

Dissolved Gaseous Mercury Production at a Marine Aquaculture Site in the Mercury-Contaminated Marano and Grado Lagoon, Italy

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Abstract

Dissolved gaseous mercury (DGM) production was examined in relation to ultraviolet radiation within a marine aquaculture site in the contaminated Marano and Grado Lagoon (Italy). The measured rates of DGM production relative to time elapsed (17.06 and 20.68 pg h⁻¹, respectively) were substantially (6–20 times) higher than what has been observed in other marine Hg studies. We measured similar levels of DGM relative to dissolved total mercury (THg_D) (0.84%–8.91%) at these sites in comparison to uncontaminated marine sites, however relative to other moderately-contaminated marine sites in Portugal the % DGM/THg_D was high. These results suggest a substantial capacity for Hg volatilization from these highly contaminated lagoons to the atmosphere due to photoreduction mechanisms.

Keywords Dissolved gaseous mercury · Photoreduction · Aquaculture · Lagoon · Contamination

Mercury (Hg) is a global contaminant found even in remote areas free from industrial pollution. It is present in several different forms in ecosystems including elemental mercury (Hg(0)), divalent mercury (Hg(II)), and methylmercury (MeHg; CH₃Hg(I)). MeHg is a neurotoxin that can bioaccumulate and biomagnify in aquatic organisms resulting in toxic effects (Kidd et al. 2005), as such the retention of mercury in ecosystems is a concern for ecosystem health. Mercury can be lost from natural water through the process of Hg(II) photoreduction to aqueous Hg(0) (known as dissolved gaseous mercury (DGM)) through primarily abiotic reactions with ultraviolet radiation (O'Driscoll et al. 2018; Qureshi et al. 2010). DGM is volatile and may undergo

evasion to the atmosphere and lessen the Hg burden in ecosystems.

Several researchers have examined Hg photoreduction in freshwater ecosystems (O'Driscoll et al. 2004, 2018; Haverstock et al. 2012), and open ocean systems (Qureshi et al. 2010), however there is much less information available for coastal marine systems. In particular, we currently do not know if the proportion and rate of Hg photoreduction is similar between contaminated and uncontaminated coastal sites, therefore making it difficult to predict long-term effects. This paper addresses this knowledge gap.

The purpose of this research was to quantify the relationships between the intensity of incident solar radiation and the degree of Hg photoreduction in a mercury-contaminated coastal lagoon in order to compare the rate and amounts of DGM production. These measurements are critical for modelling DGM loss processes in contaminated coastal waters and marine aquaculture sites.

Materials and Methods

Study sites were located in the Marano and Grado Lagoon in the northern Adriatic Sea (Fig. 1), an economically important area in northeastern Italy with substantial aquaculture development. This area has historical Hg contamination in

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Fig. 1 Location map of field sites, VN1 and VN3, within the Val Noghera fish farm in the Marano and Grado Lagoon, northern Adriatic Sea, Italy

sediment stemming from two fluvial sources: the Isonzo River which drains the catchment of the world's second largest Hg mining area (Idrija Mercury Mine, Slovenia) (Covelli et al. 2001), and the Aussa-Corno river system which received more than fifty years of industrial discharges from a now decommissioned chlor-alkali plant (Covelli et al. 2009).

The first study site (VN1) was located in the eastern sector of the Val Noghera fish farm (33T 0368213 Eastings, 5063104 Northings), an active aquaculture site with high Hg concentration in sediments ($4.20\text{--}6.87\text{ mg kg}^{-1}$), while the second study site (VN3) was located in the western sector (33T 0368213 Eastings, 5063104 Northings) where aquaculture is no longer active, and with lower Hg concentrations ($2.15\text{--}5.10\text{ mg kg}^{-1}$) (Petranich et al. 2018a). VN1 has more intense recycling and recirculation of the waters than VN3, due to the periodic opening of sluice gates, the only mechanism for water exchange between fish farm and external lagoon environment (Fig. 1). More details regarding the hydrogeology, fish farming activities and management of the area have been described in previous works (Petranich et al. 2018a, b). Sampling activities and analyses were performed at VN1 on May 11, 2018 and at VN3 on May 31, 2018.

The intensity and spectral distribution of incoming solar radiation was quantified using an OceanOptics USB 4000 spectroradiometer with a fibre-optic (10 m length, 200 μm

diameter) and spectral diffusion probe (diameter 4.3 mm). The spectroradiometer probe was fastened to a post $\sim 3\text{ m}$ above ground in an unshaded area close to the sampling site. Spectral readings were taken continuously every 1 min during the field campaign for UVA (280–320 nm), UVB (320–400 nm), and visible (400–800 nm) radiation and integrated using spectra suite software.

Water samples were collected every 30 min for 8 h during the peak sunlight period to determine total dissolved Hg (THg_D) and DGM. In parallel, temperature, pH, redox potential, salinity and dissolved oxygen in the water column were measured in situ using portable probes (pH-meter PH25, Conductivity meter CM 35+ and Oxygen meter OXI 45P by Crison Instruments).

THg_D analysis was conducted using the cold vapour atomic fluorescence spectrometry technique (CV-AFS) with a mercury specific detector (Analytik Jena, Mercury) according to the EPA Method 1631e. The calibration was performed using NIST 3133 certificated solution. The limit of detection (LOD) and quantification (LOQ) were equal to 0.63 ng L^{-1} and 2.11 ng L^{-1} , respectively. Total mercury (THg) in sediment was reported by Petranich et al (2018a) using a Direct Mercury Analyser (DMA-80, Milestone).

Gaseous elemental mercury (GEM) was measured in the headspace of a 1L fixed-volume water subsample in a glass

container in the dark, using the Lumex RA915M instrument, which uses atomic absorbance with Zeeman correction to achieve low detection limits for Hg in air (2.0 ng m^{-3}). By using a closed loop system to bubble the internal air through the water sample we created an equilibrium between DGM aqueous and GEM in air over a 30-minute measuring period (Fig. 2). O’Driscoll et al. (2003) previously reported that the efficiency of DGM to be removed from a bubbled solution was dependant upon temperature with shorter bubbling times required for warmer water temperatures. They observed >90% DGM removal with a sparging time of 5 min at a temperature of 303.15 K, suggesting rapid extraction for the temperatures used in our experiments presented here.

Calculation of DGM was performed using the dimensionless Henry’s law constant ($H' = 0.33$ for artificial sea water at 298.2 K) as determined by Andersson et al. (2008) in a similar bubbling system. 298.2 K was a relevant temperature correction given the ranges of temperatures observed in the surface waters sampled at each site (297.15–301.15 K range at VN1 and 300.15–305.15 K Range at VN3). The system blank (MilliQ) was found to be lower than the LOD (median 1.4 ng m^{-3}) and this value was reached within minutes of completing the experiments, thus it was not necessary to subtract it.

Results and Discussion

Most of the physical and chemical water parameters varied over the duration of the analysis and some similar trends were observed. For example, pH was observed to increase from 8.8 to 8.9 at site VN1 over 8 h, and from 8.2 to 8.4 at site VN3 over the same time period (Table 1). It was found that pH was significantly correlated with DGM concentrations at both VN1 ($R^2 = 0.56$, $p = 0.04$) and VN3 ($R^2 = 0.71$, $p = 0.01$), although this may be due to an auto-correlation with solar radiation. Acidity is known to decrease in natural waterbodies as photosynthesis outcompetes respiration

and aqueous CO_2 is removed from the system. As such, this small change in pH may be related to cumulative radiation received during the daylight hours, similar to the mechanisms governing Hg photo reactions (Hofmann et al. 2011).

The DGM concentrations at VN1 ranged between 237.6 and 401.5 pg L^{-1} (mean = 331.4 pg L^{-1} ; SD = 42.94; $n = 13$) and increased over the course of the field measurements with concentrations decreasing slightly after 13:00 (Fig. 3). THg_D at this site (Table 1) ranged between 3.85 and 28.22 ng L^{-1} (mean = 7.7; SD = 6.17 ng L^{-1} ; $n = 13$), which resulted in % DGM/ THg_D ranging between 0.84% – 8.24%. At VN3, DGM concentrations varied between 200.3 and 321.5 pg L^{-1} (mean = 279.5 pg L^{-1} ; SD = 46.99; $n = 12$) and increased over the course of the field measurements with a decline observed in mid-afternoon corresponding with a decrease in UV radiation due to clouds (Fig. 4). THg_D at this site (Table 1) ranged between 2.86 and 9.13 ng L^{-1} (mean = 5.04; SD = 2.06 ng L^{-1} ; $n = 12$), which resulted in % DGM/ THg_D ranging between 2.89% and 8.91%. Concentrations of DGM in water were correlated with incoming UVB measurements at both sites (Site VN1: $R^2 = 0.48$, $p = 0.09$, $n = 13$; Site VN3: $R^2 = 0.70$, $p = 0.01$, $n = 12$).

Emili et al. (2012) found that the seasonal-average concentrations of DGM within a benthic chamber experiment at the sediment–water interface in the Marano and Grado Lagoon were variable with season, ranging between 17.3 pg L^{-1} in autumn to a maximum of 795.0 pg L^{-1} in summer, with corresponding levels of THg_D of 5.47 and 5.53 ng L^{-1} . This would represent a % DGM/ THg_D of 0.3% in autumn and 14.4% in summer. This matches quite well with the measurements observed in our study at the same general location. In comparison, Sorensen et al. (2013) found that in both uncontaminated coastal areas and open-ocean areas of the West Atlantic Ocean the fraction of DGM/ THg_D ranged between 7.8% and 15.8% respectively, which is similar to our contaminated lagoon site readings.

In contrast, Cesario et al. (2017) found that DGM concentrations ranged between 13.4 and 40.0 pg L^{-1}

Fig. 2 Schematic diagram of gaseous elemental mercury (GEM) headspace analysis for the determination of aqueous Hg(0) in water samples

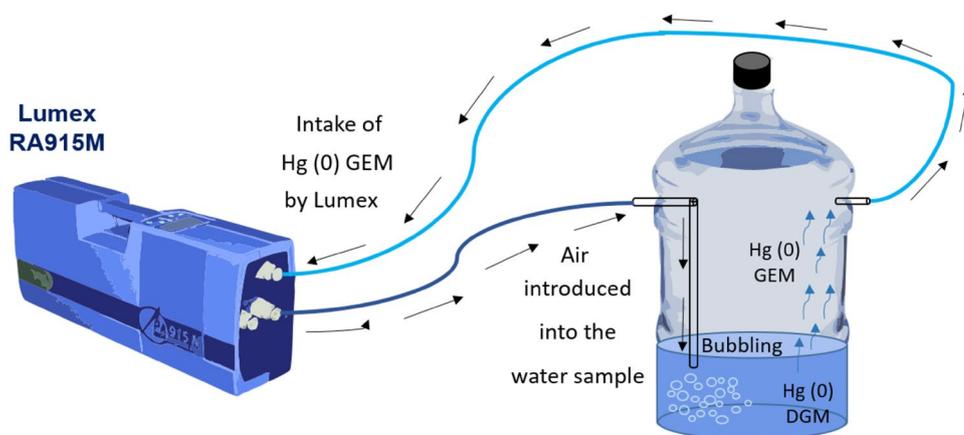


Table 1 Water chemistry parameters measured at study sites VN1 and VN3 during experiments

Hour	Eh (mV)	pH	Salinity (g/L)	O ₂ (mg/L)	O ₂ (%)	THg _D (ng/L)	THg _D SD
VN1							
9:40	107	8.81	25.8	6.83	79.5	28.22	0.10
10:05	93	8.82	25.8	6.77	79.1	10.93	0.94
10:30	84	8.79	26.1	6.83	79.3	5.77	0.08
11:00	84	8.74	26.1	6.58	77.4	3.85	0.11
11:30	85	8.79	26.2	6.63	77.4	4.40	0.07
12:00	79	8.84	26.1	6.7	78.4	5.96	0.04
12:40	83	8.86	26.2	7.26	85.6	7.54	0.05
13:10	80	8.84	26.1	7.44	88.3	4.94	0.03
13:40	75	8.89	26.0	7.24	86.9	5.49	0.05
14:10	72	8.87	26.0	7.71	92.4	4.81	0.06
14:40	76	8.89	26.2	7.7	92.9	6.59	0.27
15:10	78	8.9	26.2	7.81	93.7	4.84	0.13
15:40	72	8.91	26.1	7.7	92	6.76	0.04
VN3							
9:30	56	8.27	30.6	4.58	58.7	4.30	0.08
10:00	70	8.29	30.9	4.44	55.7	6.94	0.09
10:30	75	8.19	30.7	4.65	58.8	3.79	0.10
11:00	81	8.31	30.7	5.04	64.3	2.86	0.03
11:30	64	8.34	30.8	5.32	68.6	3.47	0.01
12:00	72	8.3	30.8	5.32	69.0	3.42	0.00
13:00	57	8.27	30.7	5.57	73.5	4.03	0.04
13:30	73	8.41	30.9	6.06	80.7	6.30	0.16
14:00	82	8.42	30.8	6.55	87.7	4.56	0.00
14:30	70	8.43	30.8	6.38	86.0	3.77	0.05
15:00	82	8.45	30.8	7.29	98.4	9.13	1.20
15:30	75	8.44	30.7	7.19	97.4	3.79	0.03

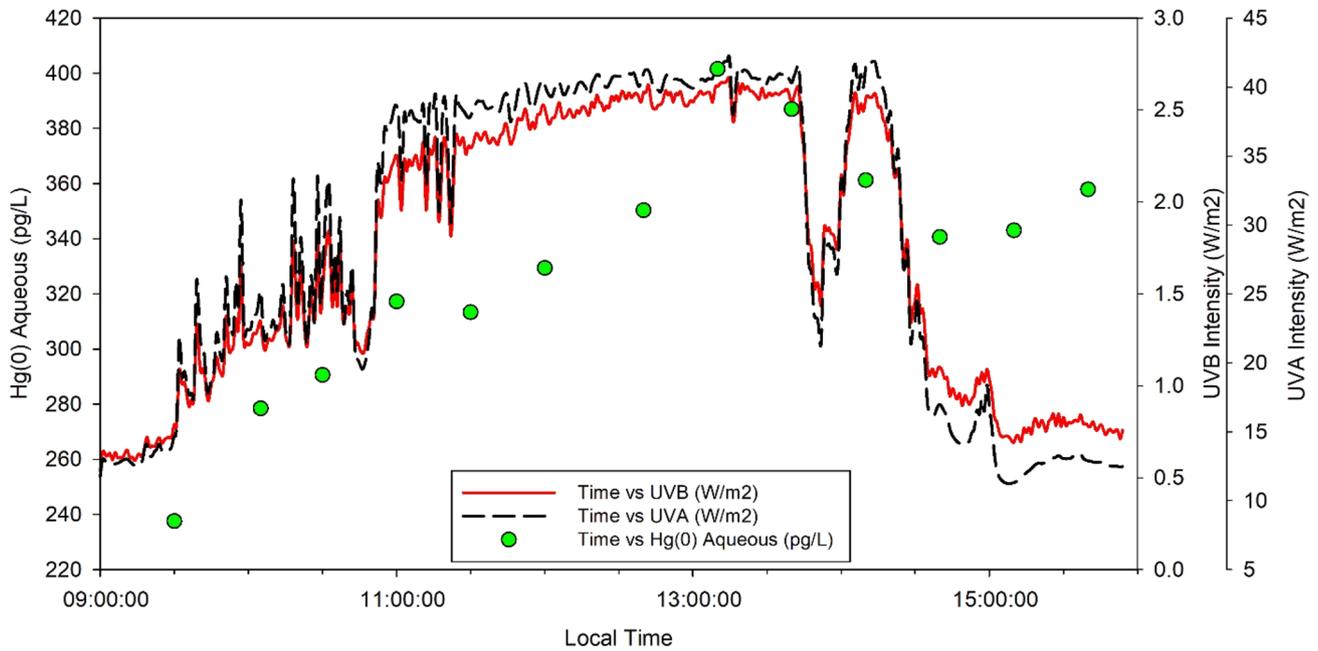


Fig. 3 Dissolved gaseous mercury (DGM; Hg(0)) concentration in surface water and UVA and UVB radiation intensities for the measurement period at VN1 aquaculture site

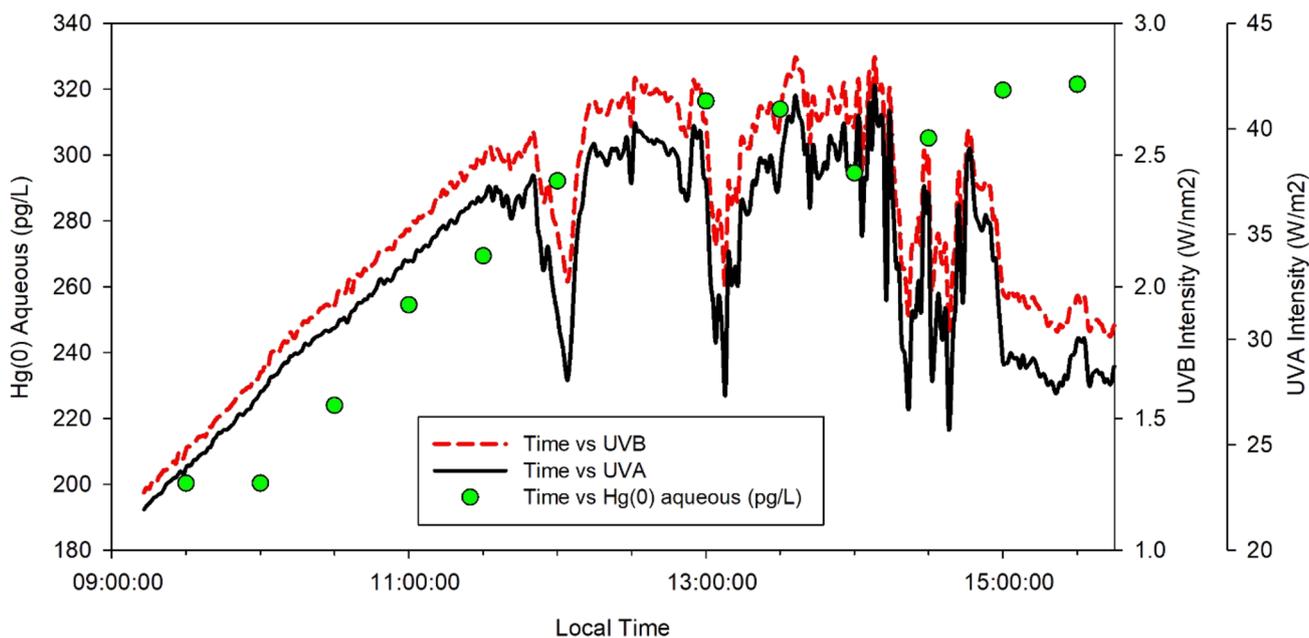


Fig. 4 Dissolved gaseous mercury (DGM; Hg(0)) concentration in surface water and UVA and UVB radiation intensities for the measurement period at VN3 aquaculture site

(mean = 19.7 pg L^{-1}) in surface waters near Alcochete in the Tagus Estuary in Portugal. This corresponds with a maximum of 0.16% of the total Hg present as DGM in the Cesario et al. (2017) research, which is substantially less than what was observed in our study. The Alcochete area is a moderately Hg-contaminated site with much lower sediment concentrations (THg $200\text{--}600 \text{ ng g}^{-1}$) than the lagoon sites in our study (THg $2150\text{--}6870 \text{ ng g}^{-1}$).

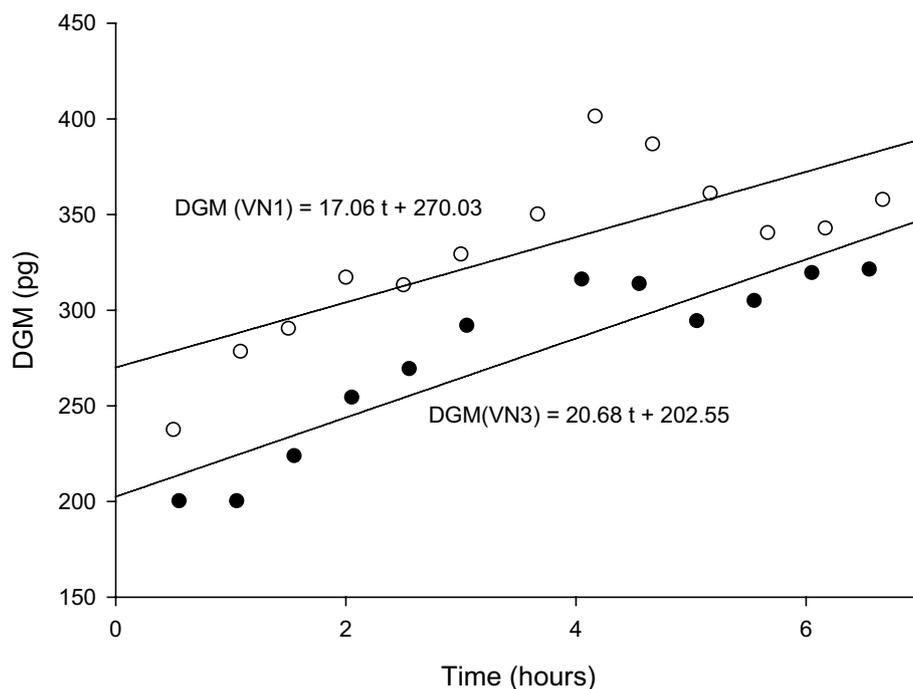
O'Driscoll et al. (2018) found that mean concentration of DGM measured in all freshwater lakes in Kejimikujik Park, Nova Scotia (ranging from 15 to 80 pg/L ; mean = $41 \pm 17.5 \text{ pg/L}$) was approximately 8.5% of the total reducible Hg(II), suggesting a high rate of Hg photoreduction under optimal conditions. While these are rates from a freshwater site, the % DGM/THg_D observed in this study are similar, suggesting high rates of Hg photoreduction in the Marano and Grado Lagoon. This may suggest an increased capacity for DGM volatilization to the atmosphere at the highly contaminated Marano and Grado Lagoon site where the % DGM/THg_D is 10–50 times higher than other contaminated marine sites in Portugal and is comparable to the highest potential photoreduction at freshwater sites.

A comparison of the rate of DGM production was performed by examining the linear relationship between the mass of DGM (pg) produced and the elapsed time in hours (Fig. 5). The rates of DGM production in a 1 L sample volume were 17.06 pg h^{-1} at VN1 and 20.68 pg h^{-1} at VN3. This zero-order rate of production is much larger (6 to 20 times) than the rate of DGM production observed by Amyot

et al. (1997) who calculated a zero-order rate of DGM production ranging $1 \text{ pg L}^{-1} \text{ h}^{-1}$ to $3 \text{ pg L}^{-1} \text{ h}^{-1}$ in coastal seawater from the Gulf of Mexico. This difference is likely due to the large availability of photoreducible mercury at our contaminated sites. This research suggests there is a substantial capacity for Hg loss to the atmosphere from the water column at these contaminated marine sites. This has recently been confirmed by Floreani et al. (2019) who measured water-to-air flux rates with a floating chamber ranging from 51.2 to $79.9 \text{ ng m}^{-2} \text{ h}^{-1}$ at the same research sites during the summer.

In conclusion, the rate of DGM production at this contaminated site is up to 20 times greater than zero-order rates observed at uncontaminated marine sites. We found that the fraction of DGM in the water column, in terms of the % DGM/THg_D, was similar to percentages observed in other uncontaminated marine sites but substantially higher than those observed at other contaminated marine sites in Portugal. We hypothesize that these differences may be attributed to larger fractions of photoreducible mercury available at the Marano and Grado lagoon site. A greater fraction of photoreducible mercury may be related to many water chemistry variables including: (i) the specific distribution of dissolved and particulate Hg(II) species in the water column; (ii) the availability of competing ions and salinity changes; and (iii) the structure and concentration of dissolved organic matter (Vost et al. 2012). Our research confirms the importance of the incident solar radiation in the photoreduction of Hg(II) to DGM, which is volatile and easily released to the

Fig. 5 Scatterplot of cumulative mass of dissolved gaseous mercury (DGM; pg) produced for sites VN1 (open circles) and VN3 (closed circles) versus elapsed time in hours of experiment. Black lines represent linear regression (VN1 $R^2=0.59$, $p<0.01$; VN3 $R^2=0.84$, $p<0.01$)



atmosphere in the form of GEM ($Hg(0)$). This research also confirms the recent work of Floreani et al. (2019) showing there is a substantial capacity for Hg loss to the atmosphere from the water column at these contaminated lagoon sites through photoreduction mechanisms. This work highlights the importance of additional research on mercury photoreaction rates in coastal areas to better predict mercury fate in contaminated marine sites.

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