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RESEARCH ARTICLE

The dynamics of mercury around an artisanal and small-scale gold mining area, Camarines Norte, Philippines

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Abstract

To elucidate the dynamics of mercury emitted and released by artisanal and small-scale gold mining (ASGM) activity and to estimate its impact on the ecosystems of the bay, the distribution of mercury in the atmosphere, soil, water, and sediment around Mambulao Bay, Camarines Norte, Philippines, was investigated. The ASGM operations use mercury to extract gold from ore and are located on the east shore side of the bay. Samplings were conducted in August 2017 and September 2018. The samples were used for determination of total mercury (T-Hg) and organic mercury (org-Hg) concentrations, total organic carbon (TOC) content, and chemical composition. The atmospheric mercury concentration on the east shore side, 6.1–25.8 ng m^{-3}, was significantly higher than the value of 1.4–9.9 ng m^{-3} observed on the west shore side. The average concentrations of T-Hg in the forest soils of the west shore side and those of the east shore side were 0.081 ± 0.028 mg kg^{-1} and 0.496 ± 0.439 mg kg^{-1}, respectively. In the vertical distribution of T-Hg in the soil of the east shore side, a higher concentration was observed near the surface. For the vertical variations in T-Hg in the marine sediment, higher values were observed near the estuary, and the vertical variations in core samples showed an increase in mercury concentration toward the surface. The highest concentration of T-Hg in sediment, 9.5 mg kg^{-1}, which was 2 orders of magnitude higher than the background levels of this area, was found near the river mouth. The T-Hg, org-Hg, and TOC levels showed a positive correlation, suggesting that the rivers are the main sources of T-Hg and org-Hg in the bay. Although the fish sample containing a mercury content higher than the regulatory level for fish and shellfish of 0.4 mg kg^{-1} in Japan was only one of 42 samples, the percentage of org-Hg in fish samples was $91 \pm 18\%$. Mercury released into the surroundings by the ASGM activities can be converted into methylmercury and affect the bay's ecosystem.

Keywords Mercury pollution · Soil · Sediment · Fish · Organic matter · Philippines

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Introduction

The toxicity of mercury is widely known due to the pollution "Minamata disease" that occurred in Japan. The chemical species of mercury that caused Minamata disease is methylmercury produced by a side reaction from inorganic mercury compounds used as a catalyst. Methylmercury contained in factory wastewater was released into Minamata Bay and concentrated through the ecosystem (Kitamura et al. 1960; Minamata City 2000), causing serious health damage to people who consume marine products (Harada 1995; Ninomiya et al. 1995; Akagi et al. 1998; Harada et al. 1998).

Artisanal and small-scale gold mining (ASGM) has increased in many developing countries (Murao et al. 2002a) as well as the Philippines (e.g., Ban Toxics! 2011; Macabuhay et al. 2018) and has become one of the major sources

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of anthropogenic mercury today (UNEP 2013), use metallic mercury to extract gold from ores. Through this activity, mercury vapor is emitted into the atmosphere by heating the gold amalgam (Straaten 2000; Drake et al. 2001; Oliveira et al. 2004; Kono et al. 2012; Kono and Tomiyasu 2013), and the mercury-contaminated slag is released into the water system. The emitted mercury causes an increase in mercury concentration at the surfaces and may be taken up by microorganisms and subjected methylation. In the Philippines, the transformation of Hg to MeHg is observed in stagnant water around ASGM sites (Corpus et al. 2011). The transport of mercury through river systems is also an important issue because transported mercury can affect ecosystems (Mohan et al. 2012) and human health in downstream regions. Many studies have demonstrated that mercury contamination in river systems is caused by ASGM activity as a result of the discharge of mining wastes: Amazon (Moreno-Brush et al. 2016), Mindanao, the Philippines (Appleton et al. 1999), Northern Colombia (Marrugo-Negrete et al. 2008), southeastern Senegal (Niane et al. 2014a), Buru Island, Indonesia (Reichelt-Brushett et al. 2017), Madre de Dios, Peru (Diringer et al. 2015), Colombia (Pinedo-Hernández et al. 2015), West Java, Indonesia (Tomiyasu et al. 2019a, b). ASGM workers and their families are exposed to mercury vapor (Calao-Ramos et al. 2021; Kristensen et al. 2014; Murao et al. 2002b), and residents of nearby and downstream communities may consume fish heavily contaminated by MeHg (Gibb and O'Leary 2014; Murao et al. 2017; Niane et al. 2014a, b). In a mining community in the Philippines, women who burn amalgam in the kitchen showed much higher Hg concentration in hair than men (Murao et al. 2002b). Although the inhalation of volatile mercury can be drastically decreased by stopping the use of mercury in gold mining, the mercury dispersed into the environment will not disappear. Leaf/soil and sediment are important reservoirs of discharged mercury, and contaminated leaf/soil/sediment may become a continuous source of mercury in ecosystems, meaning that the relative importance of exposure via the consumption of contaminated food may increase in the future (e.g., Murao et al. 2014). Takenaka et al. (2021) found that part of the Hg accumulated in leaf is converted to a water-soluble species after forest fire in the Philippines. Since ASGM activities using mercury are in most of the cases illegal and differ by region, detailed investigations for each region are indispensable to understand the entire scope of this activity and to estimate the impact of the discharged mercury on ecosystems.

In this study, the distribution of mercury in the atmosphere, soil, water, and sediment around Mambulao Bay, Camarines Norte, Philippines, was investigated to elucidate the dynamics of mercury emitted and released by ASGM activity and to estimate its impact on ecosystems of the bay. ASGM activity in the region is located in the mountainous settlements on the eastern coast of Mambulao Bay near the border between Camarines Norte and Paracale. Samaniego and Tanchuling (2018) reported that mercury-containing waste from ASGM activity flows into Gumaus Bay through rivers. On the other hand, there are no detailed reports on the influx and distribution of mercury into Mambulao Bay. Mambulao Bay is an inner bay, and if mercury contained in wastewater flows in, it is expected that mercury will stay for a long time, and the impact on the ecosystem may be more serious than that of Gumaus Bay.

Material and methods

Sampling

The study was conducted in an ASGM area of the province of Camarines Norte, Philippines (Fig. 1). ASGM is concentrated in the municipalities of Jose Panganiban, Labo and Paracale owing to the rich gold deposits. At the ASGM sites, mercury is used in the extraction of gold from ore using traditional methods. The amalgam and gold-unbound mercury are separated from the tailings by panning. After removing the excess mercury by squeezing in a piece of cloth, the amalgam is burned in an open pan using a gasoline-air torch, and the mercury is emitted into the atmosphere, causing environmental and health risks. Mercury-contaminated tailings are dumped into rivers. Annual production of gold from ASGM is estimated at 2400 kg in the province. The use of mercury in the amalgamation process in this area has been reported in detail (Samaniego and Tanchuling 2018; Murao et al. 2019). The sampling points of this study are shown in Fig. 1. The sampling was conducted along the seashore of Mambulao Bay: E1–E6 are the east side and W1–W7 are the west side of the bay. A1–A7 are active ASGM sites or a location where workplaces were found. There are likely other ASGM sites scattered around the bay that we have not discovered.

The samplings were conducted in August 2017 and September 2018. At each site, the soil samples were collected every 2 cm from the surface up to a depth of 10 cm. Marine sediment samples were collected with acrylic tubes (inner diameter 3.5 cm; length 50 cm). The length of core samples ranged from 10 to 40 cm, depending on the characteristics of the sediment, mainly grain size. The obtained core samples were cut at every 2 cm and samples were taken from the center of the column to prevent contamination. River sediment was collected with a scoop, reaching out from the riverbank.

The soil and sediment samples were placed in plastic bags with seals and were imported to Japan with the permission from the Ministry of Agriculture, Forestry and Fisheries, Japan in accordance with plant protection law. The samples brought

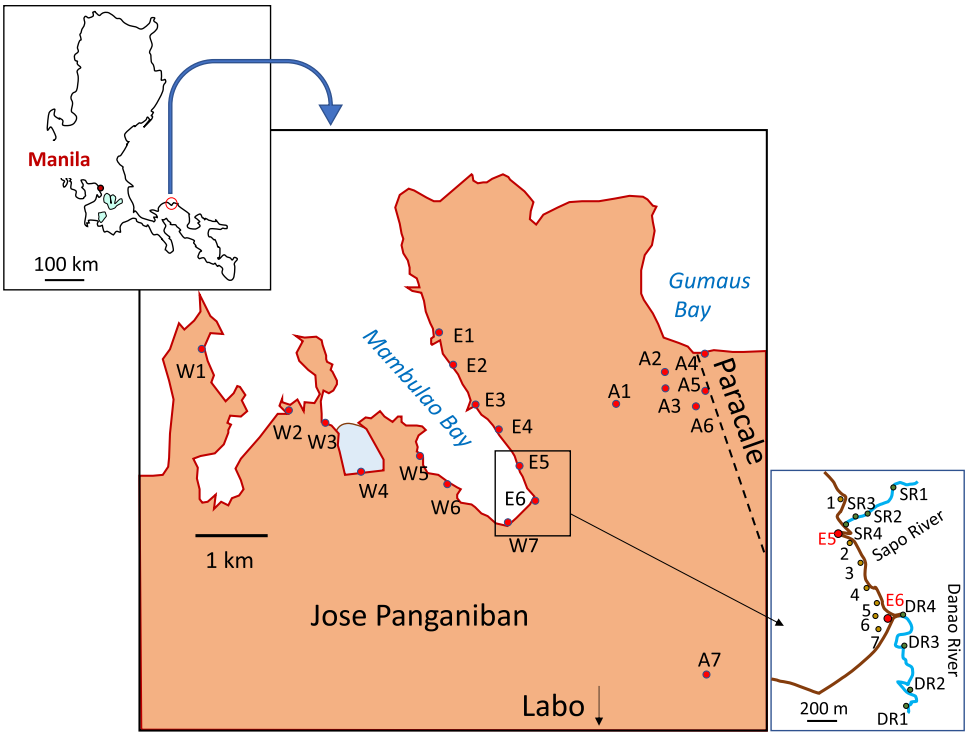

Fig. 1 Map showing the study area

back to Japan were freeze-dried, ground in an agate mortar, and used for the determination of T-Hg and org-Hg concentrations, total organic carbon (TOC) content, and soil/sediment chemical compositions as soon as possible.

The temperature, pH, and electric conductivity of the water samples were measured at sampling points using electrodes (portable pH meter D-74, HORIBA Scientific Co., Ltd., Japan; measurement range for pH 0.00–14.00 and electric conductivity 0.0–199.9 S/m). Water samples were filled into a 250-mL Teflon bottles such that no air remained, which were sealed tightly with a screw cap and then brought back to the laboratory. For filtered total mercury (FT-Hg) analysis, the water samples collected were filtered through a membrane filter (with a pore size of 0.45 µm). The suspended particles on the filter were used for particulate mercury (p-Hg) analysis.

Atmospheric mercury was collected by the gold amalgamation method using a mercury collector tube (NIC, Tokyo, Japan). At each sampling location, the collector tube was connected to an air pump (Sibata Scientific Technology, Saitama, Japan), and ambient air was sucked into the collector tube for 30–80 min at a flow rate of 0.5 L min^{-1}.

Mercury measurements

The procedure for determining the total mercury concentration in solid samples

The T-Hg concentrations were determined using the method described by Akagi and Nishimura (1991) with modifications by Akagi et al. (1995). The precision and accuracy of the method has been repeatedly verified by interlaboratory calibration exercises (Matsuo et al. 1989; Malm et al. 1995), including the analysis of reference standards (e.g., IAEA 085 and 086). In the present study, the accuracy of the T-Hg measurement was also verified on the certified reference material CRM 7302-a (marine sediment) prepared by the National Institute of Advanced Industrial Science and Technology (AIST), Japan. The values determined by this method of 0.51 ± 0.02 mg kg^{-1} ($n = 8$) agreed well with the reference value of 0.52 ± 0.03 mg kg^{-1}.

The procedure for the T-Hg measurement in solid samples was as follows. A known amount of sample (0.1–0.5 g) was placed in a 50-mL volumetric flask. After adding 1 mL of pure water, 2 mL of a 1:1 nitric acid–perchloric acid solution, and 5 mL of concentrated sulfuric acid, the flask was left to stand for a few minutes and then heated on a hot plate at 230 °C for 20 min. After cooling, the volume of the digested sample was adjusted to 50 mL with water, and a suitable aliquot of the resulting solution (< 10 mL) was analyzed for its mercury content by cold vapor atomic absorption spectrometry (CVAAS) using a semiautomated mercury analyzer (Model Hg-201, Sanso Seisakusho Co., Ltd., Japan). Separately, 1.0 mL of water and the standard mercury solution were transferred into three sample digestion flasks and treated by the above-mentioned procedure to obtain blank and standard test solutions for measuring the total mercury concentration.

The absolute limit of detection, calculated as triple the standard deviation of the blank reading ($n = 10$), was 0.02 ng; on 0.2 g of sample, the detection limit was 0.1 μg kg^{-1}. The repeatability was confirmed with duplicate measurements of the soil/sediment samples, and the variation ranged from 0.3 to 11.5% (mean, 3.9%).

The procedure for determining organic mercury concentration in solid samples

The org-Hg concentrations were determined by the method of Tomiyasu et al. (1996) with some modifications (Tomiyasu et al. 2020a, b). This method does not require special equipment; mercury species were separated by solvent extraction and measured by CVAAS. In natural soil, not only methylmercury but also ethylmercury can be present (Tomiyasu et al. 2017a, b). Thus, by this method, the total amount of organic mercury species can be determined, of which more than 90% can be accounted for by methylmercury. The procedure for org-Hg measurement was as follows. A known amount of sample (1–5 g) was placed in a centrifugation tube for org-Hg determination. After adding 0.4 g of CuCl and 10 mL of 3 M HCl (3% NaCl) solution, the tube was shaken for 20 min and then centrifuged for 10 min at 2000 rpm. The resulting supernatant was poured into another 50-mL centrifugation tube. The extraction was repeated in another 10 mL of 3 M HCl (3% NaCl) solution, and the second supernatant was combined with the first. To the combined HCl solutions in the centrifugation tube, 10 mL of toluene was added, and the tube was shaken for 10 min. After centrifugation for 2 min at 2000 rpm, the HCl solution was discarded and the remaining toluene was cleaned by adding 5 mL of 3 M HCl (3% NaCl) solution to the tube and shaking for 5 min. The mixture was centrifuged for 2 min at 2000 rpm, and 7 mL of toluene was collected into a 10-mL tube with a cap. After adding 2 mL of 0.1% cysteine solution, the tube was shaken for 2 min and centrifuged for 2 min at 1200 rpm. The toluene layer was discarded, 1.5 mL of the cysteine layer was digested with HNO_3-$HClO_4$-H_2SO_4, and the organic mercury was measured by the same procedure as that employed for the T-Hg determination. To prepare the calibration curves, aliquots of MeHg standard solutions were prepared in 50-mL centrifugation tubes as described for the soil samples. The repeatability was checked by duplicating measurements of the real soil samples. The duplicate measurements deviated by 1.11 ± 0.69 μg kg^{-1} ($n = 9$). The accuracy of the org-Hg measurement was verified on the certified reference material ERM-CC580 (an estuarine sediment) prepared by Joint Research Centre (JRC), Belgium. The results of the current methods (0.077 ± 0.004 mg kg^{-1}; $n = 7$) were consistent with the reference value for MeHg (0.075 ± 0.004 mg kg^{-1}).

The analytical method for the determination of org-Hg in fish samples comprised alkaline leaching, HCl acidification, and the extraction of org-Hg into toluene. Organic Hg in the toluene layer was extracted into a cysteine solution, followed by CVAAS measurement after wet digestion. The accuracy of the org-Hg measurement was verified using certified reference material CRM 7402-a (cod fish tissue) prepared by National Metrology Institute of Japan (NMIJ). The value determined by the current method of 0.059 ± 0.002 mg kg^{-1} ($n = 7$) was in good agreement with the reference value of 0.058 ± 0.002 mg kg^{-1} for MeHg. The absolute limit of detection, calculated as triple the standard deviation of the blank reading ($n = 10$), was 0.16 ng; on 5.0 g of sample, the detection limit was 0.032 μg kg^{-1}.

Because MeHg is predominant (> 90%) among org-Hg species in the natural environment, we can discuss the behavior of MeHg based on the org-Hg concentration obtained by this method. Indeed, the org-Hg concentration obtained by the method agreed well with the reference value for MeHg. Thus, "org-Hg" was used for the measurement value, and "MeHg" was used for the discussion of the environmental behavior of mercury in this study. A schematic diagram of the procedures for T-Hg and org-Hg measurements is shown in Fig. S1.

Procedures for determining the FT-Hg concentration in the water samples

The method for the determination of FT-Hg was based on acidification and oxidation with BrCl in combination with UV radiation (Logar et al. 2001) as follows. The BrCl solution was prepared by dissolving 1.1 g of analytical reagent grade $KBrO_3$ and 1.5 g of analytical reagent grade KBr in 20 mL of pure water. Concentrated HCl (80 mL) was then slowly added to the solution with constant stirring (Bloom and Crecelius 1983). For FT-Hg measurements, the filtered water samples were poured into Teflon bottles, and 0.5 mL of BrCl solution was added. After exposure to UV radiation overnight, 0.5 mL of 12% $NH_2OH{\cdot}HCl$ was added to decompose any excess BrCl. BrCl oxidation in combination with UV radiation decomposes mercury compounds contained in the water sample to Hg^{2+}. The water sample was poured into a glass reaction vessel and 1 mL of 10% $SnCl_2$ in 2 M HCl solution was added to reduce Hg^{2+} to Hg^0. The solution was bubbled with argon, and Hg^0 swept from the water samples was accumulated as amalgam on a porous gold collector. After that, the collector was heated, and regenerated mercury vapor was measured by cold vapor atomic fluorescence spectrometry (CVAFS; model RA3000F Gold +, Nippon Instruments Corporation, Tokyo, Japan). The

duplicate measurements' average relative percent difference was 6.4%, and the detection limit was 0.028 ng L^{-1}.

Procedures for determining the Hg concentration in the atmosphere

The Hg collected in the tube was measured using double amalgamation CVAAS with a WA-4 mercury analysis system (NIC, Tokyo, Japan). This system comprises an electric furnace, a Hg trapping chamber, an air pump for delivering the carrier gas, a multi-pass auto valve, and an atomic absorption spectrometer. The samples contained in porous gold-filled tubes were heated in the furnace at approximately 500 °C. The carrier gas transported the generated Hg vapor to the Hg trapping chamber, where it was trapped on a porous gold collector. The porous gold collector was then heated at approximately 500 °C. The liberated Hg vapor was introduced into a quartz cell, and its atomic absorption at 253.7 nm was measured. These operations were performed automatically. The detection limit (3σ) of this system (0.02 ng Hg) was obtained from replicate determinations of blanks ($n=9$). Each collector tube was calibrated individually before and after the sampling campaign by measuring a known amount of Hg vapor. The reproducibility of replicated measurements of 2 ng Hg ($n=5$) was 2.2%.

TOC in the soil samples and chemical composition analysis

The TOC content was determined as the difference between the total carbon (TC) and inorganic carbon (IC) content using a total carbon analyzer (TOC-V SCN, Shimadzu Co., Ltd., Japan) attached to a solid-sample module (SSM-5000A, Shimadzu Co., Ltd., Japan). The TC content was determined by combusting a portion of the dried sample (50 mg) at 980 °C. The IC content was determined by adding aqueous H_3PO_4 (1:1 v/v H_3PO_4:H_2O) to a 50-mg-dried soil sample, followed by heating at 240 °C. The chemical compositions of the soil samples were analyzed by the wavelength dispersive X-ray diffraction fluorescence technique (ZSX-mini II, Rigaku Co., Ltd., Japan).

Statistical analysis

The statistical analysis functions of Microsoft Excel for Mac (Microsoft Corporation, USA) was used for data analysis and to generate graphs. One-way ANOVA was used to evaluate whether there were significant differences among the average mercury concentrations from different sampling locations. Student's *t*-test was used to evaluate the results from the two locations. Regression analysis was used to establish the relationships among the variables. Correlation or multiple linear regression analysis was used to establish relationships between two variables. For all purposes, the significance was set at $p<0.05$.

Results and discussion

The variation in the atmospheric concentration of mercury

In 2017, along with collecting soil, seawater, and bottom sediments around the bay, mercury in the atmosphere was collected and measured. The geographical changes in mercury concentration in the atmosphere are shown in Fig. 2(a). The mercury concentration in the atmosphere at the sampling locations on the east shore was 6.1–25.8 ng m^{-3}, which was significantly higher than the value of 1.4–9.9 ng m^{-3} observed at the west shore (unpaired *t*-test, $p<0.05$). The average value of 3.1 ± 1.7 ng m^{-3} on the west shore excluding W2 can be considered as the background level of atmospheric mercury concentration in this area. The atmospheric mercury concentration observed at the active ASGM site

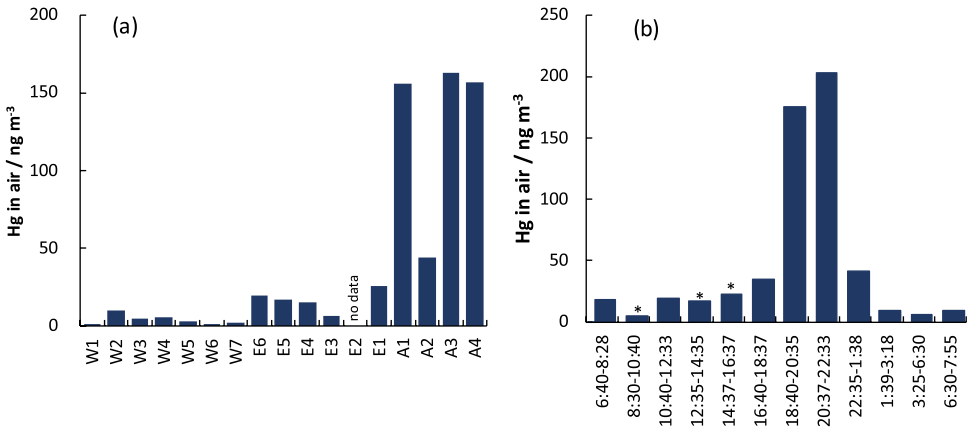

Fig. 2 The variation in atmospheric mercury along the seashore of Mambulao Bay (**a**) and time variation in atmospheric mercury in the town (**b**). A single asterisk (*) indicates the collection time is a little short due to pump trouble

was 15.4–162.6 ng m^{-3}. The mercury emitted by ASGM activities is dispersed, resulting in an increase in the mercury concentration in the atmosphere of the surrounding area.

On the other hand, it was expected that the value would fluctuate depending on the direction of the wind and the time of day depending on the work process of ASGM. Therefore, the time variation of atmospheric mercury concentration was measured every 2 h for 24 h (Fig. 2 (b)); atmospheric mercury was collected every 2 h at the balcony on the second floor of our dormitory located approximately 100 m east of E5. The mercury concentration began to rise from 16:40 to 18:37, reached a maximum from 20:37 to 22:33, and then decreased. The highest mercury value of 203 ng m^{-3} had the same order of magnitude as the value observed at the ASGM site, which suggested that amalgam burning was conducted around the dormitory area; the burning process may be performed at night while avoiding the public eye.

The distribution of T-Hg and org-Hg in soil

The analytical results of the total and organic mercury concentrations in the soil samples are shown in Table 1. The depth variations in T-Hg in soil are shown in Fig. S2. Lower values with no significant vertical variations were observed at W3 and W5. The average ± standard deviation of T-Hg concentrations of these locations, 0.047 ± 0.009 mg kg^{-1}, can be considered as the background concentration of this area. From the value, it can be said that locations showing T-Hg concentrations higher than 0.074 mg kg^{-1} (ave. + 3σ) were affected by mercury discharged from anthropogenic sources. The coastal mercury concentration distribution is shown in Fig. 3. The higher T-Hg concentrations were observed

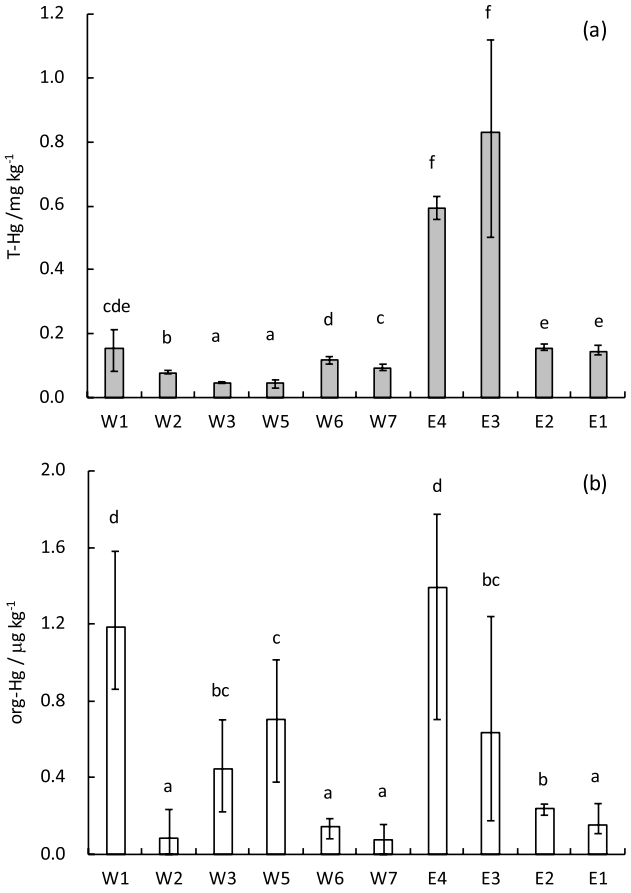

Fig. 3 The average concentrations of (**a**) T-Hg and (**b**) organic mercury in soil core samples of each location. The error bar shows the min and max values of each location. Different letters above bars indicate significant differences among measured parameters at various sites

Table 1 Total and organic mercury concentration in soil samples

Sample		T-Hg	org-Hg	org-Hg/T-Hg	TOC	IC
location	depth/cm	/ mg kg^{-1}	/ μg kg^{-1}	, %	, %	, %
W1	0-2	0.082	1.02	1.24	7.69	7.83
	2-4	0.130	1.22	0.94	6.83	8.12
	4-6	0.201	1.58	0.79	5.33	8.93
	6-8	0.212	1.23	0.58	3.74	10.06
	8-10	0.155	0.86	0.55	3.35	9.96
W2	0-2	0.085	0.23	0.28	5.60	0
	2-4	0.079	0.00	0.00	5.22	0
	4-6	0.077	0.00	0.00	4.63	0
	6-8	0.076	0.18	0.24	4.38	0
	8-10	0.074	0.00	0.00	4.39	0
W3	0-2	0.050	0.22	0.45	2.79	0
	2-4	0.044	0.30	0.68	2.50	0
	4-6	0.046	0.50	1.08	2.11	0
	6-8	0.047	0.70	1.49	1.95	0
	8-10	0.049	0.49	0.99	1.71	0
W5	0-2	0.048	1.01	2.12	1.89	0
	2-4	0.055	0.69	1.25	1.88	0
	4-6	0.053	0.72	1.35	1.46	0
	6-8	0.042	0.71	1.68	1.31	0
	8-10	0.030	0.38	1.27	0.88	0
W6	0-2	0.117	0.08	0.07	2.69	0
	2-4	0.128	0.12	0.09	2.59	0
	4-6	0.128	0.17	0.13	2.52	0
	6-8	0.119	0.19	0.16	2.50	0
	8-10	0.105	0.16	0.16	2.11	0
W7	0-2	0.101	0.00	0.00	1.63	0
	2-4	0.105	0.16	0.15	1.34	0
	4-6	0.087	0.08	0.09	1.42	0
	6-8	0.085	0.00	0.00	1.34	0
	8-10	0.085	0.13	0.15	1.18	0
	average	0.090	0.44	0.60	2.97	-
	stdev	0.045	0.44	0.60	1.78	-

Sample		T-Hg	org-Hg	org-Hg/T-Hg	TOC	IC
location	depth/cm	/ mg kg^{-1}	/ μg kg^{-1}	, %	, %	, %
E1	0-2	0.164	0.26	0.16	2.29	0
	2-4	0.146	0.14	0.10	2.10	0
	4-6	0.143	0.13	0.09	2.11	0
	6-8	0.136	0.12	0.09	1.92	0
	8-10	0.134	0.11	0.08	1.85	0
E2	0-2	0.152	0.23	0.15	6.54	0
	2-4	0.168	0.26	0.15	4.39	0
	4-6	0.155	0.20	0.13	3.50	0
	6-8	0.156	0.23	0.15	3.41	0
	8-10	0.148	0.26	0.18	2.89	0
E3	0-2	1.077	1.24	0.12	12.2	0
	2-4	1.119	1.11	0.10	7.60	0
	4-6	0.857	0.37	0.04	3.97	0
	6-8	0.501	0.30	0.06	2.70	0
	8-10	0.590	0.18	0.03	2.35	0
E4	0-2	0.590	1.77	0.30	8.54	0
	2-4	0.629	1.71	0.27	5.60	0
	4-6	0.558	1.74	0.31	4.27	0
	6-8	0.607	1.04	0.17	3.73	0
	8-10	0.577	0.70	0.12	3.15	0
	average	0.430	0.61	0.14	4.25	-
	stdev	0.327	0.60	0.08	2.66	-

Sample		T-Hg	org-Hg	org-Hg/T-Hg	TOC	IC
location	depth/cm	/ mg kg^{-1}	/ μg kg^{-1}	, %	, %	, %
A4	0-2	0.278	0.28	0.10	4.70	0
	2-4	0.275	0.14	0.05	4.61	0
	4-6	0.258	0.00	0.00	4.26	0
	6-8	0.234	0.32	0.14	3.97	0
	8-10	0.179	0.15	0.09	3.92	0
A5	0-2	0.038	0.23	0.60	0.63	0
	2-4	0.038	0.34	0.90	0.30	0
	4-6	0.033	0.40	1.21	0.26	0
	6-8	0.036	0.00	0.00	0.12	0
	8-10	0.026	0.00	0.00	0.08	0
A7	0-2	0.378	0.38	0.10	1.60	0
	2-4	0.272	0.25	0.09	0.78	0
	4-6	0.138	0.17	0.13	0.53	0
	6-8	0.085	0.16	0.19	0.32	0
	8-10	0.056	0.11	0.20	0.24	0
	average	0.15	0.20	0.25	1.75	-
	stdev	0.12	0.13	0.36	1.90	-

at locations E3 and E4, suggesting that these locations were strongly affected by dispersed mercury through the air from ASGM activity. At E4, where the highest surface mercury concentration was observed, the mercury concentration increased toward the surface and reached the maximum (Fig. S2). At an ASGM site in West Java, Indonesia, the maximum concentration in soil samples was observed at the surface, and the observed value, 9.35, 1.77, and 1.48 mg kg^{-1} were decreased with the distance from the village where mercury was used for extraction of gold toward hill (Tomiyasu et al. 2013). The highest concentration at each location decreased with depth, and similar vertical variations were observed. These facts suggested that emitted mercury from the workplace dispersed and caused an increase in mercury concentration at the soil surface. The value of 1.48 mg kg^{-1} observed at about 1 km from the ASGM village was the same order of magnitude as values observed at E3 in the current study, and the vertical variation showed similar trends. The atmospheric deposition of mercury may cause the increase in mercury concentration at E3 and E4. Since the mercury concentration in the atmosphere can be changed with wind direction, mining process, etc., it might not be compared easily. The higher mercury concentration in soils observed at E1–E4 (Fig. 3) harmonized with an observation that atmospheric mercury concentration on the east shore was significantly higher than that on the west shore. Even at the deepest layer collected at locations E3 and E4, the T-Hg concentration, 0.590 mg kg^{-1} and 0.577 mg kg^{-1}, respectively, was several times higher than the estimated background level of this area. The deposited mercury may have percolated into deeper layer of the soil via leaching of run-off water. Longer core samples (> 10 cm) will be required for quantitative estimation of the impact of mercury deposited from the atmosphere on the soil surface in this area. The locations showing the lowest organic mercury concentrations were W2, W6, W7, and E1, with an average value of 0.11 ± 0.08 µg kg^{-1} (Fig. 3(b)). The highest organic mercury concentrations were observed in E4 and W1. The second highest group included W3, W5, and E3; E3 showed the highest T-Hg concentration, but W3 and W5 showed the lowest values. As a result, the percentage of org-Hg to T-Hg of the west shore, $0.60 \pm 0.60\%$, was significantly higher than that of the east shore, $0.14 \pm 0.08\%$ (unpaired *t*-test, $p < 0.01$). The presence of methylmercury in the soil of this area may depend on a variety of factors, not just on the total mercury concentration. At the ASGM site, mercury delivered to the soil surface from the atmosphere showed a linear relationship with the soil TOC content (Tomiyasu et al. 2017a, b). TOC also plays an important role in organic mercury formation (Tomiyasu et al. 2020a, b). In the present study, significant linear relationships ($p < 0.01$, $n = 50$) were observed between the TOC vs. T-Hg ($r = 0.59$) and TOC vs. org-Hg ($r = 0.53$) and T-Hg vs. org-Hg ($r = 0.49$) plots. Organic matter in soils may be another important factor for the presence of methylmercury in soil. The correlations among T-Hg, org-Hg, and TOC are shown in Fig.S3.

Mercury concentration in seawater and surface sediment

The mercury concentrations in water and sediment samples collected along the seashore of Mambulao Bay are shown in Table S1. No significant difference was observed between the west and east shores in terms of the mercury concentration.

The distribution of mercury along the seashore is shown in Fig. 4. The highest concentration of filtered total Hg (FT-Hg), 17.6 ng L^{-1}, was observed at E6 and decreased gradually toward E1. The lowest values of 0.86 ± 0.19 ng L^{-1} were observed at W5–W1, excluding W2; since W2 is a small port, the water collected here may have been influenced by some activities of local people other than mining activity. A concentration of 0.86 ± 0.19 ng L^{-1} can be considered the background concentration of dissolved Hg in seawater in this area. The distribution of p-Hg showed a tendency similar to that of FT-Hg, in which higher values were observed at W6–E5 and decreased gradually toward the bay mouth. In the case of FT-Hg, W5 and W4 showed background concentrations, but in p-Hg, W5 and W4 appeared to be affected by mercury from the inner part of the bay. The average value at W1 and W3, 2.4 ng L^{-1}, can be considered the background concentration of p-Hg in the bay. In the distribution of Hg in SPM (mg kg^{-1}), the highest value of 2.94 mg kg^{-1} was observed at W7, which was two orders of magnitude higher than the lowest value observed at W1. In the distribution of mercury in surface sediment, the surface sediment from W4 to E2 showed significantly higher mercury concentrations than those from W1 and E1. These observations suggest that the hotspot of Hg in the bay was the innermost part of the bay and that suspended particles played an important role in mercury transport. The highest concentration of p-Hg (644 ng L^{-1}) observed at W7 was approximately 40 times higher than the highest concentration of FT-Hg. The dispersion and deposition of contaminated particles may have caused the increase in mercury concentration of surface sediment in the wide area of the bay.

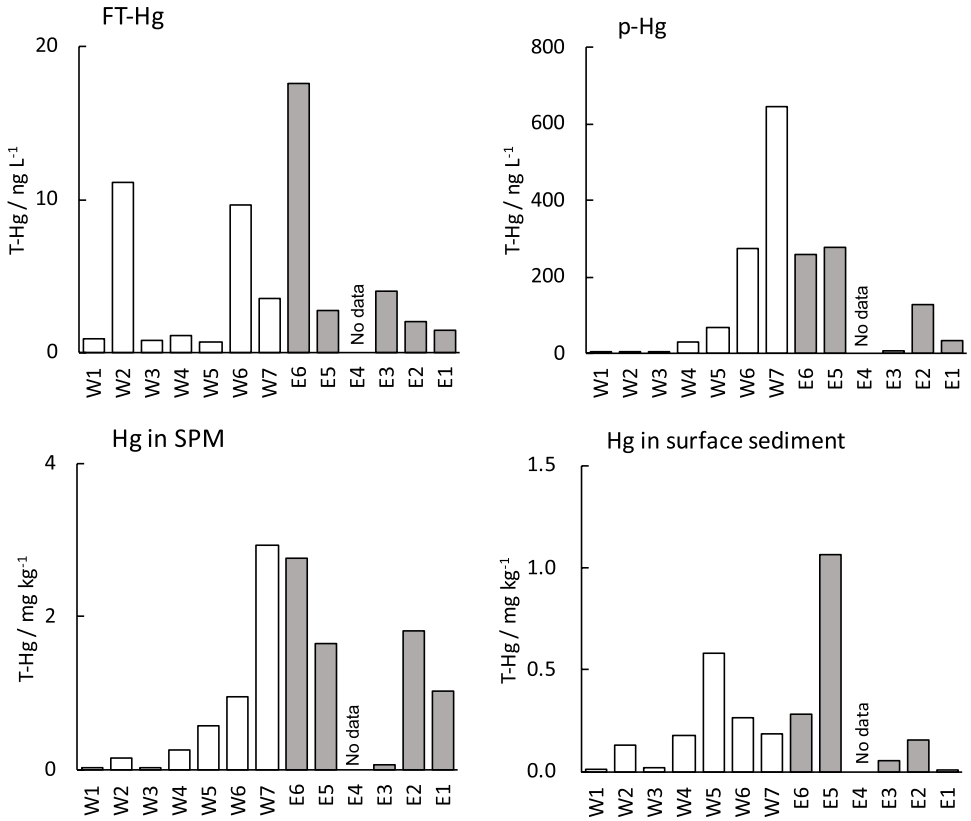

Fig. 4 The distribution of mercury along the seashore

The highest p-Hg was observed for W7, which was about twice that of E6, but the Hg in SPM was nearly equal for W7 and E6. This result means that at W7, twice of suspended solids were in seawater compared with E6. Since no rivers were found around W7, at the current, it is unknown how the suspended solids were supplied to W7 water. More detailed investigations will be required to understand the behavior of suspended solids in the bay.

Mercury concentration in the water and sediment of rivers flowing into Mambulao Bay

The Sapo River and Danao River flow into Mambulao Bay from E5 and E6, respectively. Since high concentrations of dissolved Hg in seawater (FT-Hg) and T-Hg in surface sediment were observed at these locations, the rivers were suspected to be a source of mercury in the bay (Fig. 4). The analytical results of samples from these rivers are shown in Table 2. The FT-Hg, p-Hg, and Hg SPM concentrations in

Table 2 The mercury concentration in water and surface sediment of Mamblao Bay

Location	FT-Hg ng/L	p-Hg ng/L	Hg in SPM mg/kg	Surface sediment T-Hg mg/kg	Location	FT-Hg ng/L	p-Hg ng/L	Hg in SPM mg/kg	Surface sediment T-Hg mg/kg
W1	0.94	1.4	0.03	0.01	E1	1.5	33.2	1.03	0.01
W2	11.13	6.2	0.16	0.14	E2	2.0	127.3	1.82	0.16
W3	0.75	3.5	0.04	0.02	E3	4.0	6.5	0.07	0.06
W4	1.10	29.5	0.26	0.18	E4				
W5	0.66	68.4	0.57	0.58	E5	2.8	276.8	1.65	1.07
W6	9.61	272.1	0.95	0.27	E6	17.6	258.2	2.76	0.28
W7	3.50	644.2	2.94	0.19					
min	0.66	1.4	0.03	0.01	min	1.5	6.5	0.07	0.01
max	11.13	644.2	2.94	0.58	max	17.6	276.8	2.76	1.07
Average	3.96	146.5	0.71	0.20	Average	5.6	140.4	1.46	0.31
St. dev	4.51	239.6	1.04	0.19	St. dev	6.8	124.6	1.00	0.43

the Sapo River were 54.2 ± 41.4 ng L^{-1}, 541 ± 450 ng L^{-1}, and 31.6 ± 32.3 mg kg^{-1}, respectively; their concentrations in the Danao River were 216 ± 51.8 ng L^{-1}, 8064 ± 1849 ng L^{-1}, and 154 ± 59.5 mg kg^{-1}. As shown in Fig. S4, the concentrations of mercury in the Sapo River tended to decrease toward the estuary from the upper reaches. The source of mercury of this river may be locate more upstream of SR1. On the other hand, in the Danao River, the mercury concentration in water maintained a high value from the upper stream to the river mouth. The source of mercury may be scattered along the river.

Although the total concentration of mercury in sediment of Danao River, 141 ± 136 mg kg^{-1}, was significantly higher than that of the Sapo River (5.79 ± 2.82 mg kg^{-1}), there was no significant difference in org-Hg concentrations in sediment between the Danao River (99.8 ± 80.1 μg kg^{-1}) and Sapo River (35.1 ± 35.7 μg kg^{-1}). Since a high total mercury concentration does not necessarily mean a high organic mercury concentration, the total mercury concentration is not the controlling factor for the presence of organic mercury in river sediment. On the other hand, a positive linear relationship was observed between the TOC and org-Hg concentration (Fig. S5; $n = 10$, $r = 0.72$, $p < 0.05$). Organic matter can be one of the key factors regarding the presence of org-Hg in the river sediment.

Since the concentrations of FT-Hg and p-Hg in river water are significantly higher than those in seawater, the main route of mercury discharged by ASGM activity into the bay may be the rivers. Especially for suspended particulate matter (SPM), total mercury levels as high as 213 mg kg^{-1} were observed. SPM is the major transporter of mercury, and its deposition can cause the increased mercury concentrations in the sediment of the bay.

The vertical distribution of total and organic mercury levels in marine sediment

To estimate the impact of mercury flow into the bay from the river, 10–40-cm core samples were collected around the river mouth (Fig. 1, inset), and the vertical variations in T-Hg, org-Hg, and TOC% were investigated. The results are shown in Table S2. Their values showed similar vertical variations and tended to increase toward the surface (Fig. 5). The range of T-Hg was 0.04–9.49 mg kg^{-1}, and the first and second highest concentrations of T-Hg were observed at the river mouths of the Sapo River (E5) and Danao River (E6). This fact clearly indicates that mercury transported by the rivers impacts the sediment. The longest core of 40 cm was obtained at location 7. At the depths deeper than 24 cm of the core sample, the T-Hg concentration decreased and was maintained at low levels. The average concentration of this part was 0.13 ± 0.07 mg kg^{-1}. The T-Hg at the deepest part of other core samples (10 cm of location E5 to 26 cm of location 6; see Table S2) was apparently higher than that value. Sediment in this area has been affected by the mercury discharged by ASGM at least to a depth of 20 cm.

The org-Hg concentration ranged from n.d. to 16.1 μg kg^{-1}, and the highest concentrations were also observed at E5. Since the waste from ASGM should not include org-Hg, the org-Hg found in the sediment was formed during its transport and/or after deposition: A linear relationship was observed between the T-Hg and org-Hg concentrations for each core sample (Fig. S6), which indicates that the origin of Hg contained in org-Hg is ASGM activity. From the average org-Hg percentage of the cores, it was estimated that approximately 0.04% of mercury was present as org-Hg in the sediment of Mambulao Bay (Table S2).

T-Hg and org-Hg in fish samples from Mambulao Bay

The fish samples were purchased from fishermen or fish markets after confirming that they were caught in Mambulao Bay by interview. A total of 40 samples from more than 20 species were obtained and analyzed (Table S3). The ranges of T-Hg and org-Hg concentrations in the wet weight base were 0.005–1.02 mg kg^{-1} (av. ± s.d.; 0.13 ± 0.17 mg kg^{-1}) and 0.005–0.92 mg kg^{-1} (av. ± s.d.; 0.11 ± 0.15 mg kg^{-1}), respectively. The percentage of org-Hg in fish samples was 90.7 ± 18.3%. Among the 40 samples, of the three individuals with the highest mercury concentrations, two were croaker and one was grouper; one sample showed a higher T-Hg concentration than the regulatory level of mercury for fish and shellfish of 0.4 mg kg^{-1} in Japan (Ministry of Health, Labour and Welfare 1973). Since these predator fish species showed high mercury concentrations, mercury methylated in the environment had accumulated and magnified through the food chain.

The environmental impact of mercury discharged by ASGM activity

The impact of mercury emitted into the atmosphere

At the workplace in Labo, Camarines Norte where we were able to witness amalgam burning operations, the measured mercury concentration reached 0.3 mg m^{-3}. The value is one order of magnitude higher than the regulation value of 0.025 mg m^{-3} for workplaces in Japan (Ministry of Health, Labour and Welfare 1988). Since the workplace was not closed space and had no mercury recovery systems, the emitted mercury will spread to the surroundings and will affect not only the workers but also the local people living around the workplace. Although we could not find workplaces in city area of Jose Panganiban, an apparent increase

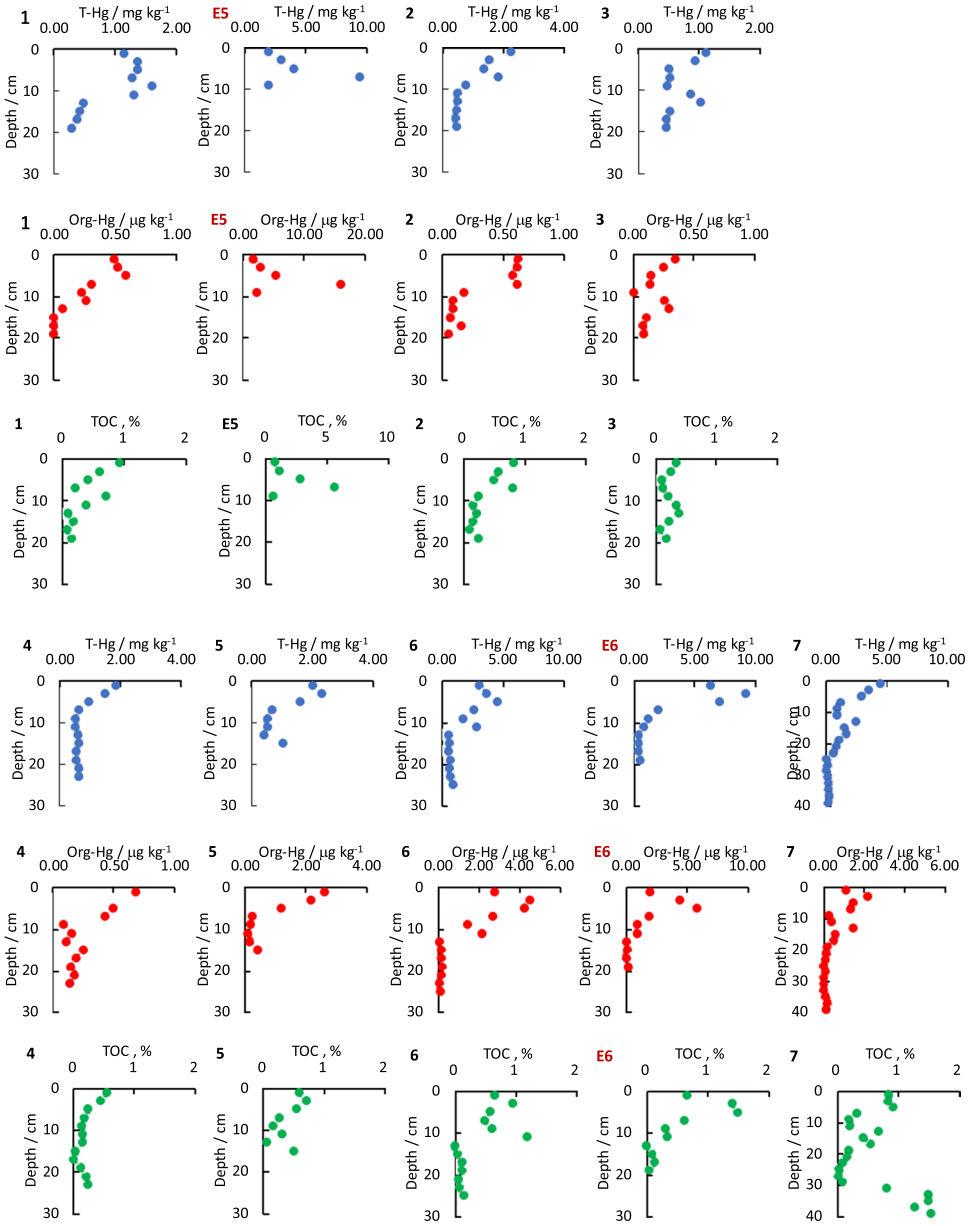

Fig. 5 Vertical variations in T-Hg, org-Hg and TOC in the sediment of Mambulao Bay

in atmospheric mercury concentration was observed at our hotel. The average mercury concentration was 68 ng m^{-3}, which was more than ten times higher than the background concentration estimated in this area. The increase in atmospheric mercury concentration can impact vulnerable groups, such as children, in the future.

In a part of the mercury deposited from the atmosphere can be converted to MeHg by microorganisms under the organic matter-rich conditions (Guimarães et al. 2000, Munthe et al. 2001; Hall and St Louis 2004; Balogh et al. 2003; Ericksen et al. 2003; Qiu et al. 2005; Tomiyasu et al. 2012; Tomiyasu et al. 2017a, b; Tomiyasu et al. 2020a, b). As shown in Fig. S3, org-Hg in soil showed a significant dependency on organic matter content in the present study. The fact suggests that organic matter plays an important role for MeHg formation also in this area. Although the org-Hg makes up only a small portion of the total mercury, the high mercury levels in the atmosphere around the ASGM site can cause a continuous increase in mercury levels on the soil surface. Continuous research is needed to track changes in mercury levels and to estimate their impact on ecosystems.

Impact of mercury discharged into water systems

Extremely high concentrations of mercury in water and sediment were observed in the Danao and Sapo rivers. The dissolved and particulate mercury concentrations in river water ranged from 0.020–0.3 μg L^{-1} and from 0.2–10 μg L^{-1},

respectively. The total concentration of mercury in sediment was in the range of 10–300 mg kg^{-1}. Since these values were several orders of magnitude higher than the background values in sea water and sediment, rivers can be the main sources of mercury into Mambulao bay. In addition to plant debris, domestic wastewater from villages along the river provides organic matter. Organic matter can be an important factor for the methylmercury formation in river sediment, and eutrophication provides a reducing condition in sediment, in which methylmercury is produced by microorganisms. Yu et al. (2012) investigated microbial methylmercury production in freshwater river sediments contaminated with industrial mercury and reported that potential mercury methylation rates changed seasonally in river sediment. The condition of Danao and Sapo River sediment may change drastically not only due to human activity but also in the rainy and the dry seasons. Corpus et al. (2011) indicated a contrasting distribution of mercury between dry and rainy season in a region which includes several ASGM sites. In the next step of the investigation, these seasonal changes should be followed throughout the year to clarify the impact of mercury transported from the rivers into the bay.

The T-Hg, org-Hg, and organic matter concentrations showed similar vertical variations in each core sample (Fig. 5), and linear relationships were observed between them (Fig. S6). A large water flow in the rainy season can transport contaminated river sediment into Mambulao bay. During the deposition of the transported muds, large coarse particles settle first, and then small particles settle, so fine particles containing organic matter settle last. As a result, mercury binding with organic matter showed vertical variations similar to those of organic matter. The org-Hg in marine sediment may have mainly been formed in river sediment and transported. One of the reasons is that the percentage of org-Hg in river sediment, 0.42%, is significantly higher than the value of 0.042% in marine sediment ($p < 0.05$). Wu et al. (2011) reported that concentrations of MeHg in mangrove sediments showed significant negative correlations with total organic matter. Hammerschmidt and Fitzgerald (2004) suggested that a principal control on MeHg production in low-sulfide, coastal marine sediments is partitioning of Hg(II) Ibetween particle and dissolved phases. In their study area, since most of the partitioning in sediments was due to Hg–organic associations, it was pointed out that an increase in Hg (II) utilized by bacteria could enhance methylmercury production. In our study area, a high positive correlation was found between TOC and org-Hg (Fig. S6), suggesting that org-Hg is produced in river sediment rather than in ocean sediment.

At depths deeper than 24 cm in the sediment at location 7 (Fig. 1, inset), the mercury concentration decreased rapidly (Fig. 5), and the relationship between TOC and T-Hg was lost (Fig. S6), which suggests that the layer deeper than 24 cm had not received mercury derived from ASGM activity. On the other hand, when the Fe content was plotted against TOC, a linear relationship ($p < 0.01$) was observed even when these deeper layers were included (Fig. S7). It has been reported that organic carbon and iron show similar distributions in marine sediments, which is attributed to their adsorption on clay mineral surfaces or direct associations between organic carbon and iron, which are formed primarily by coprecipitation and/or direct chelation (Lalonde et al. 2012; Dicen et al. 2019). The correlation between TOC and iron observed in our study may have appeared due to coprecipitation of organic matter with iron hydroxide at the mixing point of river water and seawater.

The metallic mercury used by ASGM activities is discharged into the surrounding environment and methylated. More than 90% of the mercury in fish caught in the bay was organic mercury, indicating that the mercury released by ASGM activities can enter the ecosystem and be concentrated as organic mercury through the food web. If the inflow of mercury continues, the mercury concentration in fish may increase further, and there is concern that people's health will be affected in the future.

Conclusion

In this study, we attempted to evaluate the effects of mercury released by ASGM activity around Mambulao Bay. It was shown that mercury released into river systems by such activities may accumulate in the sediment in the bay and affect the ecosystem. Although the distribution of the mercury concentration in the coastal sediment was clarified, it is possible to elucidate the diffusion of mercury throughout the bay by performing core sampling throughout the bay. In the next step, by conducting a series of surveys of rivers and the seafloor with seasonal fluctuations taken into consideration, it will be possible to more clearly understand the dynamics of mercury and predict the future impact of ASGM activities. Continuous surveying is important.

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Author contribution All authors contributed to the study's conception and design. Material preparation, data collection, and analysis were performed by Sora Yasumatsu, Hitoshi Kodamatani, Ryo Kanzaki, Chisato Takenaka, Satoshi Murao, Shuichi Miyagawa, Kenichi Nonaka, Akiko Ikeguchi, Ian A. Navarrete, and Takashi Tomiyasu. The first draft of the manuscript was written by Takashi Tomiyasu, and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Data availability All data generated or analyzed during this study are included in this published article and its supplementary information files.

Declarations

Competing interests The authors declare no competing interests.

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