quantitative and definitive estimate on the dangerous health effects on exposed populations, these methodologies offer preliminary information on the health risk level resulting from pollutant exposure. Several authors showed that selenium (Se) offers protection against Hg toxicity (Parízek and Ostádalová, 1967; Satoh et al., 1985; Ralston, 2009; Lémire et al., 2010) that suggests to take in account Se contents in fishes to assess a real risk associated to Hg intake. Positive relationships has been found between Hg and Se contents in different seawater fishes (Burger and Gochfeld, 2011; Dang and Wang, 2011; Calatayud et al., 2012). Ralston et al. (2008) showed that Se:Hg molar ratios above 1 protect against Hg toxicity. However this ratio definitively depends o species-specific toxic-kinetics processes (Watanabe, 2002; Burger and Gochfeld, 2012). This feature leads to a wide variability of Se:Hg molar ratios and makes difficult their use in risk assessment. Accordingly, here we estimated health risk for Hg intake only on THQ and EWI parameters. These indexes are widely used to assess risk associated with fish consumption (Storelli et al., 2004, 2010; Storelli, 2008; Martorell et al., 2011; Domingo et al., 2012). In particular, for no carcinogenic effects, an HQ exceeding 1.0 indicates a potential health risk (US EPA, 1989). In our dataset, either using USEPA's reference dose (TQa) that WHO acceptable daily intake (TQb), species inside the Bay exceeded the value 1 in all cases, while fishes outside the Bay only in demersal and benthic fishes (*P. bogaraveo, P. erythrinus, M. barbatus*) (Table 3). International agencies indicate a provisional tolerable weekly intake (PTWI) of Hg, ranging from 0.7 $\mu g\ kg^{-1}$ body weight (b.w.) (US-EPA, 2004) to 1.6 $\mu g\ kg^{-1}$ b.w. (FAO/WHO, 2006). These limits represent safe values for human population over lifetime. The calculated EWI index exceed the PTWI (US-EPA, 2004; FAO/WHO) in almost all the species collected inside the Bay and in demersal and benthic fishes from outside. In summary, the calculated THQ and EWI highlight that the consumption of fish from inside the Bay represents a serious risk for human health of resident populations and confirm the importance of the current fishing ban in this area. Also, the results suggest caution in the consumption of fishes from outside the Bay, especially of demersal and benthic species, confirming that Hg contamination in this area is a serious concern that calls for appropriate and timely social actions.

5. Conclusions

The main conclusions of this work can be synthesised as follows:

- The high HgT concentrations measured in benthic species from Augusta Bay suggest an active release mechanism of mercury from polluted sediments to the water column, with consequent effects of bioaccumulation in the trophic web.
- High contamination of pelagic species measured in the external zone of the bay confirms the role of the Augusta marine environment as a potential Hg source for the surrounding area and underscores the crucial risk associated with contaminant transfer from the semi-enclosed basin to the open sea.
- The THQ and EWI values advise that consumption of fish from inside the Augusta Bay represents a serious risk for human health of the local populations, while suggest caution in consuming demersal and benthic fishes from outside the Augusta Bay definitively demanding for appropriate social actions.

Conflict of Interest

The authors declare that there are no conflicts of interest.

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Attachment II

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The sea–air exchange of mercury (Hg) in the marine boundary layer of the Augusta basin (southern Italy): Concentrations and evasion flux

E. Bagnato [a,*], M. Sproveri [b], M. Barra [c], M. Bitetto [a], M. Bonsignore [b], S. Calabrese [a], V. Di Stefano [b], E. Oliveri [b], F. Parello [a], S. Mazzola [c]

[a] DiSTeM, University of Palermo, Via Archirafi 36, 90123 Palermo, Italy
[b] IAMC-CNR, Capo Granitola, Via del Mare 3, 91021 Torretta Granitola, Trapani, Italy
[c] IAMC-CNR, Naples, Calata Porta di Massa, Naples, Italy

HIGHLIGHTS

- The Hg evasion flux in the Augusta basin marine boundary layer was examined.
- The human activity has influenced in the past the marine Hg cycle in the Augusta Bay.
- The release of Hg from the Augusta Bay is a source of pollution for the Mediterranean.

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ABSTRACT

The first attempt to systematically investigate the atmospheric mercury (Hg) in the MBL of the Augusta basin (SE Sicily, Italy) has been undertaken. In the past the basin was the receptor for Hg from an intense industrial activity which contaminated the bottom sediments of the Bay, making this area a potential source of pollution for the surrounding Mediterranean. Three oceanographic cruises have been thus performed in the basin during the winter and summer 2011/2012, where we estimated averaged Hg_{atm} concentrations of about 1.5 ± 0.4 (range 0.9–3.1) and 2.1 ± 0.98 (range 1.1–3.1) ng m^{-3} for the two seasons, respectively. These data are somewhat higher than the background Hg_{atm} value measured over the land (range 1.1 ± 0.3 ng m^{-3}) at downtown Augusta, while are similar to those detected in other polluted regions elsewhere. Hg evasion fluxes estimated at the sea/air interface over the Bay range from 3.6 ± 0.3 (unpolluted site) to 72 ± 0.1 (polluted site of the basin) ng m^{-2} h^{-1}. By extending these measurements to the entire area of the Augusta basin (~23.5 km^2), we calculated a total sea–air Hg evasion flux of about 9.7 ± 0.1 g d^{-1} (~0.004 t yr^{-1}), accounting for ~0.0002% of the global Hg oceanic evasion (2000 t yr^{-1}). The new proposed data set offers a unique and original study on the potential outflow of Hg from the sea–air interface at the basin, and it represents an important step for a better comprehension of the processes occurring in the marine biogeochemical cycle of this element.

1. Introduction

Mercury (Hg) is a chronic pollutant of global concern known to be transported long distances in the atmosphere into remote ecosystems (Schroeder and Munthe, 1998). Hg flux into the atmosphere from natural and anthropogenic sources has been reviewed recently and new estimates for the worldwide distribution of anthropogenic emissions have been published (Pacyna and Pacyna, 1998; Kim et al., 2005; Travnikov, 2005; Amos et al., 2012). Although a part of the Hg emitted naturally comes from geological and geothermal sources, much of it is recycled Hg previously emitted from primary or anthropogenic sources, and subsequently re-deposited to terrestrial and ocean surfaces (Ericksen et al., 2005). Hence, as a consequence, a large part of the 2000 t of yearly emissions from natural sources is actually reemission of previously deposited mercury, much of which has an anthropogenic origin. In some instances, it has been discovered that marine sediments contaminated by industrial effluents may be secondary sources of Hg to aquatic ecosystems even though discharge has been strongly reduced or has even ceased (Bothner et al., 1980). The exchange of Hg between oceanic surfaces and the atmosphere represents an important process for the atmospheric cycling and environmental turnover of this element (Mason et al., 1994; Lam-

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* Corresponding author. Tel.: +39 3471258337; fax: +39 091 6169908.
E-mail address: emanuelabagnato@virgilio.it (E. Bagnato).

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borg et al., 1999). The ability of GEM to reemit from terrestrial and aquatic surfaces keeps this element circulating in the environment, with burial into ocean sediments as the only long term sink. According to the global model of Hg biogeochemistry proposed by Mason et al. (1994), the ocean releases about 1/3 of the total global Hg emissions to the atmosphere (about 30% of the total budget of atmospheric mercury on a global scale) and receives about 30–70% of the global atmospheric deposition (Lamborg et al., 2002). Re-emissions from the ocean of previously deposited Hg are dominated by gaseous elemental mercury (Hg^0 or GEM ~ 2000 t yr^{-1}; Mason et al., 1994), the most volatile and long-lived form of this metal. Its low solubility and high Henry's Law constant induce high GEM evasion fluxes from fresh water systems, accounting for about 7–95% of the total estimated atmospheric Hg deposition in that system. By these considerations, currently there is a clear intent to increase both qualitative and quantitative knowledge concerning the processes occurring during the exchange of Hg between sediments, the overlying water column and sea-air interface. Within the frame of the IAMC-CNR/ASP program founded by the Regional Health Department of Syracuse, we performed a short-term (1 yr) monitoring study on Hg distribution and evasional flux in the atmospheric compartment of the Augusta basin (Fig. 1), a site of the Mediterranean Sea strongly affected in the past by the uncontrolled discharge of Hg (since the 1950s) from industrial and petrochemical plants (Sprovieri et al., 2011). This work represents an important step toward a better comprehension of the processes occurring once Hg is re-emitted from the contaminated bottom sediments (which actually represent the main source of Hg for the Bay; Sprovieri et al., 2011) in the water column and finally to the atmosphere. Although the water surface area of the Augusta basin represents only a small part of the total oceanic surfaces on Earth, we aimed this study may improve the global mercury budget and cycle which lack measurements in large parts of the world's marine environments. Our purposes are threefold: (1) to characterize the regional background level of atmospheric GEM as well as evasional fluxes of Hg in the Bay and compare with other areas at various latitudes; (2) to evaluate the regional sources (if any) eventually affecting the GEM_{atm} concentrations; and (3) to discuss the deposition of atmospheric Hg in the Augusta area. With these aims, a dynamic flux chamber coupled with a real-time atomic adsorption spectrometer (Lumex-RA 915+) has been used to measure Hg evasion flux at the sea/air interface during three intensive research oceanographic cruises performed in the winter and summer 2011–2012.

2. Methodology

2.1. Site location

The Augusta basin is within a natural Bay which occupies about 30 km of the eastern coast of the Sicily (Fig. 1a). The southernmost part of the basin hosted one of the most important chlor-alkali plants of Italy (Syndial Priolo Gargallo), which with 765 kg of Hg emission made up over 20% of total Italian emissions in 2001 (Le Donne and Ciafani, 2008). The effects of indiscriminate Hg discharge of the past include high Hg levels in bottom sediments which act as a source of Hg to the water column in the Augusta Bay (ICRAM, 2005; Sprovieri et al., 2011). In detail, sediments lying in the southern part of the Bay show the highest HgT levels (0.1–527.3 mg kg^{-1}) with a large range of variability (median value 23.8 mg kg^{-1}), while the northern area is characterized by sediments containing HgT concentrations varying from 0.1 to 12.7 mg kg^{-1} (median value 1.1 mg kg^{-1}) (Sprovieri et al., 2011). An averaged outflow of total Hg (HgT) from the Bay to the Augusta coastal waters has been estimated to be in the order of about 0.162 kmol yr^{-1} (~0.032 t yr^{-1}; Sprovieri et al., 2011), which corresponds to 1–2% of the amount calculated for the entire Mediterranean area (12.5 kmol yr^{-1}; Rajar et al., 2007). By these considerations it emerges that the Augusta basin may play an important role in exporting mercury into the Mediterranean Sea and represents a point source for that system.

2.2. Atmospheric GEM measurements

Measurements of atmospheric elemental gaseous mercury (GEM) were performed across the Augusta basin on-board the Italian CNR research vessel Luigi Sanzo, during three main oceanographic cruises carried out along the same route in the winter (November 2011) and summer (July 2011–June 2012) (Fig. 1b), chosen out of practical and logistical criteria. For the sake of simplicity, GEM, Hg and Hg^0 are used without distinction in this article, unless otherwise specified. The analysis of atmospheric GEM was performed using an automated real-time atomic adsorption

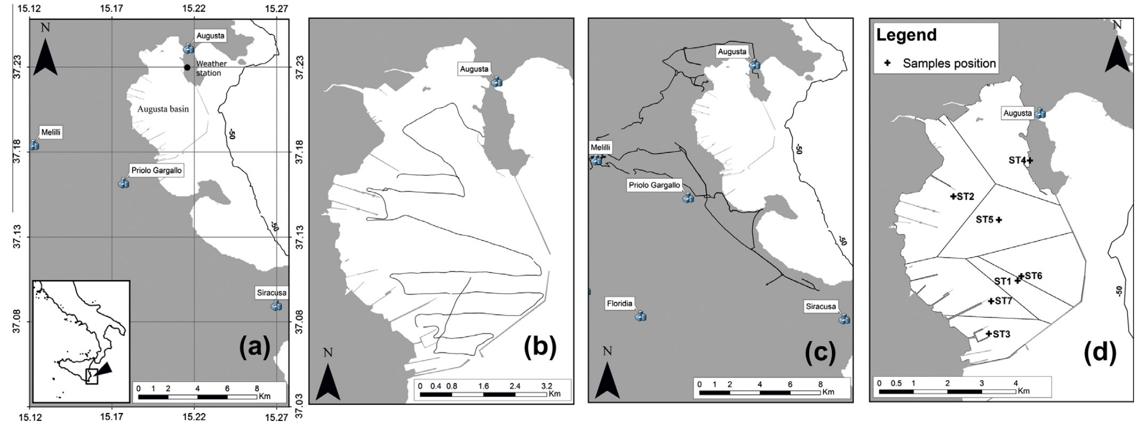

Fig. 1. Maps showing (a) the Augusta basin and the site of the installed weather station used in this study, (b) the routes of the oceanographic cruises inside the Augusta basin, (c) the land trajectories to detect GEM contents in the atmosphere along the coastal area, and (d) the stations for Hg evasion flux measurement by accumulation chamber technique (ST1–7). Map (c) also reports the partition of the entire basin into seven Voronoi polygons, each relative to one station of measurement (see text for detail).

spectrometer (Lumex-RA 915+). The Lumex sampled air at about 20 l min^{-1} directly into the instrument's sampling inlet (~3 cm diameter) at ambient temperature to the multi path detection cell which has an effective path length of 10 m. This multi-path cell has a volume of 0.7 l and air changes in the cell 3 times every 7–10 s. The instrument inlet has an external washable dust filter with a porosity of 5–10 mkm in addition to a coarse dust filter of porosity 100 mkm. The Lumex monitored gaseous elemental mercury (GEM) concentrations using differential atomic absorption spectrometry with correction for background absorption via the Zeeman Effect (Sholupov et al., 2004). A zero correction resets the baseline every 5 min during sampling. The detection limit was ~2 ng m^{-3}, and the instrument has an accuracy of 20%. The accuracy and precision of the applied instrumentation has also been assessed through comparison with the traditional gold trap/CVAFS system used at remote sites elsewhere (Aiuppa et al., 2007; Witt et al., 2008). During the cruises, the air inlet of the analyzer was installed on the upper deck about 3 m a.s.l. to avoid the contamination from ship emissions. We sampled air at 1 s intervals by covering a total marine area of about 60 km at a speed of ~10 km h^{-1}. Lumex has also been employed to measure atmospheric GEM concentration over the land along the shoreline surrounding the Augusta basin (Fig. 1c), in order to assess background Hg levels in the air masses inland. For this purpose, the inlet of the instrument unit was connected to a 1 m-long silicone tube and mounted outside of a side window of the vehicle. GEM concentrations in air were thus continuously quantified at 5 s intervals, by covering about 20 km of the coast by car at a speed of ~20 km h^{-1}. This analyzer has been successfully used in various types of atmospheric mercury measurement campaign (e.g., Kim et al., 2006; Špiric and Mashyanov, 2000; Engle et al., 2006; Wang et al., 2006; Aiuppa et al., 2007; Muresan et al., 2007; Witt et al., 2008; Ci et al., 2011) where it was successfully used for continuous measurements of Hg distribution in the atmosphere over large city areas and various geological contexts both by walking traverse and from moving vehicles.

2.3. Mercury flux assessment at the sea–air interface

For the first time in this area, we used a plexiglass open-bottom dynamic flux chamber (emerged part: 50 × 50 × 50 cm; submerged part: 50 × 50 × 30 cm) technique coupled with a real-time atomic adsorption spectrometer (Lumex-RA 915+) to estimate the sea–air Hg evasion flux in the MBL (Fig. 2). The accumulation chamber was built by the technical staff working in the laboratories of electronic at IAMC-CNR (Capo Granitola), according to the different schemes proposed in literature (Kim and Lindberg, 1995; Carpi and Lindberg, 1998; Covelli et al., 1999; Wang et al., 2006). The Plexiglas was selected since it transmits all visible and UV wavelengths in solar radiation (89% and the 64% of UV-A and UV-B, respectively; Wang et al., 2006), which are responsible for the formation of photo-induced gaseous mercury in water. The floating chamber system was placed on the sea water surface with the edges of the chamber immersed 30 cm into the water to ensure a tight seal with the water, preventing entry of outside air. To homogenize the air inside the chamber two fans have been installed, suspended at about 5 cm from the top of the chamber. After positioning the chamber on the surface and achieving good contact, we were able to reach a steady-state of internal mercury concentration within approximately 10 min. This allowed us to reduce the flux chamber's influence on the environmental parameters of the sea water surface we were investigating, mainly wind speed and waves, because the chamber remains on the water for only a short period of time. Of course, this technique is suitable during relatively calm conditions of the sea, when the influence of these factors is negligible; anyway, the large size of the chamber reduces noise caused by the waves. Mercury flux from the water surface exposed in the chamber (0.25 m^2) was then calculated according to the Eq. (1) (Lindberg and Price, 1999; Zhang et al., 2001):

$$\Phi_{GEM} = Q(C_o - C_i)/A \qquad (1)$$

where Φ_{GEM} is the GEM total emission rate per area and unit time (ng m^{-2} s^{-1}); $(C_o - C_i)$ is the difference in GEM concentrations in air exiting (C_o) and entering (C_i) the chamber (ΔC) (in ng m^{-3}); A is the basal area of the chamber in m^2; and Q is the flow rate of air flowing through the chamber in m^3 s^{-1}. Of course, the concentration differential used in the flux calculation must be greater than the system blank, which we determined based on the ΔC difference measured in the sunlight by sealing the chamber bottom to a large clean surface (a clear polycarbonate plate in our case). The QA/QC protocol of the experiment has been achieved in the field using

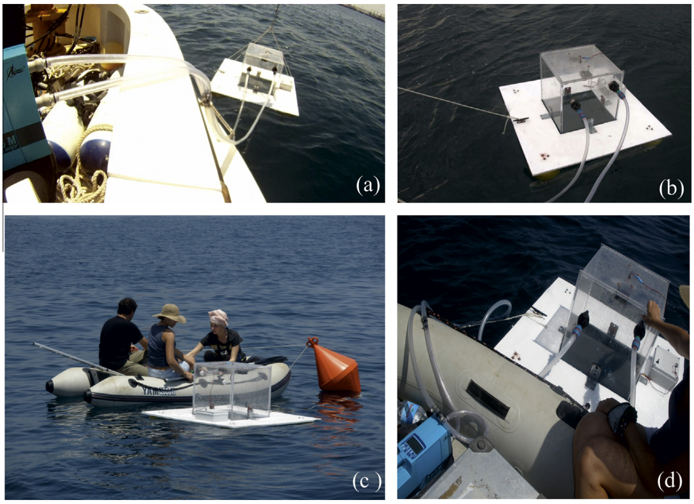

Fig. 2. Positioning (a-b), testing (c) and in real-time measurements (d) of sea–air GEM evasion flux by using the accumulation chamber technique.

blanks. Before and after each oceanographic cruise, the chamber was extensively cleaned with diluted laboratory detergent and several-fold rinsed with Milli-Q water. We find negligible blank value (GEM $_{\text{blank}} \sim 0.15$ ng m^{-3}) which agrees well with the blank tests reported in literature (~0.2 ng GEM m^{-3}; Carpi and Lindberg, 1998; Gustin et al., 1999). The theoretical Hg concentration (from the manual calibration) has been compared to the measured concentration by direct injection into the analytical device and the recovery rate from direct injection into the flux chamber. The overall QA/QC protocol showed that up to 99% of the accuracy has been achieved by the technical protocol, as also confirmed by the low relative standard deviation exhibited by our data.

2.4. Bulk deposition collection

Bulk deposition was collected using a glass-made open collector (wet + dry deposition) according to Iverfeldt (1991) and Jensen and Iverfeldt (1994), which was located on the roof of the port authorities office close to downtown Augusta close to the weather station (Fig. 1a). Rainwater samples were collected at irregular intervals in function of the rainy events which affected the examined area. Samples were analyzed for total mercury concentrations (OSPAR, 1997) by a direct analyzer (Milestone DMA-80), which uses the principle of thermal decomposition, amalgamation and atomic absorption, in operation at IAMC-CNR (Capo Granitola). Before the analysis, each rainwater sample was weighed into a quartz boat, and transferred from the analytical balance to the DMA-80. Sample boats, loaded onto the instrument auto-sampler, are first dried and then thermally decomposed in a oxygen-rich furnace. Mercury and other combustion products are released from the sample and they are carried to the catalyst section of the furnace, where nitrogen and sulfur oxides, as well as halogens and other interfering compounds, are eliminated. Mercury is selectively trapped, in a separate furnace, through gold amalgamation. Combustion by-products are flushed off. The amalgamation furnace is heated and mercury is rapidly released. Mercury is flown via the carrier gas into a unique block with a tri-cell arrangement, positioned along the optical path of the spectrophotometer, where it is quantitatively measured by atomic absorption at 253.65 nm.

3. Results and discussions

3.1. Meterological pattern of the area

A meteorological data set, including wind direction, air temperature, and precipitation amount, was developed using data from the continuous acquisition by a weather station (DAVIS – Vantage Pro 2 Wi-Fi) installed on the roof of the Augusta port authorities office (Fig. 1a). Wind rose diagrams, median wind direction and dispersion parameters were computed by means of "openair" R statistical package. The overall (whole observation period) wind rose diagram (Fig. 3a) showed that the most frequent wind directions were related to NW and NE sectors. Winds from NW sector represents about the 50% of total observations, and were characterized by prevalent N-W direction (25%), while the prevalent one for NE sector (accounting for 35% of the total) was E-NE. We did not identify any relevant relation between the measured Hg concentrations in the MBL and meteorological parameters recorded during the survey.

3.2. GEM distribution in the MBL

The GEM measurements in the MBL over the Augusta basin have been performed along the same route in winter (November 2011) and summer (July 2011–June 2012) (Fig. 1b). During the survey, the wind speed ranged from 4.5 to 9.8 m s^{-1} and T_{air} from about 12–25 °C. During the cruises we measured averaged atmospheric GEM concentrations of ~1.5 ± 0.4 (range 0.9–3.1) and ~2.1 ± 0.98 (range 1.1–3.1) ng m^{-3} in the winter and summer, respectively (Table 1). The time-weighted average GEM concentrations show to some extent seasonal variations, as previously reported in literature for other geographic areas (Sprovieri et al., 2003; Sprovieri and Pirrone, 2008; Wangberg et al., 2008). Variability in our collected Hg data may be ascribed to the different intensity of the natural sunlight between winter and summer which represents a key parameter in controlling rates of % Hg^0 produced and then escaped from seawater surface (Costa and Liss, 1999); anyway the intensity of solar radiation has not been determined in this study. Time series evidence that collected data result somewhat higher than the atmospheric background Hg level measured over the land at the downtown urban site of Augusta (averaged 1.1 ± 0.3 ng m^{-3}; Table 1 and Fig. 4a), while are similar to those detected along the shore close to the dense industrial area surrounding the basin (range 1.5 ± 1.4–2 ± 1.6 ng m^{-3}), where we sporadically measured Hg peaks of about 8–10 ng m^{-3} (Fig. 4a). Estimated GEM at background levels suggests no significant acute toxicity since generally the lowest adverse effect observed has been fixed at 15–30 μg m^{-3} (~15–30 × 10^3 ng m^{-3}; Kazantzis, 2002). Anyway, GEM$_{\text{atm}}$ level over the Augusta basin results are to some extent higher than the background atmospheric mercury values reported for the North Hemisphere (range: 1.5–1.7 ng m^{-3}; Lindberg et al., 2007; evidenced by the dashed red lines in Fig. 4b), while are similar to those reported for a few polluted marine areas, like Tokyo Bay, the South China Sea and the Yellow Sea (1.9 ± 0.6, 2.8 ± 1.5 and 2.3 ± 0.7 ng m^{-3}, respectively; Narukawa et al., 2006; Fu et al., 2010; Ci et al., 2011; Table 1). Our data are also in the range proposed for many other oceans and seas, such as the Mediterranean (1.5 ± 0.3–2 ± 0.6 ng m^{-3}, Sprovieri et al., 2010) and the Adriatic Sea (1.6 ± 0.4 ng m^{-3}, Sprovieri and Pirrone, 2008), the Atlantic Ocean (1.3 ± 0.1–2 ± 0.1 ng m^{-3}, Temme et al., 2003) and the North Pacific Ocean (2.5 ± 0.5 ng m^{-3}, Laurier et al., 2003), while are higher than those measured over the equatorial Pacific Ocean (1.0 ± 0.1 ng m^{-3}, Kim and Fitzgerald, 1986) (Table 1). Finally, our data fit with results from the 2010 MED-OCEANOR cruise campaign recently performed by Fantozzi et al. (2013) in the Eastern Mediterranean (range: 1.3–1.8 ng GEM m^{-3}, averaged: 1.6 ± 0.1 ng m^{-3}; Table 1). By displaying data as a function of latitude (Fig. 5) and for comparison with the atmospheric total gaseous mercury (TGM = GEM + RGM) contents from other marine/oceanic environments (Kim and Fitzgerald, 1986; Slemr and Langer, 1992; Fitzgerald, 1995; Mason et al., 1998; Lamborg et al., 1999; Narukawa et al., 2006; Fu et al., 2010; Ci et al., 2011; Fantozzi et al., 2013) we found a small but discernible inter-hemispheric gradient in GEM resulting from greater emissions of Hg to the atmosphere in the more industrialized Northern Hemisphere. In compiling this diagram we considered that under the normal atmospheric condition, GEM is generally taken more than 95–98% among all the atmospheric Hg species (i.e. RGM and Hg$_p$; Ci et al., 2011). Since RGM is easily adsorbed by the seawater surface, most of the literature reported TGM measurements should be considered as GEM.

3.3. Air–sea GEM flux

Mercury leaves the ocean by evasion of dissolved Hg^0 when it is present at supersaturated concentration in the surface waters with respect to the atmosphere (Kim and Fitzgerald, 1986). Sea–air Hg evasion flux has been measured at seven monitoring stations selected along the Augusta basin (ST1-7; Fig. 1c and Table 2). During the oceanographic cruises, weather conditions were optimal, therefore the effect of wind, waves and presence of clouds were

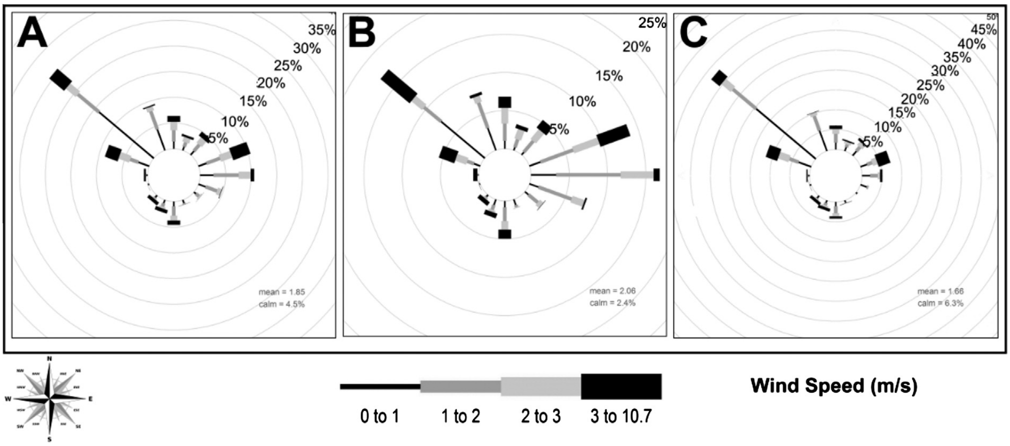

Fig. 3. Wind rose diagram built for the whole observation period showing the most frequent wind directions. Winds from NW sector represents about the 50% (c) of total observations, and were characterized by prevalent N-W direction (25%) (b), while the prevalent one for NE sector (accounting for 35% of the total) was E-NE (a).

Table 1
Gaseous elemental mercury (GEM) concentrations measured in the MBL over the Augusta basin compared to literature data for other acquatic environments. For a more detailed description on averages and methods the reader is referred to the original article.

Measurement sites	Period	GEM (ng m^{-3})		S.D. (*n*)	Methods	References
		Range	Mean			
Augusta Basin MBL						
Winter period averaged	2011/11/29–30	(0.9–3.1)	1.5	0.4 (8137)	Lumex RA-915 + analyzer	Present study
Summer period averaged	2011/07/11–12–2012/06/23–24	(1.1–3.1)	2.1	0.98 (159)	Lumex RA-915 + analyzer	Present study
Augusta downtown	11/11/2011	(0.8–1.4)	1.1	0.3 (129)	Lumex RA-915 + analyzer	Present study
Other sites						
Sweden coastal areas	October 1979–September 1980	(2.7–4)	3.4	0.4 (12)	Gold-traps	Brosset (1992)
North Atlantic ocean	October 1977–January 2000	(1.7–2)	2	0.1 (8)	Tekran 2537A analyzer	Temme et al. (2003)
South Atlantic ocean	October 1977–February 2001	(1–1.5)	1.3	0.1 (10)	Tekran 2537A analyzer	Temme et al. (2003)
South Atlantic	1996/05/20–1996/06/17	(1.2–1.9)	1.6	0.2 (14)	Gold-traps	Lamborg et al. (1999)
North pacific ocean	2002	(1.6–4.7)	2.5	0.5 (n.a.)	Tekran 2537A analyzer	Laurier et al. (2003)
Equatorial pacific ocean	1984/07/03–1984/06/08	(0.8–1.1)	1.0	0.008 (23)	Gold-traps	Kim and Fitzgerald (1986)
Indian ocean	2007	(1–1.5)	1.2	0.06 (n.a.)	Tekran 2537A analyzer	Witt et al. (2010)
Eastern Mediterranean sea	August 2003–September 2006	(1.3–2)	1.5	0.3 (5)	Tekran 2537A analyzer	Sprovieri et al. (2010)
Western Mediterranean	August 2003–July 2007	(1.2–2.7)	2	0.6 (3)	Tekran 2537A analyzer	Sprovieri et al. (2010)
East Mediterranean	2010/08/26–2010/09/13	(1.3–1.8)	1.6	0.1 (15)	Tekran 2537A analyzer	Fantozzi et al. (2013)
Baltic sea	1997/07/02–15	(1.4–2)	1.7	0.2 (11)	Tekran 2537A analyzer	Wängberg et al. (2001)
Baltic sea	1998/03/02–15	(1.2–1.6)	1.4	0.1 (9)	Tekran 2537A analyzer	Wängberg et al. (2001)
Adriatic sea	2004/10/26–2004/11/12	(0.8–3-3)	1.6	0.4 (n.a.)	Tekran 2537A analyzer	Sprovieri and Pirrone (2008)
Tokyo Bay	2003/12, 2004/10, 2005/01	(1.1–2.8)	1.9	0.6 (22)	Automated Hg analyzer	Narukawa et al. (2006)
South China sea	2008/05/09–2009/05/18	(1.5–4.5)	2.8	1.5 (n.a.)	Tekran 2537A analyzer	Fu et al. (2010)
Yellow sea	July 2007–May 2009	(1.12–7)	2.3	0.7 (1206)	Lumex RA-915 + analyzer	Ci et al. (2011)

n.a. = Not available.

not taken in consideration in discussing results. Our data range from 3.6 ± 0.3 (unpolluted site) to 72 ± 0.1 ng Hg m^{-2} h^{-1} (most polluted site) (Table 2), indicating that the sea–air evasion flux of Hg from the basin is not uniformly distributed but varies spatially (see Fig. 1c and Appendix I), while any particular trend across the two seasons (November 2011–June 2012) has been observed. Each flux value is devoid of the blank effect, since we subtracted the chamber blank value. The higher Hg evasion fluxes were estimated in the southern part of the basin (sampling stations ST1 and ST3, accounting for about 36 ± 0.3 and 72 ± 0.1 ng Hg m^{-2} h^{-1}, respectively; Fig. 1c), the most contaminated area of the basin in terms of Hg contained in the bottom sediments (0.1–527.3 mg Hg kg^{-1}, median value 23.8 mg Hg kg^{-1}; Sprovieri et al., 2011). On the other hand, the lowest Hg flux has been measured close to the northern sector of the basin (ST4, 3.6 ± 0.3 ng Hg m^{-2} h^{-1}; Table 2 and Fig. 1c), where the bottom sediments exhibited quite low Hg contents (range: 0.1–12.7 mg kg^{-1}; median value 1.1 mg kg^{-1}; Sprovieri et al., 2011). These results suggest that the marine sediments are key contributors of Hg to the marine ecosystem and hence may represent a potential source of Hg to the atmosphere. By comparing our data with literature cases for many marine environments (Table 2), GEM_{atm} flux over the Augusta basin resulted to be one order of magnitude higher than the averaged values reported for the Pacific Ocean (3 ± 2 ng m^{-2} h^{-1}; Kim and Fitzgerald, 1986), the Mediterranean Sea (2.2 ± 1.5 ng m^{-2} h^{-1}, Fantozzi et al., 2013; 2.5 ± 1.2 ng m^{-2} h^{-1}, Gardfeldt et al., 2003; 2.4 ± 1.5 ng m^{-2} h^{-1}, Ferrara et al., 2000), the Tyrrenian Sea (4.2 ± 3.2 ng m^{-2} h^{-1}, Gardfeldt et al., 2003; 1.6 ± 1.3 ng m^{-2} h^{-1}, Andersson et al., 2007), the Artic Ocean (2.4 ng m^{-2} h^{-1}, Andersson et al., 2008), the South China Sea (4.5 ± 3.4 ng m^{-2} h^{-1}, Fu et al., 2010), and the Tokyo Bay (5.8 ± 5 ng m^{-2} h^{-1}; Narukawa et al., 2006). In detail, our results are comparable both to the Hg flux

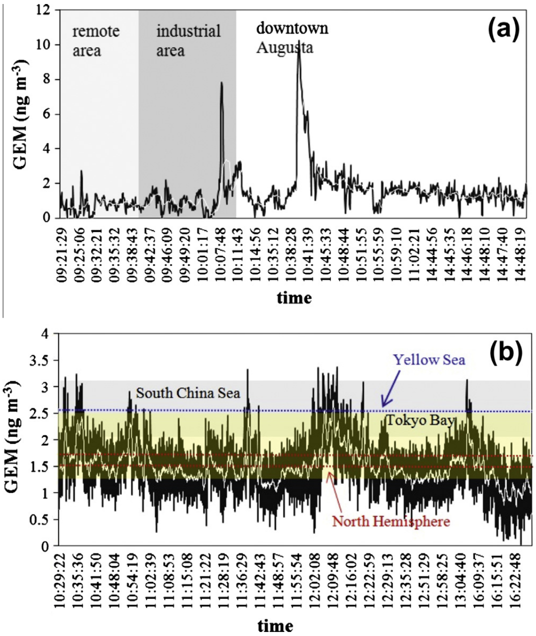

Fig. 4. Time series atmospheric GEM concentration measured (a) in the atmosphere over remote, industrial and urban areas close to the Augusta basin, and (b) at the MBL above the basin. (a) The atmospheric background Hg level measured over the land at the downtown urban site of Augusta is quite low (averaged 0.9 ± 0.5 ng m^{-3}), while we measured GEM concentrations peaks of about 8–10 ng m^{-3} along the coastline close to the dense industrial area surrounding the basin. (b) The yellow and grey areas indicate the concentration range of GEM measured over the Tokyo Bay (range: 1.3–2.5 ng m^{-3}) and the South China Sea (range: 2.1–3.1 ng m^{-3}), respectively, compiled by literature data (Narukawa et al., 2006; Fu et al., 2010). Blue dashed line indicates the averaged GEM value reported for the atmosphere over the polluted area of the Yellow Sea (Ci et al., 2011). Finally, our data result somewhat from similar to slightly higher than the range found at the North Hemisphere (red dashed lines; range: 1.5–1.7 ng m^{-3}; Lindberg et al., 2007). The simple moving average of our data (SMA) is also reported (white line) in both the graphs. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

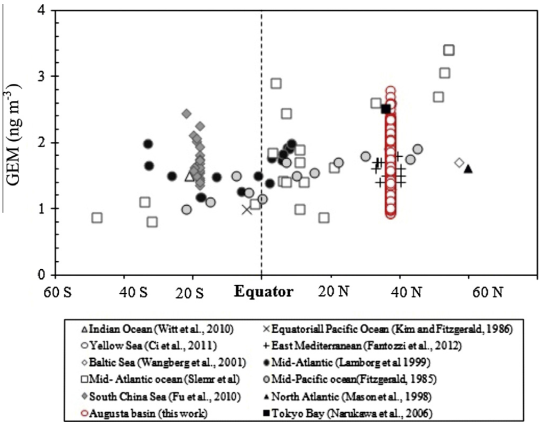

Fig. 5. Values for GEM found as a function of latitude over the Augusta basin. Also shown are compiled values for several marine/oceanic environmental systems (see text for the references).

value estimated over the Yellow Sea (3.2–44 ng m^{-2} h^{-1}; Ci et al., 2011) and the Atlantic Ocean (20–80 ng m^{-2} h^{-1}; Mason et al., 1998), this last containing extremely high dissolved gaseous mercury levels in waters. From Table 2it emerges that most of the listed worldwide Hg sea/air evasion fluxes have been calculated indirectly by using the gas-exchange model (GEM; Liss and Slater, 1974); while only two data (plus the present study) refer to Hg flux values estimated by the dynamic flux chamber technique (DFC). The use of the dynamic flux chamber technique coupled with a real-time atomic adsorption spectrometer (Lumex-RA 915+) thus represents an important step aimed to refine the estimation method to assess Hg fluxes from environmental surfaces (Wang et al., 2006). This technique also aims to reduce the uncertainty in the goodness of processing data often given by the calculation model, strongly dependent from the choice of gas transfer parameterizations (Wanninkhof, 1992) and diffusion coefficient of mercury (Liss and Slater, 1974). To evaluate the impact of Hg emissions from different sources we must have a clear understanding of the factors controlling emissions, develop a data base of emissions from substrates with a wide range of Hg concentrations, and develop a framework for scaling point source measurements to broad areas. As listed in Table 2, our data, and more in general Hg evasion rates from acquatic environments, result to be higher than Hg flux from background uncontaminated soils (~0.9 ng Hg m^{-2} h^{-1}), while are comparable to those reported from volcanic/geothermal areas and substrates associated with hydrothermal systems (~14 and 83 ng Hg m^{-2} h^{-1}, respectively; Table 2). The highest Hg fluxes measured in areas of thermal activity are most likely due to a combination of diffuse Hg-bearing hydrothermal gas flow through soil and elevated Hg concentrations in thermal area substrates (Varekamp and Buseck, 1984). Finally, Hg flux measured at the sea/air interface in the Augusta Bay results to be several orders of magnitude lower than Hg released from areas associated with important ore deposits and metal mining, which are typically enriched in Hg relative to natural background concentrations (Table 2), and have averaged fluxes ranging from background rates (2 ng Hg m^{-2} h^{-1}) to tens of thousands of ng m^{-2} h^{-1} (3730–118 000 ng Hg m^{-2} h^{-1}; Table 2). In order to calculate the total sea–air Hg evasion flux over the entire surface area of the Augusta basin (about 23.5 km^2), we used the model of territorial distribution proposed by Aurenhammer (1991) (the 'Voronoi Polygons' method). This method allowed us to split the basin in seven different areas (ST1-7, in km^2) each accounting for a different % of the total Hg evasion flux. Thus, we estimated a cumulative Hg evasion flux for the whole basin of about 0.004 t yr^{-1} (~9.7 ± 0.1 g d^{-1}), which accounts for ~0.0002% of the global mercury oceanic evasion of 2000 t yr^{-1} proposed by Mason et al. (1994). Anyway, this value (9.7 ± 0.1 g d^{-1}) results to be lower than the total Hg flux emitted from the polluted Tokyo Bay (range 19–249 g d^{-1}; Sakata et al., 2006; Narukawa et al., 2006), but it is significant if we consider that the extent of the water surface area of the Augusta basin represents only a trivial % of the total oceanic surfaces on Earth (3.6×10^8 km^2; Eakins and Sharman, 2010) and 1/5 of the Tokyo Bay surface area (1000 km^2).

3.4. Bulk depositional flux assessment

Long-range transport of atmospheric gaseous Hg, followed by wet and dry deposition, is an important process by which Hg is supplied to terrestrial and aquatic ecosystems far from its source. Our preliminary data collected during a very short-term survey (from August 2011 to April 2012) (range: 21–32 ng L^{-1}; Appendix II) are comparable to those reported for rainwaters collected at the North Pacific Ocean (10–50 ng L^{-1}; Nishimura, 1979) and the North Sea (30 ng L^{-1}; Cambray et al., 1979). We also found a good correlation with Hg levels found in precipitations collected close to a chlorine caustic electrolysis plant (industrial area; 17 ng L^{-1}) and

Table 2
Mercury evasion flux from some acquatic environments reported in literature including this study. For a more detailed description on averages and methods the reader is referred to the original article.

Measurement sites	Date	Hg(0) evasion flux (ng m^{-2} h^{-1})		Methods	References
	(year-month-day)	Range	Mean (SD; *n*)		
Augusta basin					
ST1	29/11/2011	(35.6–36.3)	36 (0.3; 2963)	DFC	Present study
ST2	29/11/2011	(14.2–14.5)	14.4 (0.1; 2965)	DFC	Present study
ST3	30/11/2011	(71.8–72.1)	72 (0.1; 2958)	DFC	Present study
ST4	29/11/2011	(3.2–3.9)	3.6 (0.3; 2963)	DFC	Present study
ST5	24/06/2012	(10.4–11.1)	10.8 (0.3; 2752)	DFC	Present study
ST6	23/06/2012	(7.1–7.3)	7.2 (0.1; 3244)	DFC	Present study
ST7	25/06/2012	(17.8–18.2)	18 (0.2; 4293)	DFC	Present study
Other acquatic sites					
Equatorial Pacific ocean	1984/07/03–1984/06/08	(0.5–8)	3 (2; 22)	GEM	Kim and Fitzgerald (1986)
Western Mediterranean	2003/08/20–23	(4.1–6.2)	5.1 (1; 275)	GEM	Andersson et al. (2007)
Western Mediterranean	2000/07/14–2000/08/09	(0.5–4.5)	2.5 (1.2; 6)	GEM	Gardfeldt et al. (2003)
Eastern Mediterranean	2000/07/17–23	(1.6–15.2)	7.9 (4.2; 10)	GEM	Gardfeldt et al. (2003)
Eastern Mediterranean	2010/08/26–2010/09/13	(0.2–4.9)	2.2 (1.5; 17)	GEM	Fantozzi et al. (2013)
Mediterranean Sea	1998/02/06–1998/09/22	(1.2–5.7)	2.4 (1.5; 6)	DFC	Ferrara et al. (2000)
Tyrrenian sea	2003/08/27–2004/10/29	(0.4–4.1)	1.6 (1.3; 675)	GEM	Andersson et al. (2007)
Tyrrenian sea	2000/07/29–2000/08/08	(0.1–9.9)	4.2 (3.2; 7)	GEM	Gardfeldt et al. (2003)
Ionian sea	2003/08/08–2004/11/11	(0.8–6.6)	2.7 (1.8; 888)	GEM	Andersson et al. (2007)
Adriatic sea	2004/11/02–10	(2–9.7)	5.4 (2.5; 401)	GEM	Andersson et al. (2007)
North Adriatic sea	2004/11/05–06	(23.7–33.2)	28.4 (4.7; 104)	GEM	Andersson et al. (2007)
Strait of Sicily	2003/08/06–2004/03/26	(0.7–3.5)	2.1 (1.4; 329)	GEM	Andersson et al. (2007)
Mediterranean coastal water	2000/07/31–2000/08/07	(2.7–4.5)	3.7 (0.8; 63)	DFC	Gardfeldt et al. (2003)
North Atlantic Ocean	2005/07/07–11	(−0.6 to 2.5)	0.4 (0.3; 559)	GEM	Andersson et al. (2011)
Baltic sea	1997/07/02–15	(6–89)	31 (25; 11)	GEM	Wängberg et al. (2001)
Artic ocean	2005/07/13–2005/09/25	(n.a.)	2.4 (n.a.)	GEM	Andersson et al. (2008)
North sea	1992/09/n.a.	(2.4–46)	20 (13; 11)	GEM	Baeyens and Leermakers (1998)
South China Sea	2007/08/11–27	(0.2–15.3)	4.5 (3.4; 40)	GEM	Fu et al. (2010)
Tokyo Bay	2003/12/10–2005/01/12	(0.1–22)	5.8 (5; 22)	GEM	Narukawa et al. (2006)
Yellow sea	2010/07/10–17	(3.2–44)	18.3 (11.8; 40)	GEM	Ci et al. (2011)
Land evasion					
Background unpolluted soils (US)	n.a.	(0.3–0.8)	0.9 (0.2; 1326)	DFC	Ericksen et al. (2006)
Volcanic/geothermal areas (LVC)	2000/04/14–15	(5.2–19.8)	13.7 (8; 12)	DFC	Engle and Gustin (2002)
Mineralized area (Peavine peak, Nevada)	2000/04/14–15	(2–15)	10 (n.a.; 16)	DFC	Engle and Gustin (2002)
Mine-waste enriched soils (Mt. Amiata)	2008/08/27–28	(250–8000)	3730 (n.a.; 56)	DFC	Fantozzi et al. (2013), in press
Gold Mines (Venezuela)	2004/05/16–31	(650–420100)	118000 (n.a.; 12)	DFC	Garcıa-Sanchez et al. (2006)
Hydrothermal systems (Lassen Park)	2004/08/20–21	(-110 to 103)	12 (n.a.; 13)	DFC	Engle et al. (2006)
Hydrothermal systems (Yellowstone)	2003/09/12–2004/09/01	(-27 to 541)	83 (n.a.; 106)	DFC	Engle et al. (2006)
Sulfur Bank geothermal area	n.a.	(436–510)	n.a (n.a.)	DFC	Gustin (2003)

DFC = dynamic flux chamber; GEM = gas-exchange model; n.a. = not available.

to the mineralized area of Mt. Amiata (Cinnabar deposits) near vapor-dominated geothermal springs (14.4 ng L^{-1}) (Ferrara et al., 1986). By attempting to calculate a first Hg bulk depositional flux (wet + dry) for the Augusta basin, we used the following relation:

$$\Phi_{Hg} = (C_{Hg} \cdot P)T^{-1} \tag{2}$$

where C_{Hg} is the concentration of Hg in rain (in ng L^{-1}), P is the amount of precipitation (in mm), and T is the exposition time of the collector (in days). We estimated a preliminary Hg bulk depositional flux ranging from 0.05 to 0.23 µg m^{-2} d^{-1} (weighted average of 0.10 µg m^{-2} d^{-1}; Appendix II). Although our estimated average Hg bulk deposition flux (35.8 µg m^{-2} yr^{-1}) at the Augusta basin is higher than the values calculated by Mason et al. (1994) to ocean (from 0.13 to 9.5 µg m^{-2} yr^{-1}) and land (0.1–19.8 µg m^{-2} yr^{-1}) at various latitudes (Downs et al., 1998), it results to be one order of magnitude lower than the annually atmospheric Hg flux released in the MBL (maximum emission ~315 µg m^{-2} yr^{-1}; this work).

4. Conclusions

Mercury has an extremely complex cycle in the Earth's ecosystems and the environmental bodies are both active sink and source for Hg. The exchange of mercury between natural surfaces and the atmosphere is an important process for the atmospheric cycling and environmental turnover of this element. The new data set proposed in this study offers a unique and original opportunity to study the potential outflow of Hg from the sea–air interface at the Augusta basin, and will serve as a basis for future estimates on Hg mass balance in this area.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2013.07.025.

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