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A FIRST INSIGHT OF Hg OCCURRENCE IN THE HELLENIC VOLCANIC ARC

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Abstract Mercury is a highly toxic element with both natural and anthropogenic sources to the marine environment, with implications to ecosystems and human health. It is recognized as a priority pollutant by the European Environmental Legislation and the United Nations Environmental Program (UNEP). The complex geodynamic and geological setting of the Hellenic Volcanic Arc (HVA) in Greece, reflects in a great variety of geochemical compositions for many thermal fluid manifestations and leads to the necessity of studying them separately.

The present paper is a preliminary presentation of Hg levels in aquatic samples from Methana peninsula, Kos and Nisyros islands and Yali islet. These study areas are affected by active fault zones which characterized as pathways of elevated heat flow. Samples were collected along the coastline, both from thermal springs and swallow-waters hydrothermal vents and analyzed for Total mercury (THg), trace metals (TM) nutrients, total alkalinity (At), Dissolved Oxygen (DO) and physicochemical parameters where measured in situ.

The concentrations of THg were quite variable, ranging from 3.48 to 278.53 pM (mean 32.56 pM), while in Kos spotted the highest (278.53 pM) with no values exceeding the limit set by the WFD (70 ng /l or 349.02 pM). It appears to have a strong positive correlation with nutrients, DO, while strong negative one with pH and At. In the area of Nisyros – Yali the measured THg falls in between the other sites , while in Methana is the lowest levels with strong positive correlation with salinity, conductivity and pH and negative with DO and temperature. Strong positive correlation of THg was with Li, Al, Mn, Fe, As, Sr, Cd in every sample area.

We hypothesize that underwater hydrothermal activity may constitute a considerable Hg source to the oceans, as fluids from thermal waters are often brackish to saline due to marine intrusion into the coastal aquifer. As a result, more research is required in these areas in order to determine the amount of Hg contribution to the oceans by the type of volcanism and tectonic activity, as well as the positive correlations between Hg and TM such as As, Cd, Mn and Fe.

Keywords: *mercury (Hg) , Hellenic Volcanic Arc, thermal springs, hydrothermal fluid*

1. Introduction

The UNEP Minamata Convention , which was ratified in 2017, has the objective of reducing human exposure to toxic mercury (Hg). The main route of exposure for humans is through the consumption of fish that accumulate Hg from the ocean (Petrova et al., 2020). Recent calculations of anthropogenic Hg emissions indicate a three-fold increase in Hg levels in the surface ocean since before industrialization (Lamborg et. al., 2014). Although extensive research has improved our understanding of anthropogenic Hg emissions, there are still fundamental questions remaining about the natural sources of Hg and its transformations in the environment (Outridge et al., 2018). One particularly significant natural source of Hg is hydrothermal vents (HV). However, estimates of Hg emissions from HV vary widely (ranging from 20 to 2,000 tons per year) and are based on measurements from only a few HV locations (German et al., 2016). Other sources of Hg, such as atmospheric deposition, riverine inputs, and submarine groundwater discharge, are considered secondary sources that contribute to the recycling of natural and anthropogenic Hg (Outridge et al., 2018). Hydrothermal systems in shallow (less than 200m depth), near-shore environments have been largely ignored, and their contribution to the global Hg cycle remains unknown. A first investigation of the Panarea site (Italy) (Bagnato, et al., 2017) shows significant Hg inputs, especially Hg0. The study finds that the Hg0 evasion flux is negligible in the MED budget. The authors state that previous assessments of total hydrothermal inputs to the MED ∼15Mgy−1 are underestimations. (Cossa et al., 2022). In the South Aegean Sea, several shallow sites are known (e.g.,Nisyros, Milos, Kolumbo) (Nomikou et al., 2013)., but this possibly important source is far from being well-constrained; obviously, more data are crucially needed in this field.

2.Material and Methods

2.1 Study area- sampling

The selected areas represent different geographic, geologic and chemical environments. Samples (coastline, surface, depth up to 14m) were collected on September of 2022 from Methana, Nisyros-Yali and Kos. SCUBA diving was utilized to collect fluids from 2 areas in Nisyros- Yali of diffuse hydrothermal venting.

Kos island is located at the eastern part of the HVA and formed at around 5 Ma, at the beginning of the Pliocene. The geologic units of Kos consist of alluvial deposits with greenschists and flysch in the northern part of the island, lacustrine and terrestrial deposits of the Pliocene age in the central part with tuffs, and ignimbrites of the Quaternary age that cover the southern part of the island. Furthermore, hydrothermal activity is noticeable along the island with the most important sites being (i) the thermal spring of Therma, which is emerging on the beach close to St. Fokas, (ii) the ferruginous spring of Kokkinonero rich in CO2, and (iii) the intensively degassing area of Paradise beach at Kefalos Bay. (Daskalopoulou et al., 2019)

Saronikos Gulf displays a complicated morphology which is strongly related to the neotectonic evolution of the gulf and the Quaternary volcanic intrusions. It can be divided into a western and an eastern part by a shallow N–S platform, part of which emerges and creates the islands of Salamina, Aegina, Angistri, Poros and the peninsula of Methana. This zone comprises several volcanic outcrops of Plio-Quaternary age, representing the northwestern edge of the HVA. The larger graben correspond to two basins: a) the Epidavros Basin with a maximum water depth of 400 m and a Plio-Quaternary sediment thickness of 250-500 m, and b) the Megara Basin with a maximum water depth of 250 m and a Plio-Quaternary sediment thickness of more than 500 m. (Lampridou et al., 2018)

The submarine region of Nisyros, extending from Kos in the north to Tilos in the south, constitutes a large basin-tectonic graben with 600 m average depth. This basin is interrupted by a complex volcanic group forming the volcanic islands of Nisyros, Pachia, Pergoussa, Yali and Strongyli and small intra-volcanic basins with less than 350 m of depth. (Nomikou & Papanikolaou, 2011)

2.2 Analytical Procedure

The analysis of THg was occurred with EPA method 1631e measuring mercury in water by oxidation, purge and trap and cold vapor atomic fluorescence spectrometry (CVAFS) by instrumentation of TEKRAN MODEL 2500. All Hg sample is oxidized to Hg(II) with BrCl. After oxidation, the sample is sequentially reduced with NH2OH•HCl to destroy the free halogens, then reduced with stannous chloride (SnCl2) to convert Hg(II) to volatile Hg(0). The Hg(0) is separated from solution by purging with nitrogen and then collected onto a gold trap. Consequently, the Hg is thermally desorbed from the gold trap into an inert gas stream that carries the released Hg(0) to a second gold (analytical) trap. The Hg is desorbed from the analytical trap into a gas stream that carries the Hg into the cell of a cold-vapor atomic fluorescence spectrometer (CVAFS) for detection . This method is accompanied by Method 1669: Sampling Ambient Water for Determination of Trace Metals at EPA Water Quality Criteria Levels (Sampling Method). The Sampling Method is necessary to preclude contamination during the sampling process.

An Agilent 7900 ICP-MS (Agilent Technologies, Santa Clara, CA, USA) was used for the determination of trace elements in samples. The 7900 ICP-MS features Ultra High Matrix Introduction (UHMI) technology, which uses an innovative aerosol dilution approach allowing samples with TDS levels of up to 25% to run. Nutrients were measured with HACH DR/4000 while physicochemical parameters were measured in situ using portable multimeter.

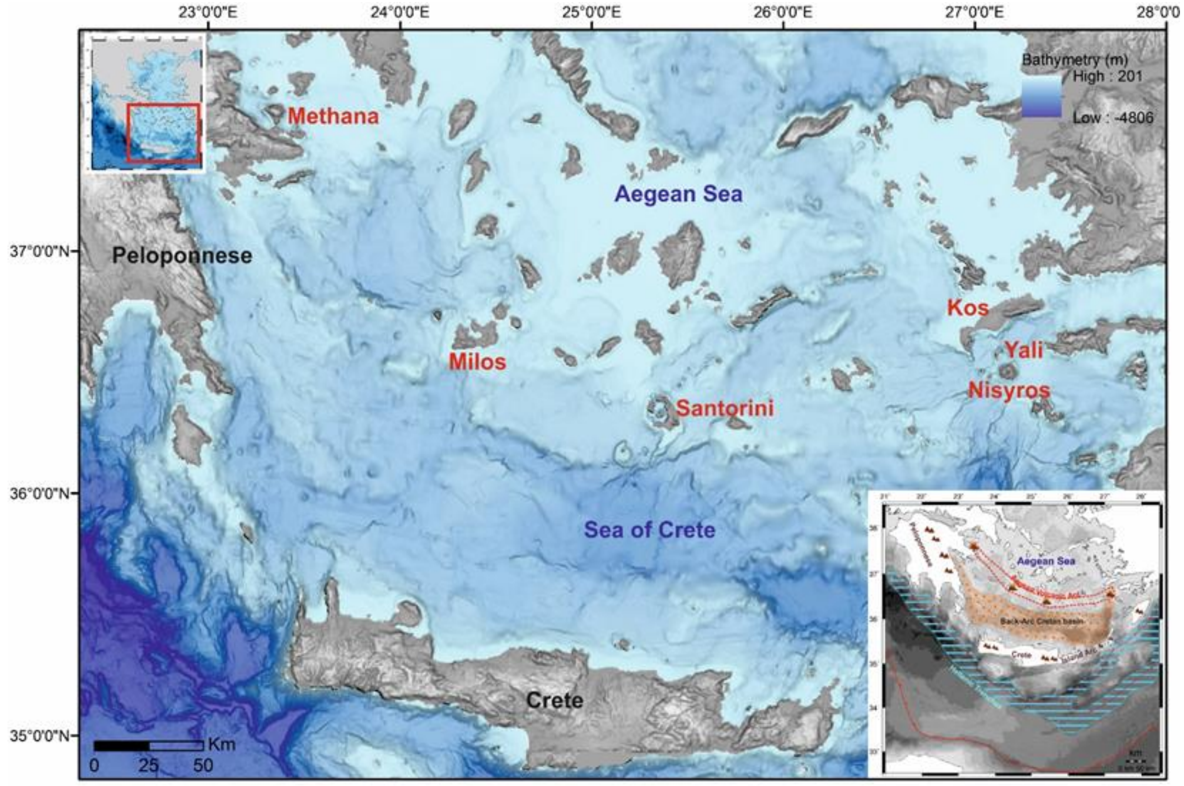

Figure 1. Synthetic map of the southern Aegean Sea combining onshore and offshore data from oceanographic surveys. The volcanic groups are indicated within red boxes together with the names of the main terrestrial and submarine volcanic centers along the volcanic arc and the specific sampling areas. (modified after Nomikou et. al., 2013).

3. Results

Table 1. Range values of pH, conductivity, salinity, T, DO, At and THg of the collected samples in Kos, Methana and Nisyros-Yali.

Site	pH	Conductivity (mS/cm)	Salinity (ppt)	T (ºC)	DO (mg/L)	At (mg CaCO3/L)	THg (pM)
Kos	1.8 - 7.7	1.03 - 58.2	0.4 - 38.7	25.2 - 41.1	0.41 - 10.25	124 - 957	3.48 - 278
Methana	5.8 – 6.0	16.4 - 58.0	9.2 - 38.4	27.3 - 37.8	0.51 - 6. 04	5.96 - 840	4.79 - 46.1
Nisyros Yali	5.9 - 7.5	49.1 - 57.4	31.9 - 38.3	25.0 - 48.5	5.9 - 11.9	99.4 - 293	13.9 - 141

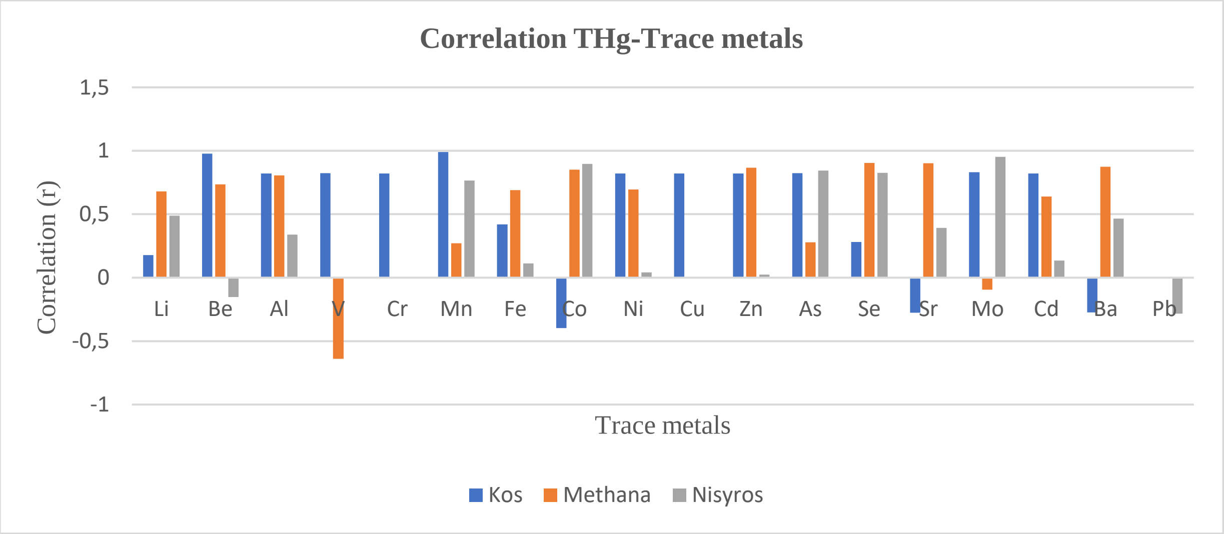

Figure 2. Correlation graph between THg and trace metals.

The range of the measured THg concentrations from sea water samples, surface and nearshore areas, are shown in the table 1, along with the range of pH, conductivity , salinity, temperature, dissolved oxygen and alkalinity.
The minimum THg concentrations were found at the hot spring of Kos Ebros Thermi- St. Fokas near the coast, while the maximum at Kokkinonero spring of Kos.
In Figure 2 it is shown the correlation graph between THg and the analysis of trace metals.
Concentrations of THg in every area appear to have a strong positive correlation with Al, Mn, As,Se and Cd. In Kos there is also a strong positive correlation with Be, Cr, Ni, Cu, Zn and Mo. In Methana strong positive correlation is shown with Co, Ni, Zn, Se, Sr and Ba , while a negative with V. In the area of Nisyros strong positive correlation appears to have with Co, As, Se and Mo.

4. Discussion/Conclusion

In the area of Kos, at spring Kokkinonero, were measured he highest levels of THg at 279 pM , Al at 2074 µM, V at 1.40 µM , Co at 105 µM, Ni at 249 µM , Cu 31,6 at µM, Zn at 137 µM and As at 54.3 µM.

Samples from nearshore areas show a wide range of THg values ranging from 3.48 pM to 169 pM, which appears to be due to the complexity of the geochemical processes. The highest Li values are observed (up to 369 µM), while the lowest values of Al and As,. In these areas we also find the highest levels of Sr with values up to 149 µM. At the same time, the highest temperature values are observed in the range of 32 ºC to 41 ºC, which points to the high activity of the hydrothermal fields and tectonics of the area.
In the area of Nisyros, samples from the open sea and near to Yali in max depth of 15m, appear to have similar values of physicochemical parameters and nutrients, as well as in the analysis of TM.
Further investigations into the role of chemical reactions and correlations with trace metals in the shallow subsurface, will be necessary to better understand the source, transport and fate of Hg.

Table 2. Values of trace metals and THg of the collected samples in Kos, Methana and Nisyros-Yali.

Site	LAT	LON	THg (pM)	Al (μM)	Mn (μM)	Fe (μM)	As (μM)	Sr (μM)	Cd (μM)
K1- Ebros Thermi St. Foka	36.844683	27.316451	3.48	nd	0.087	nd	0.17	139	nd
K2 - Agia Irini	36.826872	27.234016	169	0.12	1.714	0.790	0.39	149	nd
K3 - Coastal cold spring	36.846361	27.323137	23.7	nd	nd	nd	0.01	3.95	nd
K4 - Kokkinonero	36.855637	27.248101	278	2074	8.23	0.14	54.3	0.56	0.79
M1 - Paphsania's baths	37.637996	23.360028	46.07	8.50	6.28	269	0.03	87.8	nd
M2 - St. Anargyri thermal spring	37.578362	23.387601	35.91	2.00	30.3	6.45	1.42	103	nd
M3 - St. Nikolaos thermal spring	37.587208	23.398484	4.79	0.55	6.61	6.45	0.03	32.5	nd
N1 - Yali	36.646776	27.118233	64.3	0.98	0.33	1.59	0.03	94.5	0.001
N2 - Mandraki baths	36.61259	27.15393	141	0.47	55.9	0.87	2.92	138	0.003
N3 - Thermiani	36.619069	27.179496	28.4	0.54	4.52	1.77	0.98	140	0.01
N4 - Avlaki baths	36.55826	27.17592	13.9	0.17	22.5	0.35	0.30	111	0.001
N6 - St.Antonios Yali	36.656816	27.139265	29.2	0.12	0.16	0.41	0.03	94.4	nd

5.Acknowledgements

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