Environmental Science & Technology

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Bivalves as a Mercury Bioindicator: A National Isotopic Survey along the Coast of South Korea

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Cite This: https://doi.org/10.1021/acs.est.4c03788

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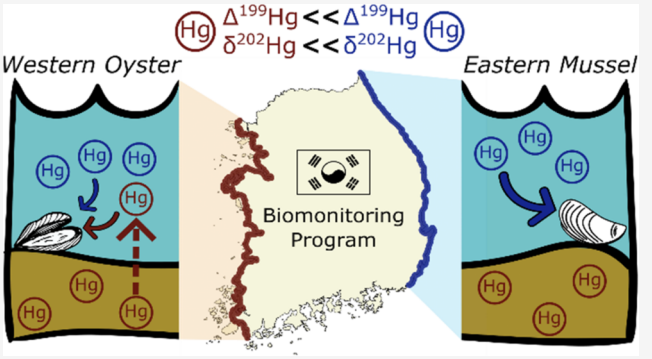
ABSTRACT: Mercury (Hg) is a contaminant that poses health risks for human populations relying on seafood consumption. To mitigate its impact, identifying and monitoring Hg sources have become priorities, notably under the Minamata Convention. Bivalves are commonly used as sentinels in contaminant biomonitoring but can accumulate Hg from diverse environmental media. To investigate their Hg sources, bivalves (blue mussel, *Mytilus edulis*, and Pacific oyster, *Crassostrea gigas*) and their associated sediment were sampled along the coast of South Korea and analyzed for Hg concentration and isotopic values. Oysters displayed low Δ^{199}Hg (0.19 ± 0.19‰) and δ^{202}Hg (−0.35 ± 0.55‰), highlighting a sedimentary source, whereas mussels exhibited higher values (0.72 ± 0.87 and 0.09 ± 0.72‰, respectively) indicating bioaccumulation from the water column. Sulfur, carbon, and nitrogen stable isotopes suggested that such a difference was not due to feeding niches. However, Hg isotopic trajectory analysis showed that environmental conditions controlling the desorption and remobilization of sediment Hg, notably via tidal flows, were likely to drive the observed source(s). While sediment Hg is not systematically reflected in biota, bivalves, which typically display Hg pools accumulated by benthic or pelagic food webs, appear valuable for Minamata Convention biomonitoring, though their fluctuating Hg sources require careful interpretation.



KEYWORDS: *mercury stable isotopes, mussel watch, pacific oyster, blue mussel, sediment, isotopic trajectory analysis, sulfur isotopes, anthropogenic contaminant*

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INTRODUCTION

Mercury (Hg) is a global pollutant, ubiquitous in marine ecosystems.[1,2] Emitted by anthropogenic activities in its inorganic form (IHg; gaseous elemental Hg^0 and oxidized Hg^{2+}), microbial processes methylate Hg to an organometallic form (MeHg; methylmercury) in aquatic sediments and the water column.[3,4] MeHg poses significant health hazards due to its toxicity and bioaccumulation into marine food webs and humans via fisheries consumption.[5] To mitigate ecological and human MeHg exposures, the United Nations has established the Minamata Convention on Mercury, a multilateral agreement that entered force in August 2017.[6] Along with the enforcement of new policies and technologies regulating anthropogenic Hg emissions, the convention also encourages signed parties to 'build upon existing monitoring networks and research programs' to track environmental Hg sources through time and space.

In coastal ecosystems, monitoring generally uses living organisms to evaluate changes in environmental quality, namely, "biomonitoring".[7−9] Biomonitoring of contaminants in such ecosystems has relied upon a large variety of taxa, including fishes and birds, but macroinvertebrates remain the most commonly used, particularly bivalves.[10,11] Mainly filter-feeders and sometimes deposit-feeders, bivalves present multiple advantages of being sessile, abundant, globally distributed, and tolerant to a wide range of environmental conditions and toxicity of contaminants.[7,12,13] Moreover, they serve as a valuable indicator for sources and concentrations of pollutants transferred from benthic and benthopelagic food webs.[14−16] The most famous example of bivalve-based monitoring is the Mussel Watch, developed in the U.S. in 1975,[17] an initiative that has spread worldwide in the form of numerous similar national-scale initiatives.[18,19] Theoretically, such programs present the opportunity to meet the biomonitoring objectives of the Minamata Convention by revisiting the records of past surveys and continuing the monitoring on a multinational scale. However, uncertainties

Received: April 17, 2024
Revised: January 6, 2025
Accepted: January 7, 2025

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remain regarding the sources of Hg and the environmental compartments traced by bivalves.[20]

Settled at the interface between the sediment and the water column, bivalves are exposed to a wide range of biogeochemical conditions, reflecting changes in Hg speciation and exposure pathways amid complex benthic cycling. Bivalves typically feed on seston, which corresponds to suspended particulate matter in their organic (e.g., phytoplankton, detritus) and inorganic (e.g., minerals) forms.[21−23] Hg bound to suspended particles are thought to be efficiently assimilated by bivalves, along with dissolved phases of Hg taken up via the water column.[24] While the latter might represent the most direct Hg exposure pathway, sediment plays a fundamental role in supplying both the water column dissolved and suspended particulate matter through sorption, diffusion, and resuspension (i.e., induced by wave strength, tidal flows, or bioturbation).[25−27] Sediment is also the major site for microbial methylation[3,5] and a net sink, storing both legacy and present Hg, which originate from continental/riverine runoff (e.g., watershed, groundwater discharge), atmospheric deposition, and direct industrial releases.[26,28,29] Although MeHg is the most efficiently assimilated form of Hg by bivalves, IHg typically predominates in their tissues, with considerable variation in the relative proportions of each form.[24,30] For example, co-occurring species may bioaccumulate different levels of MeHg or IHg due to variations in diet or physiological conditions.[31] Consequently, bivalves' Hg bioaccumulation is intricate and can reflect a wide range of complex Hg sources derived in varying proportions from sedimentary to water column origins.[14,32,33]

Because bivalves do not exhibit measurable changes in Hg isotopes during bioaccumulation, the Hg isotopic compositions of their tissues provide a direct reflection of their environmental sources.[20] Processes involving IHg photoreduction and MeHg photodegradation lead to both mass-independent and mass-dependent isotope fractionations, represented through Δ^{199}Hg and δ^{202}Hg, respectively.[34] Contrary to Δ^{199}Hg, all-known Hg biogeochemical processes induce mass-dependent fractionation, including microbial and abiotic methylation/demethylation,[35,36] and sorption/dissolution.[37,38] Sediment is typically not affected by photochemical processes and displays little to no mass-independent fractionations (i.e., near-zero Δ^{199}Hg) and instead reflects the values of sedimentary Hg sources (e.g., geogenic, terrestrial runoff, atmospheric deposition).[39] However, it encompasses a wide range of δ^{202}Hg values depending on the influence of proximate anthropogenic inputs (i.e., smelting, mining, coal combustion, chemical industries),[29,40,41] deposition pathways (i.e., terrestrial runoff, atmospheric deposition),[32,33,42] and/or local processes (e.g., sorption, dissolution, methylation).[36−38] Contrary to the sediment, both particulate and dissolved Hg phases in the water column are efficiently photoreduced, resulting in positive Δ^{199}Hg and δ^{202}Hg values in the product Hg.[43,44] Therefore, Hg stable isotopes present opportunities to elucidate between benthic and pelagic exposure pathways to bivalves due to the broad isotopic values displayed by both sources and the isotopic shifts induced by Hg biogeochemical transformations.

Since sediment acts as a long-term depository for Hg, characterizing the pathways of bivalve Hg exposure from sediment is essential, and bivalve-based biomonitoring programs could prove crucial if Hg pools in bivalves differ from those in sediments. To this end, paired sediment and bivalves were sampled in South Korea and measured for Hg concentration and isotopic compositions. Two species were studied: the blue mussel (*Mytilus edulis*) and the Pacific oyster (*Crassostrea gigas* or *Magallana gigas*). These species are abundant with global distribution and have long served as sentinels of the Mussel Watch,[17,18] and other biomonitoring programs worldwide.[19,30,45] South Korea presents the opportunity to test the influence of environmental drivers on Hg bioaccumulation, as the western, southern, and eastern coasts have unique tidal regimes, sediment proprieties, and river discharges.[46−48] Furthermore, the effect of interspecific differences in feeding modes on Hg bioaccumulation was evaluated by sulfur, carbon, and nitrogen stable isotopes, used to distinguish between pelagic and benthic dietary origins. To characterize Hg sources and compare them with the few prior studies on Hg isotopes in sediments and bivalves from various ecosystems, the isotopic (δ^{202}Hg and Δ^{199}Hg) difference between sediment and bivalve (considering both the direct comparison and the extent of divergence) were illustrated by trajectory segments plotted from sediment isotopic values to those of bivalves. Given the similar feeding modes of mussels and oysters, spatial variations in environmental and biogeochemical conditions along the coasts of South Korea are expected to result in distinct Hg exposure pathways to bivalves. Ultimately, this study informs on the potential integration of widespread biomonitoring programs such as the Mussel Watch under the Minamata Convention.

MATERIALS AND METHODS

Sample Collection. Sediments and bivalves were sampled at 49 sites along the western, southern, and eastern coasts of South Korea in February 2020 as a part of an ongoing nationwide biomonitoring program of organic and trace metal contaminants. Surface sediment samples (top 2 cm) were collected using a Van Veen grab sampler (27 cm × 27 cm × 15 cm) and sieved through a 63 mm nylon mesh. Following bivalve geographical distribution, blue mussels (*M. edulis*) were sampled on the eastern and southern coasts (n = 38), and Pacific oysters (*C. gigas*) were sampled on the western coast (n = 11 sites). These species are filter-feeders with plastic particle selection processes that depend on the composition of the seston. They typically favor the ingestion of organic and large particles, mainly phytoplankton, but they are also capable of feeding on a wide spectrum, from small bacteria and picoplankton to large zooplankton and sediment particles.[21−23] All collected bivalves were measured for shell length, width, and height using calipers. At each site, bivalve samples were constituted of a pool of 10 to 15 individuals of similar sizes (i.e., 47.8 ± 8.0 mm shell length, 26.2 ± 4.2 mm shell width, and 18.6 ± 3.2 mm shell height for the mussels; 60.2 ± 14.1, 33.1 ± 6.5, and 24.7 ± 4.0 mm, respectively, for the oysters). Upon sampling, bivalves were put in seawater and aerated for a few hours to allow the excretion of particles and sediments. Soft tissues were then separated from the shells on-site, washed with deionized water, and transported to the laboratory, where they were freeze-dried, homogenized, and pooled by site.

Mercury Concentration and Stable Isotope Analyses. All analyses were performed at the Environmental and Health Assessment Laboratory (POSTECH, Pohang, South Korea). Total mercury concentrations (THg) in all sediment and bivalve samples were measured by atomic absorption spectroscopy (AAS) using an MA-3000 direct Hg analyzer (Nippon Instruments Corporation, Japan). THg is expressed

https://doi.org/10.1021/acs.est.4c03788
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on a dry weight (dw) basis. The accuracy and reproducibility of the analysis were established by multiple measurements of Montana soil and lobster hepatopancreas reference materials (SRM-2711, NIST, 7.4 ± 0.2 ng·g^{-1} and TORT-3, NRC, 292 ± 22 ng·g^{-1}, respectively), which yielded THg recoveries within the confidence limits (n = 15, 7.3 ± 0.1 ng·g^{-1} and n = 14, 291 ± 47 ng·g^{-1}, respectively) (Table S1). Duplicate and triplicate measurements of sediment and bivalves showed a precision of ±1.2 ng·g^{-1} (n = 17) and ±0.7 ng·g^{-1} (n = 10), respectively.

Among the 49 sites, Hg isotopes of paired sediment and bivalves were measured from 27 sites. Using a dual-stage thermal furnace, samples were combusted to release Hg in the form of Hg^0. Hg^0 was then oxidized (Hg^{2+}) and preconcentrated into a potassium permanganate solution (1% $KMnO_4$) prepared in trace metal grade sulfuric acid (10% H_2SO_4). Hg isotopic compositions of the $KMnO_4$ trap solutions were measured by multicollector inductively coupled plasma mass spectrometry (MC-ICP-MS; Nu-Plasma III, Nu Instruments, U.K.) with continuous reduction of the solution by tin(II) chloride (2% $SnCl_2$) and separation of Hg^0 using a glass gas−liquid phase separator. Instrumental mass bias was corrected using the National Institute of Standards and Technology (NIST) SRM-997 standard (i.e., thallium) introduced via a desolvating nebulizer (CETAC Aridus3). Isotopic values are expressed in δ notation (‰) relative to their deviation from the NIST SRM-3133 standard and calculated by sample-standard bracketing following: $\delta^{XXX}Hg = [(({}^{XXX}Hg/{}^{198}Hg)_{sample}/({}^{XXX}Hg/{}^{198}Hg)_{NIST\ SRM\text{-}3133}) - 1] \times 1000$, where XXX represents Hg isotope masses. Hg mass-dependent fractionation is represented by $\delta^{202}Hg$, while mass-independent fractionation is expressed by Δ notation following: $\Delta^{XXX}Hg = \delta^{XXX}Hg - (\delta^{202}Hg \times a)$, where a = 0.252, 0.502, and 0.752 for isotopes 199, 200, and 201, respectively. Standard deviations of Hg isotopic values are presented as ±2SD.

SRM-2711 (n = 4) and TORT-3 (n = 9) reference materials were analyzed following the same procedure as sediments and bivalves. THg content in the $KMnO_4$ solutions was systematically checked by cold vapor atomic fluorescence spectroscopy (CV-AFS; Brooks Rand, U.S.). Combustion procedure recovered 96 ± 10, 102 ± 7, 98 ± 2, and 94 ± 6% of sample THg in the sediment, bivalve, SRM-2711, and TORT-3, respectively. Isotopic measurement reproducibility was assessed by analyzing NIST SRM-8610 (UM-Almadén, n = 30) and procedural standards SRM-2711 and TORT-3. Measured isotopic values, as well as analytical reproducibility of standards, agreed with previously published values (Table S2). Analytical uncertainties (±2SD) for sediment and bivalve samples were estimated based on SRM-2711 and TORT-3 measurements, respectively (Table S2).

To disentangle the dietary dependency of mussels and oysters to the sediment, the subset of samples selected for Hg isotope analysis was measured for sulfur ($\delta^{34}S$), carbon ($\delta^{13}C$), and nitrogen ($\delta^{15}N$) stable isotopes.[49,50] These analyses were performed on bulk bivalve tissues and surface sedimentary organic matter; the latter was obtained after resuspension of the sediment by flushing seawater.[49] The same bivalve samples were also analyzed for MeHg content (i.e., expressed as % MeHg)[51] to understand the potential effect of Hg speciation on the isotopic compositions. Details of both methodologies are available in the Supporting Information (Texts S1 and S2).

Data Treatment. Hg isotopic values measured in this study were compared with those from four previous studies that analyzed paired sediment and bivalves, including blue and ribbed (*Geukensia demissa*) mussels from U.S. northeastern estuaries by Kwon et al.,[14] zebra mussels (*Dreissena polymorpha*) from Douglas Lake (U.S.) by Kwon et al.,[32] blue mussels from Groswater Bay (Canada) by Li et al.,[33] and Asian clams (*Corbicula fluminea*) from Hyeongsan River (South Korea) by Kim et al.[20] For each study, isotopic values were selected by taking into consideration the proximity of bivalve and sediment sampling sites (Text S3). These values were used to examine bivalve Hg sources across ecosystems (i.e., coastal, lake, river) and species (i.e., mussel, oyster, and clam).

Differences in $\Delta^{199}Hg$ and $\delta^{202}Hg$ between sediments and bivalves sampled for this study and literature-extracted values were analyzed using stable isotope trajectory analysis (SITA).[52] SITA is based on trajectory segments established as Euclidean distances between isotopic coordinates inside a bidimensional δ-space. For each site, Hg isotopic trajectory segments were drawn inside the $\delta^{202}Hg/\Delta^{199}Hg$ δ-space, starting from the sediment isotopic values and ending with the bivalve isotopic values. Trajectory segments were characterized by distance- and direction-based metrics. The distance-based metric is the "net change", defined as the length between the initial (i.e., sediment) and the final (i.e., bivalve) coordinates of the trajectory segment (in ‰). The direction-based metric is the "angle" (α) of the trajectory segment (in °), considering the second axis of the δ-space (i.e., the $\Delta^{199}Hg$ axis in the $\delta^{202}Hg/\Delta^{199}Hg$ δ-space) as the North (0°). Trajectory segments were plotted inside a trajectory rose diagram, consisting of circular plots of segments where lengths correspond to net changes and angles range from 0 to 360° according to increase and/or decrease in $\delta^{202}Hg$ and $\Delta^{199}Hg$ values between sediment and bivalve (i.e., 0−90°: increase in $\delta^{202}Hg$ and $\Delta^{199}Hg$; 90−180°: increase in $\delta^{202}Hg$ and decrease in $\Delta^{199}Hg$; 180−270°: decrease in $\delta^{202}Hg$ and $\Delta^{199}Hg$; 270−360°: decrease in $\delta^{202}Hg$ and increase in $\Delta^{199}Hg$).

For statistical comparisons of concentrations, isotopic values, and net changes, data were first checked for normality (Shapiro−Wilk test) and homogeneity of variance (Bartlett's test). When the two conditions were met for multiple group comparisons, ANOVAs followed by post hoc Tukey's HSD tests were applied. For the rest of the comparisons, nonparametric analogous Kruskal−Wallis tests followed by Dunn's post hoc tests with Bonferroni's adjustments were used. The spatial Hg variations were explored by comparison among the western, southern, and eastern coasts. Interspecific differences in Hg content between bivalve species and intraspecific variations among mussels sampled in the south and east coasts were assessed through Student's t-tests or a nonparametric analogue, the Wilcoxon signed-rank test. Circular statistics were applied to the angles of the isotopic trajectory analysis. Angle homogeneity of distribution and differences in directions were assessed by Hermans−Rasson and Watson−William's tests, respectively (α = 0.05 for all statistical tests).[52−54] All statistical analyses were performed using the open-source software R (version 4.2.2, R Core Team, 2023).

RESULTS AND DISCUSSION

Sediment and Bivalve Hg Concentrations. Sediment THg differed across coasts ($\chi_{2,48}^2$ = 19.8, p < 0.001).

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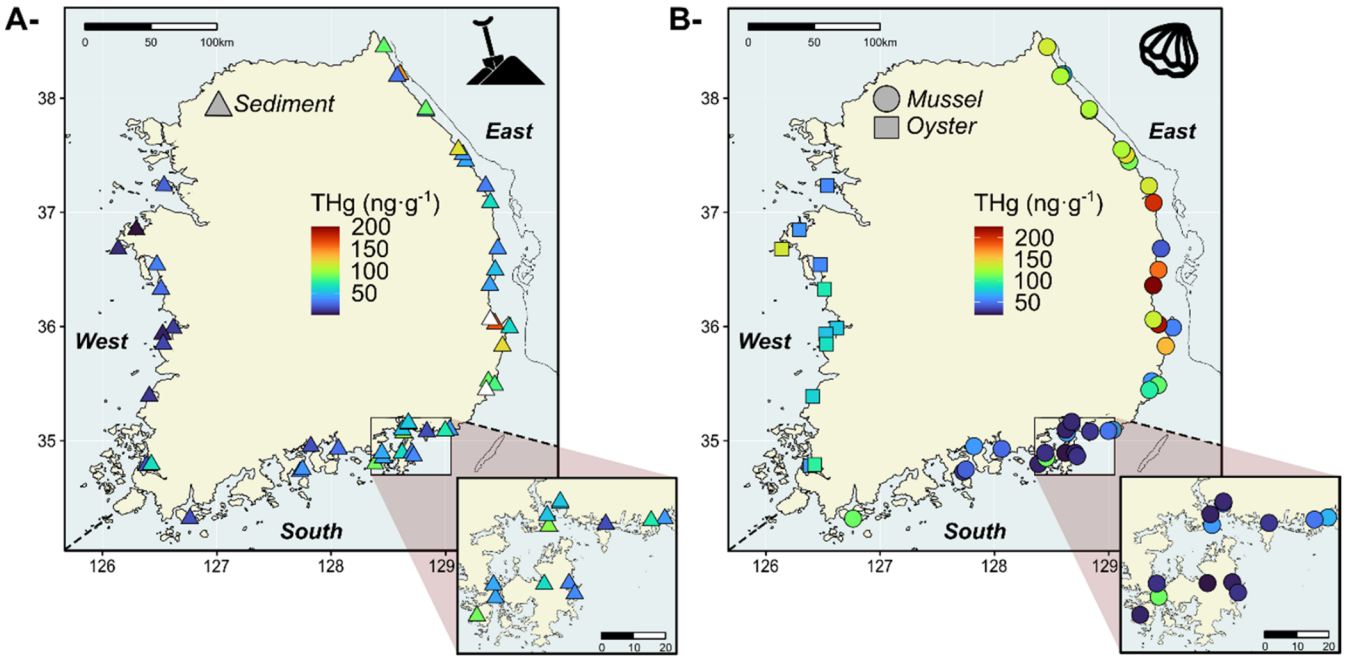

Figure 1. Distribution of total mercury (THg) concentrations measured in sediments (A) and bivalves (B) along the coast of South Korea. Sediment THg concentrations exceeding 200 ng·g^{-1} in Onsan (southernmost site, 1418 ng·g^{-1}) and in Pohang (northernmost site, 600 ng·g^{-1}) are represented in white. Sites where mussels and oysters were sampled are indicated by circles and squares, respectively. The boundary of the continental shelf is represented by the 200 m bathymetric line in black. Dashed lines mark the boundaries of the western, southern, and eastern sampled coasts.

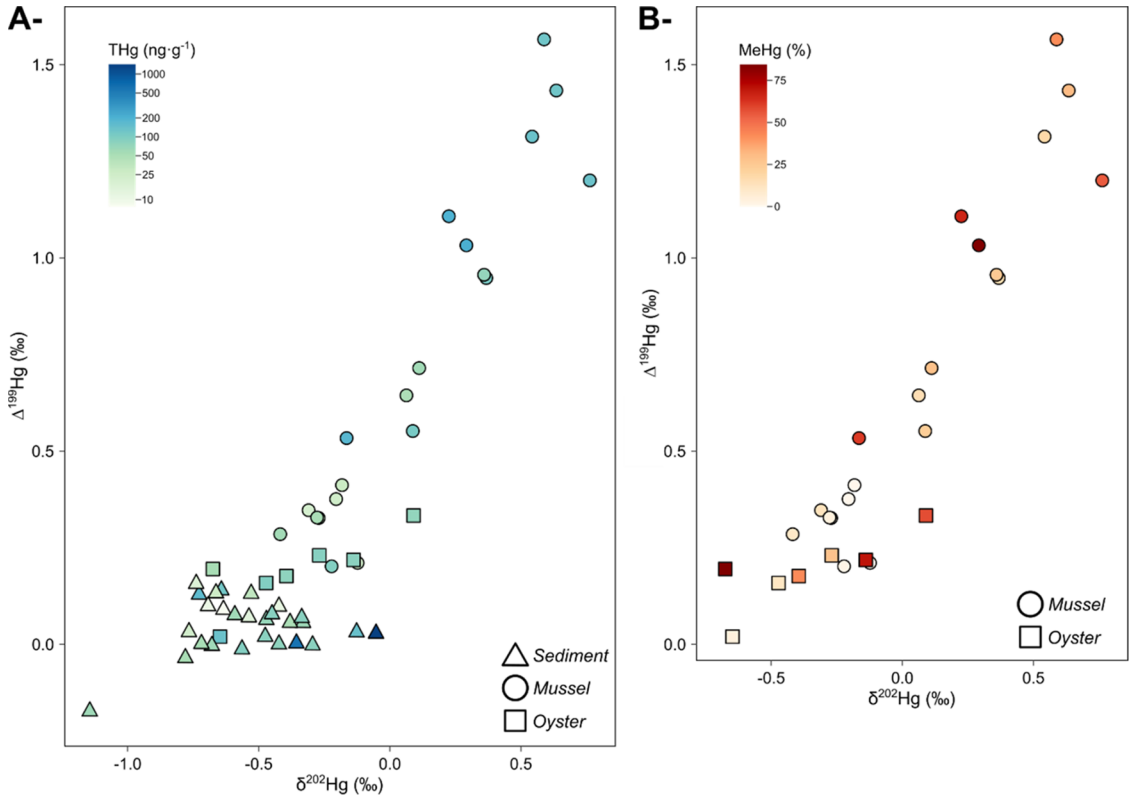

Figure 2. δ^{202}Hg and Δ^{199}Hg values in sediments (triangles) and bivalves (circles for mussels and squares for oysters). Color scales represent THg (log scale) in all samples (A) or %MeHg in bivalves (B).

Significant variations were observed between the eastern (167 ± 320, ranging from 24 to 1418 ng·g^{-1}) and western (20 ± 18, ranging from 1 to 64 ng·g^{-1}) locations (Dunn's test, $p < 0.001$), while southern sediment exhibited intermediate values (46 ± 23, ranging from 17 to 94 ng·g^{-1}) (Figure 1A). Conversely, there was no significant interspecific difference ($W = 214$, $p > 0.05$) between the mussels (90 ± 59, between 21 and 225 ng·g^{-1}) and the oysters (79 ± 24, between 55 and 138

https://doi.org/10.1021/acs.est.4c03788
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ng·g^{-1}) for THg (Figure 1B) and %MeHg (W = 98, p > 0.05). Both species displayed low mean %MeHg (i.e., 25 and 43%, respectively) as commonly observed in bivalves.[16,30,33] Intraspecific variations in %MeHg were, nevertheless, important (i.e., 0−84% for mussels and 5−84% for oysters) and likely resulted from site-specific environmental conditions governing MeHg production and mobility. No significant relationship was observed between sediment and bivalve THg across the studied species and locations (Figure S1), consistent with previous observations of coastal bivalves.[55,56] Therefore, bivalves did not appear to reflect the extent and spatial variation of sediment THg, especially in the mussel assemblages, which could be linked to the accumulation of different Hg sources.

Isotopic Characterization of Bivalve Hg Sources. The sediments displayed a wide range of δ^{202}Hg values, from −1.14 to −0.05‰ (−0.54 ± 0.23‰), and a narrow range of Δ^{199}Hg values, from −0.18 to 0.15‰ (0.05 ± 0.14‰) (Figure 2A), with no significant difference across the coasts ($F_{2,26}$ = 1.2 for δ^{202}Hg, $F_{2,26}$ = 1.3 for Δ^{199}Hg, both p > 0.05) (Figure S2). Typically, Hg in the sediment encompasses Δ^{199}Hg values near-zero or slightly positive, as it is rarely affected by photochemical reactions except when subjected to photoreduction in shallow waters or deposition of photoreduced Hg from the water column.[57,58] The Δ^{199}Hg and δ^{202}Hg of all sediments were within the ranges of coastal and nearshore sediments previously sampled in the west coast of South Korea and in the Chinese marginal seas influenced by mixtures of Hg introduced via industrial discharges (near-zero Δ^{199}Hg and slightly negative δ^{202}Hg), atmospheric deposition (positive Δ^{199}Hg and highly negative δ^{202}Hg), and riverine runoff (near-zero to negative Δ^{199}Hg and intermediate negative δ^{202}Hg) (Figure S3).[58,59] The significant but weak linear relationship between the sediment δ^{202}Hg and THg (R^2 = 0.25, F = 8, p < 0.01) suggested that, while the influence of industrial Hg releases along the coasts of South Korea generally dictates δ^{202}Hg and Hg levels in the sediments, environmental processes resulting in mass-dependent fractionations within sediments and mixtures of multiple Hg sources may result in the weak relationship.[29,60] Notably, near-zero δ^{202}Hg and higher THg found in the sediments of the east coast were consistent with the presence of numerous historical or current anthropogenic point Hg sources (e.g., shipbuilding companies, smelting plants, petrochemical/refining industries) (Text S4).[61]

As for the bivalves, Δ^{199}Hg and δ^{202}Hg values were significantly different between the mussels and oysters (W = 9, p < 0.001 for Δ^{199}Hg and t = −3, p < 0.01 for δ^{202}Hg). The mussels exhibited higher Δ^{199}Hg (0.72 ± 0.87‰) and δ^{202}Hg (0.09 ± 0.72‰) and greater ranges of values (0.20 ≤ Δ^{199}Hg ≤ 1.57‰ and −0.42 ≤ δ^{202}Hg ≤ 0.76‰) relative to the oysters (i.e., 0.19 ± 0.19‰ ranging from 0.02 to 0.33 and −0.35 ± 0.55‰ ranging from −0.67 to 0.09‰, respectively) (Figure 2). The low Hg isotopic values observed in the oysters were similar to those of the sediment despite the absence of significant THg (Figure S1) and Hg isotope relationships (Figure S4) between them. Moreover, while Hg isotopic compositions displayed no significant relationship with THg (or 1/THg, Figure S5) and %MeHg for the oysters, the mussel Δ^{199}Hg and δ^{202}Hg values were both correlated with THg (R^2 = 0.42, F = 13, p < 0.01 and R^2 = 0.33, F = 9, p < 0.01, respectively) and %MeHg (R^2 = 0.37, F = 11, p < 0.01 and R^2 = 0.28, F = 7, p < 0.05, respectively), such that the mussels with greater THg and %MeHg had higher Δ^{199}Hg and δ^{202}Hg.

Overall, sediment THg and Hg isotope values varied by the extent of proximate anthropogenic influences and appeared to serve as an effective storage site for Hg. In contrast, the bivalves displayed absence of THg relationships with their paired sediments. Despite no significant sedimentary-bivalve THg relationship, the extent to which environmental Hg sources influenced bivalves appeared to differ by species or coastlines. The oysters sampled on the west coast displayed Hg isotopic compositions similar to the sediment (i.e., near-zero Δ^{199}Hg and negative δ^{202}Hg). In marine biota, species with a sedimentary Hg origin tend to have isotopic compositions similar to their associated sediment, implying the potential contribution of sedimentary Hg sources to oysters.[40,42,43] Characterizing the isotopic shifts from sediment to bivalve using the isotopic trajectory analysis (Figure 3), this was verified as similar Hg isotopic compositions were observed

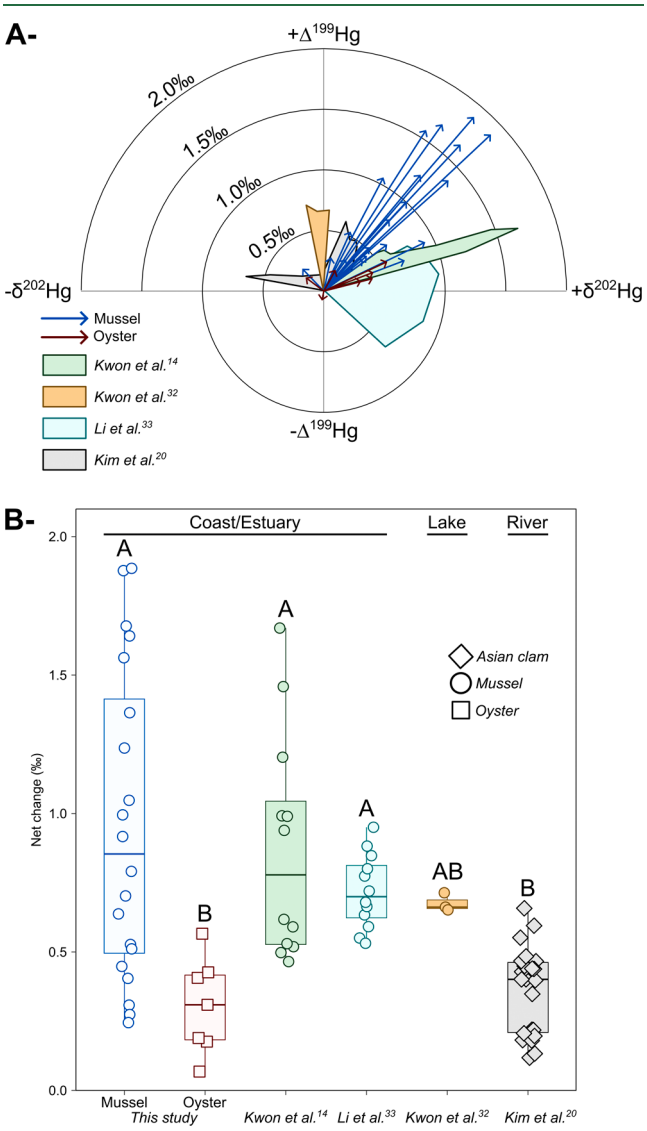

Figure 3. (A) Trajectory rose of the shifts in δ^{202}Hg and Δ^{199}Hg values between sediments and bivalves sampled along the coast of South Korea (arrows, this study) and in past studies (convex hull areas). (B) Boxplot of the trajectory net changes with significant differences between study cases indicated by letters.

https://doi.org/10.1021/acs.est.4c03788
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between the oyster and sediment (i.e., low net changes from 0.07 to 0.57‰ without homogeneous Hg isotopic trajectories across locations; HR = 6.0, $p > 0.05$). Furthermore, the linear correlation between Δ^{199}Hg and Δ^{201}Hg values, in which the slope is used to distinguish between IHg photoreduction (~1.00) and MeHg photodegradation (~1.36) prior to bioaccumulation,[34] was not observed for the oysters (R^2 = 0.22, F = 1, $p > 0.05$) (Figure S6). This further confirmed that the oysters reflected Hg from the sediment that has undergone none to negligible photoreduction or photodegradation.

Conversely, the mussels sampled on the east and south coasts had much wider ranges of Hg isotope values driven, to some extent, by Hg and MeHg bioaccumulation. Their Hg isotopic trajectories were also significantly different compared to the oysters (WW = 0.3, $p < 0.01$), pointing toward a single direction (HR = 43.0, $p < 0.001$) characterized by higher Δ^{199}Hg and δ^{202}Hg values in the mussels than their associated sediment and elevated net changes from 0.24 to 1.89‰ (Figure 3). This was consistent with the pattern of aqueous IHg photoreduction and MeHg photodegradation, which cause higher δ^{202}Hg and Δ^{199}Hg in the remaining Hg relative to the reactant, implying that water column Hg was the primary source for the mussels.[43,44,57] Furthermore, mussel Δ^{199}Hg and Δ^{201}Hg were significantly correlated (R^2 = 0.67, F = 36, $p < 0.001$) and displayed a slope of 0.96 ± 0.16 (Figure S6), consistent with the experimental slope reported for IHg photoreduction.[34]

Although biotic demethylation and adsorption of Hg^{2+} to minerals and thiol groups can cause positive shifts in δ^{202}Hg in the remaining MeHg or dissolved Hg phase, respectively, these processes alone cannot explain the net changes observed in mussels. Indeed, the δ^{202}Hg shifts in mussels were significantly larger than those typically caused by adsorption and demethylation (i.e., usually not exceeding 0.6‰) and also exhibited mass-dependent fractionations (i.e., shifts in Δ^{199}Hg) not induced by these processes.[37,38,62] Rather than external Hg sources derived from atmospheric deposition, it is also possible that mussel high Δ^{199}Hg and δ^{202}Hg could have resulted from Hg resuspended or diffused from the sediment into the water column, which has undergone photoreduction or photodegradation prior to bioaccumulation. To evaluate such alternative hypothesis, mussel δ^{202}Hg values were corrected to eliminate the effect of photoreactions (i.e., δ^{202}Hg when Δ^{199}Hg = 0‰). Previously, biota Hg have been tracked back to the sediment despite their high Hg isotope values based on the linear correlation between their δ^{202}Hg corrected values and the sediment δ^{202}Hg.[63−65] Given the low %MeHg and the Δ^{199}Hg/Δ^{201}Hg slope close to IHg photoreduction detected in the mussels, the δ^{202}Hg values were corrected using the experimental slope of Δ^{199}Hg/δ^{202}Hg reported during progressive aqueous IHg photoreduction (i.e., $\delta^{202}Hg_{MusselCorrected} = \delta^{202}Hg_{Mussel} - (\Delta^{199}Hg_{Mussel}/1.15)$, detailed in Figure S7).[34] The mussel δ^{202}Hg corrected values ranged from −0.77 to −0.28‰ and were not correlated to sediment δ^{202}Hg (Figure S7). While these corrected values must be interpreted with caution due to the variations in the concentrations and types of dissolved organic matter and ligands along the coast of South Korea,[63,66] they imply that mussels were not associated with the sediment Hg but influenced by water column Hg.

Ecological and Environmental Drivers of Hg Pathways to Bivalves. The observed interspecific difference in the Hg pools accumulated by bivalves prompts consideration of potential underlying ecological drivers, such as dietary sources (i.e., benthic vs water column feeding) or site-specific environmental characteristics (e.g., tidal influence). Based on sulfur (δ^{34}S), carbon (δ^{13}C), and nitrogen (δ^{15}N) isotopic compositions, no interspecific difference in bivalve dietary relationships with the sediment was observed. The mussel and oyster δ^{34}S (19.40 ± 0.89 and 19.55 ± 1.16‰, respectively), δ^{13}C (−18.99 ± 0.88 and −18.54 ± 1.05‰, respectively), and δ^{15}N (8.36 ± 1.10 and 9.35 ± 2.18‰, respectively) were noticeably similar ($p > 0.05$ for all pairs of comparisons). The bivalves were systematically enriched in ^{34}S, ^{13}C, and ^{15}N compared to the surface sediment-derived organic matter (i.e., δ^{34}S from −28.10 to −3.36‰, δ^{13}C from −27.21 to −19.96‰, and δ^{15}N from −2.46 to 6.85‰) (W = 0, $p < 0.001$ for δ^{34}S; W = 4, $p < 0.001$ for δ^{13}C, and t = −10, $p < 0.001$ for δ^{15}N) (Figure S8) and were within the ranges of previously reported values of bivalves feeding upon phytoplanktonic and benthic microalgae across South Korean coastal ecosystems.[67] Relative to δ^{13}C and δ^{15}N, bivalve dietary ties to organic matter sources are more easily traceable using δ^{34}S due to the large discrimination between the positive δ^{34}S of water column sulfate (SO_4^{2-}) and the negative δ^{34}S of sediment sulfide (S^{2-}).[50,68] While infauna biota or species trophically tied to sedimentary production, including bivalves, are typically characterized by near-zero to negative δ^{34}S values,[50,69,70] it was not the case in this study. Instead, the mussels and oysters seemed to rely homogeneously on the organic matter of the water column. Therefore, the Hg isotopic compositions, together with the δ^{34}S, δ^{13}C, and δ^{15}N values, strongly suggested that, despite the absence of interspecific differences in dietary sources, the oysters were exposed to sedimentary Hg, which have undergone little photoreduction in the water column, while the mussels bioaccumulated water column Hg. This raises questions regarding the potential effects of diverse environmental conditions on Hg sources and biogeochemical processing.

More than half of the mussel sampling sites were located on the eastern coast of South Korea, characterized by deep waters with sandy beaches and rocky shores, no riverine inputs, and negligible tidal influences.[46−48] In these ecosystems, Hg delivered via precipitation was expected to be the main source, undergoing photoreduction within the water column before integration into mussels. Given that Δ^{200}Hg anomalies occur exclusively via atmospheric Hg^0 oxidation, prior studies have used Δ^{200}Hg as a conservative tracer to distinguish between Hg^0 (negative to near-zero Δ^{200}Hg) and Hg^{2+} (positive Δ^{200}Hg) atmospheric depositional pathways.[71] Here, the mussel Δ^{200}Hg ranged from 0.01 to 0.32‰, while the oyster ranged from −0.04 to 0.08‰. The positive Δ^{200}Hg observed in the mussels aligned with an accumulation of Hg from the water column that has been delivered via wet deposition. This result is in accordance with the similar Hg isotopic composition of precipitation and bivalves previously observed on the eastern coast of South Korea.[20] The influence of wet Hg deposition on the entire ecosystem was further revealed by the positive relationship between the sediment and mussel Δ^{200}Hg (Figure S4). The efficient uptake of dissolved inorganic Hg phases derived from precipitation would also explain the low % MeHg and the absence of a significant relationship between the mussel and sediment Hg concentrations and isotopic values. Site-specific differences in MeHg production at the sediment−water interface probably drive the variable %MeHg in the mussels, as this interface is typically the primary zone of

https://doi.org/10.1021/acs.est.4c03788
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methylation in coastal ecosystems. Overall, these results imply relatively uniform Hg sources from the water column, with photoreduction processes occurring before bioaccumulation in mussels on the eastern coast.

In contrast, the western coastal ecosystems of South Korea, where the oysters were sampled, are marked by shallow depths and strong tidal mixing, resulting in extensive muddy tidal flats. Additionally, three major rivers (the Han, Geum, and Yeongsan Rivers) flow into the western basin, contributing to the formation of large turbid estuaries.[46−48] Tidal sediment resuspension is known to be a major source of particulate Hg to the surrounding water column filtered by bivalves, as observed in natural settings,[72,73] mesocosm and microcosm experiments.[25,74,75] The fact that Hg was sourced from the sediment despite the oysters being trophically tied to the water column by $\delta^{34}S$, $\delta^{13}C$, and $\delta^{15}N$ values suggests that resuspended Hg was quickly bioconcentrated by phytoplankton and, then, biodiluted to the water column bivalves and nekton, as previously demonstrated in some coastal ecosystems.[16,28] The strong tidal flows of the west coast probably led to the active resuspension of particulate-bound Hg from the sediment, which was observed in the oysters. Presumably, Hg delivered via precipitation had an equally important role as a source to the west, south, and east coasts, but the diurnal tidal export on the western coast likely suppressed aqueous photoreduction in such a turbid environment[47] and allowed atmospheric Hg to be quickly flushed out with other Hg sources introduced via riverine/continental runoff and those resuspended from the sediment.[28] Alternatively, Hg exported via rivers and terrestrial runoff typically bound to particulate phases encompass lower $\Delta^{200}Hg$ relative to dissolved Hg phases, which also may explain the western coast oyster low $\Delta^{200}Hg$ relative to the mussel on the eastern coast.[76] As the transfer and equilibrium distribution of Hg between the sediment and the surrounding surface water is known to be favored in organic-rich sediment of small particle sizes, the muddy fine-grained sediment of the western coast might also have contributed to the higher sedimentary Hg exposure to oysters compared to the sandy coarse-grained sediment of the eastern coast.[25,77,78]

Finally, the mussels were also sampled on the south rocky shore coast. Significant intraspecific differences were observed in the mussels with the eastern individuals displaying higher $\Delta^{199}Hg$ (0.91 ± 0.93‰), $\delta^{202}Hg$ (0.22 ± 0.80 ‰), and net changes (1.15 ± 0.63‰) than the southern ones (0.45 ± 0.34, −0.10 ± 0.34, and 0.66 ± 0.24‰, respectively) ($t = 3$, $p < 0.01$ for $\Delta^{199}Hg$; $t = 3$, $p < 0.05$ for $\delta^{202}Hg$; $t = 2$, $p < 0.05$ for net changes). The intermediate environmental conditions of the south, characterized by small tidal ranges but with muddy sediments more prone to Hg transfer to the water column, might explain a potential narrow influence of sedimentary Hg for mussels sampled on the southern coast compared to the eastern coast. Such potential intraspecific difference further highlights the significant impact of coastal environmental drivers on the bivalve Hg sources.

Revisiting Bivalve Hg Sources across Various Ecosystems. The diversity of bivalve Hg sources in South Korea raises questions about which compartment is being monitored when bivalves are used as a bioindicator. To further assess the potential suitability of bivalves for Hg biomonitoring, the diversity of bivalve Hg sources across other coastal, riverine, and lacustrine ecosystems was assessed. For that purpose, the Hg isotopic trajectory analysis was applied to previous studies reporting the Hg isotopic compositions of bivalves with their associated sediment along the coast of Canada (Groswater Bay) and U.S. northeastern estuaries, in the Hyeongsan River (South Korea), and Douglas Lake (U.S.) (Figure 3). The trajectories of each study case pointed in a preferred direction that was significantly different from one another (Table S3) and were characterized by significantly higher net changes in mussels sampled in coastal ecosystems compared to oysters in this study and Asian clams in riverine ecosystems ($\chi_{5,75}^2 = 36.5$, $p < 0.001$).

In coastal and estuary habitats, the mussels globally displayed an increase in $\Delta^{199}Hg$ and $\delta^{202}Hg$ values compared to their respective sediments with high net changes. This corresponded to a pool of Hg biogeochemically processed and derived from the water column for which the extent of photochemical processes likely governed the net changes, as described for the mussels sampled in South Korea. Despite the prevalence of water column Hg exposure to the mussels was recognized by Li et al. in Groswater Bay,[33] Kwon et al.[14] suggested that the primary Hg source originated from the sediment with a substantial photochemical reduction in the water column postresuspension and preintegration to mussels.[14] This study proposes the alternative possibility that the mussels from these U.S. northeastern estuaries could have been exposed to water column Hg rather than to Hg derived from the sediment. The varying extent of Hg resuspension (driven by local environmental conditions), along with the variations in sediment biogeochemical properties (i.e., carbon/sulfide content, redox conditions, IHg/MeHg vertical distribution, sulfate-reducing bacterial activities),[16,79,80] likely explain the large variability in Hg isotopic trajectories observed across coastal habitats globally and should be the focus of future researches.[4,78,81] While the case of Lake Douglas was singular (i.e., similar $\delta^{202}Hg$ but higher $\Delta^{199}Hg$ in the mussels than sediment),[32] the importance of water column Hg processing was highlighted by bivalves' highly positive $\Delta^{199}Hg$. Methylation within the water column, resulting in negative shifts in $\delta^{202}Hg$ in the product MeHg,[36] could have offset the positive $\delta^{202}Hg$ resulting from photodegradation.

In the riverine ecosystem, two clusters of trajectories were observed: one characterized by low net changes and diminishing $\delta^{202}Hg$ between the sediment and Asian clams and the second by an increase in both $\Delta^{199}Hg$ and $\delta^{202}Hg$. This is in direct accordance with the investigations described by Kim et al., including a remote site where bivalves accumulated Hg from the water column (i.e., higher influence of photochemical reactions and greater Hg isotopic values) and Hg-contaminated sites for which they were at equilibrium state isotopically with the sediment (i.e., low net changes).[20] From a biomonitoring perspective, it appears that in lotic environments where resuspension can be active, the Hg concentration of the sediment could dictate the magnitude of sediment association. Overall, these study cases further support inconsistent Hg exposure pathways to bivalves and reinforce the conclusion that bivalve Hg sources are likely to be driven by the strength of environmental processes highly depending on each ecosystem characteristics.[15] In coastal habitats, even if the water column Hg seems to represent the dominant pathway to bivalves, the different trajectories exhibited by each ecosystem suggest Hg accumulation from different sources and distinct local biogeochemical processes. While the compartments tracked by bivalves could be different between lentic

https://doi.org/10.1021/acs.est.4c03788
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lacustrine and lotic river habitats, more evidence needs to be gathered in these ecosystems to confirm such a hypothesis.

Perspectives on Bivalves as a Hg Bioindicator and the Role of Hg Isotopes. Environmental factors resulted in the context-dependent extent of Hg derived from the sediment or the water column by bivalves. At the national scale of South Korea, it leads to the western coast oysters appearing to better reflect sediment Hg than the mussels in the eastern and southern coasts.[82] These results have important consequences when studying Hg pathways to bivalves, the interpretation of Hg concentrations in biomonitoring programs using bivalves, and their potential role in achieving the objectives of the Minamata Convention, including the implementation of Hg isotopes.

Future studies exploring bivalve and sediment bulk Hg concentrations should consider the influence of water column sources, and biota sediment accumulation factors should not be applied for Hg without demonstrating or justifying a sedimentary origin, even for benthic species. This study could not test for potential interindividual factors influencing bivalve Hg bioaccumulation patterns.[13,72,83] Differences among bivalve Hg biodynamics, including active Hg transport and passive metabolic processes, should be better considered in the future.[13,31] For example, bivalve visceral mass (kidney, liver, digestive tract, and gland) can bioaccumulate more Hg than muscle, suggesting potential internal Hg transformation and redistribution processes[55] that can ultimately affect Hg isotopic compositions.[35] Moreover, suspension-feeding bivalves can rely on varying plankton size and handle particles differently due to distinct ctenidial architecture and laterofrontal cilia microstructure or physicochemical affinity with particles, which could contribute to interspecific differences in Hg uptake pathways and isotopic values.[21−23] Ultimately, multicompartment (i.e., sediment, seawater, inorganic particles, organic seston, different bivalve tissues, co-occurring bivalve species) measurements of THg and MeHg concentrations and isotopes coupled to environmental parameters (i.e., physical, chemical, and biological) would enhance the understanding of the complex Hg interactions between bivalves, sediment, and the water column.

Bivalve-based biomonitoring programs have been considerably useful in identifying contaminated sites and characterizing temporal and spatial Hg trends worldwide.[30,45,84] This study further supports the use of bivalves for Hg biomonitoring by illustrating that sediment repertories are not homogeneously reflected in the biota. Nevertheless, bivalves provide multiple-compartment traceability, which can be used to improve the accuracy of Hg data interpretation. The Mussel Watch and other national-scale biomonitoring programs based on bivalves typically cover an extensive range of environmental conditions, are often multispecific,[19,30] and are based on pooled specimens that encompass potential biological variabilities (e.g., growth, dietary conditions, spawning status) even if these are mitigated by sampling bivalves during specific seasons and at particular sizes.[13,72,83] As the systematic incorporation of Hg isotopes appears limited because of the methodology scarcity and associated time and cost, screening sites for Hg isotopes may be implemented to identify Hg biogeochemical processes and exposure pathways to bivalves. Idealistically, Hg isotopes could help develop a conceptual model predictive of Hg sources, offering more realistic and comprehensive applications for all stakeholders.

In the context of the Minamata Convention, biomonitoring programs using bivalves could prove beneficial for tracing patterns relevant to new policies in sites where the variability of Hg sources is assessed beforehand. Due to the observed mismatch between Hg concentrations and sources, revisiting the records of past surveys will require new analyses of Hg isotopes. This will help verify if changes in concentrations are related to shifts in sources, including dilution or bioaccumulation of point-source anthropogenic Hg contamination through δ^{202}Hg values. This study shows that bivalves cannot represent a substitute for the sediment, which remains a key compartment to monitor for the identification of anthropogenic contaminations and hotspots in environmental media.[39] To date, fish have been mainly studied regarding Hg biomonitoring in the context of the Minamata Convention for biota and human exposure.[39] Both fish and bivalves can accumulate Hg originating from the sediment or atmospheric deposition in the water column, and their consumption worldwide represents one of the Hg pathways to humans that should be monitored. While fish present the advantage of consistently accumulating MeHg with a low range of %MeHg, the standardization of the information on Hg sources and pathways required for spatial and temporal comparisons by the Minamata Convention is difficult to achieve given the plasticity of their movement and foraging behavior even when similar species or life stages are considered. Conversely, bivalves are sessile organisms that reflect local Hg concentrations and processes facilitating standardization but their various accumulation of MeHg can question their relevance to assess the transfer of toxic Hg forms through food webs to human populations.[39] Still, this study advocates for the use of bivalves in the context of the Minamata Convention, including the many biomonitoring programs developed worldwide, and future research centered on bivalve MeHg concentrations and isotopic values will clarify their relevance for human exposure.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.4c03788.

Additional experimental details; the selection process of literature-extracted values; supplementary tables summarizing data and statistical analyses; figures illustrating THg, %MeHg, and Hg isotopic compositions, their spatial distributions, and the relationships between sediment and bivalves; and the complete dataset (PDF)

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https://doi.org/10.1021/acs.est.4c03788
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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank the Korea Marine Environment Management Corporation for the collection and provisioning of the sediment, mussel and oyster samples. This work was supported by the Korea Institute of Marine Science & Technology Promotion (KIMST) funded by the Ministry of Oceans and Fisheries (grant number-20220534) and by the National Research Foundation of Korea (NRF) funded by the Korea government (MSIT; grant number-2021R1C1C1008429).

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https://doi.org/10.1021/acs.est.4c03788
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