





Application of copper(II)-based chemicals induces CH_3Br and CH_3Cl emissions from soil and seawater

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Methyl bromide (CH_3Br) and methyl chloride (CH_3Cl) are major carriers of atmospheric bromine and chlorine, respectively, which can catalyze stratospheric ozone depletion. However, in our current understanding, there are missing sources associated with these two species. Here we investigate the effect of copper(II) on CH_3Br and CH_3Cl production from soil, seawater and model organic compounds: catechol (benzene-1,2-diol) and guaiacol (2-methoxyphenol). We show that copper sulfate (CuSO_4) enhances CH_3Br and CH_3Cl production from soil and seawater, and it may be further amplified in conjunction with hydrogen peroxide (H_2O_2) or solar radiation. This represents an abiotic production pathway of CH_3Br and CH_3Cl perturbed by anthropogenic application of copper(II)-based chemicals. Hence, we suggest that the widespread application of copper(II) pesticides in agriculture and the discharge of anthropogenic copper(II) to the oceans may account for part of the missing sources of CH_3Br and CH_3Cl , and thereby contribute to stratospheric halogen load.

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Methyl bromide (CH_3Br) and methyl chloride (CH_3Cl) are the most abundant brominated and chlorinated hydrocarbons in the atmosphere¹. They have average tropospheric lifetimes of 0.8 and 0.9 years¹, respectively, which are long enough for them to reach the lower stratosphere and disassociate, releasing bromine and chlorine radicals that catalyze stratospheric ozone depletion. However, the sizes of identified sources of CH_3Br and CH_3Cl are smaller than those of the sinks with a -39 Gg yr^{-1} imbalance for CH_3Br and a -748 Gg yr^{-1} imbalance for CH_3Cl , respectively¹. A recent reevaluation on CH_3Cl emissions from tropical plants², which was seen as the largest CH_3Cl source, showed it may be overestimated by about 1300 Gg yr^{-1} , suggesting the existence of even larger missing CH_3Cl sources than previously thought. These discrepancies need to be resolved to better understand stratospheric halogen chemistry and to predict future ozone recovery. The present atmospheric CH_3Br and CH_3Cl originate from predominantly natural sources. These natural sources tend to be amplified under anthropogenic-induced influences, such as biomass burning³, global warming^{4,5}, sea level rise^{6,7}, agricultural cultivation⁸, land use change⁹, etc., posing persistent and growing challenges for the recovery of stratospheric ozone^{10,11}.

Among the known sources and sinks of CH_3Br and CH_3Cl , soil is an important bi-directional interface with simultaneous abiotic production^{12,13} and biotic degradation^{14,15}. Within the soil, abiotic Fenton-like reactions that involve Fe(III) oxidizing organic matter in the presence of halide ions are responsible for the production of methyl halides¹². This pathway is ubiquitous and makes a significant contribution to the global methyl halide budgets. It is reasonable to postulate that the Fenton-like mechanism may be catalyzed by other transition metal ions, such as copper(II).

A setting that copper may be present in abundance is in global agriculture, where copper(II)-based pesticides, herbicides, and fungicides, such as copper(II) sulfate (CuSO_4), are widely used, especially in the fields of rice, oranges, walnuts, and grapes¹⁶. For example, in 2008 in the U.S., copper compounds accounted for 17% (the second most) of total fungicides applied in agriculture¹⁷. Roughly $2.0 \times 10^{11} \text{ kg CuSO}_4$ per year are used in global agriculture (Supplementary Note 1), in addition to other copper products.

Here, we incubate agricultural soil, seawater, and model compounds of soil organic carbon with different copper treatments, and quantify CH_3Br and CH_3Cl production rates, in order to explore and evaluate the potential effect of copper(II) chemicals on CH_3Br and CH_3Cl production. The results provide insight on copper-catalyzed production mechanisms of CH_3Br and CH_3Cl , as well as the potential impact of copper chemical application on atmospheric CH_3Br and CH_3Cl budgets.

Results and discussion

CH_3Br and CH_3Cl flux from soil. Live, unamended agricultural soil samples were net sinks of methyl bromide (CH_3Br) and methyl chloride (CH_3Cl) with average fluxes at $-0.06 \text{ ng kg}^{-1} \text{ hr}^{-1}$ and $-3.7 \text{ ng kg}^{-1} \text{ hr}^{-1}$, respectively (Fig. 1). After being autoclaved, they switched to CH_3Br and CH_3Cl sources at $0.45 \text{ ng kg}^{-1} \text{ hr}^{-1}$ and $6.9 \text{ ng kg}^{-1} \text{ hr}^{-1}$, respectively, supporting the conventional idea that soils act as a bi-directional interface of CH_3Br and CH_3Cl with simultaneous enzymatic degradation and abiotic production^{5,12,18}. The deactivation of methyl halide-consuming microorganisms following heat treatment¹⁹ in autoclaved soil results in the unidirectional interface of CH_3Cl and CH_3Br emissions, possibly catalyzed by endogenous Fe(III) in the soil¹². CH_3Br and CH_3Cl fluxes declined to near zero after organic matter depletion, demonstrating that soil organic matter provides the carbon substrate for CH_3Br and CH_3Cl formation rather than atmospheric CH_4 or CO_2 .

Cu(II) amendment induces the production of CH_3Br and CH_3Cl . Addition of copper(II) sulfate (CuSO_4) at different dosages yielded enhancements in CH_3Br and CH_3Cl productions from both live and autoclaved soil samples, and the increments were positively correlated to the amount of CuSO_4 added (Fig. 1). No such trend was observed from the organic matter-depleted mineral soil. It has been previously demonstrated that halide ions can be alkylated to produce volatile halogenated carbons when soil or sediment organic matter is oxidized by Fe(III) without the mediation of sunlight or microbial activities¹². The results suggested that Cu(II), as an electron acceptor, may oxidize organic matter in a similar manner as Fe(III) during the halogenation process to produce volatile CH_3Br and CH_3Cl .

Notably, live soils produced 4–6 times more CH_3Cl than CH_3Br on molar basis (e.g., amended with 10 ml of 5 mM or 10 mM CuSO_4), despite Cl^- being ~135 times more abundant than Br^- in the soils (Supplementary Table 1). For autoclaved soil, CH_3Br production rate was even up to 15 times that of CH_3Cl (e.g., amended with 10 ml of 5 mM CuSO_4). These results suggested that Cu(II)-catalyzed methylation reaction favors bromide over chloride when both ions are present, possibly due to relative electronegativities and polarizabilities of the halogens²⁰. This is a similar trend as found in the Fe(III)-catalyzed production of methyl halides^{12,13,21}.

The increases of CH_3Br and CH_3Cl production rates induced by copper(II)-addition were much larger in autoclaved soil samples than in live soil samples. For example, as the Cu(II) addition increased from 0 to 10 mM, average CH_3Br fluxes from live soil samples gradually switched from -0.06 to $0.69 \text{ ng kg}^{-1} \text{ hr}^{-1}$, while emissions from autoclaved soils increased from 0.45 to $578 \text{ ng kg}^{-1} \text{ hr}^{-1}$. For CH_3Cl fluxes, they shifted from -3.7 to $2.1 \text{ ng kg}^{-1} \text{ hr}^{-1}$, and from 6.9 to $25.2 \text{ ng kg}^{-1} \text{ hr}^{-1}$, respectively. It is possible that thermal treatment promoted the fracture of labile humic substances in soil^{22–24}, making the organic carbon more readily available for the formation of volatile halogenated compounds.

In conjunction of Cu(II), H_2O_2 further promotes CH_3Br and CH_3Cl production. The addition of H_2O_2 also enhanced CH_3Br and CH_3Cl production in both live and autoclaved soils (Fig. 2), but not as large as those caused by the addition of Cu(II). However, H_2O_2 amplified the effect of Cu(II) on CH_3Cl and CH_3Br production in both live and autoclaved soil samples (Fig. 2). Compared to experiments with Cu(II) addition only, the amendment of both H_2O_2 and Cu(II) increased the production rates of CH_3Br and CH_3Cl by about 93-fold and 7-fold, respectively, in live soils; and by about 1.2-fold and 5-fold, respectively, in autoclaved soils. It is postulated that the combination of Cu(II) and H_2O_2 produced hydroxyl radicals ($\bullet\text{OH}$)²⁵, which provides a powerful, nonspecific oxidant agent. Subsequently, the $\bullet\text{OH}$ radicals react with organic compounds, halide ions, and/or copper ions to enhance the copper-mediated reaction to form volatile organochlorine compounds, such as CH_3Br and CH_3Cl .

Catechol (benzene-1,2-diol) is regarded as a precursor of soil humic substances, and it is often used as a model substance of monomeric phenols that are commonly formed during the microbial degradation of many naturally occurring and anthropogenic aromatic substances²⁶. To elucidate abiotic chemical reactions, in the absence of soil microbes or complex soil organic matter in soils that may be chemically altered during the autoclaving process, an experiment was designed with catechol to further test the essentiality of Cu(II) and H_2O_2 in CH_3Br and CH_3Cl production.

Water solutions containing catechol (10 mM), KBr or KCl (20 mM), CuSO_4 (50 mM), and H_2O_2 (50 mM) produced large

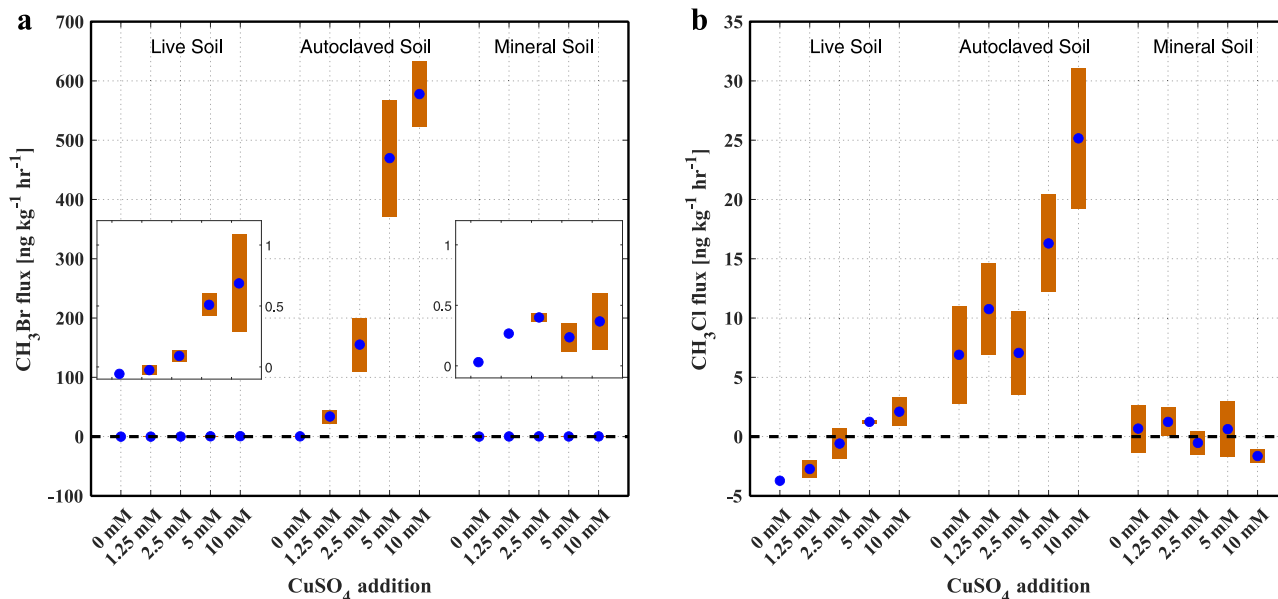


Fig. 1 Methyl halide fluxes from soil samples amended with different amount of CuSO₄. **a** Methyl bromide (CH₃Br) and **b** methyl chloride (CH₃Cl) fluxes from live, autoclaved, and mineral soil samples mixed with 10 ml of different concentrations of CuSO₄ solution. The blue dots represent the average fluxes of two replicate incubations (*n* = 2) and the upper and lower boundary of the bars represent the two individual fluxes. The inserted plots in **(a)** are the enlarged view of CH₃Br fluxes from live and mineral soils.

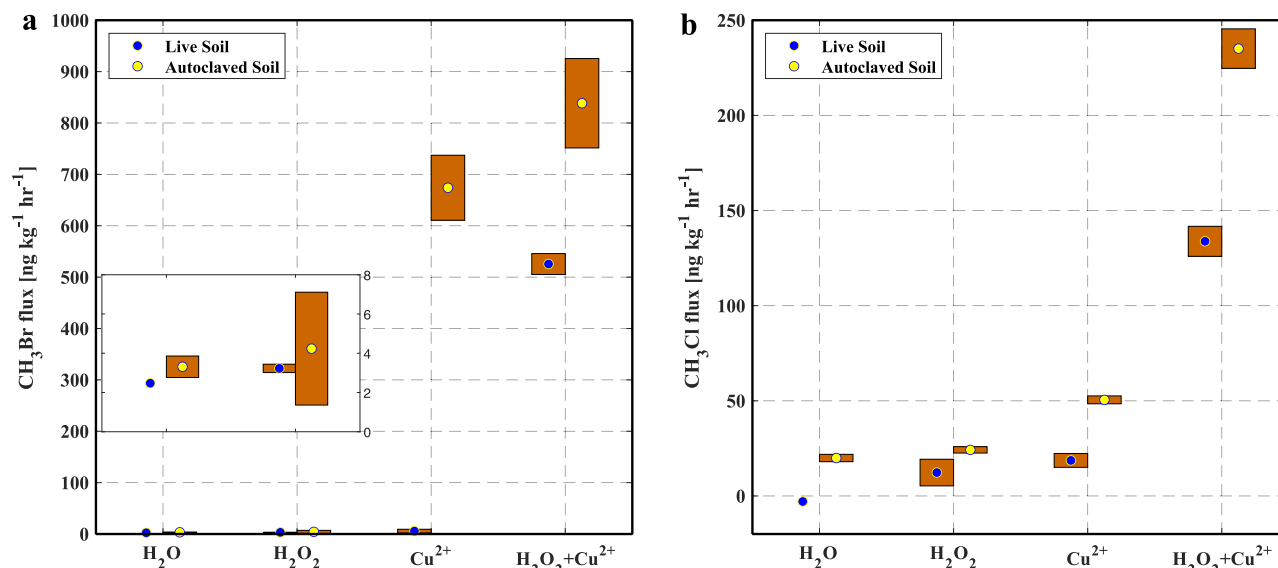


Fig. 2 Methyl halide fluxes from soil samples amended with different chemicals. **a** Methyl bromide (CH₃Br) and **b** methyl chloride (CH₃Cl) fluxes from live and autoclaved soil samples under different treatments. (i) 20 ml of deionized water was added; (ii) 10 ml each of deionized water and 50 mM H₂O₂ was added; (iii) 10 ml each of deionized water and 50 mM CuSO₄ was added; (iv) 10 ml each of 50 mM H₂O₂ and 50 mM CuSO₄ at were added. The dots represent the average fluxes of two replicated incubations (*n* = 2) in each treatment and the upper and lower boundary of the bars represent the two individual fluxes. The inserted plots in **(a)** are the enlarged view of CH₃Br fluxes from soils in the first two treatments.

amounts of CH₃Br and CH₃Cl, respectively (Supplementary Fig. 1), associated with an abrupt color change from clear to brownish with visible precipitates (Supplementary Fig. 2). CH₃Br and CH₃Cl production rates also increase with increasing concentrations of CuSO₄ and H₂O₂, which further demonstrate the enhancing effect of Cu(II) and H₂O₂.

Time and sunlight effect. The experiments described so far showed that the addition of CuSO₄ induces production of CH₃Br and CH₃Cl from the reaction with soil organic carbon.

In addition, Cu(II) works in conjunction with H₂O₂, an oxidizing agent, to further increase CH₃Br and CH₃Cl production. In natural ecosystems, the formation of H₂O₂ results principally from exciting humic substances by solar radiation^{27,28}. Therefore, time-series light vs. dark experiments were conducted with soil samples to explore how long the Cu(II) effect can persist, and to find out if a potential photochemical pathway involving ambient sunlight exists.

The time-series experiments showed that, in the dark experiments (Fig. 3, dark incubations), the production rates of CH₃Br and CH₃Cl were highest immediately following the addition of CuSO₄,

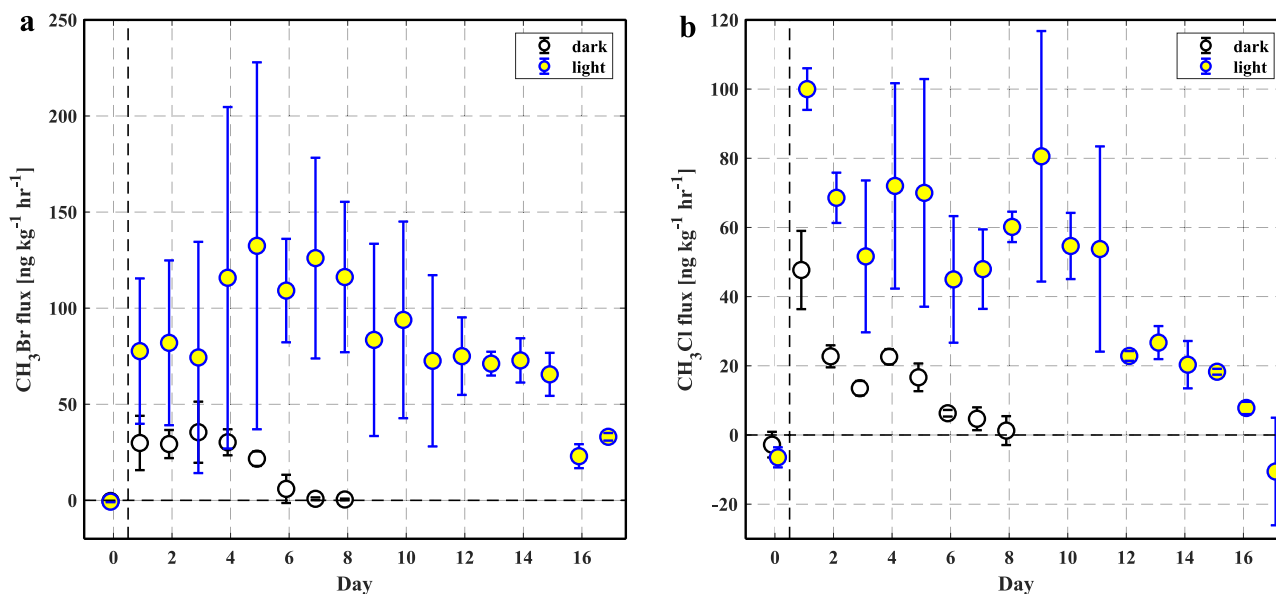


Fig. 3 Time-series fluxes of methyl halide from soil samples. **a** Methyl bromide (CH_3Br) and **b** methyl chloride (CH_3Cl) from light vs. dark incubations of live soil samples. On day 1, 10 ml of 50 mM CuSO_4 was added to soil samples (50 grams); the dark incubation lasted for 8 days while the light incubation was 17 days. The circles represent the average fluxes of triplicate incubations ($n = 3$) and the error bars represent the standard deviations.

and then declined to negligible levels over the following week. The depletion of Cu(II) may contribute to the persistent decline of CH_3Br and CH_3Cl production. Therefore, under natural conditions where copper can undergo aerial oxidation²⁰, it may apply a longer enhancing effect on CH_3Br and CH_3Cl production. It is noted that CH_3Cl fluxes started to turn negative on day 8, indicating net consumption of CH_3Cl from the ambient air, which might be attributable to the re-habitation of methyl halide-consuming microbial communities²⁷ after the addition of Cu(II) chemical.

For sunlight experiments (Fig. 3), the average CH_3Br and CH_3Cl fluxes were persistently higher than those from the dark experiments. Although the decline of CH_3Br and CH_3Cl fluxes over time was also observed, it took a longer period (17 days vs. 8 days) for them to resume near-background levels. These results suggested that solar radiation may amplify the effect of Cu(II) on CH_3Br and CH_3Cl production, and Cu(II) might be recycled under the light conditions to exert the longer enhancement effect.

Sunlit incubations of catechol were also conducted to further test the essential role of solar radiation played in CH_3Cl production. Results showed rapid production rates occurred when the chemical solutions with Cu(II) were exposed to sunlight, while the omission of sunlight yielded slow production of CH_3Cl (Supplementary Fig. 3a). It indicates the likely existence of a photochemical production pathway, in which copper may be reoxidized to exert a persistent enhancement effect on methyl halide production.

A few studies have proven the importance of irradiation in the production of methyl halides^{29–32}. For example, artificial ultraviolet irradiation ($\lambda = 254 \text{ nm}$) can catalyze the reaction between dissolved organic carbon and chlorine in seawater to generate CH_3Cl ³². However, in natural environments, UV radiation with such a short wavelength would have been absorbed by stratospheric ozone before it can reach earth's surface, which makes this pathway only plausible in sewage treatment industries. Similar to some other studies^{29–31}, the light involved in our experiments was ambient sunlight. It has been proposed that the UVB region of sunlight may bring the complex of Cu(II) and halide ions to a redox excited state²⁰, promoting methyl halide production. Therefore, the larger CH_3Br and CH_3Cl fluxes in samples with copper sulfate and sunlight imply that sunlight is an important driver for the reaction.

On the other hand, the glass jars used in the sunlight experiments attenuated UVB ($\lambda = 265\text{--}322 \text{ nm}$), UVA ($\lambda = \sim 320\text{--}390 \text{ nm}$), and photosynthetic active radiation (PAR, $\lambda = 410\text{--}655 \text{ nm}$) by about 75%, <1%, and 23%, respectively (Supplementary Table 3), suggesting that CH_3Br and CH_3Cl emissions may be even higher under natural conditions.

CH_3Br and CH_3Cl production in seawater. Natural seawater from San Francisco Bay produced relatively small amounts of CH_3Br and CH_3Cl under dark or light conditions, in comparison to the Cu(II) addition treatments. The treatment with both Cu(II) amendment and ambient sunlight exposure showed the greatest positive average fluxes of both CH_3Br and CH_3Cl (Fig. 4), while samples undergoing other treatments without this combination displayed relatively smaller fluxes. Similar to the results of soils and model compound incubations, the large production of CH_3Br and CH_3Cl was contingent upon the presence of both Cu(II) and sunlight. Similarly, a cruise study in the Atlantic Ocean also identified a photochemical production pathway for methyl iodide (CH_3I) production under ambient sunlight conditions³⁰.

Many discharge routes of anthropogenic copper to the oceans exist, such as copper leaching from boat antifouling paint and aquaculture nets, copper residue from automobile brake pads in urban runoff, and atmospheric aerosol deposition^{33,34}. Therefore, this study also suggests a previously unaccounted for, primarily anthropogenically driven CH_3Br and CH_3Cl source from seawater through the interaction of copper, sunlight, and dissolved organic matter.

Potential mechanism of the observed phenomenon. It has been well established that Fe(III) can foster the reaction between guaiacol and chloride ions to produce CH_3Cl ¹²; during this process, the only byproduct of this reaction was 1,2-benzoquinone and the aromatic ring remained intact (Fig. 5). To test if Cu(II) can also catalyze this reaction, the mixture of guaiacol, KCl , and Cu(II) was incubated, which generated CH_3Cl at a higher production rate than the mixture with catechol (Supplementary Fig. 3b).

This may be attributed to the more readily liberated methyl group from the methoxy group of guaiacol, either through an

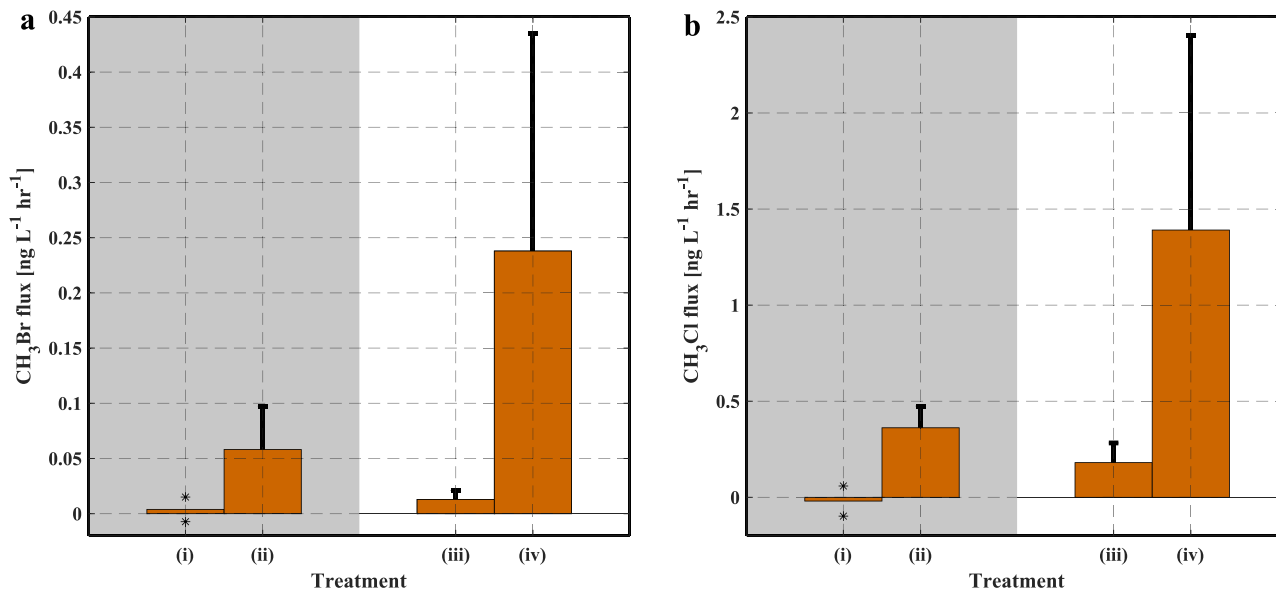


Fig. 4 Methyl halide fluxes from seawater samples under different treatments. **a** Methyl bromide (CH₃Br) and **b** methyl chloride (CH₃Cl) fluxes from the ocean water under four treatments. (i) seawater incubated under dark conditions ($n = 2$); (ii) seawater with Cu(II) amendment incubated under dark condition ($n = 4$); (iii) seawater incubated under ambient sunlight ($n = 5$); and (iv) seawater with Cu(II) amendment incubated under ambient sunlight ($n = 7$). The bars represent the average fluxes from replicate incubations of each treatment, and the error bars represent the standard deviations. For treatment (i), the two individual fluxes were presented in the figure (*), instead of the standard deviation.

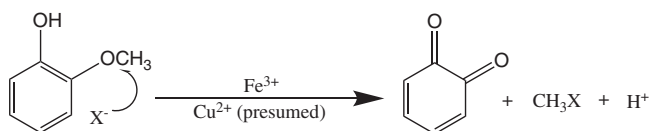


Fig. 5 Fe(III)-catalyzed¹² and presumed Cu(II)-catalyzed reaction pathway of guaiacol and halide ions to form methyl halides. X represents Cl, Br, or I.

SN₂ reaction (nucleophilic attack by Cl⁻) or cleavage of ·CH₃ radical. The bond dissociation energy (BDE) required to cleave the ·CH₃ radical from the methoxy group of guaiacol is approximately 240 kJ/mol^{35,36}, the least within the structure. In comparison, the carbon bonds within the aromatic ring could possess up to 600 kJ/mol of BDE. Production of CH₃Br and CH₃Cl from catechol, which has no such methoxy group, must follow a different pathway, whereby the aromatic ring is fractured to provide ·CH₃ radicals.

Other studies showed that thermal decomposition of catechol and other aromatic compounds produces a range of C₁–C₆ products^{22–24}, suggesting the existence of thermal-facilitated ring-opening reactions. This could also potentially help explain the phenomenon that the same amount of Cu(II) addition would trigger a higher production of CH₃Br and CH₃Cl from the autoclaved soil than from the live soil. Hence, it is speculated that autoclaved soil produced non-aromatic carbon fragments, which reacted more readily in the production of halogenated volatile compounds.

Studies have identified multiple C₁–C₆ productions, such as furans^{37,38}, oxalic acid³⁹, carbon suboxide⁴⁰, chloroethane, iodoethane, and other chloroalkanes^{21,41,42}, chlorinated acetic acid^{43,44} and other organic acids^{39,45–47} (such as acetic acid, formic acid, fumaric acid, maleic acid, malonic acid, and muconic acid) as byproducts of the Fenton-like reactions of catechol⁴⁸. We find this reaction also produces chloroform (CHCl₃) and CO₂ (Supplementary Table 4), compounds that have already been observed in previous similar studies^{47,49}. Thus, it is suggested that Fenton-like or photo-Fenton reactions also

resulted in multiple ring-opening reactions of catechol and produced radicals, such as ·CH₃, which facilitated the formation of halogenated organic compounds when halide ions were present (Supplementary Fig. 5).

Environmental implications. The mechanism as noted in this study, in which Cu(II) and radiation enhance the methylation of bromide and chloride to produce CH₃Br and CH₃Cl, have been originally identified and used in bromide²⁰ and chloride⁵⁰ determination in aqueous samples at ultra-trace levels. This study presents a consideration of the environmental consequence of this process in both conventional and organic agriculture where large amounts of copper sulfate and other Cu(II)-based chemicals are applied, as well as in coastal marine environments where Cu(II)-containing runoff is discharged⁵¹.

CH₃Br and CH₃Cl production induced by Cu(II)-based chemical usage may depend on several environmental variables, such as sunlight intensity, soil organic matter (content, composition, and structure), halide concentrations, etc. It has also been shown that pH of soil and water has an important influence on the occurrence of volatile halogenated compounds^{31,43,49}. However, a simplified estimation without considering these factors suggests this process may be responsible for 4.1 ± 1.9 Gg CH₃Br yr⁻¹ and 2.5 ± 0.7 Gg CH₃Cl yr⁻¹, respectively (Supplementary Note 1). Similar to Fe(III)-induced production of methyl halides¹², this study indicates that application of copper(II)-based chemicals may increase atmospheric concentrations of methyl halides, especially for CH₃Br (~10% of the missing sources), contribute to stratospheric halogen load, and thereby affect ozone levels.

Methods

Experimental procedure. Three sets of experiments were conducted. The first set involved the incubation of soil samples with either unamended conditions or with chemical reagent supplements, such as copper(II) sulfate (CuSO₄) or hydrogen peroxide (H₂O₂) or both, and different light conditions, light vs. dark, to investigate their impact on CH₃Br and CH₃Cl production in soils. The second set of experiments involved incubations of solutions with catechol (benzene-1,2-diol) and guaiacol (2-methoxyphenol), compounds with (methoxy-) phenolic structures, which are often used as chemical models for natural organic matter in soil^{12,37}.

The third set involved incubation of seawater samples under different conditions: Cu(II) vs. no Cu(II) amendment, and light vs. dark. All three sets of incubations followed the same experimental set-up, as described in the section “Incubation and sampling”, unless otherwise stated.

Soil sample reactions

Soil sample preparation. Surface soil was collected from Oxford Tract (37°52′34″N 122°16′02″W), an agricultural research facility of the University of California, Berkeley. The soil type was a Tierra (Fine, montmorillonitic, thermic Mollic Palexerafls)—Urban land complex with a clay loam texture (soil properties in Supplementary Table 1). Before incubation, rocks and visible litter were removed, and the soil was sieved through a 2 mm standard test sieve (Fisher Scientific Company, New Hampshire, USA) to homogenize its texture. The soil was sealed and stored at about 5 °C and incubated within six months of collection. Part of the soil samples was oven-dried at 60 °C until constant weight to calculate soil water content based on the weight loss.

Autoclaved soil preparation (Supplementary Fig. 4): To differentiate between microbial and abiotic geochemical processes on CH₃Br and CH₃Cl production and degradation¹², a parallel set of soil samples was autoclaved at 105 °C overnight to sterilize the soil microorganisms and enzymes.

Mineral soil preparation (Supplementary Fig. 4): To test the necessity of soil organic matter, a parallel set of soil samples had their organic matter content depleted using the loss-on-ignition method: oven-dried soil samples were sieved through a 2 mm mesh and then heated in a muffle furnace (Thermolyne™, Thermo Fisher Scientific, Massachusetts, USA) at 375 °C for 24 hours to combust the soil organic matter.

Incubation of soil samples. Experiment I (results are presented in Fig. 1): To examine the effect of Cu(II) on CH₃Br and CH₃Cl production, live, autoclaved, and mineral soil samples (50 g each, dry weight, same hereafter) were mixed with 10 mL of solution containing CuSO₄ at 0 mM (deionized water), 1.25 mM, 2.5 mM, 5 mM or 10 mM. The glass jars containing all these mixtures were sealed and situated in a thermostatted bath (circulating water and ethylene glycol mixture, VWR Model 1180S, Pennsylvania, USA) at 20 °C during the experiments. Incubations to determine CH₃Br and CH₃Cl fluxes started within 30 min after the mixture preparation, and followed the method as described in the section “Incubation and sampling” below. Each treatment was conducted twice ($n = 2$).

Experiment II (results are presented in Fig. 2): To examine the combined effect of Cu(II) and H₂O₂ on CH₃Br and CH₃Cl production, live and autoclaved soil samples (50 g each) were incubated in glass jars under four different treatments. (i) soil samples were mixed with 20 ml of deionized water; (ii) soil sample was mixed with 10 ml of deionized water and 10 ml of H₂O₂ at 50 mM; (iii) soil sample was mixed with 10 ml of deionized water and 10 ml of CuSO₄ at 50 mM; (iv) 10 ml each of H₂O₂ at 50 mM and CuSO₄ at 50 mM were added into the soil samples. Incubations to determine CH₃Br and CH₃Cl fluxes started within 30 min after the mixture was completed, and followed the method described in the section “Incubation and sampling”. Each treatment was conducted twice ($n = 2$).

Experiment III (results are presented in Fig. 3): To explore the persistence of the Cu(II) effect and to find out if a potential photochemical pathway involving ambient sunlight exists, a time-series light vs. dark experiment was conducted as follows.

Two groups of soil samples (50 g each) were mixed with 10 ml 50 mM CuSO₄ first in sealed glass jars and then incubated under dark and ambient sunlight conditions, respectively. Sunlight treatment was accomplished by exposing the glass jars under ambient sunlight on the roof of a building (10:00–17:00 PDT, July in 2021, 37°52′26″N 122°15′35″W). To account for the potential effect of temperature associated with sunlight exposure, the temperature within the light glass jars was measured in the beginning and the end of the experiment; then the dark glass jars were incubated at the same temperature as the immediate prior light experiments by situating in a temperature-controlled thermostatted bath (circulating water and ethylene glycol mixture, VWR Model 1180S, Pennsylvania, USA).

Prior to headspace air sampling, the glass jars were vented and flushed with ambient air for 1 min. After sealing the jars, 20 ml of headspace air was drawn into a glass syringe with Teflon plunger (SampleLok, Hamilton, Reno, Nevada, USA) and stainless steel needle through a septum on the cover of the glass jars at 30 min intervals for three samplings⁵². Sample storage time in the syringe was less than 5 min. The air samples were cryotrapped and then cryo-focused prior to injection into a gas chromatograph-mass spectrometer (Agilent 6890 N/5973, Agilent Technologies, California, USA) for CH₃Br and CH₃Cl analysis^{8,53}.

Each of these treatments was repeated three times ($n = 3$). The incubations for the dark experiment lasted for 8 days while the light experiment lasted for 17 days, until negative CH₃Cl fluxes were finally observed. The solar radiation strength, such as, UVA ($\lambda = \sim 320\text{--}390$ nm), UVB ($\lambda = 265\text{--}322$ nm), and photosynthetic active radiation (PAR, $\lambda = 410\text{--}655$ nm), was also measured by UVA/UVB/PAR-BTA sensors (Vernier Inc., Beaverton, Oregon, USA) inside the glass jar in the sunlight experiments (Supplementary Table 2). Before the start of the experiment, parallel soil samples were mixed with 10 ml deionized water and incubated as controls.

Model substance reactions

Chemicals. The following chemicals were used in the model substrate experiments: catechol, C₆H₄(OH)₂ ($\geq 99\%$, Sigma-Aldrich); guaiacol, C₆H₄(OH)(OCH₃) ($\geq 99\%$, Sigma-Aldrich); potassium chloride, KCl ($\geq 99.0\%$, Sigma-Aldrich);

potassium bromide, KBr ($\geq 99.0\%$, Sigma-Aldrich); hydrogen peroxide, H₂O₂ (35%, Acros Organics, Thermo Fisher Scientific); copper(II) sulfate, CuSO₄ ($\geq 99.99\%$, Sigma-Aldrich).

All the chemicals above were prepared as solutions with deionized water (Ultra-pure type I, ChemWorld, Utah, USA) and stored in volumetric flasks. Catechol and guaiacol were configured at 10 mM (millimole per liter; same hereafter); KBr and KCl were configured at 20 mM; CuSO₄ and H₂O₂ were configured at 50 mM.

Incubation of model substances. Experiment IV (results are presented in Supplementary Fig. 1): Control experiments were conducted with a mixture of 10 ml of 10 mM catechol, 20 ml water and 10 ml of 20 mM KBr (Br-control) for CH₃Br studies or 20 mM KCl (Cl-control) for CH₃Cl studies.

In order to investigate the response of CH₃Br and CH₃Cl formation to varied oxidizing environments, 10 ml of 50 mM CuSO₄ solution was first added to a set of parallel control mixtures (both Br-control and Cl-control), after which, 10 ml of H₂O₂ solution at 0 mM (deionized water), 10 mM, 20 mM, 30 mM, 40 mM or 50 mM were added into the mixture for incubation.

In order to investigate the response of CH₃Br and CH₃Cl formation to varied amount of Cu(II) addition, 10 ml of 50 mM H₂O₂ was first added to a set of parallel control mixtures (both Br-control and Cl-control), after which, 10 ml of CuSO₄ at 0 mM, 10 mM, 20 mM, 30 mM, 40 mM or 50 mM were added into the mixture for incubation.

All the aforementioned mixtures were incubated to determine CH₃Br and CH₃Cl fluxes following the method as described in the section “Incubation and sampling” below. Each of the incubation treatments was conducted twice ($n = 2$).

Experiment V (results are presented in Supplementary Fig. 3):

Effect of solar radiation: The potential role of solar radiation was tested as follows: 10 ml each of 10 mM catechol and 20 mM KCl was mixed in a sealed glass jar. Subsequently, 10 ml of 50 mM CuSO₄ was added. The mixture was exposed under sunlight for three hours (12:00–15:00 PDT, 2019/10/23, 37°52′26″N 122°15′35″W, Supplementary Table 3) and then brought indoors to the laboratory for incubation to get CH₃Cl fluxes. For comparison, the same mixture without sunlight exposure was also incubated.

Reactions with guaiacol: In the presence of Fe(III), the methoxy group of guaiacol can undergo nucleophilic attack by chloride to produce CH₃Cl, without needing sunlight or microbial mediation¹². To determine if Cu(II) behaved similarly to Fe(III) in this known pathway, two additional sets of experiments were conducted with 10 ml each of either 10 mM guaiacol or 10 mM catechol, 20 mM KCl, and 50 mM CuSO₄.

All the aforementioned mixtures were incubated following the method as described in the section “Incubation and sampling” below, from which CH₃Cl fluxes were determined. Each treatment was conducted twice ($n = 2$).

Seawater sample reactions

Seawater sample preparation. Unfiltered seawater samples were collected from the San Francisco Bay (37°51′45″N 122°18′50″W) using glass jars ($V = 1.9$ L, Ball Corporation, California, USA). The jars were previously acid washed and then rinsed with deionized water, ethanol, and acetone to ensure purity. Samples were stored at 5 °C after collection, prior to the testing.

Incubation of seawater. Experiment VI (results are presented in Fig. 4): Seawater incubations consisted of 500 ml samples in glass jars, subjected to the following 4 treatments: dark control ($n = 2$), sunlight control ($n = 5$), dark Cu(II) addition ($n = 4$), and sunlight Cu(II) addition ($n = 7$). The dark control experiment entailed storing the sample unsealed for 1.5 h in a dark environment. The sunlight control experiment entailed storing the sample unsealed for 1.5 h under ambient light (noontime, sunny day). The Cu(II) experiments entailed the addition of 0.3 mg CuSO₄ to the seawater, which were mixed and dissolved in the solution, before situating under dark or light conditions. Immediately following the above treatments, all the seawater samples were sealed for a closed headspace and incubated following the method described in the section “Incubation and sampling”.

Incubations and halocarbon analysis

Incubation and sampling. For all incubations (except for experiment III), the soils, seawater, or chemical mixtures were first mixed well in glass jars and then situated in a thermostatted bath (circulating water and ethylene glycol mixture, VWR Model 1180S, Pennsylvania, USA) at 20 °C. The jars were sealed with a stainless steel lid and Viton gasket and connected to a previously-evacuated stainless-steel loop (14.5 mL, which served as a sampling volume. The sample valve is at the top of the jar while the samples are at the bottom. The initial headspace was filled with ambient air, either outdoor air or laboratory air. Headspace air samples from the jars were drawn into the sampling loop at 30 min intervals, and then drawn through a cryotrap, followed by desorption, cryofocusing, and injection into a gas chromatograph-mass spectrometer (Agilent 6890N/5973, Agilent Technologies, California, USA) for CH₃Br and CH₃Cl analysis^{8,53}.

Flux calculation. CH₃Br and CH₃Cl fluxes from the samples were calculated based on the hourly averaged change of headspace concentration multiplied by moles of headspace air⁵, and normalized to the dry mass of the soil ($\text{ng kg}^{-1} \text{hr}^{-1}$) or the

volume of the seawater ($\text{ng L}^{-1} \text{hr}^{-1}$); or were reported as the total mass of CH_3Br and CH_3Cl produced in pure chemical experiments (ng). Positive fluxes represented production of CH_3Br and CH_3Cl while negative fluxes represented consumption of CH_3Br and CH_3Cl from the headspace air. At least two ($n \geq 2$) incubations were conducted for each treatment of the soils, seawater, and chemical mixtures.

Calibration. Weekly calibration curves were constructed using whole ambient air standards collected at Niwot Ridge, Colorado, and calibrated at the Global Monitoring Division Laboratory of the National Oceanographic and Atmospheric Administration. Each calibration curve was made up of 10–18 data points by trapping various volumes of standard gas to capture the full range of chromatogram peak areas observed in the samples. The daily drift of instrumental signals was also corrected using multiple daily runs of the same standard⁸. The averaged instrumental precisions for CH_3Br and CH_3Cl after applying drift corrections were 1.9% and 1.0%, respectively⁸. Using the precision estimates, ambient concentrations, and sample size, the minimum detectable fluxes from soils were about $\pm 0.02 \text{ ng kg}^{-1} \text{ hr}^{-1}$ for CH_3Br and $\pm 0.58 \text{ ng kg}^{-1} \text{ hr}^{-1}$ for CH_3Cl .

Data availability

The authors declare that the data generated or analyzed in this study are available within the paper and its supplementary information files. Source data for figures are provided at the Zenodo repository (<https://doi.org/10.5281/zenodo.5706329>).

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Author contributions

Y.J. and R.C.R. conceived of this study with preliminary experiments conducted by J.Y.K. and J.V.; Y.J., W.Z. and J.Y.K. carried out the main experiments; W.Z., M.J.D. and R.C.R. provided essential insight in data interpretation; Y.J. wrote the manuscript with inputs from all authors.

Competing interests

The authors declare no competing interests.

Additional information

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