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Methylmercury Production in Estuarine Sediments: Role of Organic Matter

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Supporting Information

ABSTRACT: Methylmercury (MeHg) affects wildlife and human health mainly through marine fish consumption. In marine systems, MeHg is formed from inorganic mercury (Hg^{II}) species primarily in sediments, then accumulates and biomagnifies in the food web. Most of the fish consumed in the United States are from estuarine and marine systems, highlighting the importance of understanding MeHg formation in these productive regions. Sediment organic matter has been shown to limit mercury methylation in estuarine ecosystems, as a result it is often described as the primary control over MeHg production. In this paper, we explore the role of organic matter by looking at the effects of its changing sediment concentrations on the methylation rates across multiple estuaries. We measured sedimentary MeHg production at eleven estuarine sites that were selected for their contrasting biogeochemical characteristics, mercury (Hg) content, and location in the Northeastern U.S. (ME, NH, CT, NY, and NJ). Sedimentary total Hg concentrations ranged across 5 orders of magnitude, increasing in concentration from the pristine, sandy sediments of Wells (ME), to industrially contaminated areas such as Portsmouth (NH) and Hackensack (NJ). We find that methylation rates are the highest at locations with high Hg content (relative to carbon), and that organic matter does not hinder mercury methylation in estuaries.

INTRODUCTION

In the Northeast United States, estuaries are particularly impacted by mercury (Hg) contamination as the coastal region is heavily industrialized, has a high population density, and has coal-fired power plants as the main source of electricity.[1] Additionally, many locations are impacted by historical discharges from wastewater treatment facilities and various industrial processes. Although anthropogenic Hg emissions in the Northeastern U.S. have been significantly reduced since the 1970s, the U.S. remains one of the larger emitters.[2] Continued release of Hg from local sources and the buried "legacy Hg" in coastal sediments continue to support methylmercury (MeHg) production in these locations.

Anthropogenic Hg is released into the atmosphere in its elemental (Hg^0) and inorganic (Hg^{II}) forms, mostly by coal-fired electric utilities and incinerators.[2] Hg^0 and Hg^{II} then enter the water column through gas exchange and wet/dry deposition, where it can subsequently be converted into MeHg, in the water column or sediments. External sources of MeHg to the estuarine and coastal zones are generally limited (some exceptions exist, e.g. New York–New Jersey Harbor where watershed export and river supply dominate), and most MeHg is produced in situ[3−5] within the sediment. Most methylation occurs in sediments and is mediated by sulfate- and iron-reducing bacteria,[6,7] although the mechanisms driving the conversion are complex and still poorly understood. The conversion has been shown to depend on physical and biogeochemical factors that can affect methylating bacteria activity,[8] and the supply of bioavailable Hg^{II} species.[7]

Multiple studies[9−12] have examined differences and factors affecting estuarine Hg methylation and concluded the following: (i) sediment organic matter (OM) is the most important factor for MeHg production as it hinders mercury methylation by changing Hg^{II} bioavailability; and (ii) methylation rates are elevated in low organic content (often pristine) sediments compared to contaminated, high-OM sediments. However, these studies looked at methylation within a single ecosystem or across a small spatial range, where OM can appear as the main control over methylation if all other factors remain constant.

In this paper, we examined the importance of sediment OM for Hg methylation over a broad geographic and Hg contamination range. To this purpose, we measured changes in bulk sediment and porewater total Hg (HgT) and MeHg concentrations, and Hg^{II} methylation rates across a range of ecosystems from rural (e.g., Wells, ME) to industrial (e.g., Hackensack, NJ) locations. We found that neither OM nor Hg sediment–porewater partitioning explain the changes in mercury methylation rates, and that the highest MeHg production rate are found in more contaminated organic-rich sediments.

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METHODS

Site Description. We sampled eleven Northeastern U.S. sites with contrasting sediment characteristics (Supporting Information Figure S1 and Table S1). Three sites, all sampled in July 2009, were located in the beach town of Wells (ME, Gulf of Maine), a sparsely populated pristine area located in proximity of 9.1 km^2 of protected land: Drakes Rd (WD), Harbor Rd (WH), and Mile Rd (WM). In New Hampshire, three sites sampled in July 2009 were located in industrialized Portsmouth: Jackson Estuarine Laboratory (JEL), Barberry Rd (BB), and Portsmouth Naval Shipyard (PNS). The U.S. EPA has placed PNS on the National Priority List (1945 to approximately 1978) as 25 acres of tidal flats between two of the islands were filled with wastes including Hg-containing material. Long Island Sound (LIS) was sampled (May 2010) at locations noted E, C, and W, with site W being the most anthropogenically impacted, and E being the least impacted site.[4,12,13] Berry's Creek (BC) and Mill Creek (MC) are tidal tributaries to the Hackensack River (NJ), which discharges to New York/New Jersey Harbor Estuary (NY/NJ Harbor). These NJ sites are heavily contaminated as they are located near the Ventron/Velsicol Superfund site where 30−400 tons of mercury compounds were released from 1929 to 1974.[14,15]

Sampling. LIS sediment cores (9-cm O.D. polycarbonate tubes) were obtained using a multicorer (Ocean Instruments, Inc.); a minimum of eight cores were collected at each station to provide enough material for bulk Hg, MeHg, methylation rate measurements, and sulfide. Portsmouth (NH), Hackensack (NJ), and Wells (ME) cores were sampled by hand using 4.8-cm O.D. polycarbonate tubes. Sediment cores collected for methylation rate measurements were preserved at ambient bottom water temperature prior to further processing. Cores were sectioned into 1- or 2-cm intervals (to a depth of 10 cm) within 24 h of collection in a low-oxygen, nitrogen-filled glovebag and/or glovebox.

At each site, we extracted sediment core porewater from 2-cm sediment subsections using direct vacuum filtration with acid-washed Nalgene polystyrene filter units and 0.22-μm cellulose nitrate filters. Filter units were rinsed with deionized water prior to use, and sediments were typically centrifuged prior to filtration. Porewater collection required 4−8 cores from each site and water from separate cores was pooled at each depth. Aliquots of porewater for HgT and MeHg analyses were stored in Teflon bottles and acidified to 0.5% with optima grade HCl.

Aliquots of porewater for sulfide analysis were preserved in sulfide antioxidant buffer (SAOB) and analyzed immediately using an ion-selective electrode (Orion Sulfide Electrode).[16] The SAOB buffer was prepared daily, using deoxygenated water. The detection limit (DL) was ∼100 nM.

Sediment OM content was determined by loss on ignition (LOI) at 550 °C overnight. Carbon was measured using a CHN elemental analyzer (Forno Fisons Instruments) for Long Island Sound sediments. For the samples without carbon content measurements, carbon was estimated using the slope of the relationship between %LOI and sediment carbon content (Figure S2).

Mercury methylation rates (k_{meth}) were estimated using the methylation rate of an enriched stable isotope spike of ^{200}Hg or ^{201}Hg (purity of 96.41% and 98.11%, respectively, obtained from Oak Ridge National Laboratory). The stock solutions were diluted with filtered bottom water (0.22 μm) and equilibrated for an hour before injection into replicate intact sediment cores.[9,17−19] Capped sediment cores were then incubated for 2 h in July and August, and for 7 h in May at ambient bottom water temperature to mimic in situ conditions. The DL for k_{meth} was estimated to be 0.0001 day^{-1} for LIS samples and 0.0006 day^{-1} for all other samples,[20] and methylation rates were above the DL in all samples except at MC. The ratios of ambient Hg 200:202 and Hg 201:202 in laboratory standards were found to have relative standard deviations of 3.83% and 3.04%, respectively.

RESULTS

Sediment Total Mercury and Methylmercury Content. Sediment HgT and MeHg concentrations (expressed on a dry weight basis) varied greatly across sites. Surficial (0−4 cm, average of four 1-cm slices or two 2-cm slices) sediment HgT concentrations ranged from 0.02 nmol g^{-1} in Wells (WH site) to 7.54 nmol g^{-1} in Hackensack (BC; Table S2). Sediment MeHg content followed a pattern similar to that of HgT with the lowest concentrations measured in Wells (WH site) and the highest in Hackensack (MC). The lowest porewater HgT concentration (0.011 nM) was detected at western LIS location, while the highest porewater HgT (0.951 nM) was measured in Wells (WM).

Sediment Organic Matter Content. Organic matter content of the sediment ranged from 0.68% in Wells to 11.39% in western LIS (Table S2). %LOI was significantly correlated with sediment carbon content (Figure S2; C (mmol g^{-1}) = 0.30 [LOI(%)], r^2 = 0.89)

Pore Water Sulfide. All porewater sulfide concentrations were below 10 μM with the exception of WM (98.5 μM), see Table S4.

Mercury Methylation. Table S3 summarizes the average surficial methylation rates (k_{meth}). The highest average rate (3.44% day^{-1}) was measured in Portsmouth (PNS). We measured the lowest rates in Wells (WH; 0.20% day^{-1}).

DISCUSSION

Pristine to Anthropogenically Impacted Sediments. The wide range of HgT concentrations across sites was evident after HgT was normalized to organic carbon content (Hg to C molar ratio expressed as pHg/C = −log[Hg/C]). This ratio allows for better comparison between biogeochemically distinct sites and can be used as a proxy for mercury contamination[9] (Figure 1). If the binding capacity to OM were the only factor influencing sediment Hg concentration, then the ratio would be constant among sites. Figure 1 confirms that the least contaminated sites are located in Wells (ME), mean pHg/C of 7.3, and that the most anthropogenically impacted site is BC on the Hackensack with a pHg/C of 5.2. While differences in pHg/C among sites were generally small within regions, in LIS the Hg content relative to C greatly increased from east to west. The spread in pHg/C at MC is due to large depth variability in sediment HgT content, where high surficial sediment HgT levels suggest more recent contamination.

Significance of the Methylation Rate. Numerous studies have explored the ability of added Hg isotopes to mimic the behavior of local Hg^{II},[10,22,23] and concluded that k_{meth} relationship to %MeHg is evidence for k_{meth}'s environmental significance. Our finding is consistent with other studies, as we show (Figure 2) that k_{meth} and %MeHg are correlated in most locations. Highly contaminated sediments are an exception,

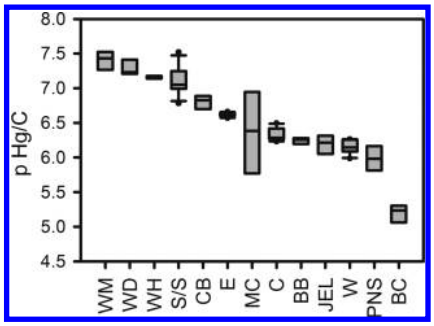

Figure 1. Sediment HgT concentration (0–10 cm) normalized to carbon for each site in the current study and Chesapeake Bay (CB), shelf and slope (S/S).[9,21] Each bar is an average of sections from 2–3 sediment cores (the bottom and top of the box represent the 25th and 75th percentile, the band near the middle is the median, and the whiskers represent the minimum and maximum value for each location).

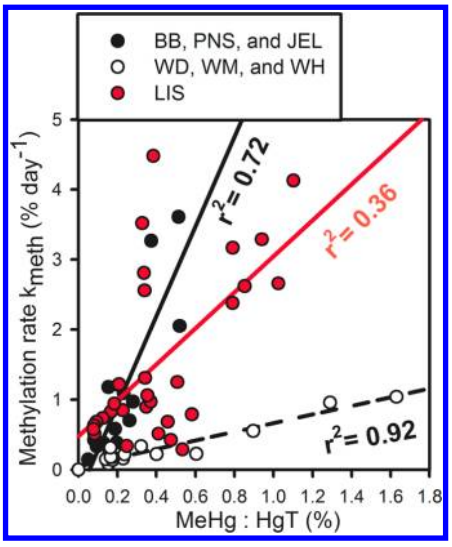

Figure 2. Methylation rate vs %MeHg of NH sites (BB, PNS, and JEL) in black, ME sites (WD, WM, and WH) presented as open symbols, and LIS sites (W, C, and E) as red symbols.

where we believe that %MeHg is mostly a function of the Hg loading rather than MeHg formation rate. The methylation rate and %MeHg are not correlated across regions, but positive linear relationships were found among sites in NH, LIS, and ME with large differences in linear regression slopes between the locations (6.39 in NH and 0.61 in ME). The linear relationships within those regions suggest that when all other factors such as physical sediment characteristics and Hg loadings are equal, the methylation rate becomes the main control over relative MeHg content. The difference in slopes between regions is not related to any of the measured ancillary parameters, but could be associated with changes in bacterial communities.[24] Although %MeHg is a good proxy for methylation rate within site, it cannot substitute k_{meth} in multisystem studies, where the linear regression slopes can be very different. As mentioned before, %MeHg is also sensitive to Hg loading; because HgT and OM are often positively correlated, a decrease in %MeHg with increasing OM does not necessarily equate to a decreasing k_{meth} with increasing OM.[25]

Methylation rates are highest at Hg impacted sites (low pHg/C) with a clear downward trend at sites with less Hg contamination. Figure 3 depicts our study sites and a compilation of published August and July k_{meth} and OM from

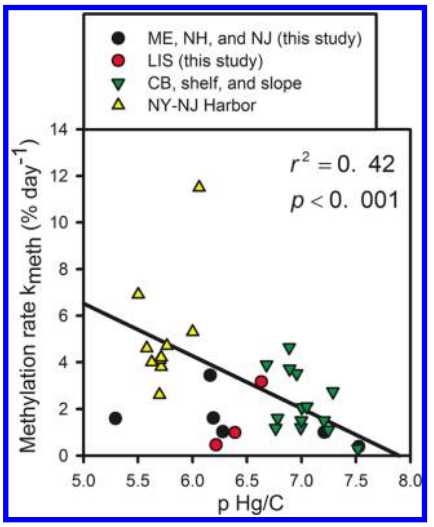

Figure 3. Methylation rate versus pHg/C of the sediment. Black circles: ME, NH, and NJ (this study); red circles: LIS (this study); green triangles: Chesapeake Bay and the adjacent shelf/slope;[9,21] and yellow triangles: NY-NJ Harbor.[11]

New York–New Jersey (NY-NJ) Harbor,[11] the Chesapeake Bay and its adjacent shelf/slope.[9,21] We propose that at low pHg/C more dissolved Hg^{II} is available for methylation; this is supported by an upward trend in porewater Hg^{II} concentration with decreasing pHg/C (Figure S4). However, there is no a direct relationship between k_{meth} and porewater Hg^{II} concentration as reported by many others,[5,12] although this lack of correlation is not limited to our work.[20,26]

Mitchell and Gilmour[20] discussed the lack of relationship between porewater Hg^{II} and k_{meth} in their study of salt marshes in Chesapeake Bay. They proposed that correlations were only significant in studies encompassing geochemically diverse sites with low OM and porewater sulfide,[12,27] thus allowing Hg partitioning coefficient, K_d, to become a major factor for methylation. K_d is the ratio of Hg concentration in the solid phase to that of porewater and is expressed in L kg^{-1}. Our study sites have low sulfide and OM, variable Hg^{II} concentration, and present a range of biogeochemical conditions, but just as in Chesapeake Bay salt marshes, k_{meth} and K_d are not inversely correlated (Figure S4).

While k_{meth} is unrelated to Hg^{II}, many other large-scale trends are maintained, suggesting that there are common factors (or factor) controlling MeHg production. For example, we find that MeHg and HgT are well correlated across all sites (Figure S3 [MeHg, pmol g^{-1}] = 4.7 [HgT, nmol g^{-1}], r^2 = 0.91, p < 0.01; BC was excluded from the regression because of large variability in MeHg content between cores). Using the slope, we can calculate the fraction of HgT as MeHg (%MeHg) to be 0.47 ± 0.04% which is the same as that previously reported (c.a. 0.5%) for a range of marine coastal systems.[3] Another example is the decreasing methylation rates with increasing pHg/C; although this trend is significant overall, the opposite trend is found in LIS (Figure 3).

Mercury Methylation and Sediment Organic Matter. The "eutrophication hypothesis" was derived from the relationship among k_{meth}, K_d, and OM,[11,12] as illustrated by Figure 4. An inverse relationship (black line) between sediment

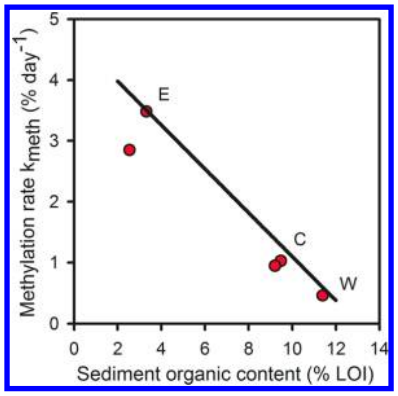

Figure 4. Relationship between methylation rate, k_{meth}, and sediment organic matter content for LIS (red circles, each symbol represents the average methylation rate in surficial sections (four 1-cm sections) of the same core). Solid line is the June relationship previously established (k_{meth} = 4.7 − 0.36 [%LOI]).[12]

OM and k_{meth} was found by Hammerschmidt and Fitzgerald,[12] and confirmed by LIS data obtained in the current study (Figure 4, red circles). The major implication of this relationship is that reducing sediment organic content by minimizing anthropogenic nutrient loading could lead to increased methylation.[25]

Yet, we do not find an inverse relationship between methylation rate and OM at our other study sites (Figure 5). On the contrary, OM-rich sites have (on average) higher methylation rates (Figure 5 left) which is consistent with the notion that OM helps support microbial communities and perhaps enhances methylation.[28−30] Moreover, Figure 5 (right) confirms that the lack of strong OM-driven inhibition of mercury methylation is not limited to our study sites. Overall, these data sets suggest that the empirical relationship between methylation rate and sediment organic content in estuaries is more complex than previously described.

Organic Matter Content and Hg Partitioning. The premise for the "eutrophication hypothesis" is that Hg^{II} conversion to MeHg is influenced by the efficiency of methylation by microorganisms, and the concentration and bioavailability of Hg^{II}, which are in turn controlled by inorganic and organic complexing agents in both the solid and porewater phases.[12,25] Numerous studies have reported that sediment OM, by strongly influencing Hg partitioning behavior, is the main control of Hg methylation,[8,11,12,31] and have demonstrated this, primarily, by using correlations between k_{meth} and %LOI (or K_d). Elevated sediment binding capacity, characterized by higher K_d values, has been linked to decreased methylation.[3,11,12] But, as we mentioned earlier, k_{meth} and Hg^{II} concentration are not related in this study, and high partitioning coefficients do not result in inhibited methylation (Figure S4). Despite the significant correlation in Figure 6, the

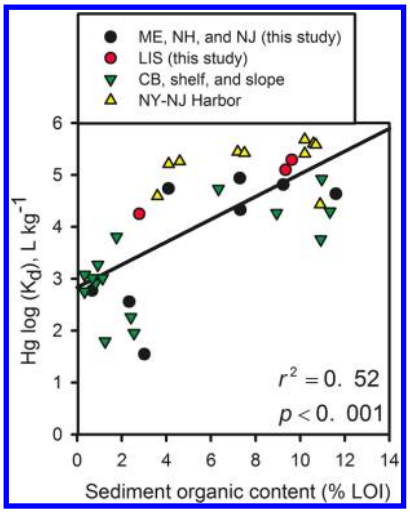

Figure 6. Variation of mercury (total Hg for all the sites and Hg^{II} for NY-NJ Harbor) distribution coefficient (K_d) with organic content of the sediment, measured as percent loss-on-ignition (%LOI). Black circles: ME, NH, and NJ (this study); red circles: LIS (this study); green triangles: Chesapeake Bay and the adjacent shelf/slope; and yellow triangles: NY-NJ Harbor.

log K_d levels off at about 6%LOI, and that the accumulation of sites at both %LOI extremes drives the linear relationship. Sites with nearly identical binding capacity, PNS and BC (Table S3) have organic contents of 11.16% and 3.75%. Conversely, sites like WM and E have similar %LOI (3.02 and 2.79) but drastically different log (K_d) (1.55 and 4.25 L kg^{-1}).

Sediment OM content does not explain variations in Hg partitioning, although it is possible that only a limited fraction of OM is relevant for Hg complexation.[9] Additionally, the role

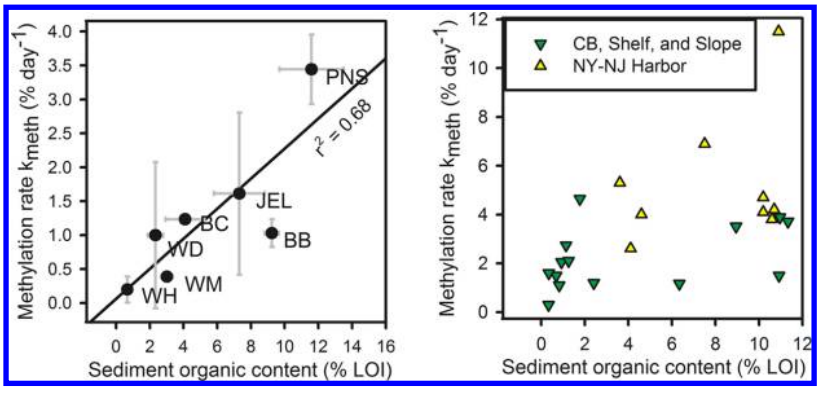

Figure 5. Left: Relationship between methylation rate, k_{meth}, and sediment organic matter content (%LOI) for ME, NH, and NJ. Each symbol represents the site average (n = 2 or 3 cores, except for BC where n = 1) for 0−4 cm depth sediment, and the error bars represent standard deviation. Right: Relationships between the methylation rate (k_{meth}) and sediment organic content (%LOI) for Chesapeake Bay, its adjacent shelf/slope,[9,21] and NY-NJ Harbor.[11] The Chesapeake Bay and shelf/slope is an average of data from the upper 4 cm of sediment, and the mean of the upper 6 cm in NY-NJ Harbor sediments.

of dissolved organic matter cannot be neglected;[32] dissolved OM is known to participate in porewater Hg^{II} speciation and thus to affect Hg^{II} bioavailability. It is possible that the sites with high Hg loadings are also receiving OM and dissolved OM that enable the formation of more bioavailable Hg forms.[33,34] We also believe that high K_d or %LOI alone cannot explain the trends found in LIS, as sites with similar (and higher) %LOI can have higher methylation rates. Furthermore, this limitation cannot be attributed to inhibited methylation due to high porewater sulfide content[35,36] as surficial sulfide content was 0.12 μM for W and below detection limit for site C (Table S4). Porewater sulfide is often mentioned as an important factor in mercury methylation, and multiple studies reported significant inverse correlations between sulfide and k_{meth}, though no such relationship was found in this study.

By expanding our study area to cover multiple estuaries across the U.S. east coast, we tested the hypothesis whether large biogeochemical differences in the study sites would isolate OM (K_d) as main control over Hg methylation. We found that overall OM is not a good indicator of sediment's binding capacity, or of sediment's potential to methylate Hg. Two major implications can be derived from our work: reducing the load of Hg can lower MeHg production, and a reduction in OM content will not necessarily lead to a spike in methylation, as suggested by the "eutrophication hypothesis".

In LIS, OM can pass for a factor controlling methylation if it is correlated to one. Indeed, Hammerschmidt and Fitzgerald[12] found that acid volatile sulfur (AVS) was related to k_{meth} (and OM), but AVS did not explain all the variability. This is expected as AVS is only a small fraction of the total reduced sulfur content of the sediment,[9] and all sulfur phases need to be considered.[21] It is also possible that the composition, rather than amount, of OM controls Hg^{II} partitioning into porewater and its subsequent methylation. Dissolved OM[30,32] and sulfide ligands (e.g., polysulfides)[37−39] have been proposed as alternative complexing agents for Hg^{II}.

Our work demonstrates the need for more thorough investigations of factors affecting methylation in the field. While laboratory experiments have demonstrated the complexity of mercury methylation, marine field studies have mostly relied on simple correlations and small-scale studies because of obvious logistic and technical limitations (such as handling reduced sulfur species in the field). Multi-estuary comparison studies, integrating advanced Hg, OM, and sulfur speciation work, will help decipher what factors truly control Hg methylation on a large scale, and help build strong global MeHg models. While HgT measurements are easy to obtain and good global models are available, MeHg analyses are tedious and good models are scarce. Models are needed to predict how global changes in Hg loading and climate change affect MeHg concentrations in fish.

■ ASSOCIATED CONTENT

Supporting Information

Maps of sampling locations, tables with sites and surface sediment characteristics, additional methods, and figures referred to in this manuscript. This information is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

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