nature COMMUNICATIONS

ARTICLE

Received 16 Mar 2014 | Accepted 9 Jul 2014 | Published 19 Aug 2014

DOI: 10.1038/ncomms5633

Fumigant methyl iodide can methylate inorganic mercury species in natural waters

Yongguang Yin[1,2,3], Yanbin Li[4], Chao Tai[2,5], Yong Cai[2,3] & Guibin Jiang[1]

Methyl iodide or iodomethane (CH_3I) has recently been registered as a fumigant in many countries, although its environmental impacts are not well understood. Here we report the results of a study on the methylation of mercury by CH_3I in natural water by incubation experiments using both Hg ($^{199}HgCl_2$ and $CH_3{}^{201}Hg^+$)- and hydrogen (CD_3I)-stable isotope addition techniques. We find that methylation of Hg^0, Hg_2^{2+} and Hg^{2+} by CH_3I can occur in natural water under sunlight, while only Hg^0 and Hg_2^{2+} can be methylated in deionized water. We propose that the methylation of Hg by CH_3I in natural waters is mediated by sunlight and involves two steps, the reduction of Hg^{2+} to Hg^0/Hg_2^{2+} and the subsequent methylation of Hg^0/Hg_2^{2+} by CH_3I. Further quantitative assessment suggests that CH_3I-involved methylation of inorganic Hg could be an important source of CH_3Hg^+ in an environment where CH_3I has been used in large amounts as a fumigant.

[1] State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, No. 18, Shuangqing Road, Haidian, Beijing 100085, China. [2] Department of Chemistry and Biochemistry, Florida International University, University Park, Miami, Florida 33199, USA. [3] Southeast Environmental Research Center, Florida International University, University Park, Miami, Florida 33199, USA. [4] Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education, Ocean University of China, Qingdao 266100, China. [5] Institute of Resources and Environment, Henan Polytechnic University, Jiaozuo 454000, China. Correspondence and requests for materials should be addressed to Y.C. (email: cai@fiu.edu) or to G.J. (email: gbjiang@rcees.ac.cn).

Methyl iodide or iodomethane (CH_3I) is one of the most abundant organoiodine compounds in natural environments[1]. Anthropogenic input of CH_3I to the environment has been rapidly increasing since the 1990s, after it was suggested as a replacement for the ozone-depleting fumigant methyl bromide (CH_3Br). CH_3I is preferred over CH_3Br because it is similar to, or more effective than, CH_3Br in controlling a wide variety of soil pests and weeds[2], and it has less impact on the ozone layer owing to its rapid photodegradation in the troposphere[2]. The U.S. EPA approved the use of CH_3I as a fumigant in 2008 (ref. 3). A commercially available CH_3I formulation was then registered in many countries, such as the USA, Japan, and New Zealand.

The potentially negative impact of using CH_3I has not been adequately addressed[4], despite its increasing use on farmland. Compared with CH_3Br, CH_3I degrades more slowly in soil, hence increasing its chance of being transported to an aquatic environment via runoff[5,6]. CH_3I is known to have the capability of methylating several metals and metalloids, including Sn^{2+}, As^{3+}, Pb^{2+} and Hg^0, following an oxidative addition mechanism[7–10]. Among these metals/metalloids, mercury deserves special attention because its methylation product, methylmercury (CH_3Hg^+), is among the most widespread of all highly toxic contaminants. Previous work has demonstrated that CH_3I can be used as a methylation reagent for synthesizing CH_3Hg^+ from Hg^0 in a laboratory setting[10]. However, such a methylation reaction has not been confirmed in natural waters with low concentrations of Hg^0 and CH_3I (ref. 11). The undetectable CH_3Hg^+ in the previous study could be attributed to the possible degradation of CH_3Hg^+, which was not monitored during the experiment[11]. It is understandable that direct methylation of Hg^{2+} by CH_3I has not been observed[12–14], as this reaction is theoretically impossible according to the mechanism of the oxidative addition reaction. However, recent studies have indicated that a rapid conversion of Hg^{2+} to Hg^0 can occur in natural waters[15,16], suggesting that Hg^{2+} could also play an important role in the CH_3I-involved methylation of inorganic mercury in the environment.

In this study, we show that CH_3I has the potential of methylating inorganic mercury in aquatic environments under sunlight. We used both mercury ($^{199}HgCl_2$ and $CH_3\,^{201}Hg^+$)- and hydrogen (CD_3I)-stable isotopes to examine the possible methylation of inorganic mercury species by CH_3I in natural water. Various concentrations of $^{199}HgCl_2$, $Hg_2(NO_3)_2$, Hg^0 and CH_3I were added to deionized water or natural water and incubated with or without sunlight. $CH_3\,^{201}Hg^+$, spiked in the incubation media, was used as a control to correct for the degradation of produced CH_3Hg^+. CD_3I was used to validate the source of the methyl group in CH_3Hg^+. Our results demonstrate that methylation of inorganic mercury by CH_3I could be an important source of CH_3Hg^+ in CH_3I-contaminated surface water.

Results

Methylation of inorganic mercury by CH_3I in natural water. Natural water samples were collected from a pond located at the Florida International University (FIU). Methylation experiments were carried out in a closed 0.5-l Teflon bottle under natural sunlight or in darkness. The methylation of inorganic mercury species (Hg^{2+}, Hg_2^{2+} and Hg^0) by CH_3I was measured (Fig. 1). Significant production of CH_3Hg^+ was observed in waters exposed to sunlight for all tested mercury species. For samples tested in the dark, no significant formation of CH_3Hg^+ occurred for Hg^{2+} and Hg^0 ($P>0.1$) (Fig. 1a,c), and a 90% reduction in the formation of CH_3Hg^+ was observed for Hg_2^{2+} ($P<0.05$) when compared with that under sunlight (Fig. 1b). Most previous studies also showed that sunlight is necessary for the methylation of Hg^0 by CH_3I[10,11,17], although contrast results were also observed[18]. In sunlight, the methylation rates of these three mercury species (r, equation (9), see Methods) were in the order of Hg^0 (1.67 ± 0.09 pmol l^{-1} E^{-1} m^2) > Hg_2^{2+} (0.424 ± 0.025 pmol l^{-1} E^{-1} m^2) > Hg^{2+} (0.125 ± 0.010 pmol l^{-1} E^{-1} m^2). These results suggest that methylation of mercury by CH_3I can occur in natural water and this process is driven by sunlight. The 1-day methylation yield of Hg^0 by CH_3I was calculated to be 0.6%, comparable with the results of Celo *et al.*[18,19] and Hall *et al.*[11] (1.1 and 0.29%, respectively). Although methylation rates of Hg^0 and Hg_2^{2+} were ~13- and 4-fold higher than that of Hg^{2+}, methylation of Hg^{2+} by CH_3I should be more important as Hg^{2+} is the main inorganic mercury species in natural water. The formation of $CH_3\,^{199}Hg^+$ with the addition of $^{199}Hg^{2+}$ demonstrated that the generated CH_3Hg^+ was from the methylation of spiked $^{199}Hg^{2+}$ (Supplementary Fig. 1a). Further experiments were conducted to examine the origin of the methyl group of CH_3Hg^+ using a CD_3I tracer method. When natural water containing Hg^{2+} was spiked with CD_3I and incubated under sunlight for 4 days, formation of CD_3Hg^+ was detected using gas chromatography–mass chromatography (GC–MS) (Supplementary Fig. 1b) (detailed description is given in Supplementary Note 1). Based on the oxidative addition theory, Hg^{2+} cannot be directly methylated by CH_3I. It is therefore

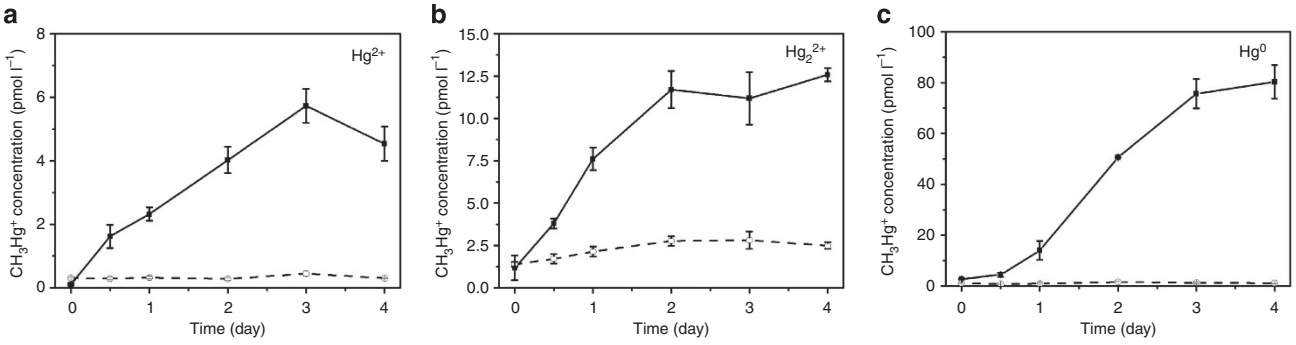

Figure 1 | Methylation of inorganic Hg by CH_3I in pond water. (**a**) Hg^{2+}, (**b**) Hg_2^{2+} and (**c**), Hg^0. Solid line and dashed line represent the methylation of inorganic Hg under sunlight and in the dark, respectively. CH_3I was spiked into the pond water to form a final concentration of 1 mmol l^{-1}. The final concentrations of Hg^{2+}, Hg_2^{2+} and Hg^0 were 4.99, 4.99 and 4.24 nmol l^{-1} (as Hg), respectively. The methylation rates for Hg^{2+}, Hg_2^{2+} and Hg^0 were calculated to be 0.125 ± 0.010, 0.424 ± 0.025 and 1.67 ± 0.09 pmol l^{-1} E^{-1} m^2, respectively. All the tests were conducted in triplicate, and the error bars indicate the s.d. of three repeated measurements.

proposed that the observed methylation of Hg^{2+} in natural water may proceed through a two-step reaction mechanism, the reduction of Hg^{2+} to Hg^0 or Hg_2^{2+} followed by the methylation of Hg^0 or Hg_2^{2+} by CH_3I (Equations (1–5)). Considering the electronegativity of the iodine atom, CH_3I is expected to dissociate to $CH_3.$/I. or CH_3^+/I^-, but not CH_3^-/I^+ (ref. 20). $CH_3.$ and CH_3^+ can then methylate Hg_2^{2+} or Hg^0. According to the density functional theory, the methylation reaction of Hg^0 and CH_3I is thermodynamically favourable[17]. The requirement of sunlight for this reaction indicates the existence of a high activation barrier[17]. This proposed mechanism of Hg^{2+} methylation is supported by the facts that 95.2 pmol l^{-1} Hg^0 was detected in the pond water spiked with 4.99 nmol l^{-1} Hg^{2+} (Supplementary Fig. 2) and that the methylation rate of Hg^{2+} was only 7.5% and 29.5% compared with that of Hg^0 and Hg_2^{2+} (Fig. 1). The formation of Hg_2^{2+} during Hg^{2+} photoreduction in the presence of dissolved organic matter (DOM, Suwannee River humic acid) was also confirmed using Raman spectrometry (Supplementary Fig. 3). These results provide strong evidences to support the proposed two-step reaction mechanism of CH_3I-involved methylation of mercury in natural water.

$$CH_3I \xrightarrow{h\nu} CH_3\cdot + I\cdot \quad (1)$$

$$CH_3I \xrightarrow{h\nu} CH_3^+ + I^- \quad (2)$$

$$Hg^{2+} + \text{natural water} \xrightarrow{h\nu} Hg^0 \text{ or } \frac{1}{2}Hg_2^{2+} \quad (3)$$

$$CH_3\cdot + \frac{1}{2}Hg_2^{2+} \rightarrow CH_3Hg^+ \quad (4)$$

$$CH_3^+ + Hg^0 \rightarrow CH_3Hg^+ \quad (5)$$

$$2I\cdot \rightarrow I_2 \quad (6)$$

$$4H^+ + 4I^- + O_2 \rightarrow 2I_2 + 2H_2O \quad (7)$$

To evaluate the importance of CH_3Hg^+ formed through CH_3I-involved process in aquatic environments, additional experiments were performed in natural waters from the Florida Everglades. In these experiments, the methylation of Hg^{2+} by CH_3I was also observed (Supplementary Fig. 4), indicating that this process may widely occur in aquatic environments. Methylation rates (r) were calculated to be 0.025 ± 0.001 pmol l^{-1} E^{-1} m^2 and 0.125 ± 0.010 pmol l^{-1} E^{-1} m^2 for surface water of the Florida Everglades and FIU pond water, respectively.

Methylation of inorganic mercury by CH_3I in deionized water. Experiments were conducted in deionized water, where factors (for example, DOM, Fe^{2+}) possibly facilitating the reduction of Hg^{2+} are absent, to validate the aforementioned mechanism of photoinduced methylation of Hg^{2+} by CH_3I. The presence of CH_3Hg^+ under sunlight was observed after 1 day of incubation when Hg_2^{2+} or Hg^0 was used as a precursor, while the methylation of Hg^{2+} was not detected (Supplementary Fig. 5). The formation of CH_3Hg^+ was not observed for all three inorganic mercury precursors in the dark. These results demonstrate that Hg^{2+} cannot be directly methylated by CH_3I.

In deionized water, the experimentally generated CH_3Hg^+ became undetectable after 3 days (Supplementary Fig. 5). This loss of CH_3Hg^+ is not probably the results of photodegradation as previous studies showed that CH_3Hg^+ present in deionized water cannot be photodemethylated[21,22]. During the course of the experiments, rapid degradation of CH_3Hg^+ was always accompanied with a change in solution colour from clear to brown. The brown substance was identified to be I_2 based on the results of the following two experiments. A purple colour appeared in the organic phase when an extraction was performed with CH_2Cl_2 (ref. 23), indicating this substance could be I_2 (Supplementary Fig. 6). The brown solution turned blue when starch was added, indicating the formation of I_3^- amylose complex. Furthermore, ultraviolet-visible spectra analysis showed that the brown substance in water and the purple substance in CH_2Cl_2 gave a maximum absorbance similar to that of I_3^- in water and I_2 in CH_2Cl_2, confirming the formation of I_2 (Supplementary Fig. 6). I_2 may be produced from the combination of $I\cdot$ or through the oxidation of I^- by dissolved oxygen (equations 6 and 7)[5]. Thus, it was assumed that I_2, originating from CH_3I, caused the degradation of CH_3Hg^+ in deionized water. To test this hypothesis, I_2 or I^- solution was added to deionized water containing $CH_3{}^{201}Hg^+$. For trials with I_2, immediate analysis of the solution indicated that $CH_3{}^{201}Hg^+$ disappeared completely (Supplementary Fig. 7a). An increase in the amount of $^{201}Hg^0$ and $^{201}Hg^{2+}$ was also observed, confirming the degradation of $CH_3{}^{201}Hg^+$. However, the concentration of $CH_3{}^{201}Hg^+$ showed no significant change in the presence of I^- (Supplementary Fig. 7b), indicating that I^- could not degrade $CH_3{}^{201}Hg^+$.

In contrast to deionized water, the degradation of $CH_3{}^{201}Hg^+$ in natural water showed no significant difference ($P > 0.1$) in the presence or absence of CH_3I (Fig. 2). In addition, the water colour did not change to brown during the 5 days of incubation (Supplementary Fig. 6). It is proposed that any I_2 formed would be quickly reduced to I^- in the presence of humic substances[24], thus inhibiting the degradation of CH_3Hg^+ by I_2. This assumption was partially supported by the fact that the rapid degradation of $CH_3{}^{201}Hg^+$ in the presence of CH_3I was not observed when Suwannee River humic acid was added to deionized water (Supplementary Fig. 8). The degradation of $CH_3{}^{201}Hg^+$ in Suwannee River humic acid solution correlated with cumulative photosynthetic active radiation (PAR) photon flux (Supplementary Fig. 8), indicating that sunlight was the

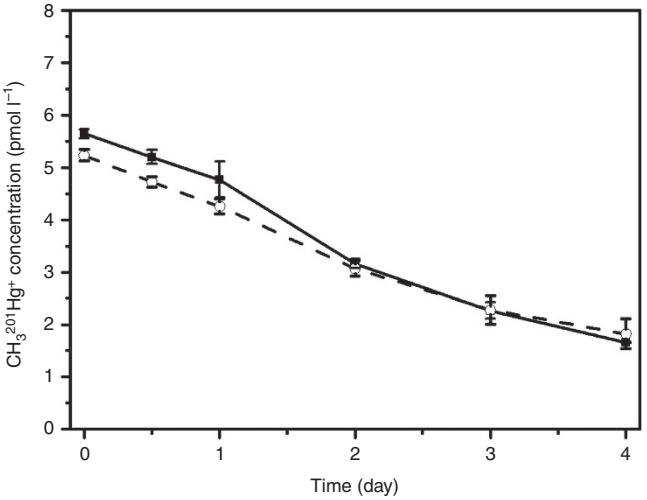

Figure 2 | Degradation of $CH_3{}^{201}Hg^+$ in pond water. Solid line and dashed line represent the degradation of CH_3Hg^+ in the presence (1 mmol l^{-1}) or absence of CH_3I, respectively. The degradation rate of $CH_3{}^{201}Hg^+$ was calculated to be 0.015 ± 0.001 m^2 E^{-1} in the presence of CH_3I and 0.013 ± 0.002 m^2 E^{-1} without CH_3I. The degradation of CH_3Hg^+ showed no significant difference in the presence or absence of CH_3I ($P > 0.1$). All the tests were conducted in triplicate, and the error bars indicate the s.d. of three repeated measurements.

driver for the degradation of $CH_3{}^{201}Hg^+$. The rapid degradation of CH_3Hg^+ by I_2 would explain why the methylation of Hg^0 by CH_3I was not detected under sunlight in deionized water in a previous study[11].

Pathway of methylation of inorganic mercury by CH_3I. Based on the results obtained in deionized and natural waters, a pathway of photoinduced methylation of inorganic mercury by CH_3I in natural water was proposed (Fig. 3). Under the influence of solar irradiation, Hg^{2+} can be reduced to Hg^0 or Hg_2^{2+} (probably facilitated by DOM) in natural waters[25], while CH_3I can be decomposed to $CH_3\cdot/I\cdot$ or CH_3^+/I^-. $CH_3\cdot$ radicals and CH_3^+ ions can then methylate Hg_2^{2+} or Hg^0 through oxidative addition reactions. DOM may play an important role in this process. On one hand, DOM can be an effective scavenger of I_2, therefore inhibiting the degradation of CH_3Hg^+ induced by I_2. On the other hand, DOM may facilitate the reduction of Hg^{2+} to Hg^0 or Hg_2^{2+} under sunlight[25], subsequently enhancing the oxidative methyl transfer.

Assessment of CH_3I-involved CH_3Hg^+ formation in environments. After being applied in farmland, CH_3I could be transported into surrounding ponds or lakes via runoff water. The levels of CH_3I in runoff water were estimated by laboratory column-leaching experiments (Supplementary Fig. 9). CH_3I applied to soils can be quickly leached out with concentration reaching 0.20–2.22 mmol l^{-1} depending on the soil type used (Supplementary Fig. 9), which is two to five order of magnitude higher than its concentration in coastal waters[26]. The reaction of Hg^{2+} and CH_3I in pond water can be described as a pseudo-second-order reaction (Fig. 4). The photomethylation rate constant of Hg^{2+} by CH_3I (k_M, see equation (13)) was then calculated to be $(1.51\pm0.19)\times10^{-2}$ l mol^{-1} E^{-1} m^2 in pond water. By using the obtained methylation rate constant and assuming that the increased CH_3I concentration in aquatic water was in the range of 0–7 mmol l^{-1} (comparable to its concentration in leachates obtained in column experiments), the differences in CH_3Hg^+ concentration at steady state in natural water with or without the presence of CH_3I were estimated (equation (17)). Figure 5 showed that the increased steady-state concentration of CH_3Hg^+ is highly dependent on the concentration of CH_3I and Hg^{2+}. If we assume that the concentration of CH_3I entering natural water is 1 mmol l^{-1} (comparable with that obtained in leachates) and Hg^{2+} concentration is 6.1–3265.4 pmol l^{-1} (literature reported

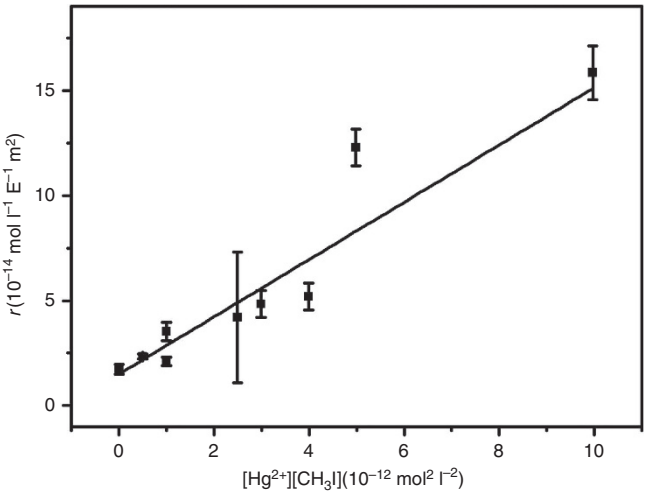

Figure 4 | Relationship between the formation rate of CH_3Hg^+ and the product of Hg^{2+} and CH_3I concentrations in a pond water. To calculate the relationship between the formation rate of CH_3Hg^+ (r) and concentrations of Hg^{2+} and CH_3I, various concentration of CH_3I (0, 0.1, 0.2, 0.5, 1.0 and 2.0 mmol l^{-1}) and $^{199}HgCl_2$ (0, 1.0, 2.0, 3.0, 4.0 and 5.0 nmol l^{-1}) were prepared using pond water containing 1 ng l^{-1} (5.0 pmol l^{-1}) $CH_3{}^{201}Hg^+$. The formation rate was observed to be positively related to the product of Hg^{2+} and CH_3I concentrations. Photomethylation rate constant of Hg^{2+} by CH_3I (k_M, see equation (13) in main text) was calculated to be $(1.51\pm0.19)\times10^{-2}$ l mol^{-1} E^{-1} m^2. All the tests were conducted in triplicate, and the error bars indicate the s.d. of three repeated measurements.

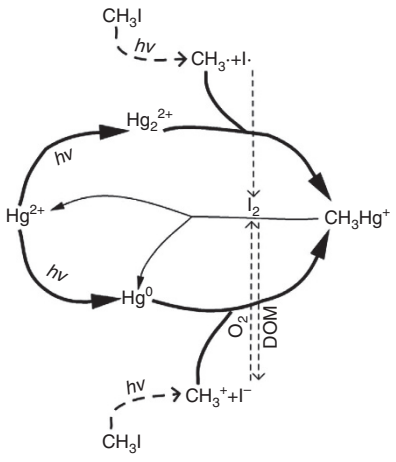

Figure 3 | Proposed pathway of photoinduced methylation of inorganic Hg by CH_3I in natural water. The methylation of Hg by CH_3I is proposed to include two steps, the reduction of Hg^{2+} to Hg_2^{2+} or Hg^0 and the subsequent methylation of Hg_2^{2+} or Hg^0 by $CH_3\cdot$ or CH_3^+ (solid line), which are photo-decomposition products of CH_3I (dashed line). I_2, which is produced from the combination of $I\cdot$ or oxidation of I^- by dissolved oxygen, can rapidly degrade the generated CH_3Hg^+. However, this process is negligible in natural waters as I_2 can be quickly reduced to I^- by DOM.

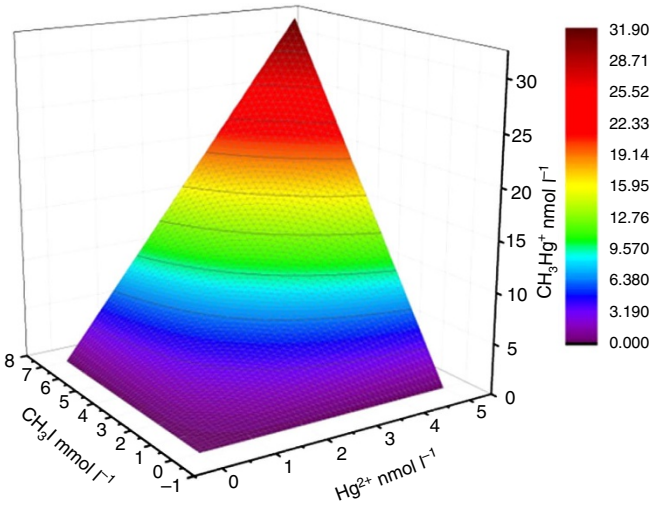

Figure 5 | The effects of CH_3I and Hg^{2+} on the increased steady-state concentration of CH_3Hg^+. The obtained photomethylation rate constant of Hg^{2+} by CH_3I ($k_M = 1.51\times10^{-2}$ l mol^{-1} E^{-1} m^2) and photodemethylation rate constant of CH_3Hg^+ ($k_D = 0.015$ m^2 E^{-1}) in the pond water were used to calculate the increased steady-state concentration of CH_3Hg^+ (equation (17)). The concentrations of Hg^{2+} and CH_3I are assumed to be in the range of 0–5 nmol l^{-1} and 0–7 mmol l^{-1}, respectively.

mercury levels in natural waters)[27,28], the steady-state concentration of CH_3Hg^+ in natural waters was estimated to increase by 0.005–2.966 pmol l^{-1} through the CH_3I-involved methylation of mercury (see Supplementary Table 1). This increase in CH_3Hg^+ is comparable to the concentration of CH_3Hg^+ in these natural waters ($<$0.025–5.085 pmol l^{-1})[27,28]. To evaluate the relative importance of CH_3I-involved methylation versus biotic methylation in sediments, we further compared the formation rate of CH_3Hg^+ from photomethylation by CH_3I in water body and the diffusion rate of CH_3Hg^+ from sediment (generated by biotic methylation) with water (see Supplementary Table 2). The results showed that the calculated formation rates of CH_3Hg^+ from photomethylation by CH_3I are in the range of 0.53–258.5 pmol m^{-2} d^{-1}, comparable with the diffusion rates of CH_3Hg^+ from sediment ($-$3.0–327.0 pmol m^{-2} d^{-1}) (Supplementary Table 2), indicating that CH_3I-involved formation of CH_3Hg^+ could be comparable with that diffused from sediment (mainly generated by biotic methylation). Both estimations suggest that photomethylation of mercury by CH_3I could be an important source of CH_3Hg^+ in areas with CH_3I fumigant application.

Discussion

Methylation of mercury by sulphate-reducing[29] or iron-reducing bacteria[30] has been deemed to be the main source of CH_3Hg^+ in aquatic environments. However, this study shows that methylation of inorganic mercury by CH_3I could be another important source of CH_3Hg^+. This would be particularly true in an environment where CH_3I is used in large amounts as a fumigant. In addition to acting as a methylation agent, CH_3I can also serve as a potential mobilizing agent for mercury sulfide (HgS)[12]. It has been demonstrated that CH_3I could methylate sulphide into volatile $(CH_3)_2S$ and $(CH_3)_2S_2$, and then liberate free Hg^{2+} into water from insoluble HgS[12]. Considering HgS is an important inorganic mercury species in anoxic environments such as soil[31], sediment[32] and sulphidic water[33], this dissolution process of HgS could increase the leaching and release of Hg^{2+} from soil and sediment into surface water, and therefore enhance the potential formation of CH_3Hg^+. As CH_3Hg^+ is a neurotoxin, the impact of CH_3I application to farmland on biogeochemical cycling of mercury should be carefully evaluated.

With respect to the production of CH_3Hg^+, most previous studies focused on the methylation of Hg^{2+} in the environment; however, there is a lack of knowledge on the methylation of Hg^0. Results of this study imply that methylation of Hg^0 can occur in the environment (for example, by CH_3I). Although Hg^0 is present at low concentrations in water and sediment, Hg^{2+}, through photomediated reduction in natural waters, provides a sufficient and continuous source of Hg^0. Additionally, Hg^0 is the main Hg species in the atmosphere, and the co-occurrence of Hg^0 and released CH_3I from fumigated fields by volatilization, makes the photochemical methylation of Hg^0 possible in the atmosphere. Therefore, the methylation of Hg^0 by CH_3I and its contribution to the CH_3Hg^+ pool needs to be considered.

Fumigants are widely applied in agricultural fields to control pests and weeds. With the phase out of CH_3Br, the use of CH_3I is expected to increase dramatically in the future. CH_3I is a pulmonary and dermal irritant[26], and is also suspected to be carcinogenic[34], neurotoxic[18,26] and endocrine disrupting[4]. This study shows that CH_3I could also indirectly threaten the health of humans and wildlife by forming a toxic chemical, CH_3Hg^+, suggesting the necessity of a more comprehensive risk assessment of CH_3I use as a fumigant.

In summary, we have demonstrated that the registered fumigant CH_3I could methylate inorganic Hg species, including Hg^0, Hg_2^{2+} and Hg^{2+}, into toxic CH_3Hg^+ in natural water under sunlight. The photoinduced CH_3Hg^+ formation mechanism by CH_3I is proposed, which involves the reduction of Hg^{2+} to Hg^0/Hg_2^{2+} and the subsequent methylation of Hg^0/Hg_2^{2+} by CH_3I, following an oxidative addition reaction. Quantitative assessment suggests that methylation of inorganic Hg by CH_3I could be an important source of CH_3Hg^+ in CH_3I-contaminated surface water.

Methods

Reagents. CH_3Hg^+ standard was purchased from Ultra Scientific (North Kingstown, RI). Enriched ^{201}HgO and ^{199}HgO were purchased from Oak Ridge National Laboratory (Oak Ridge, TN). $CH_3{}^{201}Hg^+$ was synthesized from enriched ^{201}HgO using methylcobalamin[35]. Enriched $^{199}HgCl_2$ solution was prepared by dissolving ^{199}HgO in 10% HCl. Elemental mercury (Hg^0) and $Hg_2(NO_3)_2$ were purchased from Fisher Chemicals (Pittsburgh, PA). Hg^0 stock solution was freshly prepared following the method by Whalin and Mason[36]. One drop of Hg^0 was first transferred into a piece of silicon tubing. After capping at both ends with Teflon plugs, the tubing was immersed into deionized water. Next, the gaseous Hg^0 was equilibrated with water for over 48 h under anoxic conditions. The concentration of Hg^0 in water was determined before the experiment was conducted. CH_3I and CD_3I were purchased from Fisher Chemicals and Hengye Zhongyuan Chemicals (Beijing, China), respectively. Deionized water was prepared from a Barnstead NANOpure Diamond Life Science (UV/UF) ultrapure water system (Barnstead International, Dubuque, IA).

Methylation of inorganic mercury by CH_3I. Water samples were collected from a pond in FIU (25°45′N, 80°22′W) and the Florida Everglades (25°45′N, 80°44′W), and stored in pre-cleaned 2-L Teflon bottles using trace metal clean procedures. The samples were kept in a cooler and transported to the laboratory within 3 h. Methylation experiments were conducted immediately on arrival at the laboratory. The methylation experiments were carried out in a 0.5-l Teflon bottle under natural sunlight or in darkness (wrapping bottles with aluminum foil). $^{199}HgCl_2$, $Hg_2(NO_3)_2$ or Hg^0 was spiked into each bottle to form a final concentration of about 1,000 ng l^{-1} (4.99 nmol l^{-1}) as mercury, respectively. CH_3I and $CH_3{}^{201}Hg$ were then added to each bottle to form a final concentration of 141.9 mg l^{-1} (1 mmol l^{-1}) and 1 ng l^{-1} (4.975 pmol l^{-1}), separately. For the experiments conducted in deionized water, $^{199}HgCl_2$, $Hg_2(NO_3)_2$ or Hg^0 was spiked to each bottle to form a final concentration of about 1,000 ng l^{-1} (4.99 nmol l^{-1}) as mercury, respectively. CH_3I were then added to each bottle to form a final concentration of 141.9 mg l^{-1} (1 mmol l^{-1}). To investigate the effects of Hg^{2+} and CH_3I concentrations on the methylation rate, various concentration of CH_3I (0, 0.1, 0.2, 0.5, 1.0 and 2.0 mmol l^{-1}) and $^{199}HgCl_2$ (0, 1.0, 2.0, 3.0, 4.0 and 5.0 nmol l^{-1}) were spiked into pond water containing 4.99 pmol l^{-1} $CH_3{}^{201}Hg^+$. Bottles were incubated under ambient temperature and light conditions for 4 days. During the experiment, the intensity of ambient *PAR* was measured at 15min intervals routinely using LI-192 Quantum Sensor (LI-COR Biosciences, Lincoln, NE). Triplicates (three separate bottles) were employed for each trial. $CH_3{}^{202}Hg^+$, $CH_3{}^{201}Hg^+$ and $CH_3{}^{199}Hg^+$ in the incubated samples were determined after 0, 0.5, 1, 2, 3 and 4 days of incubation using the aqueous phenylation purge-and-trap followed by the GC inductively coupled plasma–MS (ICP-MS) detection. A CD_3I addition technique was adopted to investigate the origin of the methyl group in the generated CH_3Hg^+. $HgCl_2$ and CD_3I were added to 2 l of environmental water to form a final concentration of 9.97 μmol l^{-1} as Hg^{2+} and 20 mmol l^{-1}, respectively. The bottle was then incubated under ambient temperature and light conditions for 4 days. The formation of CD_3Hg^+ was verified by the aqueous phenylation–solid phase microextraction (SPME)–GC–MS.

Analysis of CH_3Hg^+. Water samples (20 ml), L-ascorbic acid (100 mmol l^{-1}, 1 ml), concentrated HCl (1 ml) and CH_2Cl_2 (5 ml) were added into a 50-ml polypropylene centrifuge tube (Corning Inc, Lowell, MA) sequentially. After shaking for 30 min, the samples were left to stand for 5 min to let CH_2Cl_2 separate from water. CH_2Cl_2 (2.5 ml) phase was then transferred to a 50-ml polypropylene centrifuge tube containing 35 ml 1% (v/v) HCl. The tube was purged with N_2 at 150 ml min^{-1} to completely volatilize CH_2Cl_2 and release CH_3Hg^+ into aqueous phase. CH_3Hg^+ in the aqueous phase was analysed by aqueous phenylation and purge-and-trap pre-concentration followed by GC–ICP–MS[37]. The artificial formation of CH_3Hg^+ using this method has been demonstrated to be negligible, attributing to the omission of the distillation procedure and the replacement of the derivatization reagents (from sodium tetraethylborate or sodium (n-propyl)borate to sodium phenylborate ($NaBPh_4$))[37].

Aqueous phenylation reactions were performed in 300-ml glass bubblers from Exeter Scientific Glass Co. (Birdsboro, PA). The prepared sample (35 ml) was added to a 100 ml solution containing 30% (w/v) NaCl and 0.17% (w/v) NaOH. Two millilitres of citric buffer (pH 5.0, 2 mol l^{-1}) and 1 ml of 1% (w/v) $NaBPh_4$ (Fisher Chemicals, Fairlawn, NJ) were added. After 15 min of reaction, the phenylation products were purged from the bubbler at 45 °C for 45 min with

200 ml min^{-1} of N_2, and trapped on a Tenax trap. The trap was dried for 5 min by 200 ml min^{-1} of N_2. Finally, the trapped mercury species were thermally desorbed and separated using a fused silica capillary column (15 m × 0.53 mm i.d., coated with DB-1 film of 1.5-μm thickness) and then measured with an Elan DRC-e ICP-MS (PerkinElmer Sciex, Waltham, MA).

Phenylation–SPME–GC–MS[38] was used to validate the origin of the methyl group in produced CH_3Hg^+. Natural waters (2,000 ml) were transferred to 2-l Teflon bottles and spiked with 4 mg Hg^{2+} and 40 mmol CD_3I. The solution was incubated under ambient temperature and sunlight for 4 days. The produced CD_3Hg^+ was extracted from each 40-ml water sample after adding 1 ml concentrated HCl and 5 ml CH_2Cl_2. The CH_2Cl_2 phase (4 ml) was transferred into a 100-ml polypropylene centrifuge tube containing 35 ml 1% HCl and purged with N_2 at 150 ml min^{-1} to remove CH_2Cl_2. Then, pH was adjusted to 7 using 0.17% (w/v) NaOH. Sample solution (35 ml), 2 mol l^{-1} HAc-NaAc buffer (5 ml, pH 4.9) and 15 g NaCl were added to a 100-ml glass vial sealed with a polytetrafluoroethylene-coated septum. One millilitre 1% (w/v) $NaBPh_4$ solution was injected into the vial using a syringe. The vial was stirred by a magnetic stirring bar and maintained at 55 °C for 30 min in an oven. Next, headspace SPME extraction was carried out at 55 °C for 10 min. After extraction, the fibre was introduced into the GC injection port (200 °C) for thermal desorption and GC–MS analysis in splitless mode. The GC temperature programming is as following: 80 °C for 1 min, increased to 280 °C at a rate of 8 °C min^{-1} and held there for 10 min.

Analysis of Hg^0. Hg^0 in water was purged and trapped onto a home-made gold trap and detected by atomic fluorescence spectrometer. Hg^{2+} solution was used as the calibration standard. Hg^{2+} standard and 0.5 ml $SnCl_2$ solution (10% (w/v)) were added to 100 ml 1% (v/v) HCl. The mixture was left to react for 15 min and then purged for 20 min with 400 ml min^{-1} of N_2 at room temperature to let Hg^0 completely volatilize and adsorb on the gold trap. The trap was dried for 5 min by 400 ml min^{-1} of N_2. Finally, the trapped Hg^0 was thermally desorbed and determined by a PS Analytical mercury speciation system (Orpington, Kent, UK). The analytical procedure for purgeable Hg^0 in water samples was similar to that for the Hg^{2+} standards, except that $SnCl_2$ and HCl were not added.

Characterization of Hg_2^{2+} using Raman spectrometry. Formation of Hg_2^{2+} during the photoreduction of Hg^{2+} was investigated using surface-enhanced Raman spectrometry. Suwannee River humic acid and Hg^{2+} were added into deionized water to form a final concentration of 40 mg l^{-1} dissolved organic carbon and 0.5 mmol l^{-1} Hg^{2+}, respectively. After incubation under sunlight for 3 days, Raman-scattering spectra of Hg_2^{2+} in the solution with and without the addition of KI (1.0 mol l^{-1}) were collected using the following method. Au nanoparticle (AuNPs) solution was prepared by heating the solution containing 1 mol l^{-1} $AuCl_4^-$ and 5 mg l^{-1} dissolved organic matter (pH 6.8) at 80 °C for 24 h[39]. AuNP-coated Si wafer was then made by dropping AuNPs on Si wafer and then dried in a vacuum desiccator at room temperature. Next, water samples containing mercury species were dropped on the wafer and dried in a vacuum desiccator at room temperature. The AuNPs-enhanced Raman-scattering spectra of samples were obtained by using a Leica microscope in a confocal Raman spectroscopy system (Renishaw InVia Raman microscope, Britain). Spectra collections were carried out using a × 50 objective lens and 60-s scan between 155.48 and 1,132.18 cm^{-1} with a 532-nm laser (5 mW) and 2,400 lines per mm grating.

Column experiments for evaluating the leachability of CH_3I. The leachability of CH_3I was investigated using columns (16 cm length × 5 cm i.d.) containing vegetable soil, sandy soil or quartz sand. To minimize the losses of soil during the experiment, a well-permeable quartz plate was placed at the bottom of the column and the top 3 cm of the columns was filled with quartz sand. The columns were pre-saturated with deionized water and then 27.36 mg CH_3I (corresponding to an application rate of 125 lb ac^{-1}) was added into the columns. The columns were then leached with deionized water at a rate of 4.1 ml min^{-1} for 3 h. Leachates (50 ml) were continuously collected at an interval of ~12 min.

Leachates (10 ml) in 15-ml polypropylene centrifuge tube were extracted with CH_2Cl_2 (2 ml) (Corning Inc, Lowell, MA). After shaking for 30 min, the samples were left to stand for 5 min to let CH_2Cl_2 separate from water. One ml CH_2Cl_2 phase was collected for GC–MS analysis.

The determination of CH_3I was performed using an Agilent 7,890 gas chromatograph system, coupled to a quadruple Agilent 5,975 electron ionization mass spectrometric detector (Agilent Technologies, Palo Alto, CA, USA) equipped with a DB-624 fused silica capillary column (30 m × 0.25 mm i.d., 1.4-μm film thickness). The gas chromatograph system was equipped with a split/splitless injection port operating in split mode (50:1) at 120 °C. The injection volume was 2 μl. The oven temperature was programmed from 40 °C (2 min) to 90 °C at 5 °C min^{-1}, and then to 240 °C at 15 °C min^{-1}. The carrier gas was helium with a constant flow of 1 ml min^{-1}. The mass spectrometer was operated in SIM mode (m/z = 127 and 142). Solvent delay was set at 2 min. Quantification was conducted using an external standard curve method.

Data analysis. The methylation rates of Hg^0, Hg_2^{2+} and Hg^{2+} (r) were calculated by nonlinear regression of CH_3Hg^+ concentration $(C_{CH_3Hg^+})_t$ against t using equation (9) (Origin, Version 6.0 for Windows, OriginLab Corp., Northampton, MA). The net production rate of CH_3Hg^+ can be described as the difference of the photomethylation rate of inorganic mercury by CH_3I ($r \times PAR$) and the photodegradation rate of CH_3Hg^+ ($k_D \times C_{CH_3Hg^+} \times PAR$) at t time (equation (8)). Next, the function of $C_{CH_3Hg^+}$ at t time could be obtained (equation (9)) by integrating equation (8). Degradation of CH_3Hg^+ can occur in natural waters and this process was deemed to be driven by sunlight[21,40]. In this study, the spiked $CH_3{}^{201}Hg^+$ was also observed to be rapidly degraded under sunlight in both tested waters, while degradation of $CH_3{}^{201}Hg^+$ was not observed in the dark. The effect of CH_3Hg^+ photodegradation was taken into account in the calculation, represented by the photodegradation rate constant k_D. A model based on the first-order chemical kinetics was used to describe the photodegradation of $CH_3{}^{201}Hg^+$ in water (equation (10))[21,40]. The rate constant of $CH_3{}^{201}Hg^+$ photodegradation, k_D, was calculated by linear regression of $\ln(C_{CH_3{}^{201}Hg^+})_t$ against t.

$$\frac{dC_{CH_3Hg^+}}{dt} = r \times PAR - k_D \times C_{CH_3Hg^+} \times PAR \quad (8)$$

$$(C_{CH_3Hg^+})_t = \frac{r - (r - k_D \times (C_{CH_3Hg^+})_0) \times e^{-k_D J}}{k_D} (k_D > 0)$$

$$(C_{CH_3Hg^+})_t = r \times J + (C_{CH_3Hg^+})_0 (k_D = 0)$$

$$\frac{dC_{CH_3{}^{201}Hg^+}}{dt} = -k_D \times C_{CH_3{}^{201}Hg^+} \times PAR \quad (10)$$

$$\ln(C_{CH_3{}^{201}Hg^+})_t = \ln(C_{CH_3{}^{201}Hg^+})_0 - k_D \times J \quad (11)$$

where $(C_{CH_3Hg^+})_0$ and $(C_{CH_3Hg^+})_t$ are the concentrations of CH_3Hg^+ at the beginning and t time, respectively (pmol l^{-1}), k_D is the rate constant of CH_3Hg^+ photodegradation (m^2 E^{-1}), PAR is the photosynthetically active radiation (E m^{-2} d^{-1}), J is the cumulative PAR photon flux (E m^{-2}) and r is the PAR normalized formation rate of CH_3Hg^+ (pmol l^{-1} E^{-1} m^2).

The differences in CH_3Hg^+ concentrations at steady state with or without the presence of CH_3I were calculated and used to evaluate the influence of CH_3I on CH_3Hg^+ production. In natural waters, the concentration of CH_3Hg^+ was assumed to be determined by several key processes, including photodegradation of CH_3Hg^+, input of CH_3Hg^+ from sediment and runoff, methylation in water body and methylation by CH_3I. Next, the changing rate of CH_3Hg^+ could be calculated by the photodegradation rate $k_D \times C_{CH_3Hg^+} \times PAR$, the CH_3Hg^+ input rate from sediment and runoff (R_0), the methylation rate (R') and the rate of photomethylation by CH_3I ($r \times PAR$). As r was found to be positively related to the product of $C_{Hg^{2+}}$ and C_{CH_3I} (equation (13), Fig. 4) and equation (14) could be obtained by combining equation (13) with equation (12).

$$\frac{dC_{CH_3Hg^+}}{dt} = R_0 + R' + r \times PAR - k_D \times C_{CH_3Hg^+} \times PAR \quad (12)$$

$$r = k_M \times C_{Hg^{2+}} \times C_{CH_3I} \quad (13)$$

$$\frac{dC_{CH_3Hg^+}}{dt} = R_0 + R' + k_M \times C_{Hg^{2+}} \times C_{CH_3I} \times PAR - k_D \times C_{CH_3Hg^+} \times PAR \quad (14)$$

where R_0 is the rate of CH_3Hg^+ input from sediment and runoff (pmol l^{-1} d^{-1}), R' is the non-CH_3I involved methylation rate in water body (pmol l^{-1} d^{-1}), k_M is the PAR-normalized formation rate constant of CH_3Hg^+ (l pmol^{-1} E^{-1} m^2), $C_{Hg^{2+}}$ is the concentration of Hg^{2+} (pmol l^{-1}), C_{CH_3I} is the concentration of CH_3I (pmol l^{-1}). The predicted concentration of CH_3Hg^+ at steady state in the presence of CH_3I ($C^{II}_{CH_3H_g^+}$) can be calculated by making the right side of equation (14) equal to zero (equation (15)).

$$C^{II}_{CH_3H_g^+} = \frac{R_0 + R' + k_M \times C_{Hg^{2+}} \times C_{CH_3I} \times PAR}{k_D \times PAR} \quad (15)$$

The predicted concentration of CH_3Hg^+ at steady state in the absence of CH_3I ($C^{\Phi}_{CH_3H_g^+}$) can be calculated by making C_{CH_3I} of equation (15) equal to zero (equation (16)).

$$C^{\Phi}_{CH_3H_g^+} = \frac{R_0 + R'}{k_D \times PAR} \quad (16)$$

Next, the differences in CH_3Hg^+ concentrations at steady state with or without the presence of CH_3I ($\Delta C_{CH_3Hg^+}$) can be calculated by equation (17).

$$\Delta C_{CH_3Hg^+} = C^{II}_{CH_3H_g^+} - C^{\Phi}_{CH_3H_g^+} = \frac{k_M \times C_{Hg^{2+}} \times C_{CH_3I}}{k_D} \quad (17)$$

The parameters for calculating $\Delta C_{CH_3Hg^+}$ are given in Supplementary Table 1.

To evaluate the relative importance of CH_3I-involved methylation versus biotic methylation, the CH_3Hg^+ photomethylation rate within the entire water column was calculated as follows. The sunlight intensity at Z depth (m) is calculated from the light intensity in the surface water (PAR (0)) by exponentially decreasing it with depth according to the Beer-Lambert equation. Combined with the calculation of the photomethylation rate of CH_3Hg^+ in the surface water, the photomethylation

rate at Z depth can be described as equation (18). Next, mercury methylation is integrated with respect to water column depth to obtain the methylation rate within the entire water column (equation (19)).

$$\frac{dC_{CH_3Hg^+}(Z)}{dt} = k_M \times C_{Hg^{2+}} \times C_{CH_3I} \times PAR(0) \times e^{(-kZ)} \quad (18)$$

where $C_{CH_3Hg^+}(Z)$ is the concentration of CH_3Hg^+ at depth Z (pmol l^{-1}), $PAR(0)$ is the PAR above the surface of the water (E m^{-2} d^{-1}) and k is the light attenuation coefficient of sunlight (m^{-1}).

Then,

$$\int \left(\frac{dC_{CH_3Hg^+}(Z)}{dt}\right) dZ = \int k_M \times C_{Hg^{2+}} \times C_{CH_3I} \times PAR(0) \times e^{(-kZ)} dZ \quad (19)$$

The parameters for calculating $\int \left(\frac{dC_{CH_3Hg^+}(Z)}{dt}\right) dZ$ are given in Supplementary Table 2.

References

1. Yokouchi, Y. *et al.* Global distribution and seasonal concentration change of methyl iodide in the atmosphere. *J. Geophys. Res. Atmos.* **113,** D18311 (2008).
2. Ohr, H. D., Sims, J. J., Grech, N. M., Becker, J. O. & McGiffen, M. E. Methyl iodide, an ozone-safe alternative to methyl bromide as a soil fumigant. *Plant Dis.* **80,** 731–735 (1996).
3. Pelley, J. Methyl iodide, a fumigant under fire. *Environ. Sci. Technol.* **43,** 6898 (2009).
4. Mileson, B. E., Sweeney, L. M., Gargas, M. L. & Kinzell, J. Iodomethane human health risk characterization. *Inhal. Toxicol.* **21,** 583–605 (2009).
5. Gan, J. Y. & Yates, S. R. Degradation and phase partition of methyl iodide in soil. *J. Agr. Food Chem.* **44,** 4001–4008 (1996).
6. Guo, M. X., Zheng, W., Papiernik, S. K. & Yates, S. R. Distribution and leaching of methyl iodide in soil following emulated shank and drip application. *J. Environ. Qual.* **33,** 2149–2156 (2004).
7. Dai, S., Huang, G. & Cai, Y. A study of methylation of inorganic tin by iodomethane in an aquatic environment with ^{13}C carbon isotope tracer technique. *Appl. Organomet. Chem.* **3,** 115–120 (1989).
8. Chen, B. W. *et al.* Simulate methylation reaction of arsenic(III) with methyl iodide in an aquatic system. *Appl. Organomet. Chem.* **20,** 747–753 (2006).
9. Ahmad, I., Chau, Y. K., Wong, P. T. S., Carty, A. J. & Taylor, L. Chemical alkylation of lead (II) salts to tetraalkyllead (IV) in aqueous solution. *Nature* **287,** 716–717 (1980).
10. Baldoni, A. A. & Miyashiro, J. J. Preparation of organo mercuric compounds. United States Patent 2914451 (1959).
11. Hall, B., Bloom, N. S. & Munthe, J. An experimental study of two potential methylation agents of mercury in the atmosphere: CH_3I and DMS. *Water Air Soil Poll.* **80,** 337–341 (1995).
12. Thayer, J. S., Olson, G. J. & Brinckman, F. E. Iodomethane as a potential metal mobilizing agent in nature. *Environ. Sci. Technol.* **18,** 726–729 (1984).
13. Minganti, V., Capelli, R., Drava, G. & De Pellegrini, R. Solubilization and methylation of HgS, PbS, and SnS by iodomethane, a model experiment for the aquatic environment. *Chemosphere* **67,** 1018–1024 (2007).
14. Celo, V. & Scott, S. L. Kinetics and mechanism of the mercury(II)-assisted hydrolysis of methyl iodide. *Inorg. Chem.* **44,** 2507–2512 (2005).
15. Amyot, M., Mierle, G., Lean, D. R. S. & McQueen, D. J. Sunlight-induced formation of dissolved gaseous Hg in lake waters. *Environ. Sci. Technol.* **28,** 2366–2371 (1994).
16. O'Driscoll, N. J., Siciliano, S. D., Lean, D. R. S. & Amyot, M. Gross photoreduction kinetics of mercury in temperate freshwater lakes and rivers: Application to a general model of DGM dynamics. *Environ. Sci. Technol.* **40,** 837–843 (2006).
17. Castro, L., Dommergue, A., Larose, C., Ferrari, C. & Maron, L. A theoretical study of abiotic methylation reactions of gaseous elemental mercury by halogen-containing molecules. *J. Phys. Chem. A* **115,** 5602–5608 (2011).
18. Algren, D. A., Schwartz, M. D. & Schier, J. G. Acute neurologic toxicity associated with inhalational exposure to methyl iodide and iodine-131. *Clin. Toxicol.* **44,** 722–723 (2006).
19. Celo, V., Lean, D. R. S. & Scott, S. L. Abiotic methylation of mercury in the aquatic environment. *Sci. Total Environ.* **368,** 126–137 (2006).
20. Craig, P. J. & Rapsomanikis, S. Methylation of tin and lead in the environment: Oxidative methyl transfer as a model for environmental reactions. *Environ. Sci. Technol.* **19,** 726–730 (1985).
21. Zhang, T. & Hsu-Kim, H. Photolytic degradation of methylmercury enhanced by binding to natural organic ligands. *Nat. Geosci.* **3,** 473–476 (2010).
22. Hammerschmidt, C. R. & Fitzgerald, W. F. Iron-mediated photochemical decomposition of methylmercury in an Arctic Alaskan lake. *Environ. Sci. Technol.* **44,** 6138–6143 (2010).
23. Lyday, P. A. in *Ullmann's Encyclopedia of Industrial Chemistry* (Wiley-VCH, 2000).
24. Skogerboe, R. K. & Wilson, S. A. Reduction of ionic species by fulvic acid. *Anal. Chem.* **53,** 228–232 (1981).
25. Nriagu, J. O. Mechanistic steps in the photoreduction of mercury in natural waters. *Sci. Total Environ.* **154,** 1–8 (1994).
26. Schwartz, M. D., Obamwonyi, A. O., Thomas, J. D., Moorhead, J. F. & Morgan, B. W. Acute methyl iodide exposure with delayed neuropsychiatric sequelae: Report of a case. *Am. J. Ind. Med.* **47,** 550–556 (2005).
27. Horvat, M. *et al.* Total mercury, methylmercury and selenium in mercury polluted areas in the province Guizhou, China. *Sci. Total Environ.* **304,** 231–256 (2003).
28. Barringer, J. L. *et al.* Mercury and methylmercury dynamics in a coastal plain watershed, New Jersey, USA. *Water Air Soil Poll.* **212,** 251–273 (2010).
29. Gilmour, C. C., Henry, E. A. & Mitchell, R. Sulfate stimulation of mercury methylation in freshwater sediments. *Environ. Sci. Technol.* **26,** 2281–2287 (1992).
30. Fleming, E. J., Mack, E. E., Green, P. G. & Nelson, D. C. Mercury methylation from unexpected sources: Molybdate-inhibited freshwater sediments and an iron-reducing bacterium. *Appl. Environ. Microb.* **72,** 457–464 (2006).
31. Barnett, M. O. *et al.* Formation of mercuric sulfide in soil. *Environ. Sci. Technol.* **31,** 3037–3043 (1997).
32. Jonsson, S. *et al.* Mercury methylation rates for geochemically relevant Hg-II species in sediments. *Environ. Sci. Technol.* **46,** 11653–11659 (2012).
33. Graham, A. M., Aiken, G. R. & Gilmour, C. C. Dissolved organic matter enhances microbial mercury methylation under sulfidic conditions. *Environ. Sci. Technol.* **46,** 2715–2723 (2012).
34. Moser, F., Horwitz, A., Chen, J., Lim, W. A. & Voigt, C. A. Genetic sensor for strong methylating compounds. *ACS Synth. Biol.* **2,** 614–624 (2013).
35. Bancon-Montigny, C., Yang, L., Sturgeon, R. E., Colombini, V. & Mester, Z. High-yield synthesis of milligram amounts of isotopically enriched methylmercury ($CH_3{}^{198}HgCl$). *Appl. Organomet. Chem.* **18,** 57–64 (2004).
36. Whalin, L. M. & Mason, R. P. A new method for the investigation of mercury redox chemistry in natural waters utilizing deflatable Teflon bags and additions of isotopically labeled mercury. *Anal. Chim. Acta* **558,** 211–221 (2006).
37. Mao, Y. X., Liu, G. L., Meichel, G., Cai, Y. & Jiang, G. B. Simultaneous speciation of monomethylmercury and monoethylmercury by aqueous phenylation and purge-and-trap preconcentration followed by atomic spectrometry detection. *Anal. Chem.* **80,** 7163–7168 (2008).
38. Yin, Y. G. *et al.* Possible alkylation of inorganic Hg(II) by photochemical processes in the environment. *Chemosphere* **88,** 8–16 (2012).
39. Alvarez-Puebla, R. A., dos Santos, D. S. J. & Aroca, R. F. SERS detection of environmental pollutants in humic acid-gold nanoparticle composite materials. *Analyst* **132,** 1210–1214 (2007).
40. Lehnherr, I. & Louis, V. L. S. Importance of ultraviolet radiation in the photodemethylation of methylmercury in freshwater ecosystems. *Environ. Sci. Technol.* **43,** 5692–5698 (2009).

Acknowledgements

We thank Leo Scinto for providing the instrument for PAR measurement, and Bruce McCord and Watson Lees for commenting on an earlier version of the manuscript. This research was supported by the National Natural Science Foundation of China (21120102040, 20937002), National Basic Research Program of China (2013CB430002), the U.S. Department of Energy (DE-FG01-05EW07033) and the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB01020300).

Author contributions

Y.Y., Y.L., Y.C. and G.J. designed research; Y.Y., Y.L. and C.T. performed research; Y.Y., Y.L., Y.C. and G.J. wrote the paper.

Additional information

Supplementary Information accompanies this paper at http://www.nature.com/naturecommunications

Competing financial interests: The authors declare no competing financial interests.

Reprints and permission information is available online at http://npg.nature.com/reprintsandpermissions/

How to cite this article: Yin, Y. *et al.* Fumigant methyl iodide can methylate inorganic mercury species in natural waters. *Nat. Commun.* 5:4633 doi: 10.1038/ncomms5633 (2014).