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 Idrija (Slovenia), whereas the second source is the discharge of effluents from a chlor-alkali plant (Forvincosa, 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 remobilized when redox conditions change2. The result is the occurrence of dissolved reactive mercury (Hg(D)) in the water column, which can be reduced to elemental mercury (Hg0). This form is volatile and easily released into the atmosphere. This represents a potential detoxification path for the water environment3. The Hg0 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 (V1N and V3N), which has previously been investigated for Hg contamination4, 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.

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 (V3N-summer), without significant daily variations. These values are close to the natural background (3.1±0.12 ng m-3) estimated for this lagoon environment5 likely due to the atmospheric dilution of Hg emitted, amplified by the wind.

2) GEM concentrations inside the DFC constantly increased during the 10-min measurement intervals at 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 up to 79.9±114 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 areas6. Also in this case, a clear seasonal trend can be observed, showing the highest values in the summer season. Despite the highest DfG concentrations found in the water column (up to 71±410 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 V1N and V3N which prevents the photooxidation 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 formation through photooxidation of the oxidized forms (Hg0) in the water column.

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