Gaseous elemental mercury concentration and diurnal evasion fluxes from the water-air interface in the coastal environments of the Northern Adriatic Sea

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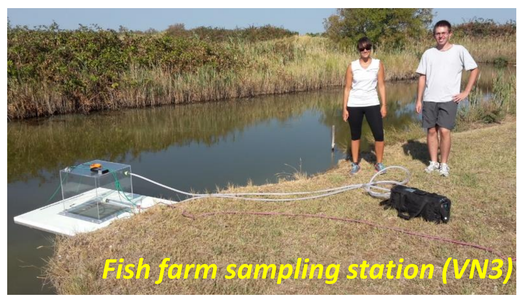
INTRODUCTION

The Marano and Grado Lagoon (Northern Adriatic Sea, Italy) is affected by mercury (Hg) contamination coming from two sources: the first and most significant is the historical mining activity from Idrjia (Slovenia), whereas the second source is the discharge of effluents from a chlor-alkali plant (Torviscosa, Italy) **[1]**. Hg contamination affects both the water column and the sediments, where Hg contents decrease from east to west. Mercury can be found as insoluble sulphide (cinnabar, HgS), bound to oxides and hydroxides or to organic matter. The fraction present in these last forms is easily remobilised when redox conditions change **[2]**. The result is the occurrence of dissolved reactive mercury (Hg^{2+}) in the water column, which can be reduced to elemental mercury (Hg^0). This form is volatile and easily released into the atmosphere. This represents a potential detoxification path for the water environment **[3]**. The Hg^0 is also the most abundant Hg form in the atmosphere (95% of the total) and is usually indicated as gaseous elemental mercury (GEM).
In this work, the evasion of Hg in terms of fluxes were determined at four sites: two are located at a fish farm in the Lagoon (VN1 and VN3), which has previously been investigated for Hg contamination **[4]**, the third site is in the open Lagoon environment (G) and the last site is in a pristine area of the Gulf of Trieste, the Bay of Piran (P) in Slovenia.

OBJECTIVES

In order to better understand some aspects of the Hg biogeochemical cycle in these environments, the aim of this work was to estimate the diurnal evasion fluxes of Hg at the water-air interface by means of a floating chamber. Results were related to both the seasonal variability of the meteorological data and the physico-chemical parameters of the water column. Moreover, considering the high level of contamination of the Lagoon environment, GEM concentrations in the air were monitored in order to highlight possible anomalous high values which can be potentially harmful for human health after exposure through inhalation.

MATERIALS AND METHODS

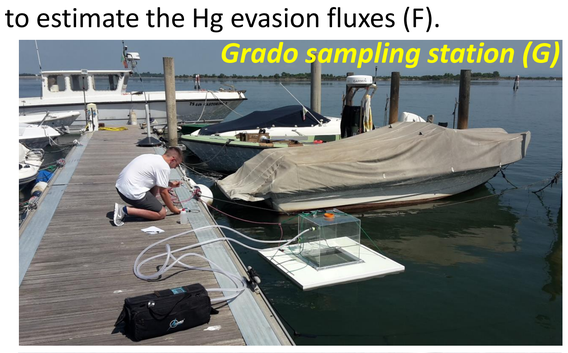

Fish farm sampling station (VN3)

- Three seasonal campaigns (summer: Jul-Aug ‘17; autumn: Oct-Nov ‘17; winter: Jan-Mar ’18) were carried out. During each sampling, continuous measurements of GEM were taken inside the chamber 5 or 6 times per day for 10 minutes each time. The time interval between each set of measurements was approximately 90 minutes. A dynamic flux chamber (DFC) coupled with a real-time adsorption spectrometer (Lumex RA915M) was used to estimate the Hg evasion fluxes (F).

$$F = \frac{(C_f - C_i)\,Q}{A}$$

Final (C_f) and initial (C_i) average concentrations of GEM inside DFC
Q = flow rate of air flowing through the chamber (1.2 $m^3\ h^{-1}$)
A = surface area occupied by the chamber (0.25 m^2)

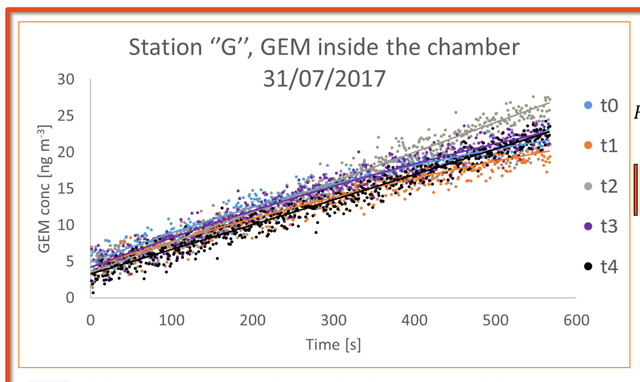
- GEM concentrations outside the chamber were measured before employing the chamber.
- Physico-chemical parameters of the water column (T, salinity, Eh, pH, O_2) and air temperature were measured in situ using portable probes.
- Water samples were collected during each sampling in order to determine the total dissolved Hg (DHg) using the CV-AFS technique.
- Meteorological data were collected from OSMER-ARPAFVG website (www.osmer.fvg.it)


Grado sampling station (G)

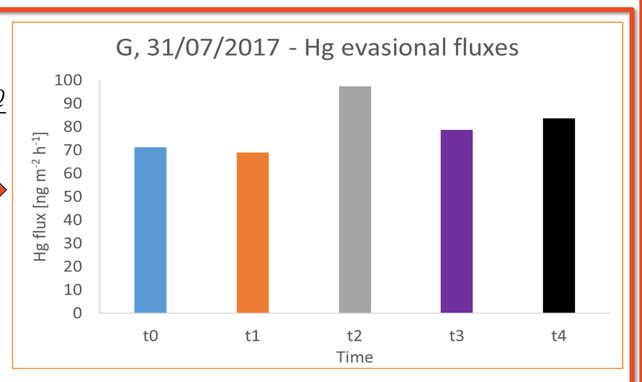

Piran sampling station (P)

RESULTS AND DISCUSSION

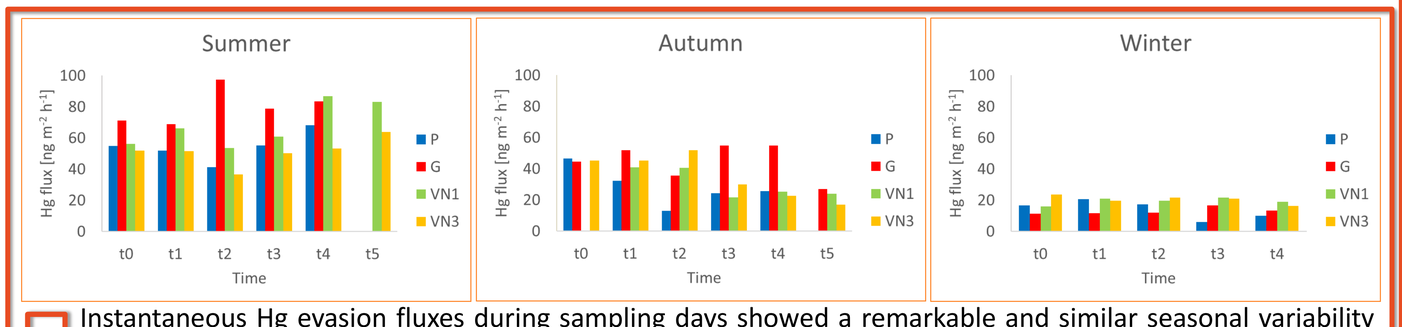
1 Regarding the GEM concentrations, the average daily values found in this work were similar in all experimental sites and in all seasons, ranging from 1.60 (G-summer) to 2.87 ng m^{-3} (VN1-summer), without significant daily variations. These values are close to the natural background (3.1±0.12 ng m^{-3}) estimated for this lagoon environment **[5]** likely due to the atmospheric dilution of Hg emitted, amplified by the wind.



$$F = \frac{(C_f - C_i)\,Q}{A}$$

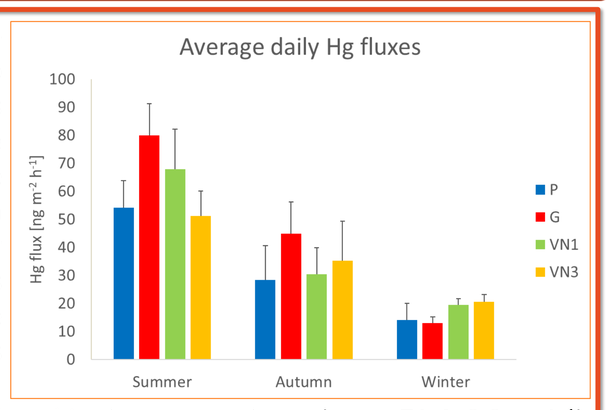


2 GEM concentrations inside the DFC constantly increased during the 10-min measurement intervals in all the sampling stations, different seasons notwithstanding. For example, experimental site G (in the Lagoon) is shown in the above pictures.

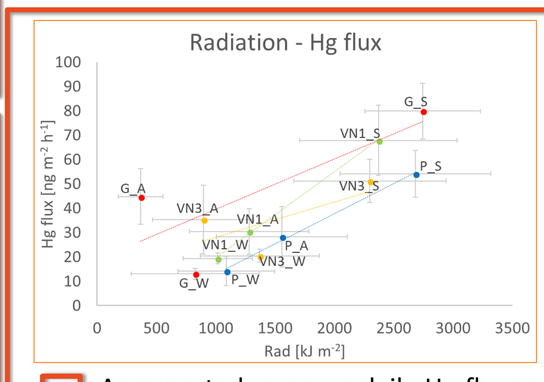


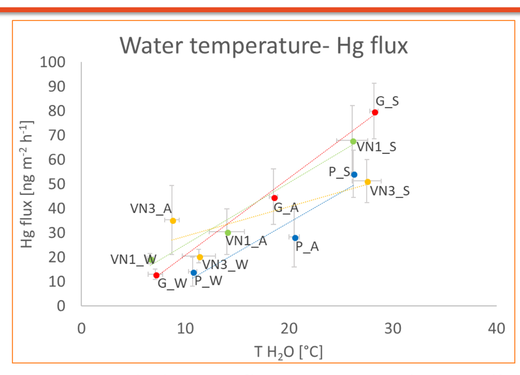
3 Instantaneous Hg evasion fluxes during sampling days showed a remarkable and similar seasonal variability for all the experimental sites. In addition, it was not possible to identify a common diurnal trend in Hg fluxes among sites, thus suggesting a high site-specific variability. These differences are most likely attributed to factors such as hydrodynamics, volatile Hg availability in the water column and turbidity.

4 Average daily Hg fluxes at the water-air interface ranged from 13.0±2.2 up to 79.9±11.4 ng $m^{-2}\ h^{-1}$. These results are higher than those reported in the literature for other marine environments but comparable with those observed in other contaminated areas **[6]**. Also in this case, a clear seasonal trend can be observed, showing the highest values in the summer season.



Despite the highest DHg concentrations found in the water column (up to 71.4±0.9 ng L^{-1}), both the fish farm sites showed lower Hg evasion fluxes than the open lagoon site (G). This is likely due to the low hydrodynamics and high water turbidity found at VN1 and VN3 which prevents the photoreduction of Hg by limiting the penetration of solar radiation.





5 As expected, average daily Hg fluxes showed a good correlation to solar radiation, thus confirming its role in promoting volatile Hg^0 formation through photoreduction of the oxidised forms (Hg^{2+}) in the water column.

Average daily Hg fluxes were also well correlated to the water temperature. High water temperatures can promote biotic reduction of Hg^{2+} to Hg^0, thus favouring its volatilisation. Moreover, Hg^0 solubility decreases with an increase in water temperature.

CONCLUSIONS

- Hg evasion fluxes at the water-air interface were significantly high in this Lagoon environment and strongly influenced by site-specific variables.
- The high Hg evasion fluxes found confirm that they play a significant role in the detoxification path of the water column.
- Although no clear diurnal trend was observed during the experiments, a clear seasonal variability exists and it correlates to solar radiation and water temperature. The highest fluxes were found in the summer season in all the experimental sites.
- GEM concentrations were significantly lower than the threshold level of attention for human health (1000 ng m^{-3} **[7]**), despite the high effusive fluxes at the water-air interface.

References

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