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Dissolved elemental mercury accumulation by freshwater phytoplankton species: A pilot study

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ABSTRACT

Bioaccumulation of dissolved elemental mercury (DGM) by various organisms has been demonstrated, but no study has shown its uptake and sequestration by phytoplankton species. The present study aims to investigate the accumulation of mercury by phytoplankton species exposed to DGM. Diatoms (*Cyclotella meneghiniana* and *Navicula pelliculosa*) and green algae (*Chlamydomonas reinhardtii* and *Haematococcus pluvialis*) were exposed to constant high level of atmospheric gaseous Hg (~7.7 μg m^{-3}). Total mercury concentrations (THg) in the medium (dissolved fraction) and algae cells (cellular fraction) were determined using cold vapor atomic fluorescence spectroscopy. Results revealed a partitioning of Hg(0) between the atmosphere and phytoplankton cultures, with THg predominantly found in the algae cells. THg in the algae cultures decreased in the order: *C. reinhardtii* > *H. pluvialis* > *N. pelliculosa* > *C. meneghiniana*. However, the cellular concentration (mol $cell^{-1}$) decreased in the order: *H. pluvialis* > *C. reinhardtii* > *C. meneghiniana* > *N. pelliculosa.* These results highlight species specificity in Hg accumulation upon exposure to DGM, further linked to the phytoplankton surface area. Our findings reveal for the first time that phytoplankton species significantly influence the partitioning of atmospheric Hg(0) in aquatic environments, with important implications for the understanding of the aquatic mercury cycle.

1. Introduction

Understanding Hg dynamics in the different ecosystem compartments (e.g. aquatic, terrestrial, and atmospheric) is crucial to understanding the Hg cycle and potential impacts. Mercury enters the atmosphere mainly in its gaseous form (elemental mercury, Hg(0)) through the action of natural sources and anthropogenic activities (Lehnherr, 2014; Teng and Altaf, 2022). Eventually, Hg(0) can be transformed into oxidized mercury - Hg(II), which can then be sorbed on particulate matter. Ultimately, Hg(0) and Hg(II) species are deposited in the terrestrial or aquatic systems mainly through dry and wet deposition, respectively (Sather et al., 2014). In the terrestrial system, 60–90 % of dry deposited Hg(0) ends up being taken up by vegetation (Zhou et al., 2021). In aquatic systems, the deposited or formed Hg(0) is present as dissolved elemental Hg (DGM) as a result of its partitioning in water (Du et al., 2023). DGM can either be (re-)volatilized back to the atmosphere or be oxidized through reactions in the surface zones, such as photochemical reactions (Luo et al., 2020), or by dark chemical reactions (Si et al., 2022) (e.g., DGM oxidation mediated by oxygen in the absence of light) in deeper zones of the water system. The prevailing reactions are important since the oxidation of DGM not only leads to its retention in the aquatic system but also increases its bioaccumulation (Soto Cárdenas et al., 2018) and methylation (Colombo et al., 2013; Regnell and Watras, 2018), thereby raising the total mercury concentrations in the aquatic systems. So far, the uptake of DGM by microorganisms has been demonstrated in bacteria (Colombo et al., 2013; Hu et al., 2013; Siciliano et al., 2002; Smith et al., 1998) and yeast (Oyetibo et al., 2019). However, to the best of our knowledge, no study demonstrating the bioaccumulation in phytoplankton species exposed to DGM has been yet published.

The primary objective of the present study is to investigate if phytoplankton species can play an important role in the air-water partitioning of Hg(0) by accumulating mercury when exposed to DGM. For this purpose, two green algae, *Haematococcus pluvialis* and

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Chlamydomonas reinhardtii, and two diatoms, *Cyclotella meneghiniana* and *Navicula pelliculosa*, were selected as representatives of two major phytoplankton groups and incubated in a gaseous Hg(0) contaminated atmosphere (~7.7 μg m^{-3}) and compared with ambient air. This represents the first pilot study in addressing phytoplankton interaction with gaseous mercury - Hg(0). Phytoplankton species play crucial roles in aquatic ecosystems, primarily acting as the foundation of the trophic food chain and sequestering carbon (Pal and Choudhury, 2014). Moreover, they directly and indirectly influence Hg bioavailability and speciation (Cossart et al., 2022; Li et al., 2024). We hypothesize that phytoplankton species significantly affect atmospheric Hg(0) partitioning with the aquatic system in a species-dependent manner by accumulating Hg when exposed to DGM.

2. Materials and methods

2.1. Culture preparation

Phytoplankton cultures were prepared for two experimental assays: assay 1 aimed to evaluate total mercury (THg) concentration in the whole system cultures after exposure to gaseous Hg(0) contaminated atmosphere, while assay 2 focused on the increase of THg concentration in the dissolved and cellular fractions after exposure to both contaminated and ambient atmospheres. Green alga *C. reinhardtii* CPCC11 (Canadian Phycological Culture Centre, Waterloo, Canada) was grown in 4× diluted Tris-Acetate-Phosphate (TAP) medium as described in (Millet et al., 2024) and 2-(N-morpholino)ethanesulfonic acid (MES)--Volvox medium (Starr and Zeikus, 2004) for experiment assay 1 and assay 2, respectively. *H. pluvialis* (UTEX Culture Collection of Algae, UTEX 2505) was grown in MES-Volvox medium (as per UTEX Culture Collection of Algae). The diatom *C. meneghiniana* (CCAC 0036 strain, Collection of Algal Cultures, University of Duisburg-Essen, Germany) and *N. pelliculosa* (SAG 1050–3, Culture Collection of Algae, University of Göttingen) were grown in synthetic freshwater medium (SFM) as described elsewhere (Millet et al., 2024). All materials were prepared using trace metal clean procedures, followed by sterilization using an autoclave cycle as previously described (Santos et al., 2024). All cultures were grown and incubated under visible light with an intensity of 100 photons m^{-2} s^{-1}, 20 °C, rotary shaking of 80–100 rpm, and 14:8 h light/dark cycle in a specialized incubator (Fitotron, model SGC120, Weiss Technik UK Ltd., Loughborough, UK).

2.2. Exposure experiments

Two experimental assays were performed to verify our hypothesis that phytoplankton species can sequester Hg(0). All experiments were conducted at 20 °C with a light intensity of 100 μmol photons m^{-2} s^{-1} and a light regime of 14:10 h. In the first experimental assay (Fig. 1**a**), the

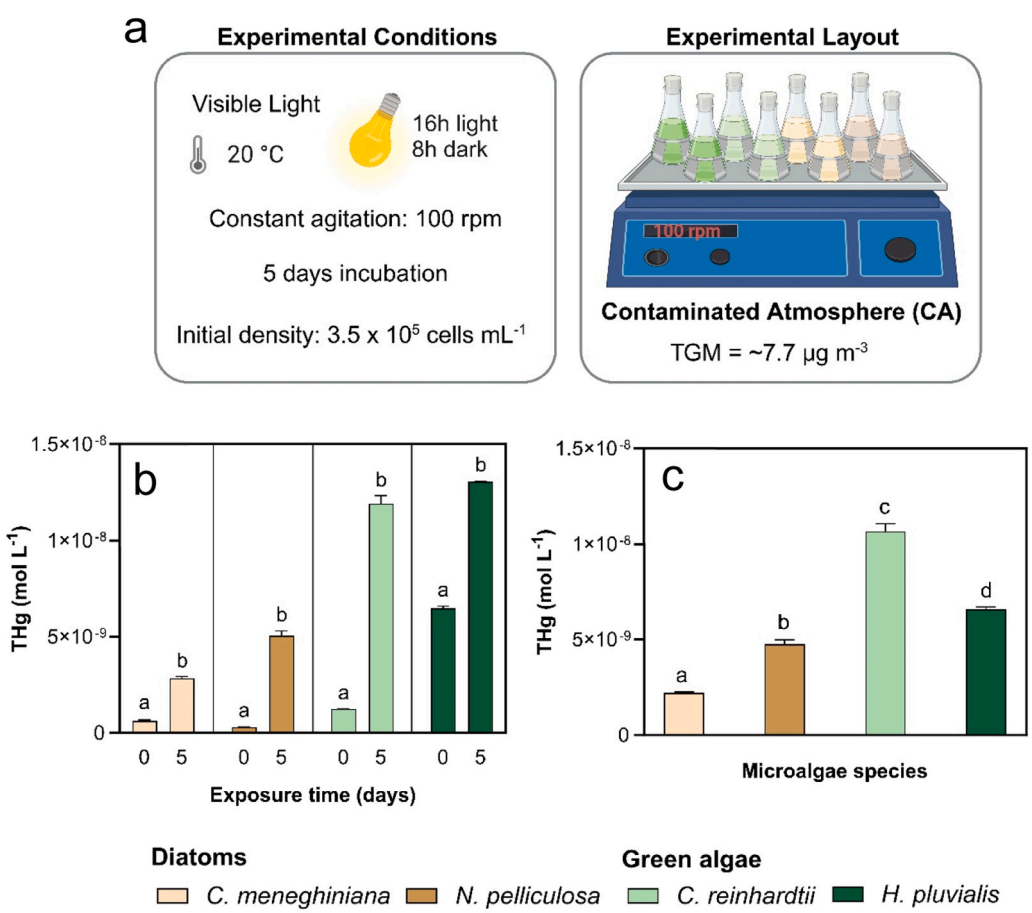

Fig. 1. Illustrative description of the experimental assay 1, used for incubating the cultures of diatoms (*C. meneghiniana* and *N. pelliculosa*) and green algae (*H. pluvialis* and *C. reinhardtii*) in 250 mL Erlenmeyer flasks under a constant gaseous Hg(0) atmosphere (~7.7 μg m^{-3}) (**1a**). Total mercury concentration (THg) in mol L^{-1} in the whole system (representing both dissolved + cellular fractions) at the beginning (T0) and after 5 days of incubation for each culture (**1b**). The concentration of THg in the whole system (representing both dissolved + cellular fractions) after 5 days, with the initial THg concentration subtracted for the different cultures (**1c**). Bar plots represent mean and their respective standard deviation. Significant differences within exposure time (**1b**), and between species (**1c**) is presented by different letters. One-way ANOVA followed by Šídák's post-hoc test was used. Fig. 1a was created in BioRender. Santos, J. (2024) BioRender.com/w62e106.

capability of the algal cultures to sequester atmospheric Hg(0) was evaluated in open settings in a contaminated atmosphere inside a culture incubator (RUMED Series 3000, Rubarth Apparate GmbH, Germany). Here, diatom species were resuspended in 100 mL SFM medium, while green algae were resuspended in 4× TAP and MES-Volvox medium, respectively for *C. reinhardtti* and *H. pluvialis*. All cultures started with an initial cell density of 3×10^5 cells mL^{-1} in duplicate. The incubation period had a duration of 5 days under a constant contaminated atmosphere (CA) of gaseous Hg(0) (~ 7.7 ± 2.2 μg m^{-3}). Hg originated from a contamination source inside the experimental incubator that maintained a constant level of gaseous Hg(0) (~ 7.7 ± 2.2 μg m^{-3}). This concentration is representative of highly contaminated environments near point sources (e.g. Hg-producing facilities, chlor-alkali plants, among others) which can vary between 0.03 and 240 μg m^{-3} (Gworek et al. (2017). The level of gaseous Hg(0) was monitored using sorbent Anasorb® C300 (SKC Ltd), followed by analysis using cold vapor atomic fluorescence spectroscopy (CVAFS) based on the Occupational Safety and Health Administration (OSHA) Method ID-140 (OSHA, 1991), and by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) based on National Institute for Occupational Safety and Health (NIOSH) Method

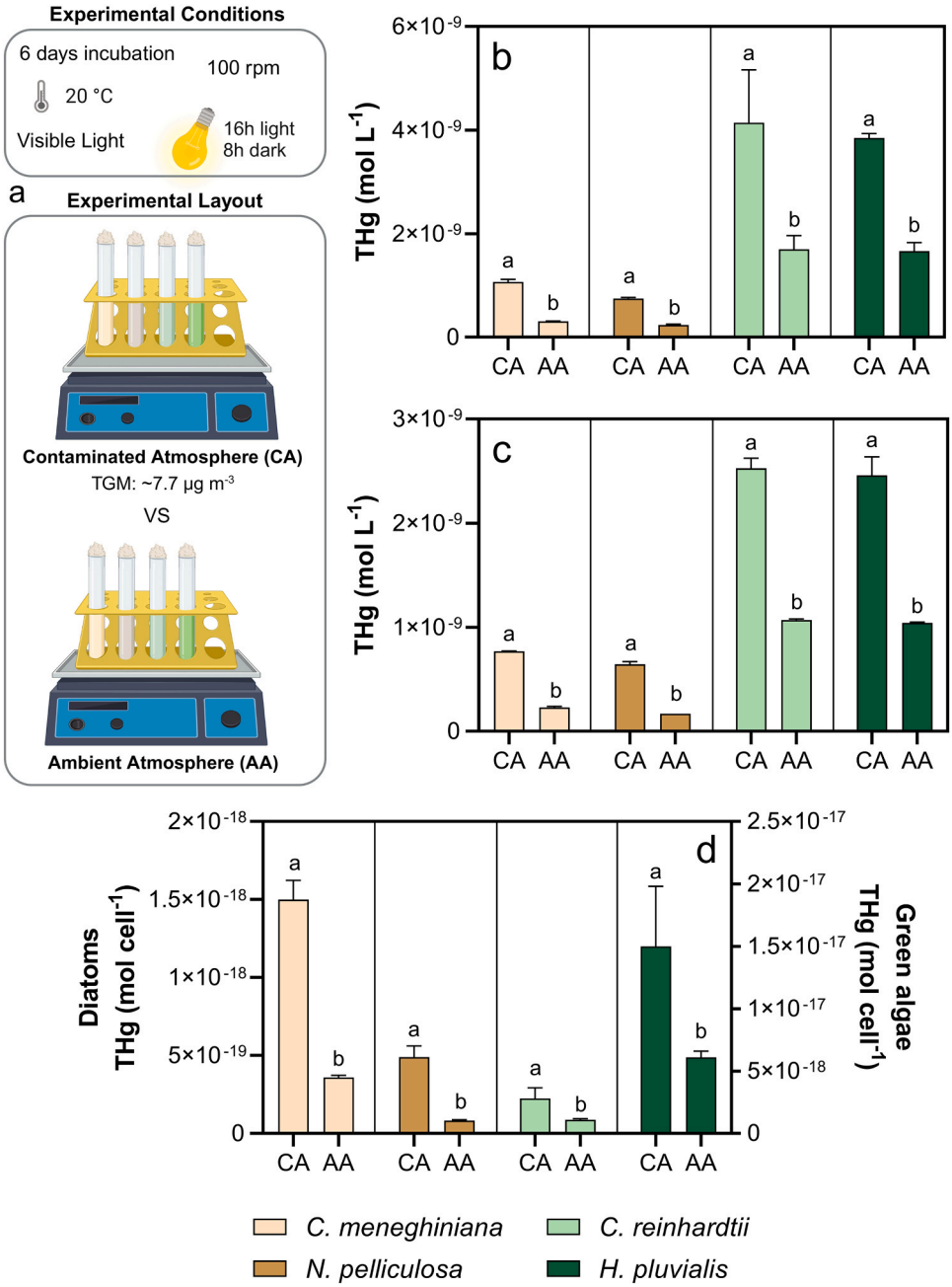

Fig. 2. Illustrative description of the experimental assay 2, performed by incubating different cultures of diatoms (*C. meneghiniana* and *N. pelliculosa*) in SFM medium and green algae (*H. pluvialis* and *C. reinhardtii*) in MES-Volvox medium. All cultures were incubated in glass tubes with a final volume of 50 mL under a constant gaseous Hg(0) atmosphere (~7.7 μg m^{-3}) vs a ambient atmosphere (**2a**). Total mercury concentration (mol L^{-1}) in the cellular fraction (**2b**) and the dissolved fraction (**2c**) of the different cultures after being exposed to contaminated atmosphere (CA) and ambient atmosphere (AA) for 6 days in open settings. Cellular mercury content (THg mol per cell) in the different cultures after 6 days incubation to CA or AA in open settings (**2d**). Significance differences between CA and AA for each species is presented by different letters (Two-way ANOVA followed by Šídák's post-hoc test). Fig. 2a was created in BioRender. Santos, J. (2024) BioRender.com/v19f884.

6009 (Eller and Cassinelli, 1994). Whole system samples (equivalent to dissolved + cellular fractions) were collected and acidified in 65 % w/w HNO_3 (HNO_3 for analysis (max. 0.005 ppm Hg) EMSURE®), at the beginning of exposure and after 5 days, for total mercury (THg) analysis using CVAFS as described elsewhere (Millet et al., 2024).

In the second experimental assay (Fig. 2**a**), the capacity of different algae cultures to accumulate THg in the dissolved and cellular fractions was evaluated. Here, SFM medium and MES-Volvox were used for diatom and green algae cultures, respectively. The cultures of *C. meneghiniana*, *N. pelliculosa*, *H. pluvialis*, and *C. reinhardtii* started with initial cell densities of 2×10^5, 3×10^5, 1×10^5, and 3×10^5 cells per mL, respectively in duplicate. Two scenarios were considered: a contaminated atmosphere (CA) under constant gaseous Hg(0) source exposure ($\sim 7.7 \pm 2.2$ μg m^{-3}) inside the same incubator as in experimental assay 1, with open (cotton plugs) and hermetically closed (Teflon caps - Brooks Rand Instruments, Seattle, USA) cylindrical glass vials, and an ambient atmosphere (AA) in another incubator (INFORS HT Multitron Pro) with open cylindrical glass vials. The levels of Hg(0) in the ambient atmosphere were below the detection limit (0.8 μg m^{-3}) of the method based on ICP-MS analysis, nevertheless, a recent study has shown indoor ambient Hg(0) concentrations of $(4.2 \pm 2) \times 10^{-3}$ μg m^{-3} (Wohlgemuth et al., 2020). The closed vials were used as secondary controls representing the THg concentration at time 0, since no gas exchange occurred (see SI). In parallel, each growth media without cells was incubated as an abiotic control under CA and AA conditions following the same conditions (opens settings and closed settings). After 6 days of incubation, the whole system samples were directly taken. The cellular and dissolved fractions were separated by centrifugation (4062 g, 4 °C, 10 min) and then acidified (65 % w/w HNO_3, for analysis (max. 0.005 ppm Hg) EMSURE®) until analysis by CVAFS.

2.3. Mercury analysis

Total mercury (THg) concentration in the different samples was measured using a MERX® Automated Total Mercury Analytical System (Brooks Rand Instruments, Seattle, WA, USA), with algae cell samples being digested for 12 h prior analysis in 65 % w/w HNO_3 under 85°C (Santos et al., 2022). The instrumental linear working range of MERX-T is between 0.08 and 400 ng/L. Linearity was assessed over the range of 20–10,000 pg of the analyte mass by constructing a calibration curve with seven standard concentrations. Each standard was analysed at least twice. The calibration curve was plotted and displayed a 99 % confidence level ($R^2 > 0.99$). All accepted values met the quality control acceptance criteria defined by US EPA method 1631 (EPA, 2002). The accuracy of the measurements was validated by analysing IAEA-450 certified reference material of unicellular microalga *Scenedesmus obliquus*. The recovery efficiency was 92.0 ± 9.0 %. For both experimental assays, the distinction between the purgeable Hg (corresponding to DGM, usually removed through purging of samples previous to acidification (Du et al., 2023; Oyetibo et al., 2019)) and non-purgeable Hg (corresponding to oxidized Hg) was not performed. Instead, all samples were directly acidified in 65 % w/w HNO_3, which promoted a fast DGM oxidation (Irei, 2021), resulting in THg measurements of the purgeable Hg plus the non-purgeable Hg.

2.4. Data analysis

Statistical analyses were performed using GraphPad Prism 10 Software. A one-way or two-way ANOVA was utilized to determine if there were statistically significant differences between two or more groups of an independent variable. Significant differences between and within results from different exposure times were determined using post hoc Šídák's multiple comparison tests.

3. Results

After 5 days of incubation in open settings (experimental assay 1) with exposure to a gaseous Hg(0) contaminated atmosphere, the concentration of total mercury (THg) in the whole system (including both dissolved and cellular fractions) was higher in all phytoplankton cultures in comparison with the initial T0 measurements (Fig. 1**b, c**). THg concentration was higher in cultures of green algae compared to diatoms, following the order: *C. reinhardtii* > *H. pluvialis* > *N. pelliculosa* > *C. meneghiniana*. To better understand how different algal species influence the partitioning of Hg(0) between the atmosphere and cell suspensions, phytoplankton cultures were incubated for 6 days in open settings exposed to both a contaminated atmosphere (CA) and an ambient atmosphere (AA) (Fig. 2**a**). Experimental assay 2 in CA revealed significant THg concentrations in both the cellular (Fig. 2**b**) and dissolved (Fig. 2**c**) fractions. These results are consistent with experimental assay 1 in CA (Fig. 1), where a greater THg accumulation was seen in green algae than in diatoms (Fig. 2). In general, the highest cellular concentration (mol $cell^{-1}$, Fig. 2**d**) followed the order *H. pluvialis* > *C. reinhardtii* > *C. meneghiniana* > *N. pelliculosa*. This finding confirms the significant role of algae cultures in THg sequestration when exposed to DGM, and its species specificity.

The THg concentration (Fig. 2**b-c,** Table S1) were significantly higher ($p<0.05$, two-way ANOVA) for the CA exposure compared to AA exposure across all species, in both cellular and dissolved fractions analyzed.

The cellular THg concentration ranged between 0.3 and 1.7×10^{-9} mol L^{-1} in AA, and 0.8–4.1×10^{-9} mol L^{-1} in CA, while for THg concentration in the dissolved fraction, it ranged between 0.2 – 1.1×10^{-9} mol L^{-1} in AA, and 6.4–2.5×10^{-9} mol L^{-1} in CA. In both fractions, green algae presented higher concentrations compared to diatoms. Within the CA exposure, a significantly higher THg ($p < 0.05$, two-way ANOVA) was found in the cellular fraction compared to the dissolved fraction for green algae (Fig. 2**a-b,** Table S1). Overall, the gaseous Hg(0) partitioning between the air and cell suspensions leads to a significant THg accumulation in the algae cultures.

When comparing the THg concentrations between biotic and abiotic exposures (Fig. 3), a significantly higher concentration was found for suspensions of phytoplankton species compared to their respective abiotic conditions for CA exposure, confirming the key role of phytoplankton species for the partitioning of atmospheric Hg(0).

4. Discussion

The results of the present study highlight the potential direct role of microalgae, namely green algae and diatoms, in DGM sequestration as well as the species specificity of this process. Nevertheless, it is important to take into account that once in the aquatic medium, DGM could be directly accumulated by the algae or oxidized first and then taken up by the algae as Hg(II). Nonetheless, it is crucial to note that purgeable Hg (corresponding to DGM) and non-purgeable Hg (corresponding to oxidized Hg) were not distinguished in this study. Instead, we monitored the THg concentration which is the combined result from the partitioning of Hg(0) between air and the growth medium and subsequent oxidation processes. Thus, two main processes could occur individually or simultaneously, involving the direct and indirect participation of algae cells.

In the direct algae involvement, DGM is bioaccumulated directly by the different phytoplankton species, similar to studies previously showing that Hg(0) can be directly taken up by plants, and lichens (Zhou et al., 2021). In such a case, the uptake of DGM will depend on different characteristics of the algae species, such as growth rate, cell wall structure, cell surface area, and cell volume (Tables S2-4). For example, (**i**) higher growth rates, reflected in higher cell density (Tables S2-3), presented higher THg accumulation (which can be either DGM or oxidized Hg(II)) by the different species after the incubation period in

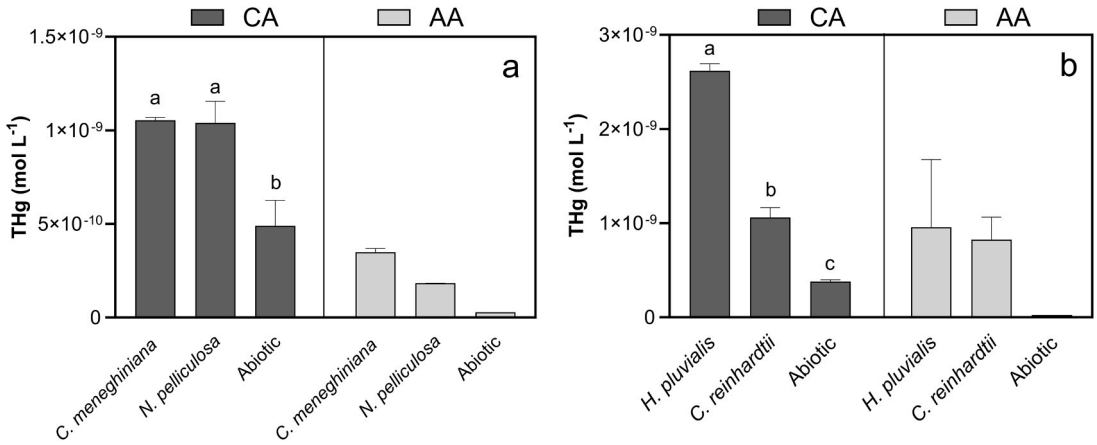

Fig. 3. Whole system concentration (mol L^{-1}) after 6 days of incubation for contaminated atmosphere (CA) and ambient atmosphere (AA) in open settings. Diatoms (*C. meneghiniana* and *N. pelliculosa*) and its respective abiotic condition (SFM medium without cells) (**3a**), and green algae and its respective abiotic condition (MES-Volvox medium without cells) (**3b**). Significance difference between algae and abiotic conditions in CA is presented by different letters (One-way ANOVA followed by Šídák's post-hoc test). No statistical analysis was performed for the AA conditions, as the abiotic condition has only one replicate.

both experiments. However, a high correlation coefficient was obtained in the linear regression analysis between algae cell density and THg concentration, which was stronger in diatoms (Fig. S1), indicating potential group-specific mechanisms or characteristics involvement; (**ii**) higher surface area could allow for a higher uptake of DGM, thus supporting the differences seen between organisms (e.g. despite *H. pluvialis* presenting the lowest growth rate, it displays the highest cell surface). Likewise, studies with lichens have associated growth rate and surface area with their capacity to uptake gaseous Hg(0) (Zhou et al., 2021). In our study, a similar relationship was found with a high correlation coefficient between cellular THg (mol $cell^{-1}$) and the surface area or volume of species (Fig. S2). (**iii**) The difference in cell wall compositions displayed by green algae and diatoms (Hildebrand et al., 2018; Poulhazan et al., 2024) can also impact the uptake of DGM (assuming that it is taking place). DGM could have entered through passive diffusion. For example, the phospholipid bilayer membranes of green algae have been shown to allow gases to diffuse at significant rates (Cooper and Hausman, 2000). While diatoms porous silica cell wall allows the passage of gases. For instance, the facilitated transport of gases, namely CO_2 and NH_3, has been associated with aquaporin channels in diatoms (Matsui et al., 2018). Nevertheless, this study did not explore the potential mechanisms of DGM uptake in diatoms and green algae, which are unknown and likely distinct (Tables S2, S3 and S4).

Another possibility, is for DGM to be adsorbed to the cell wall of the algae cells, which could then (**i**) be released back into the dissolved fraction, (**ii**) be oxidized into Hg(II), and (**iii**) be internalized via previously described mechanisms. Further research is needed, including in distinguish between DGM and oxidized Hg, and Hg absorbed and internalized by the cells.

In the indirect involvement, DGM is oxidized in the exposure media, and afterward, the formed Hg(II) is readily adsorbed and internalized by the cells depending on its speciation (Dranguet et al., 2017; Le Faucheur et al., 2014). The DGM oxidation can be driven through different mechanisms. For instance, photooxidation of Hg(0) has been shown to occur, however, under visible light (same as in our study), it was shown to present significantly low rates compared to visible + UV radiation ($k = 0.09\ h^{-1}$ vs $k = 0.6–0.7\ h^{-1}$) (He et al., 2014; Lalonde et al., 2004); other studies have shown the occurrence of photo and chemical oxidation of Hg(0) in the presence of oxidants (e.g., hydroxyl, carbonate and chlorine radicals) (He et al., 2014; Hines and Brezonik, 2004; Lin and Pehkonen, 1998). In fact, when looking at the abiotic controls, results presented higher THg concentration in CA compared to AA exposure in open settings (Fig. 3), which can be explained by different factors: (**i**) a higher concentration of gaseous Hg(0) will increase the Hg(0) partitioning between air and water leading to higher concentrations of DGM (Bouchet et al., 2011; Floreani et al., 2022; Kuss, 2014). By applying the Henry Law constant determined by Andersson et al. (2008) under our conditions (e.g. 20°C, 1 atm), we estimated an approximate equilibrium concentration of DGM in the system of 1.32×10^{-10} M under CA. This concentration represents approximately 27 and 35 % of the THg in the dissolved fraction for SFM and MES-Volvox medium, respectively (abiotic conditions, Figs. 3**a**, 3**b**). Since the purgeable Hg(0) fraction was not removed from our samples, this percentage is likely originated from DGM (Du et al., 2023); (**ii**) the occurrence of potential photo and/or chemical oxidation of DGM could increase Hg(0) partitioning, ultimately leading to higher THg concentrations (Si et al., 2022).

Another potential oxidizing factor is the extracellular polymeric substances (EPS) and thiols produced by the different algae (Mangal et al., 2019), which was not investigated in our study. These have also been shown to promote the oxidation of DGM to Hg(II). Biogenic organic materials produced by algae were reported to promote DGM oxidation under dark conditions (Poulain et al., 2007). Further, thiol functional groups from natural organic matter were shown to promote Hg(0) oxidation via oxidative complexation (Zheng et al., 2019; Zheng et al., 2012), Additionally, EPS were linked to increased Hg(0) dissolution, making it more available for uptake or oxidation in the aquatic system (Oyetibo et al., 2019). Different thiol compounds significantly promoted DGM oxidation, however, the experiments occurred under anoxic conditions, opposite to our study, whose oxic condition would promote rapid thiol oxidation (Giles et al., 1986; Schilter, 2017). Nonetheless, Zheng et al. (2013) reported that thiols exhibited little or no reactivity with DGM at pH 7.0, which is the same as in our study. Despite this corroboration, future studies should explore the role of algae EPS and thiols in DGM oxidation under different oxygen and DGM concentrations.

5. Conclusions

The results of this pilot study highlight for the first time the importance of phytoplankton in capturing atmospheric Hg(0), which could have profound implications for the mercury cycle in aquatic environments. Despite the high Hg(0) concentrations used, the results obtained provide useful indications for future studies on the dynamics of Hg0 phytoplankton interactions. Notably, phytoplankton species might play a significant, but still to elucidate, role in DGM uptake and/or oxidation and further Hg sequestration of atmospheric Hg(0). Nonetheless, further research is necessary to investigate DGM accumulation by different

species, and oxidation processes facilitated by phytoplankton species under different lower gaseous Hg(0) concentrations.

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CRediT authorship contribution statement

João P. Santos: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **David Amouroux:** Writing – review & editing, Validation, Supervision, Conceptualization. **Vera I. Slaveykova:** Writing – review & editing, Validation, Supervision, Funding acquisition, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.hazl.2024.100128.

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