The abundance, distribution and speciation of mercury in waters and sediments of the Adriatic Sea – a review

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This review focuses on mercury speciation in the Adriatic Sea, a marginal sea of the Mediterranean, which represents its distinct biogeochemical subunit due to anthropogenic mercury loadings. The current knowledge about mercury cycling in the Adriatic is presented through an overview of the state of the art of research in this area: temporal and spatial distributions and occurrence of mercury species in seawater and sediment, and chemical transformations. We summarised research results of mercury speciation in order to describe its presence and fate in the Adriatic Sea. The Adriatic Sea represents a net source of mercury to the Mediterranean Sea due to the highest total mercury concentrations observed in the North Adriatic Sea and the highest methylmercury concentrations in the South Adriatic Pit. However, the biogeochemical cycle of mercury is not completely known and our understanding of mercury transport between compartments and its (bio)transformations is limited. Future research needs to focus on microbial and chemical processes of mercury transformations to improve our understanding of the impacts of mercury contamination on the environment and human health in the Adriatic Sea.

Key words: mercury, chemical speciation, methylmercury, Adriatic, Mediterranean

INTRODUCTION

Among trace metals, mercury (Hg) is one of the contaminants of most concern because of its high toxicity, persistence and accumulative behaviour in the environment and biota (UNEP, 2013). The atmosphere is the most important medium that transports Hg around the globe (SPROVIERI *et al.*, 2010). Gaseous mercury can reside in the atmosphere and be transported over large geographical distances and exchanged with land or surface waters. Hence, mercury contamination is a global environmental prob-lem (AMAP/UNEP, 2013; UNEP, 2013). Due to transformation and transport processes, mercury can travel between environmental compartments: from atmosphere to water, soil and biota. The pathways and fate of mercury in the aquatic environment are important due to chemical and biological processes affecting speciation, partitioning and bioavailability of mercury (UNEP, 2013).

The chemical form of Hg in aquatic systems strongly depends on environmental conditions that determine its mobility and reactivity (AMAP/UNEP, 2013), and the concentration of inorganic

and organic complexing agents (FITZGERALD *et al.*, 2007). In seawater, mercury has a very reactive chemistry. It can be present in different forms, whether dissolved or bound to particulates. The main dissolved Hg fractions are dissolved elemental mercury (DEM), Hg(II) complexes with organic and/or inorganic ligands, reactive mercury (RHg), and organomercury compounds (methylmercury (MeHg) and dimethylmercury (DMHg)) (HORVAT *et al.*, 2003; O'DRISCOLL *et al.*, 2005). Binding of mercury species onto particulate matter in water causes their settling and burying in sediments, which is a major pathway for removal of mercury from the biologically active environment (UNEP, 2013). Remobilisation from sediments is an important source of Hg to coastal and open marine systems and potentially to biota (ŽAGAR *et al.*, 2013). Most mercury enters the marine environment by wet or dry deposition, with a significant fraction in oxidised form (SOERENSEN *et al.*, 2010; ZHANG *et al.*, 2009). Exceptions are small, semi-enclosed basins where river discharges, coastal erosion and ocean currents account for half of mercury input (UNEP, 2013). Rivers are the most important sources of mercury contamination from land. While riverine Hg inputs dominate in coastal watershed systems, combined atmospheric and riverine inputs are observed in "multiple-input" waters (CHEN *et al.*, 2016). Major part of deposited mercury into the ocean is re-emitted to the atmosphere. Due to supersaturation, mercury emitted from open ocean to the atmosphere is mostly Hg^0, whereas the majority of deposited Hg is oxidised mercury (SPROVIERI *et al.*, 2010). It is easily deposited to surface waters by wet deposition because of high solubility (HEDGECOCK *et al.*, 2003; HOLMES *et al.*, 2009; SPROVIERI *et al.*, 2003).

Surface seawater, especially its euphotic zone, is an important compartment for the global Hg biogeochemical cycle (UNEP, 2013). Volatile Hg species (DGM; sum of DEM and DMHg) diffuse from deep ocean waters to the surface and evaporate into the atmosphere. The major sources of DGM are biological processes in deep and surface waters (DRISCOLL *et al.*, 2013; LANZILLOTTA *et al.*, 2002), as well as geothermal/ hydrothermal fields at the sea bottom (FANTOZZI *et al.*, 2009; FERRARA *et al.*, 2000; HORVAT *et al.*, 2003; PIRRONE *et al.*, 2010). In surface waters, photoreduction and photooxidation are two important driving forces for the DEM cycle (COSTA & LISS, 1999; LANZILLOTTA *et al.*, 2002; QURESHI *et al.*, 2010). DMHg can be the dominant Hg specie in the deeper waters (MASON *et al.*, 2012) but it readily evades from surface waters and is photochemically degraded (FITZGERALD *et al.*, 2007; FITZGERALD & LAMBORG, 2003). Mercury chemistry in the open Mediterranean waters is very reactive, which results in elevated MeHg and DGM concentrations (MONPERRUS *et al.*, 2007a). MeHg produced in the sediments by sulphate reducing bacteria can be released to the overlying water (EMILI *et al.*, 2011, 2014; KORON & FAGANELI, 2012; MONPERRUS *et al.*, 2007b) and could constitute an important source of the MeHg content in marine biota. However, the estimated methylated mercury fluxes in the ocean suggest that riverine input, coastal sources and atmospheric deposition are insufficient to explain observed methylated Hg sinks in the ocean (bioaccumulation, removal by fisheries, photochemical and biological degradation, and direct removal to the deep ocean and sediments) (MASON *et al.*, 2012). Findings based on detailed MeHg profiles support the hypothesis that *in situ* sources of MeHg are dominant over advection (COSSA *et al.,* 2009). There are two zones of MeHg productivity connected to the re-mineralisation of organic carbon in the water column: first in the bottom of the euphotic layer (COSSA *et al.*, 2009, 2011; HEIMBÜRGER *et al.*, 2010) and the other at the oxygen minimum in the sub-thermocline (BOWMAN *et al.*, 2015; HAMMERSCHMIDT & BOWMAN, 2012; HEIMBÜRGER *et al.*, 2010). Conversely, photochemical and microbial demethylations of MeHg are the major removal processes of MeHg in the ocean (FITZGERALD *et al.*, 2007; LEHNHERR *et al.*, 2011).

Microbial activity can convert inorganic mercury into MeHg, which is rapidly incorporated into the food web and biomagnifies throughout trophic levels. MeHg is a powerful neurotoxin affecting fish and wildlife (UNEP, 2013). Due to its toxicological properties, pos-

sible presence in food, and transfer to humans, MeHg is the most important form of mercury; fish and aquatic biota are the predominant food sources involved in human exposure (AMAP/UNEP, 2013).

Sea represents a significant part of the mercury cycle in the environment. The Mediterranean and Adriatic Sea are especially important due to the presence of natural and anthropogenic sources of mercury contamination. Research results in the Mediterranean and Adriatic Sea have demonstrated that mercury is present in elevated concentrations in biota (BERTO *et al.*, 2006; CULLAJ *et al.*, 2004; GIANI *et al.*, 2012; HORVAT *et al.*, 2014; KLJAKOVIĆ-GAŠPIĆ *et al.*, 2006; MIKAC *et al.*, 1989; STORELLI *et al.*, 1998; TROMBINI *et al.*, 2003) compared to the Atlantic Ocean. The objective of this paper is to describe mercury contamination and emphasise the importance of its speciation in the Adriatic Sea as a biogeochemical subunit of the Mediterranean Sea. We

evaluate the current state in the Adriatic Sea by presenting relevant spatial and temporal changes in mercury concentration in different compartments.

STUDY AREA

The Mediterranean Sea is an enclosed basin that includes large but diverse coastal and marine ecosystems. Strait of Sicily separates Western and Eastern basins, each comprised of four seas (Fig. 1). The Mediterranean Sea connects to the Atlantic Ocean through the Strait of Gibraltar and to the Black Sea through the Bosporus-Marmara-Dardanelles system. The Adriatic Sea is an elongated basin and the northernmost part of the Mediterranean Sea with which water is exchanged through the Strait of Otranto (Fig. 1). The Adriatic Sea is 783 km long and about 200 km wide (UNEP, 2012). It is divided into three regional basins (north, central and south)
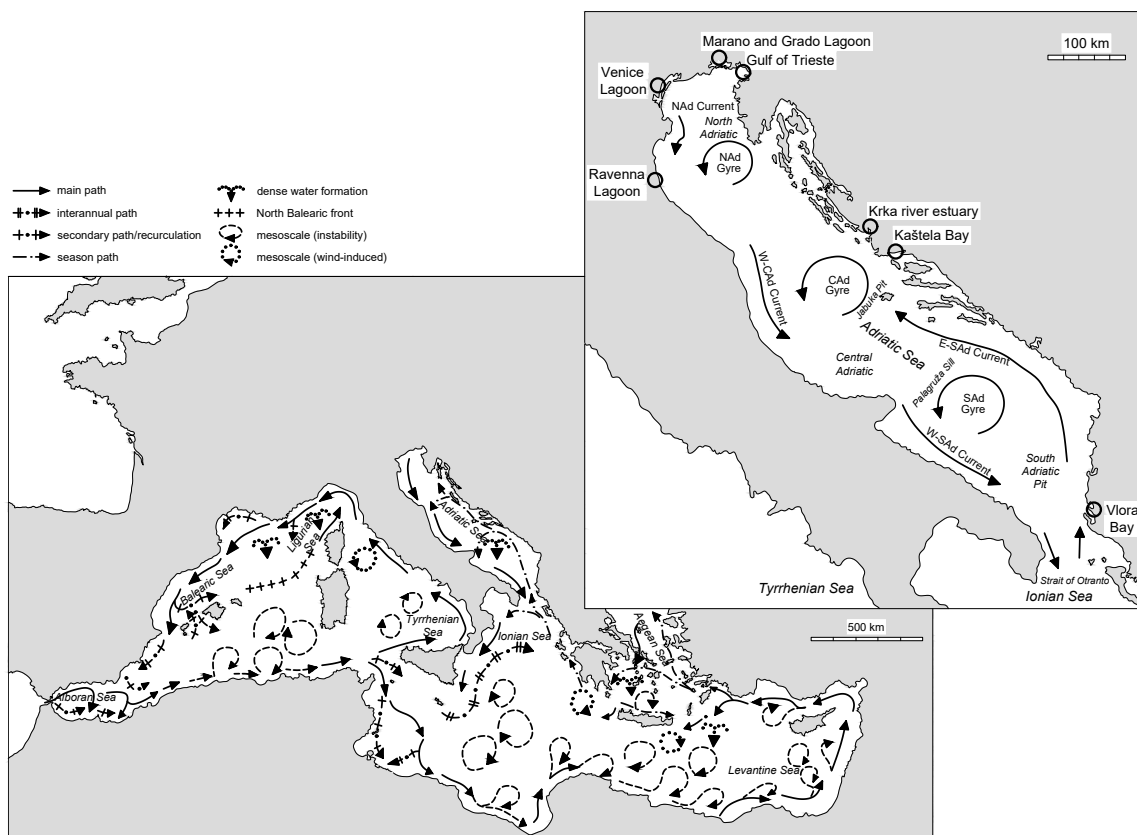

Fig. 1. Surface water circulation flows and geographical divisions of the Mediterranean and the Adriatic Sea. Redrawn from KOTNIK et al. (2015) and MILLOT & TAUPIER-LETAGE (2005)

which differ in latitude, bathymetry, physiography and biogeochemical characteristics (UNEP, 2012). Northern Adriatic is very shallow with an average bottom depth of 35 m. The central part is on average 140 m deep while the southern end is characterised by a wide depression (~1250 m) (BENSI et al., 2014). The Adriatic water circulation (Fig. 1) is dominated by North Adriatic current (N-Ad current), cyclonic Central and Southern Adriatic gyres (CAd and SAd), eastern South Adriatic current (E-SAd current) and western South Adriatic current (W-SAd current). Three water masses (surface water, Levantine intermediate water and deep water) were identified in three sub-basins of the Adriatic Sea by their physical properties (ARTEGIANI et al., 1997). Thermocline is present in spring and summer down to 30 m, 50 m and 75 m in the North, Central and South Adriatic Sea, respectively (ARTEGIANI et al., 1997). The Po River is the most important river regarding freshwater discharge (1550 m^3 s^{-1}) (ŽAGAR et al., 2013) and contributes to 46.5% of the overall freshwater input (UNEP, 2012). Most of the freshwater input is in the north-western Adriatic, while only 27% is discharged in the eastern side (UNEP, 2012). Sediments input from the Po River is ~15×10^6 t a^{-1} (NITTROUER et al., 2004) while the overall input to the northern and central Adriatic is 46.6×10^6 t a^{-1} (FRIGNANI et al., 2005). Sediments originating from the Po River consist mainly of silt and clay (COMBI et al., 2016; NITTROUER et al., 2004). The sea bottom in the eastern Adriatic is rocky with corallogenic concretions along the islands (UNEP, 2012).

MERCURY IN THE MEDITERRANEAN SEA

The Mediterranean Sea is subject to mercury contamination from natural and anthropogenic sources. Although it covers only about 1 % of the world oceans, almost 65 % of the world mercury reserves are situated in the cinnabar belt under the Mediterranean area (ŽAGAR et al., 2013). The most important Hg sources in the Mediterranean (in t a^{-1}) are atmospheric deposition (38), river inflow (13) and sediments (19), while the main outputs are evasion to atmosphere (68)
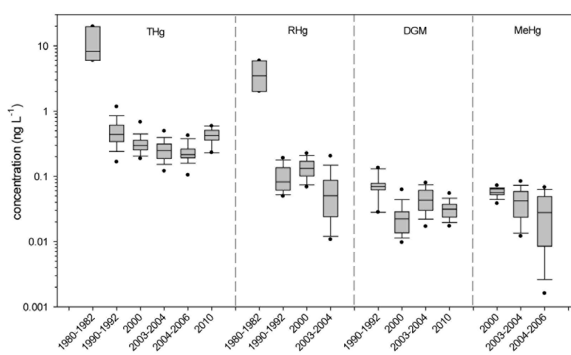

Fig. 2. Box-and-whisker plots of THg, RHg, DGM and MeHg concentrations in the Mediterranean Sea from 1980-2010 (median with 5, 10, 25, 75, 90 and 95th percentiles). Data from COSSA et al., 1997, 2009; FANTOZZI et al., 2013; FERRARA et al., 1986, 2003; HORVAT et al., 2003; KOTNIK et al., 2007

and burial in the sediments (25) (ŽAGAR et al., 2013). The Mediterranean Sea is slowly coping with mercury contamination because Hg output exceeds the input by about 5 t a^{-1}.

In the 1970s, THg values in some Mediterranean pelagic fish were two fold higher than those in the same species living in the Atlantic Ocean (COSSA & COQUERY, 2005), which raised questions about Hg contamination in the Mediterranean. High THg concentrations were also observed in water. Even though BERNHARD (1988) reported THg concentrations higher than 10 ng L^{-1}, it was stated that the validity of this data is doubtful. Since then, measured concentrations have been decreasing in the last decades (Fig. 2), mainly because more attention has been given to sample contamination during sampling, storage and analysis (BERNHARD, 1988; HORVAT, 2005), and because of using more sensitive instrumentation, mainly atomic fluorescence spectrometry (HORVAT, 2005).

Average THg concentration in the entire open Mediterranean Sea is 0.29±0.12 ng L^{-1} and is comparable in all measured water masses in the basin (KOTNIK et al., 2013). The highest concentrations are always found in coastal areas (FANTOZZI et al., 2013; KOTNIK et al., 2015). The highest open sea THg (0.71 ng L^{-1}) is found in the surface water in the Strait of Sicily, probably due to elevated geotectonic activity in this area (KOTNIK et al., 2007). Most of mercury in the open waters is present in dissolved form (avg.
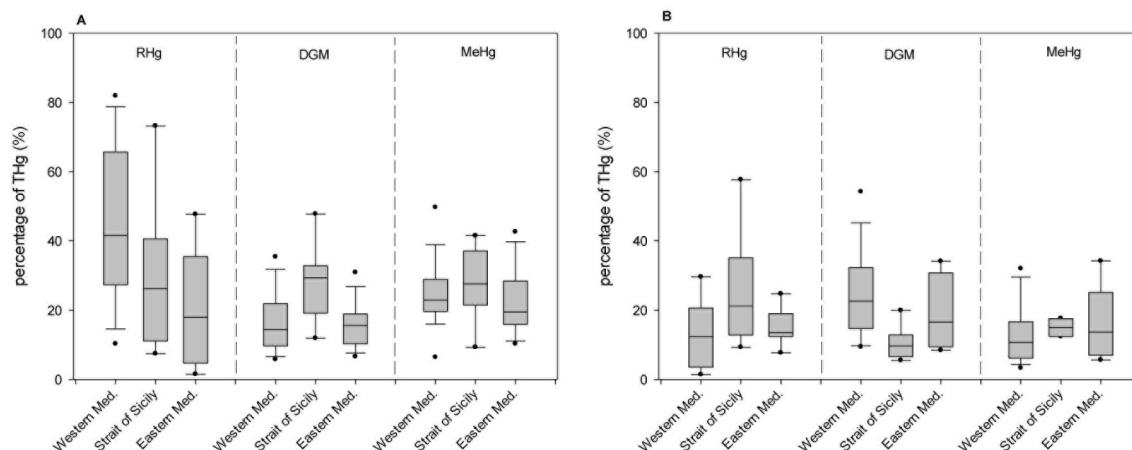
Fig. 3. Box-and-whisker plots of the geographical distribution of RHg, DGM and MeHg percentage of THg during spring (A) and summer (B) in the Mediterranean Sea. Data from KOTNIK et al., 2007

70%), due to the low abundance of particulate matter (HORVAT *et al*., 2003). The concentrations of various Hg compounds are lower than those in world oceans, despite the geological mercury anomaly (KOTNIK *et al*., 2013). Major factors influencing the distribution of RHg in the Mediterranean Sea are the presence of volcanic, geotectonic and biological activity, and photochemical reactions (KOTNIK *et al*., 2007). RHg is lower in the summer than in the spring (KOTNIK *et al*., 2007), as is its percentage of THg (Fig. 3). RHg vertical profiles are mostly the opposite of DGM, as inorganic Hg is a substrate for DGM production (KOTNIK *et al.,* 2013). Most of DGM is DEM, indicating its geotectonic origin. DGM generally increases with depth; this suggests the existence of volatile Hg sources in deeper waters (KOTNIK *et al*., 2013), bacterial activity in the oxygen-depleted waters (KOTNIK *et al*., 2007), or the oxidation of Hg^0 in the presence of UV light and chlorine/bromine (HORVAT *et al*., 2003) or hydroxyl radical (GÅRDFELDT *et al*., 2001) in the surface waters. The average MeHg concentration is higher during the spring (56.2±24.1 pg L^{-1}) than during the summer (32.1±20.1 pg L^{-1}) (KOTNIK *et al*., 2007). The highest concentrations are usually found in the bottom water layer, indicating input from sediment (OGRINC *et al*., 2007), microbially mediated methylation in deeper waters, or photochemical/microbial remineralisation of sinking organic matter from the surface waters (KOTNIK *et al*., 2007). In addi-

tion, particulate scavenging can remove MeHg from surface waters and release it into deeper waters through particulate dissolution (COSSA *et al*., 2009). MeHg/THg ratio (Fig. 3) follows the variability of MeHg concentration; it is higher in spring than in summer. This could be due to the higher biological activity (significantly higher chlorophyll levels) occurring in spring; however, MeHg concentrations are only slightly elevated, not statistically significant (KOTNIK *et al*., 2007). The vertical distribution of DMHg depends on the presence of the thermocline. Levels below limit of detection are found in the surface layer, while the highest concentrations (2.43 pg L^{-1}) are measured in the deep waters (COSSA *et al*., 1997; HORVAT *et al.,* 2003; KOTNIK *et al.,* 2007). Similar to MeHg, DMHg/THg ratio is higher during spring than summer. Since the Mediterranean deep waters are ~10°C warmer than the Atlantic waters of the same depth, more microbially mediated methylation could occur due to its temperature dependence (COSSA *et al*., 1997; COSSA & COQUERY, 2005).

Mercury accumulation rates in the Mediterranean sediments range from 10.3-30.9 ng m^{-2} d^{-1} and 2.59-4.93 ng m^{-2} d^{-1} in the Western and Eastern basins, respectively (OGRINC *et al*., 2007). THg concentrations in the sediments of the western basin decrease from the surface (78.2-90.3 ng g^{-1}) and at a depth of 10 cm the concentrations are within the range of the earth crust values (OGRINC *et al*., 2007; COSSA &

COQUERY, 2005). THg concentrations in the East-
ern Mediterranean sediment are lower (COSSA
& COQUERY, 2005). THg distribution in deeper
layers may reflect redistribution during diage-
netic processes or changes in the sedimentation
conditions (OGRINC *et al.*, 2007). The highest
MeHg concentrations (up to 2.97 ng g^{-1}) are
generally found in the uppermost sediment layer
and decrease with sediment depth. Methylation
potentials for surface sediments are in the range
0.16-0.71% d^{-1} and generally follow the MeHg
depth profile (OGRINC *et al.*, 2007).

MERCURY IN THE ADRIATIC SEA

Distribution of mercury species in seawaters

Total mercury in the seawater exhibits a con-
centration gradient: the lowest values are found
in the southern area and increase in the central
part, while the highest values are found in the
Northern Adriatic (Fig. 4A) (FERRARA & MASER-
TI, 1992; KOTNIK *et al.*, 2015). As in the Mediter-
ranean Sea, there is a decrease in measured THg
concentrations with time in the Adriatic Sea
(Fig. 5), probably due to questionable validity of
older data and possible sample contamination.
Another possibility is a real decrease of Hg con-
centrations due to the closure of the Idrija mine
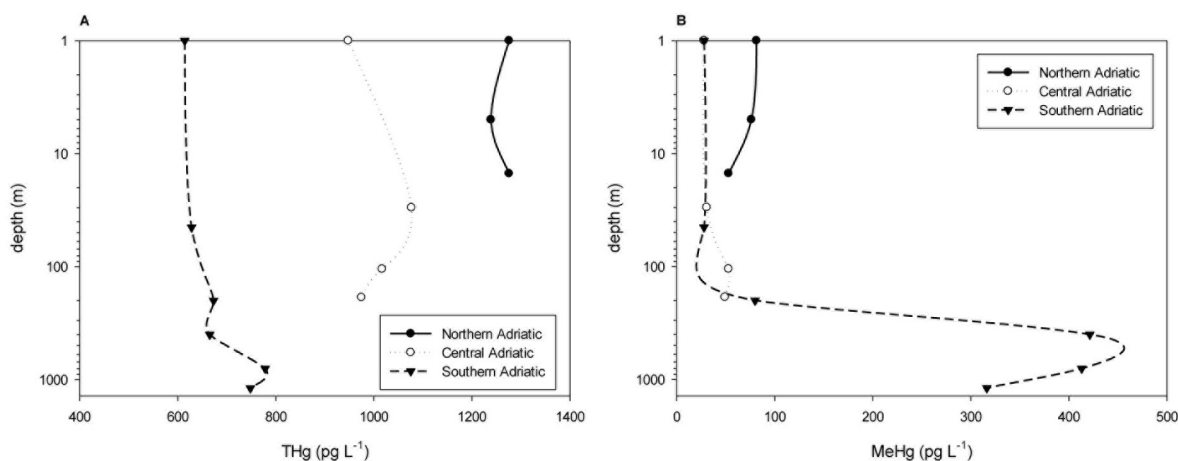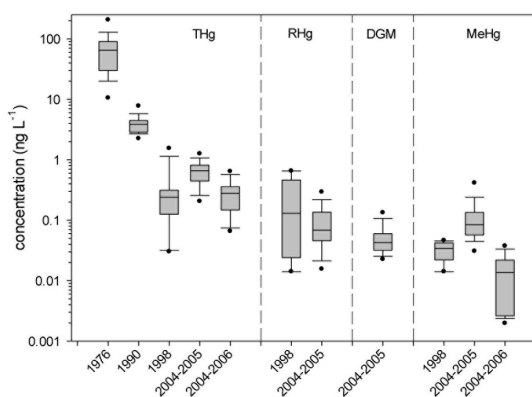in 1994 (FAGANELI *et al.,* 2003).

*Fig. 5. Box-and-whisker plots of THg, RHg, DGM and
MeHg concentrations in the Adriatic Sea from 1976-
2005 (median with 5, 10, 25, 75, 90 and 95th percen-
tiles). Data from COSSA et al., 2009; FERRARA &
MASERTI, 1992; HORVAT et al., 2003; KOSTA et al.,
1978; KOTNIK et al., 2015*

Generally, average THg concentrations in
the open Adriatic Sea are low (up to 0.32 ng
L^{-1} in uncontaminated sites), which is similar to
the values found in the open Mediterranean Sea
(HORVAT *et al.*, 2003). The highest THg values are
observed at the Otranto Strait at a depth of 40 m
in summer (0.381 ng L^{-1}) and at 600 m in spring
(0.379 ng L^{-1}) (KOTNIK *et al.*, 2007). Vertical salin-
ity gradient indicates downwelling of surface
Adriatic seawater; anthropogenic mercury pol-
lution could be the reason for observed Hg peaks
within this gradient (KOTNIK *et al.*, 2007). Elevat-

*Fig. 4. Vertical seawater profiles of THg (A) and MeHg (B) in the Northern, Central and Southern Adriatic Sea. Data
from KOTNIK et al., 2015*

ed THg concentrations in the bottom water layer of the southern Adriatic Sea (Fig. 4A) could be due to southward transfer of the downwelling surface waters from the contaminated northern Adriatic Sea. Wide range in the THg associated with suspended particulate matter (SPM) can be observed in the three parts of the Adriatic Sea, with the highest values found in the northern Adriatic. The major sources of mercury bound to SPM are the Isonzo River (microcrystalline cinnabar), the Marano and Grado lagoon and the Po river delta. Generally, the amount of Hg associated with the SPM is often comparable or higher than that of the dissolved fraction (COVELLI *et al.*, 2006b, 2007; FERRARA & MASERTI, 1992).

COSSA *et al.* (2009) made vertical profiles of methylated mercury species (MeHg+DMHg) in the Mediterranean Sea, which were the first high-resolution profiles showing consistent features. All the vertical profiles, including Adriatic, exhibit similar patterns: very low concentrations of methylated mercury species in the surface waters, a sharp gradient within the biologically most active zone (0-600 m), an intermediate maximum (200-1000 m) and lower concentrations in the deep waters (COSSA *et al.* 2009; HEIMBÜRGER *et al.* 2010). KOTNIK *et al.* (2015) obtained a similar vertical profile in the southern Adriatic (Fig. 4B). The highest MeHg concentrations (0.50 ng L^{-1}) and the highest percentage of THg as MeHg (Fig. 6) were measured in the bottom water of the eastern South Adriatic shore. These concentrations were considerably higher than values reported in the Mediterranean Sea (COSSA *et al.*, 2009; HORVAT *et al.*, 2003; KOTNIK *et al.*, 2007). Even in the most contaminated northern Adriatic, no significant increase in MeHg concentration along the water column is observed. The highest concentrations of methylated mercury species are not found near the shelf edge, suggesting that the sediments of the continental shelf are not the main MeHg source for the water column in the open sea (COSSA *et al.*, 2009). MeHg production is the greatest in the deeper central and southern Adriatic waters (southern Adriatic Pit), probably due to biological or chemical processes, an unknown benthic source or slower removal of MeHg from the
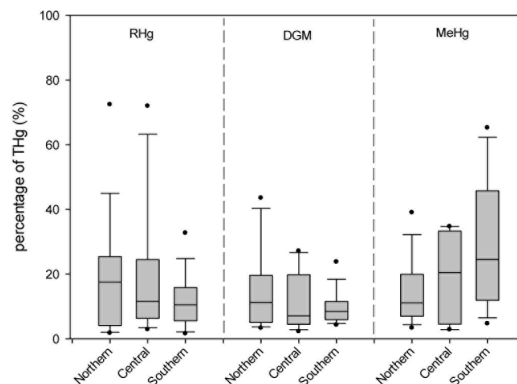

Fig. 6. Box-and-whisker plots of the geographical distribution of RHg, DGM and MeHg percentage of THg in the Adriatic Sea. Data from KOTNIK et al., 2015

water column (KOTNIK *et al.*, 2015). KOTNIK *et al.* (2007) measured DMHg below the detection limit (80 fg L^{-1}) at the Strait of Otranto. The average concentration of DMHg in Adriatic waters is 1.1 pg L^{-1}, while significantly lower values are found in the northern Adriatic (KOTNIK *et al.*, 2015). However, elevated concentrations of DMHg (up to 4.7 pg L^{-1}) are found near the island of Vis above the sea bottom, and in deep waters of the Southern Adriatic Sea. On average, DMHg represents 1.7% of THg. Differences between concentrations in the Adriatic and Mediterranean Sea are probably due to various anthropogenic sources (e.g. chlor-alkali plants, the Idrija mercury mine) (KOTNIK *et al.*, 2015) which provide sufficient substrate for methylation in this semi-enclosed sub-basin.

DGM is relatively low in surface waters and usually shows a steady increase towards the bottom during summer and spring (KOTNIK *et al.*, 2007), which reflects the importance of evasion and photochemical reactions at the surface (HORVAT *et al.*, 2003). In deeper waters, DGM distribution indicates the importance of redox processes, microbial production, diffusion from sediment and/or geothermal/hydrothermal fields, especially at locations in the southern Adriatic Pit, which is tectonically very active (KOTNIK *et al.*, 2013). DGM spatial distribution mostly follows THg distribution; the highest concentrations and percentages are found in the northern Adriatic (Fig. 6), reflecting anthropogenic sources (KOTNIK *et al.*, 2015). Correlations between maximum

DGM and RHg, and the oxygen-depleted zone are usually observed (KOTNIK *et al.*, 2013). Spatial distribution of RHg usually follows that of THg; the highest concentrations are found in the most contaminated parts of the northern Adriatic (up to 0.37 ng L^{-1}) (KOTNIK *et al.*, 2015).

Mercury in the Adriatic sediment

Mercury distribution in the open Adriatic sediments was investigated in the 1970s and 1980s, but these research mostly covered the open northern Adriatic. We will present results from these studies, and although some values can be compared with recent results, it cannot be systematically performed due to lack of data, mainly MeHg concentrations. Mercury in the sediment of the Gulf of Trieste mainly originates from the discharge of the Soča/Isonzo River, which has been draining cinnabar-rich deposits of the Idrija mine for centuries (COVELLI *et al.*, 2001, 2007; FAGANELI *et al.,* 2003). The effect of fluvial contribution, sediment re-suspension and the presence of localized natural and anthropogenic mercury sources can explain the observed highest THg levels in the northern Adriatic Sea

(Fig. 7). The largest anthropogenic Hg sources are chlor-alkali/PVC factories that had used mercury in their technological processes (ACQ-UAVITA *et al.*, 2012; CULLAJ *et al.*, 2004; GUÉDRON *et al.*, 2012; KWOKAL *et al.*, 2002).

Previous studies found that THg in the sediments of the open northern Adriatic range from <0.1-16.9 µg g^{-1} (DONAZZOLO *et al.*, 1984) with an average of 0.78 µg g^{-1} (MANTOVAN *et al.*, 1985). Frequency histogram shows that 64% of samples have <0.4 µg g^{-1} (DONAZZOLO *et al.*, 1984). The same percentage was reported by GUERZONI *et al.* (1984) for the open Adriatic sediments between Ancona and the Po River mouth. Decreasing THg gradient from the Po River mouth (0.97 µg g^{-1}) to Pesaro (0.06 µg g^{-1}) indicates that the Po River has an outstanding role in the trace metal pollution of this area (FRIGNANI *et al.*, 1976, 1978). The average THg concentrations in the Gulf of Venice (0.56 µg g^{-1}) (DONAZZOLO *et al.*, 1981), in surface sediments offshore the Po River mouth (0.4 µg g^{-1}) (FRASCARI *et al.*, 1988; GUERZONI *et al.*, 1985), and at the dredge disposal site outside the Ravenna harbour (0.28 µg g^{-1}) (GIANI *et al.*, 1994; PELLEGRINI *et al.*, 1992) are in the range observed for the open northern Adri-
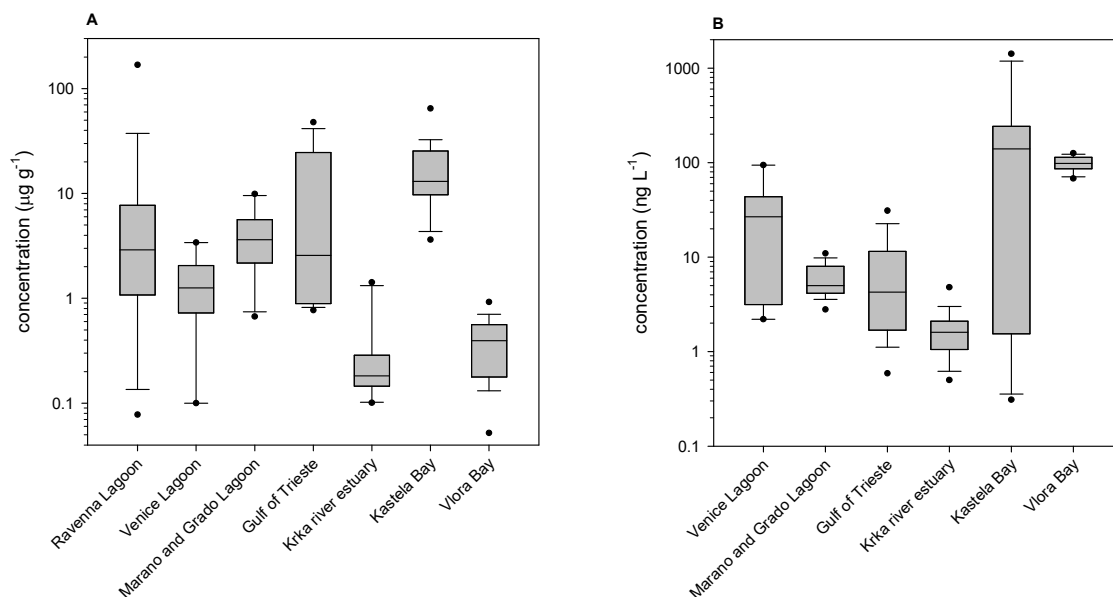
Fig. 7. Box-and-whisker plots of THg in sediments (A) and water (B) of the case studies. Data obtained from: ACQUAVITA et al., 2012; ANCONELLI et al., 1980; BERTO et al., 2006; BILINSKI et al., 2000; BLOOM et al., 2004; CULLAJ et al., 2004; FAGANELI et al., 2003; HINES et al., 2000; HORVAT et al., 1999, 2003; KOTNIK et al., 2015; KWOKAL et al., 2002; KWOKAL & LOVRIĆ, 2006; LAZO & CULLAJ, 2002; MELAKU CANU et al., 2015; MIKAC et al., 2006; QARRI et al., 2014; TROMBINI et al., 2003

atic sediments. In the southern Adriatic, THg in sediments range from 0.07-0.97 μg g⁻¹, with a median of 0.1 μg g⁻¹ (SELLI *et al.*, 1973). FERRARA & MASERTI (1992) measured THg concentrations in the sediments of all three sub-basin of the Adriatic Sea. The concentration ranges are 0.05-8.63, 0.02-0.13 and 0.03-0.07 μg g⁻¹ in the northern, central and southern Adriatic sediments, respectively. This is in a good agreement with the results from KOSTA *et al.* (1978) (0.01-15.1, 0.02-0.07, and 0.01-0.11 μg g⁻¹ in the northern, central and southern Adriatic sediments, respectively). These concentrations exhibit the north-south gradient and emphasize the influence of localised natural and anthropogenic sources on Hg distribution. Mercury is mostly (95%) accumulated in the fine fraction of the sediment (DONAZZOLO *et al.*, 1984). The average THg concentration in offshore surface muds (0.34 μg g⁻¹) is higher than in offshore relict of the northern Adriatic (mostly sand; 0.10 μg g⁻¹) which reflects the observed positive correlation between THg and clay/mud (DONAZZOLO *et al.*, 1981; GUERZONI *et al.*, 1984).

Recent research shows that THg concentrations in the Adriatic sediments can vary more than 150-fold among locations, depending on the loading sources (KOTNIK *et al.*, 2015). In the offshore sediments, THg concentrations (0.02-0.26 μg g⁻¹) are in range with the values observed in the Mediterranean. The average concentration in unpolluted areas of the Central and South Adriatic is 0.12 μg g⁻¹ (KOTNIK *et al.*, 2015) and is comparable with the previous measurements. In the coastal sediments (not including industrial hot-spots), THg values range from 0.10 μg g⁻¹ in the Krka river estuary (KWOKAL *et al.*, 2002) to 47.8 μg g⁻¹ in the Gulf of Trieste (HINES *et al.*, 2000). In the sediments contaminated by industrial activity, THg range from 0.05-250 μg g⁻¹ (Fig. 7A). Based on the sedimentation rates, sediment porosity and density, calculated mercury accumulation rates in the Adriatic sediments range from 12.0-148 ng m⁻² d⁻¹ (KOTNIK *et al.*, 2015). These values are up to 14 and 57 times higher than in the Western and Eastern Mediterranean, respectively.

In front of the Po river plume, THg concentrations in sediment are characterised by a two-fold decrease from the top layer to the deep core (FOWLER *et al.*, 1999; GUERZONI *et al.*, 1985). Similarly, THg vertical profile is characterised by 2 to 6-fold surface enrichment with respect to background levels outside the Ravenna harbour (GIANI *et al.*, 1994), and 3 to 11-fold in the northern Adriatic sediment (FABBRI *et al.*, 2001). The background THg levels in the northern Adriatic cores are estimated to 0.10-0.12 μg g⁻¹ (DONAZZOLO *et al.*, 1984; GUERZONI *et al.*, 1984, 1985; FRASCARI *et al.*, 1988). The maximum concentration of THg and MeHg at 22 cm depth is probably related to the year of maximum Hg production (i.e. 1913) when the Idrija mine produced double the annual Hg amount (FOWLER *et al.*, 1999). THg concentrations in the southern Adriatic sediment decrease from the surface (12.2 ng g⁻¹) to the deeper levels. Similarly, vertical profile of MeHg concentrations at the Strait of Otranto shows maximum in the surface sediment (2.94 ng g⁻¹) and decreases with depth to the range of the crust values (OGRINC *et al.*, 2007). Elevated MeHg concentrations at the Strait of Otranto are possibly a consequence of relatively high content of MeHg in the SPM, which is transported by water currents exiting the Adriatic Sea. During winter, sinking of surface water could cause the deposition of these particles onto the sediments (OGRINC *et al.*, 2007).

In the uppermost two centimetres, MeHg in porewaters has the highest average value found for the whole Mediterranean (8.78 ng L⁻¹) (OGRINC *et al.*, 2007). Vertical distribution of RHg and MeHg in porewaters are different; RHg is mostly constant while MeHg is constant in the uppermost four centimetres and then decreases with depth. Methylation potential for surface sediment is 0.14% d⁻¹; this is one of the lowest values for the whole Mediterranean, which is unusual when taking into account high MeHg concentration in the sediment and porewaters. Sedimentation of SPM rich in MeHg at the Strait of Otranto could explain this observation (OGRINC *et al.*, 2007). Estimated diffusive fluxes at the Strait of Otranto are 35.1 ng m⁻² d⁻¹ and 6.0 ng m⁻² d⁻¹ for RHg and MeHg, respectively. These values are 3 to 5-fold higher than corresponding fluxes in the western Mediterra-

nean Sea (OGRINC *et al.*, 2007). KOTNIK *et al.* (2015) calculated lower MeHg diffusive fluxes in the Adriatic (up to 3.35 ng m^{-2} d^{-1}) indicating local restriction on input of MeHg from the sediment.

Transport of mercury species in the Adriatic

KOTNIK *et al.* (2015) estimated mercury transport and mass balance in the Adriatic Sea based on several contributions (Table 1). They calculated overall deficit of more than 5 t a^{-1} of THg and 2.3 t a^{-1} of MeHg, and attributed it to additional Hg sources such as tectonic activity, dry deposition, and evasion overestimation. The greatest input fluxes are inflow from the Mediterranean Sea, terrestrial freshwater contributions (mainly Isonzo and Po rivers), and atmospheric deposition. Considering only seawater masses, the mass balance shows net import of inorganic Hg (0.6 t a^{-1}) and net export of MeHg (2.4 t a^{-1}) to the Mediterranean Sea. As the South Adriatic Deep Water flows out to the Mediterranean Sea at ~800 m depth (CIVITARESE & GAČIĆ, 2001), it is carrying Hg to the Mediterranean deep waters. Considering that the highest MeHg concentrations are found in the South Adriatic Deep Water (KOTNIK *et al.*, 2015), the Adriatic Sea exports methylated mercury into the Mediterranean Sea. The highest THg concentrations are usually found in the North Adriatic Surface Water. During cold and dry winters in the North Adriatic, this water mass cools, sinks and forms North Adriatic Deep Water (ARTEGIANI *et al.*, 1997) resulting in southward transfer of mercury. Due to the marine current system in the Adriatic Sea (Fig. 1) that carries particulate matter from

the river Po delta in anticlockwise direction, the western coast of the central Adriatic Sea exhibits elevated Hg concentrations in SPM (FERRARA & MASERTI, 1992). Similarly, the greatest fraction of THg as RHg is found in the northern and central Adriatic (Fig. 6), but mostly along the western shore, indicating that inflowing water is not as reactive as outflowing water (KOTNIK *et al.*, 2015). Alongside the outflow to the Mediterranean, evasion to the atmosphere is the most important route for Hg removal from the marine environment. Due to supersaturation of surface water with DEM, it easily escapes to the atmosphere (GÅRDFELDT *et al.*, 2003), exceeding atmospheric deposition by a factor of 8. DGM in surface water shows higher values in the summer than in spring due to higher water temperatures and higher evaporation rates (KOTNIK *et al.*, 2007). Based on the sedimentation rates, it appears that sediment is slowly removing both THg and MeHg from the water column.

Case studies in the Adriatic Sea

Coastal environments are areas of great ecological and economic importance, but also some of the most affected environments due to human activities. In the Adriatic Sea, coastal sites that bear the greatest Hg contamination are Ravenna Lagoon, Venice Lagoon, Marano and Grado Lagoon, the Gulf of Trieste, the Bay of Kaštela and the Bay of Vlora (Fig. 1). Pristine environment of the Krka river estuary is also a subject of mercury research. Different conditions in these coastal areas (redox potential, temperature, salinity, presence of methylating bacteria,

Table 1. Mercury mass balance in the Adriatic Sea. Data from KOTNIK et al., 2015. Negative values represent output fluxes from seawater

Source	THg (t a^{-1})	MeHg (t a^{-1})
Terrestrial freshwater contributions	9.1	0.014
"Hot spots"	1.1	0.006
Atmospheric deposition	2.2	
Evasion to atmosphere	-16.2 (as DGM)	
Sedimentation	-2.0	-0.62
Resuspension from sediment	0.5	0.114
Inflow from the Mediterranean	11.2	2.8
Outflow to the Mediterranean	-13.0	-5.2
Present is seawater	22.9 t	4.2 t

etc.) cause specific biogeochemical transformations of mercury.

Ravenna Lagoon (Pialassa Baiona)

Pialassa Baiona Lagoon mostly consists of shallow ponds. This lagoon received ~38 t of the estimated 100-200 t of Hg discharged by an acetaldehyde plant (1958-1978) (COVELLI *et al.*, 2011). THg concentrations in sediments are variable and follow pollution gradient caused by northward water transport (TROMBINI *et al.*, 2003). The highest THg concentrations (250 µg g^{-1}) are found in the channel connected to the discharge of the plant, indicating the presence of dissolvable Hg in the surface sediment (FABBRI *et al.*, 1998). Deep sediment profiles show an Hg concentration peak (40 µg g^{-1}) at 3-7 cm depth, which matches the time of industrial site conversion (MATTEUCCI *et al.*, 2005). COVELLI *et al.* (2011) found that Hg^0 represents the dominant fraction (87.5%) in the sediment. Differences in mercury speciation across the lagoon might reflect different biogeochemical cycling (TROMBINI *et al.*, 2003). MeHg concentrations in sediments (0.13-44.6 ng g^{-1}) represent a small fraction of THg (up to 0.07% in surface sediments) which TROMBINI *et al.* (2003) attributed to bacterial detoxification; this value is smaller than the characteristic ~0.5% for estuarine environments (COVELLI *et al.*, 2011). MeHg porewaters concentrations show the highest values in the first centimetre (COVELLI *et al.*, 2011), suggesting that methylation occurs in a thin layer, close to sediment-water interface. Calculated distribution coefficient K_D for THg (log K_D 6.27) is almost constant with depth, indicating a steady-state equilibrium between two phases that controls THg distribution in the presence of sulphide (COVELLI *et al.*, 2011). Mercury is still present in surface sediments and can pose a "time bomb" for the ecosystem (FABBRI *et al.*, 1998).

Venice Lagoon

Venice Lagoon is the largest lagoon in the Mediterranean. Two chlor-alkali plants (1951-1988) were the main contributors to Hg con-tamination (GUÉDRON *et al.*, 2012) with an estimated discharge of 100-300 t (BLOOM *et al.*, 2004). In the most contaminated areas, THg in water is up to 201 ng L^{-1}. Dissolved THg accounts for 4-39% of THg, while dissolved MeHg represents up to 2.8% of THg (BLOOM *et al.*, 2004). Mercury distribution in SPM shows weak concentration gradient from the northern (1.17 µg g^{-1}) to the southern part (0.76 µg g^{-1}) of the lagoon. The highest value (3.26 µg g^{-1}) is found in the industrial canal (BLOOM *et al.*, 2004). In surface sediments, THg has slightly higher values, while MeHg shows 4-10 times higher values in SPM (log K_D 6.89) (BLOOM *et al.*, 2004). Therefore, tidal flushing may enhance dispersal of particulate MeHg throughout the lagoon (GUÉDRON *et al.*, 2012). MeHg in sediments never excided 0.45% of THg; it acts as a net source of MeHg for SPM and a sink for particulate inorganic Hg (GUÉDRON *et al.*, 2012). MeHg is highly correlated to THg and organic matter, suggesting their influence on methylation in the sediments (GUÉDRON *et al.*, 2012). Specific methylation rates are usually the highest in the surface layers (up to 5.5% d^{-1}) (KIM *et al.*, 2011). GUÉDRON *et al.* (2012) found three MeHg peaks in sediment porewaters at the depths corresponding to the reduction of Fe oxides, oxidation of fresh OM, and sulphate reduction. Their results indicate that the Fe reduction zone is the most important source of MeHg for the water column. High molecular diffusion fluxes (9.46 and 1.09 ng m^{-2} d^{-1} for Hg(II) and MeHg, respectively) (GUÉDRON *et al.*, 2012) indicate that open lagoon sediments may represent an important source of dissolved MeHg (GUÉDRON *et al.*, 2012). BLOOM *et al.* (2004) estimated 1.1 t a^{-1} Hg flux into the Adriatic Sea, which makes the Venice Lagoon one of the biggest exporters of Hg to the Adriatic Sea.

Marano and Grado Lagoon

The Grado-Marano wetland system consists of the western, shallow Grado sector, and eastern Marano sector, which is largely covered in saltmarshes (FONTOLAN *et al.*, 2012). Source of Hg pollution was a chlor-alkali plant (1949-1984) and 186 t of Hg were deposited

into the lagoons (ACQUAVITA *et al.*, 2012). Hg^0 from chlor-alkali plant is the main fraction in the Marano sector and sulphide-bound Hg from Isonzo River in the Grado sector (ACQUAVITA *et al.*, 2012). Presence of Hg from the Isonzo River is observed through the THg gradient in surface sediments; from 11 µg g^{-1} in Grado to 1 µg g^{-1} in Marano (COVELLI *et al.*, 2011). The highest THg concentrations are usually found in the top core sections with almost exponential decrease from about 30 cm depth to the basal core where background values are found (average 0.13 µg g^{-1}), indicating recent contamination (COVELLI *et al.*, 2012). MeHg in sediments accounts for up to 0.2% of THg (COVELLI *et al.*, 2008). MeHg is the highest in surface sediments (up to 21.9 ng g^{-1}) and decreases with depth almost exponentially, suggesting that MeHg accumulation and production occur just below the sediment-water interface (COVELLI *et al.*, 2008). MeHg accounts for only 0.03% of THg in SPM, and therefore additional MeHg must be produced by microbial activity (COVELLI *et al.*, 2008). The average concentrations of THg and MeHg in porewaters are 99.1 ng L^{-1} and 0.84 ng L^{-1}, respectively (EMILI *et al.*, 2012). COVELLI *et al.* (2008) found that THg in porewaters of the Grado sector increased with depth which could be due to Hg scavenging by soluble Fe and Mn (oxy)hydroxides at low oxygen and sulphide conditions. The log K_D for MeHg is ~3 (COVELLI *et al.*, 2008; HINES *et al.*, 2012), indicating low affinity for sediment matter. Diffusive fluxes range from –37-570 ng m^{-2} d^{-1} for THg and from -5.5-16.3 ng m^{-2} d^{-1} for MeHg (EMILI *et al.*, 2012). High benthic fluxes (2.54-41.1 µg m^{-2} d^{-1} for THg and 0.08-2.29 µg m^{-2} d^{-1} for MeHg) (EMILI *et al.*, 2012) suggest that sediments in the lagoon are an important source of mercury for the water column (COVELLI *et al.*, 2008, 2011). Sulphate reducing bacteria (SRB) are mostly responsible for Hg methylation and the oxidative demethylation of MeHg (HINES *et al.*, 2012). Demethylation rates are ~10 times higher than methylation rates (HINES *et al.*, 2012), which might decrease the rate of MeHg accumulation.

The Gulf of Trieste

The Gulf of Trieste is a shallow water basin (up to ~25 m) located in the northeastern part of the Adriatic Sea. Mercury contamination originates from the Isonzo River, which drains the cinnabar deposits from the world's second largest Hg mine in Idrija, Slovenia (HORVAT *et al.*, 1999). Over 5×10^9 kg of Hg ore was excavated and 73% (estimation) of the mercury was recovered (COVELLI *et al.*, 1999). THg in the surface water layer of the central part of the Gulf is relatively low, but higher concentrations (up to 64.5 ng L^{-1}) are found in the area in front of the Isonzo River mouth as a consequence of sediment re-suspension (Fig. 7B) (FAGANELI *et al.*, 2003). MeHg shows low surface values and higher bottom values (up to 126 pg L^{-1}) (FAGANELI *et al.*, 2003). In the Gulf waters, THg is highly associated with SPM (log K_D 5-6). Particulate Hg accounts for <10% to >90% of THg present in the seawater, with the highest values found in the surface layer near the Isonzo River outflow (FAGANELI *et al.*, 2003). During high river floods, concentrations of particulate Hg in front of the river outflow are 5-40 times higher than during low river discharge (COVELLI *et al.*, 2007). Low log K_D for MeHg (<1) indicates much weaker binding of MeHg to SPM (FAGANELI *et al.*, 2003; HORVAT *et al.*, 1999). THg in sediments and short cores (0-10 cm) shows homogeneous distribution of mercury (HORVAT *et al.*, 1999). On the contrary, cores below 100 cm depth have THg concentrations around the background values (0.17 µg g^{-1}) while the sudden increase is observed toward the surface layers (COVELLI *et al.*, 2001, 2006a). MeHg concentrations in surface sediments (0.2-60.1 ng g^{-1}) correspond to 0.3-1.0% of THg. This value increases with the distance from the river mouth (HORVAT *et al.*, 1999), suggesting that coastal areas where methylation occurs are not necessarily areas with the highest THg concentrations (COVELLI *et al.*, 2001). Methylation activity in sediments (up to 2.0% d^{-1}) decreases with depth, indicating that recent sediment could represent a source of MeHg for the water column (COVELLI *et al.*, 1999; HORVAT *et al.*, 1999). SRB mediated oxidative demethylation is mostly active in the

uppermost layer of sediment, while reductive demethylation is negligible (<10%) (HINES *et al*., 2000). THg concentration in porewaters is relatively high (107 ng L^{-1}). This elevated value could be related to the solubility changes of Fe and Mn (oxy)hydroxides (COVELLI *et al*., 1999), similarly as in the Marano and Grado Lagoon. Diffusive fluxes range from -2.12-41.3 ng m^{-2} d^{-1} and from -1.77-4.39 ng m^{-2} d^{-1} for THg and MeHg, respectively (COVELLI *et al*., 1999). Benthic fluxes (71-665 ng m^{-2} d^{-1} for THg and 238-577 ng m^{-2} d^{-1} for MeHg) (EMILI *et al*., 2014) are much lower than those observed in the Marano and Grado Lagoon. Dissolved Hg in the benthic chamber water is dominantly in the methylated form during anoxic phase (EMILI *et al*., 2011, 2014). About 75% of THg is buried in the sediment and the rest is recycled at the sediment-water interface. Methylated form represents ~23% of recycled THg (COVELLI *et al*., 1999), making the Gulf of Trieste an efficient trap for THg and a source of MeHg to the bottom waters (HINES *et al*., 2000).

Kaštela Bay

The Bay of Kaštela is the largest bay in the central Adriatic. It is an area of high primary production due to the weathering of nutrients from surrounding fields (ZVONARIĆ, 1991). The Bay was contaminated with at least 150 t of Hg (estimated) originating from a chlor-alkali plant (1950-1990) (KWOKAL *et al*., 2002; ZVONARIĆ, 1991). Concentrations of THg in surface waters close to the chlor-alkali plant are high (up to 145 ng L^{-1}). Even higher concentrations in bottom waters suggest re-suspension from sediments or partial dissolution (KWOKAL *et al*., 2002). The lowest THg concentrations are found at the exit of the bay (Fig. 7B) (HORVAT *et al*., 2003). Approximately 70-100% of THg in water column is associated with SPM (KWOKAL *et al*., 2002). MeHg concentrations in waters are in the range 0.01-0.04 ng L^{-1} (HORVAT *et al*., 2003). Percentages of dissolved MeHg vary, but the highest value (46.8%) is found near the chlor-alkali plant (HORVAT *et al*., 2003). Elevated THg concentration in the sediment (Fig. 7A) can be explained by the fact that the chlor-alkali plant discharged

~1 t a^{-1} of Hg^0 until 1990 (KWOKAL *et al*., 2002). Very high concentrations are also found at up to 0.5 m depth (MIKAC *et al*., 2006). Depth distribution of THg is irregular near the chlor-alkali plant due to human perturbation of sediments, which are a mixture of coal ash and natural sediments (MIKAC *et al*., 2006). MeHg concentrations are typical for slightly to highly contaminated estuarine sediments (KWOKAL *et al*., 2002) but the MeHg/THg ratio in sediments is rather low (<0.18%). Even though the sediments are highly anoxic, this indicates that requirements for *in situ* methylation do not exist (KWOKAL *et al*., 2002). Therefore, most of Hg remains in the discharged form. Hg^0 is probably the only stable phase or perhaps Hg is bound to sulphide or sulphydryl groups (KWOKAL *et al*., 2002).

Vlora Bay

The Bay of Vlora represents the natural boundary between the Ionian and the Adriatic Sea. Pollution arises from the use of metallic Hg for chlor-alkali electrolysis. During factory operation (1976-1992), liquid wastewaters containing 1.1 mg L^{-1} of mercury was discharged directly into the sea (CULLAJ *et al*., 2004). It has been estimated that about 65 t of mercury had been discharged in the environment from 1977-1983 (CULLAJ *et al*., 2004). In the sediment, mercury can reach up to 0.92 µg g^{-1} (Fig. 7A). Pollution zone is not restricted to the plant area: CULLAJ *et al.* (2004) observed Hg relocation to the SW part of the Bay of Vlora and attributed it to hydrological factors. These factors do not favour Hg transportation to the open sea due to restricted communication. The biggest contributor to Hg transport is the fine sediment fraction. Mercury is mostly present in the fine fraction of the sediment (<63 µm; 0.60 µg g^{-1}), contrary to the coarse fraction (<250 µm) that contains only 0.23 µg g^{-1} of mercury (CULLAJ *et al.*, 2004). THg concentrations in seawaters are high (Fig. 7B) and the highest values are found in front of the chlor-alkali plant (QARRI *et al.*, 2014; LAZO & CULLAJ, 2002). Organic mercury fraction represents 50-59% of THg (LAZO & CULLAJ, 2002). Although the mercury-polluted soil was encap-

sulated in 2011, previous emissions of metallic mercury can still be observed in the sediments of the Bay of Vlora due to soil erosion (QARRI *et al.*, 2014).

Krka River estuary

The Krka river estuary is a stratified estuary located in the central part of the Eastern Adriatic coast. The biggest contamination sources are industrial and municipal wastewaters from the town of Šibenik. In comparison with other sites, this region can be characterised as relatively pristine (KWOKAL *et al.*, 2002). THg concentrations in the sediment of Krka river estuary are generally low (Fig. 7A). Slightly elevated values are found in the vicinity of urbanized areas near the city of Šibenik. MeHg has the lowest values among all case studies (0.50-2.96 ng g^{-1}) (KWOKAL *et al.*, 2002). In the water, MeHg values are in the range of 0.03-0.14 ng L^{-1}. The highest values are found within the freshwater-seawater interface (FSI) which can be explained by the association of Hg with mineral particles and dissolved organic compounds in the FSI (KWOKAL & LOVRIĆ, 2006). Presence of hydrophobic heterodispersed substances provides evidence that Hg is bound to hydrophobic particulate matter (BILINSKI *et al.*, 2000). THg concentrations in the water column (up to 12.5 ng L^{-1}) vary with depth and within each layer. THg maximum can be found in freshwater, at the FSI, below the FSI, or not at all (BILINSKI *et al.*, 2000). Input of atmospheric mercury into the estuary *via* precipitation can be observed through the Hg maximum in the freshwater layer. Strong winds can affect mercury concentration in the water column. During Bura wind (NE), mercury is transported to the sediments, resulting in low water column concentrations (<1 ng L^{-1}). On the contrary, during Jugo wind (SE) the outflow of brackish water decreases and water current in the marine layer goes from the sediment to the FSI (BILINSKI *et al.*, 2000; KWOKAL & LOVRIĆ, 2006).

ROLE OF PLANKTON IN MERCURY BIOGEOCHEMISTRY

In the Mediterranean Sea, several fish species (STORELLI *et al.*, 1998) show elevated mercury levels compared to the same species in the Atlantic Ocean, although THg concentrations in these two water masses are comparable (ŽAGAR *et al.*, 2013). The hypothesis that above average natural environmental levels in the Mediterranean are responsible conflicts with measured concentrations and distribution of mercury in the Mediterranean Sea (HORVAT *et al.*, 2003). In the open sea, oligotrophic environment plays an important role in mercury biogeochemistry. With relatively few nutrients, low primary productivity and low phytoplankton biomass, the Mediterranean Sea is classified as oligotrophic (UNEP, 2012). Oligotrophic conditions are characterised by higher proportions of dissolved rather than particulate carbon (ŠOLIĆ *et al.*, 2010). In oligotrophic systems, picoplankton dominates the biomass and the production (ŠOLIĆ *et al.*, 2010). Heterotrophic picoplankton (mostly heterotrophic bacteria) and autotrophic picoplankton (*Prochlorococcus*, *Synechococcus* and picoeukaryotes) represent the major components of the marine picoplankton community, especially in oligotrophic areas such as the Adriatic Sea (ŠOLIĆ *et al.*, 2010, 2016). Vertical profiles of methylated mercury species show nutrient-like patterns within the biologically active zone (COSSA *et al.*, 2009). HEIMBÜRGER *et al.* (2010) showed that Hg methylation was promoted during oligotrophic periods in the hypoxic water layer when primary production was dominated by nano- and picophytoplankton. These microorganisms may favour Hg methylation due to their great surface/volume ratio, which enables efficient accumulation of particle-reactive trace metals. Two MeHg maxima exist in the water column in which phytoplankton-derived dissolved organic carbon and particulate organic carbon are the main bacterial carbon sources in the photic and aphotic zone, respectively (HEIMBÜRGER *et al.*, 2010). Elevated MeHg concentrations in the surface and bottom water in the southern Adriatic Sea are probably the result of similar biological processes (KOT-

NIK *et al.*, 2015). Concentrations of MeHg in the seawater are correlated with chlorophyll *a* and oxygen concentrations, emphasising the role of planktonic production and mercury regeneration through methylation/demethylation processes (KOTNIK *et al.*, 2013, 2015). Also higher temperature of the deep waters may promote microbiologically mediated formation of MeHg in the water and sediment (COSSA & COQUERY, 2005). The structure of the microbial food web and the microbial role in biogeochemical processes in aquatic environments can vary considerably and depends on environmental trophic status (ŠOLIĆ *et al.*, 2010).

CONCLUSIONS

The Adriatic Sea exhibits the complexity of mercury cycling and the importance of the anthropogenic influence, especially in coastal areas. Mercury in the Adriatic seawaters and sediments shows a concentration gradient from the north to the south; the highest THg concentrations in the whole Mediterranean Sea are found in the northern Adriatic Sea. Changes in concentrations of mercury species with time can be observed in both the Mediterranean and the Adriatic Sea, especially for THg and RHg concentrations in seawater. These changes are probably connected to the closure of the Idrija mine and chlor-alkali plants, or possible sample contamination in the past. The trend cannot be accurately assessed for other Hg fractions in seawater because most of them were not measured prior to 1990s. In the sediments, THg concentrations are comparable with the newer results. However, THg values in the central and southern Adriatic sediments, and Hg speciation in sediments are too scarce to comprehensively assess Hg biogeochemistry in the Adriatic sediments. From the available data, it is evident that Hg contamination is mostly limited to the surficial sediments, while concentrations in the deeper cores are near background values.

Although the waters of the northern Adriatic Sea, along with the coastal lagoons, have the highest THg values in the whole of Adriatic, this does not reflect the distribution of MeHg.

Recent data indicate that MeHg production in the water column is the major source of MeHg in the Adriatic waters (especially in the southern Adriatic Pit), and that diffusion from the sediments cannot account for all observed MeHg. This indicates the important role of plankton in the methylation processes. However, in the coastal areas, bacterial methylation in the sediments plays an important role. Mercury methylation rates in the sediments of the Gulf of Trieste and the Venice lagoon are the highest in the whole Adriatic Sea. Water circulation can transfer produced MeHg and disperse it into the open Adriatic.

The spatial distribution of Hg in the marine environment depends on the seawater circulation, and biological and geological factors. These factors influence the transformations of Hg, leading to production of substantial amounts of MeHg, which can represent a major ecological burden, especially to the marine biota in the Adriatic Sea. In order to fully assess the impact of contamination in the Adriatic Sea, future research needs to focus on parameters that control Hg transformations in the environment. Thorough determination and speciation of Hg in all environmental compartments, together with the identification of specific biological (microbial methylation/demethylation), physical (diffusion, solubility, volatility) and chemical processes (redox, radical and photoreactions, methylation/demethylation, stable isotopes fractionation), could provide a better insight into Hg biogeochemistry and the susceptibility of the Adriatic Sea to contamination.

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Zastupljenost, raspodjela i specijacija žive u vodama i sedimentima Jadranskog mora – pregled

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SAŽETAK

Ovaj pregledni članak usredotočuje se na specijaciju žive u Jadranskom moru, rubnom moru Mediterana, koje predstavlja njegovu posebnu biogeokemijsku podjedinicu zbog antropoloških izvora žive. Trenutno znanje o kruženju žive u Jadranu je predstavljeno kroz pregled vrhunskih istraživanja na ovom području o vremenskim i prostornim raspodjelama i pojavnostima živinih specija u vodi i sedimentu te kemijskim transformacijama. Sumirani su rezultati istraživanja o specijaciji žive kako bi se opisala njena prisutnost i sudbina u Jadranskom moru. Jadransko more predstavlja neto izvor žive u Sredozemlju zbog najviših koncentracija ukupne žive uočenih u sjevernom Jadranu te najviših koncentracija metilžive u južnojadranskom ponoru. Međutim, biogeokemijski ciklus žive nije u potpunosti poznat te je ograničeno naše razumijevanje živinog transporta između odjeljaka i njenih (bio)transformacija. Buduće istraživanje se treba usredotočiti na mikrobne i kemijske procese živinih transformacija kako bi se bolje razumio utjecaj kontaminacije živom na okoliš i zdravlje ljudi u Jadranskom moru.

Ključne riječi: živa, kemijska specijacija, metilživa, Jadran, Sredozemlje