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Mercury in the coastal waters of Greece under the implementation of the Water Framework Directive (WFD)

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Abstract Mercury (Hg) is an environmentally hazardous metal and a priority element in Mediterranean environmental monitoring. Hg is a priority pollutant in the main pieces of European legislation pertaining to the marine environment (the Marine Strategy Framework Directive - MSFD and the Water Framework Directive WFD).

Despite the environmental importance of Hg there is limited knowledge on levels in Greek waters. The Laboratory of Environmental Chemistry (LEC) analyses very low Hg concentrations (above 0.5ng/L) using state of the art equipment in clean room facilities and participates in the national WFD coastal zone monitoring since 2012 in collaboration with the Hellenic Centre for Marine Research (HCMR).

This paper presents the first attempt to evaluate Hg levels in the coastal waters of Greece in the last 8 years (2012-2020) and identify trends and spatial patterns. The Hg levels measured in all areas were well below the European Legislation threshold of 70ng/L (EC 2013/39). Increased levels of Hg were found, as expected, near the major cities of Greece (Athens, Thessaloniki) and the major rivers of Northern Greece as well as in some of smaller ports.

Keywords: Hg, Greece, coastal waters, WFD, Cold vapour atomic fluorescence spectroscopy

1. Introduction

Mercury (Hg) is recognized as one of the most toxic elements to wildlife and humans, and characterized by a complex biogeochemical cycle. In the environment Hg is found in three oxidative states: Hg^0, Hg^{+1}, Hg^{+2}, as well as inorganic and organic forms [(ionic Hg (II) complexes, elemental Hg, dissolved gaseous mercury (DGM), methyl- (MHg) and dimethyl- (DMHg) mercury]. Various natural (erosion, volcanoes, hydrothermia) and human induced (fossil fuel combustion, mining, industrial waste) sources contribute to the enrichment of mercury in the environment. Particular characteristics of Hg are; enhanced lability and transport through environmental compartments; re-emission to the atmosphere (existing Hg forms in water, soil and sediments are naturally converted into volatile elemental Hg). Mercury is known to accumulate in marine organisms and biomagnify along trophic webs. Thus, higher trophic level consumers, i.e. predatory fish, accumulate higher levels of mercury (Rainbow 1995, Rajar et al. 2007, UNEP 2013, Kehrig 2010, Davis 2016).

The study of Hg is of great importance for the Mediterranean region due to its increased abundance in the geological background. It has been reported that fish of the Mediterranean exhibit higher levels of Hg than populations inhabiting other seas. Mercury accumulated in aquatic biota can subsequently be transferred to humans via fish and seafood consumption. Quite often Hg levels in fish and seafood exceed the limits for safe human consumption. Long term consumption of contaminated fish can lead to accumulation of toxic metals in vital organs and potential health hazard (Horvat, et al. 1999, Marcotrigiano et al. 2005, Kousteni et al. 2006, Damiano et al. 2011, Renieri et al. 2014). Therefore, Hg constitutes a priority element in Mediterranean environmental monitoring of biotic and abiotic components.

At European level, Hg is a priority pollutant as designated in environmental legislation [Marine Strategy Framework Directive (MSFD) 2008/56/EC and Water Framework Directive (WFD) 2000/60/EC]. Mercury also constitutes a contaminant of priority concern in the Mediterranean Action Plan MEDPOL of the Barcelona Convention, whereas the Minamata Convention on Mercury, a United Nations Environment Programme global treaty to protect human health and the environment from the adverse effects of mercury, entered into force in 2017.

According to the WFD and its derivative directives 2008/105/EC and 2013/39/EU, Hg is a priority hazardous substance. The Hg Environmental Quality Standard (EQS) for all types of water (inland, coastal and transitional) is set at 70ng/L. In the MSFD, marine chemical pollution is addressed through Descriptor 8 “Concentrations of contaminants are at levels not giving rise to pollution effects” and Descriptor 9 “Contaminants in fish and other seafood for human consumption do not exceed levels established by Community legislation or other relevant standards". The MSFD introduces the concept of 'Good Environmental Status' (GES) to be achieved in European Seas. For the needs of GES assessments, the established standards (EQS) should be coupled with biological effects to aquatic organisms at the individual or ecosystem level as well the possible adverse effects to human health through dietary exposure. (Tzempelikou et al. 2021)

This paper presents the first attempt to evaluate Hg levels and spatial patterns in the coastal waters of Greece for the last 8 years (2012-2020) of monitoring.

2. Materials and methods

2.1. Sampling and study area

Water sampling was conducted during 8 years (2012, 2013, 2014, 2015, 2017, 2018, 2019 and 2020) of monitoring. With the exception of year 2017 the sampling stations were within the Greek WFD operational and surveillance network. The WFD network covers the major coastal areas and gulfs of Greece (Cretan coast, Messiniakos, Lakonikos, Argolikos, Kyparisiakos, Patraikos, Amvrakikos, Ionian Sea island and mainland sites, Korintiakos, Saronikos, Evoikos, Maliakos, Pagasitikos, Thermaikos, sites of the Northern Greece coastline and finally ports and sites on selected Aegean Sea Islands). The 2017 campaign focused only on subareas of Saronikos gulf. The samplings were conducted with the oceanographic vessels R/V Aegaeo and R/V Philia of HCMR and water samples for total Hg were collected with Niskin bottles from 2 depths, surface and bottom, using ultraclean handling (EPA 1669). In total 580 water samples were collected and analysed for Hg.

2.2. Hg chemical analysis and statistical data evaluation

In this paper we present concentrations of Total Hg, i.e. all BrCl-oxidizable mercury forms and species found in an unfiltered seawater sample. The method of determination (EPA 1631) consists of oxidation of all species to Hg(II), purge and trap onto a gold trap, desorption and cold-vapor atomic fluorescence spectrometry (CVAFS) by a TEKRAN 2500 total mercury. The analyses were carried out in a Class 10000 clean room. The limit of quantification for Total Hg achieved is 0.5ng/L. On each analytical day a reference solution (OPR Ongoing Precision and Recovery) is prepared and analysed with a frequency of one after every seven unknown samples and a reference material or a matrix spike is analysed at least once a day for recovery estimation. Indicatively, for the analysis of 56 samples of the October 2020 campaign over two analytical shifts, 8 replicates of the OPR solution gave a relative percept standard deviation (RSD) of 8% and a recovery of 98% and 4 replicates of diluted reference material gave a recovery of 101%. The method specifications (EPA 1631) allow for maximum RSD of 21% and recovery range 77-123%.

Exploratory statistical analysis of the Hg data was carried out with SPSS 17.0. Data normality was checked using Kolmogorov- Smirnov and Shapiro Wilk tests and significant differences among data sets was carried out using non-parametric tests (Kruskal Wallis-Median). No results were excluded for this work. A more exhaustive statistical evaluation is planned upon completion of the monitoring campaigns after 2023.

3. Results and Discussion

During the last 8 years 580 samples from coastal areas of Greece were analysed for total Hg. The median Hg concentration of the entire dataset was calculated at 2.2ng/L. The Hg levels measured in all areas were well below the European Legislation threshold of 70ng/L (EC 2013/39) except for one sample. The measured concentrations of all samples were further examined in detail in order to identify spatial trends and possible hot spots for Hg. Values above 4ng/L (2 times the dataset median) along with outliers and extremes in each sub-area will be further discussed. The sub-areas, samples and % of values above 4ng/L in each area are presented in Table 1. The mean, median and range of Total Hg (ng/L) are presented in Table 2.

Table 1. Number of samples and % values above 4ng/L

Coastal Area	Total Samples	Samples and % of samples 4ng/L	
Crete coastline	10	2	20
Aegean Islands	37	16	43
Ionian Sea*	37	10	27
Amvrakikos	32	8	25
Patraikos	4	1	25
Korinthiakos	28	11	39
S. Peloponnese	59	9	15
Outer Saronikos-Attiki	14	1	7
West Saronikos	29	8	27
Inner Saronikos	59	13	22
Elefsina	40	25	62
Evoikos	55	16	29
Maliakos	10	1	10
Pagasitikos	42	12	29
Thermaikos	54	16	30
N. Greece coastline	69	22	32

*Ionian Sea: stations located in islands and on the Ionian coast of mainland Greece

The area which is clearly differentiated and can be identified as a ''hot spot'' is Elefsina bay. The mean and median Hg in Elefsina is above 4ng/L since 62% of measurements were above this limit (25 of 40 values). The three outlier values in Elefsina all refer to the station closer to the port (S1). Increased values were measured in the bottom waters of the central and west part (stations EL7 and S2) in summer and autumn months that could be attributed to release from the sediments due to anoxic / hypoxic conditions arising every year. Some elevated values were also found in the surface waters and could be attributed to atmospheric sources of Hg from industries located on the coast of Elefsina.

In all other areas the median values were close to the dataset median of 2.2ng/L as would be expected. However in some areas mean Hg levels were slightly elevated affected by several outlier and extreme measurements as seen in Figure 1. In the areas of Thermaikos, Northern Greece coastline, Inner Saronikos and Evoikos several outliers and extremes are observed as well as a significant number of measurements above 4ng/L.

In Thermaikos and the Northern Greece coastline relatively increased Hg concentrations were measured in stations affected by the major rivers (Axios, Aliakmon, Strymonas, Evros), in Thessaloniki bay, and in the gulf of Ierissos. The highest value of the entire dataset was measured in the surface water of Ierissos gulf / Stratoni (90.2ng/L) in the March sampling of 2018 (omitted from Figure 2). This station also gave an outlier value (15.2ng/L) in September of 2014.

In Evoikos some elevated concentrations were measured in Rafina, and Larymna possibly associated with marine traffic and a metallurgic industry, respectively, as well as offshore Asopos River. The maximum Hg concentration was measured in the bottom water offshore Asopos in 2014 (28.1ng/L).

In Inner Saronikos the increased Hg concentrations are associated with the Waste Water Treatment Plant (WWTP) outfall and atmospheric contributions of the metropolitan city of Athens. Two extreme Hg concentrations were found in the bottom waters of station S7 at the WWTP outfall (12.4 and 17.4 ng/L in both autumn and winter months). Station S11 offshore a major coastal highway of Athens also presented an extreme surface Hg value (18.2ng/L).

Table 2. Mean, median and range of Total Hg (ng/L) in the coastal areas of Greece

Coastal Area	Mean / Median	Range
Crete coastline	3.2 / 2.0	1.0 – 12.4
Aegean Islands	4.0 / 2.4	0.50-10.9
Ionian Sea*	3.1 / 1.6	0.5 – 18.2
Amvrakikos	3.1 / 1.9	0.5 – 11.8
Patraikos	2.6 / 2.4	0.9 – 4.6
Korinthiakos	3.3 / 2.8	0.5 – 7.0
South Peloponnese coast	2.3 / 1.6	0.5 – 10.0
Outer Saronikos-Attiki	2.8 / 2.9	0.7 – 4.5
West Saronikos	2.7 / 2.3	0.5 – 11.8
East (Inner Saronikos)	3.6 / 1.9	0.5 – 21.7
Elefsina	6.8 / 4.6	1.4 – 23.9
Evoikos	4.0 / 2.0	0.5 – 28.1
Maliakos	2.3 / 1.6	0.8 – 9.4
Pagasitikos	3.4 / 2.6	0.5 – 17.2
Thermaikos	4.8 / 1.9	0.8 – 36.9
Northern Greece coastline	5.0 / 2.0	0.50 – 90.2

*Ionian Sea: stations located in islands and on the Ionian coast of mainland Greece

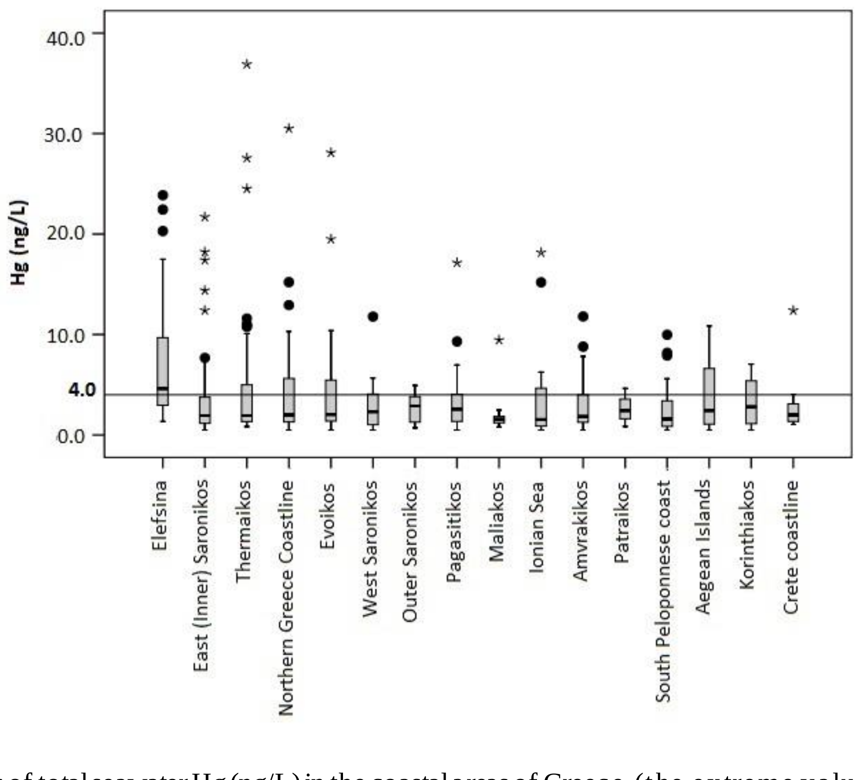

Figure 1. Boxplots of total seawater Hg (ng/L) in the coastal areas of Greece (the extreme value of 90.2ng/L was omitted for improved representation of the other areas)

Some other examples of elevated concentrations were found in the following areas: In volcanic environments (Santorini, Milos) Hg levels ranged from 5.5-6.6ng/L. In smaller ports (Volos-Pagasitikos, Igoumenitsa-Ionian Sea, Gytheio-Peloponnese, Souda-Crete) some extreme and outlier values were measured (Volos 17.2ng/L, Souda 12.4ng/L, Gytheio 7.9ng/L, Igoumenitsa 15.2ng/L). In the enclosed bays of Kalloni and Gera in Lesvos Hg levels ranged from 7.5 to 10.9ng/L. In areas affected by rivers and agricultural activities such as Maliakos with an extreme bottom value of 9.4ng/L and Messiniakos with outlier values of 8.2 and 10ng/L. In the coastal areas of the Ionian Sea affected by the rivers Louros and Arachthos elevated Hg values were also found (4.0-11.8ng/L).

Summarizing all of the above it becomes apparent that stations near ports, major cities, motorways, river estuaries and mining/metallurgical activities presented some of the highest values.

The Kruskal-Wallis and Median tests were applied and Hg levels in Elefina were found statistically higher. There were no statistical differences in the levels of Hg between the other coastal areas of Greece.

The dataset was also evaluated for differences with depth. No statistical differences were found between the surface and bottom sample neither for the entire dataset nor for each of the sub-areas.

4. Conclusions

The Hg levels measured in all coastal areas of Greece since 2012 were well below the European Legislation Threshold (EQS) of 70ng/L. However, since there are some indications of elevated Hg levels in fish and seafood of the Aegean and Ionian seas further research is required. Specifically the seawater Hg levels of the coastal waters of Greece monitored under the implementation of the WFD and the Hg levels of deep waters of the Aegean and Ionian seas monitored under the implementation of the MSFD should be correlated with Hg levels in fish and seafood. Furthermore estimations of possible risks for human health from fish and seafood consumption are also necessary. The combined approach of Hg as a contaminant in seawater and edible marine biota will allow for the proposal of the most suitable and safe 'Good Environmental Status' (GES) limit for this highly toxic element.

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