1 # Abiotic formation of methyl iodide on synthetic birnessite: A

2 # mechanistic study

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1 **Abstract**
2 Methyl iodide is a well-known volatile halogenated organic compound that contributes to the
3 iodine content in the troposphere, potentially resulting in damage to the ozone layer. Most
4 methyl iodide sources derive from biological activity in oceans and soils with very few abiotic
5 mechanisms proposed in the literature. In this study we report that synthetic manganese oxide
6 (birnessite δ–MnO_2) can catalyze the formation of methyl iodide in the presence of natural
7 organic matter (NOM) and iodide. Methyl iodide formation was only observed at acidic pH (4
8 – 5) where iodide is oxidised to iodine and NOM is adsorbed on δ–MnO_2. The effect of
9 δ–MnO_2, iodide and NOM concentrations, nature of NOM and ionic strength was
10 investigated. High concentrations of methyl iodide were formed in experiments conducted
11 with the model compound pyruvate. The Lewis acid property of δ–MnO_2 leads to a
12 polarization of the iodine molecule, and catalyzes the reaction with natural organic matter. As
13 manganese oxides are strong oxidants and are ubiquitous in the environment, this mechanism
14 could significantly contribute to the global atmospheric input of iodine.
15

16 **Keywords: Methyl iodide, manganese oxide, natural organic matter, iodine, iodide,**

17 **ozone depletion, volatile halogenated organic compound, atmospheric iodine.**

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1. Introduction

Iodoalkanes, such as methyl iodide are volatile compounds that participate in the depletion of ozone in the atmosphere (Davis et al., 1996; Solomon et al., 1994). Methyl iodide was first analysed in seawater and air in the early seventies by Lovelock et al. (1973), and was found to be the most abundant iodo-organic compound in the atmosphere (Sive et al., 2007). It was therefore suggested to be responsible for the transfer of iodine from the ocean to the atmosphere, and the subsequent destruction of the ozone layer. Alkyl iodides contribute to the pool of volatile halogenated organic compounds, and participate in the tropospheric chemistry of iodine as a source of iodine radicals and other reactive iodine species, such as HOI and HI (see Table S1 for list of acronyms) (Carpenter et al., 1999).

The major source of iodoalkanes in the environment is considered to be from oceans (Saiz-Lopez et al., 2012; Smythe-Wright et al., 2006). Nanograms to micrograms per gram of dry algae per day is the estimated release rate for volatile halogenated organic compounds in the ocean (Gschwend et al., 1985), with concentrations of alkyl iodide in air near oceanic region up to 10-20 pptv due to the high biomass productivity (Rasmussen et al., 1982). However, terrestrial sources of methyl iodide were also identified e.g. volcanic emissions (Jordan et al., 2000), rice fields (Redeker et al., 2000) and peat bogs (Dimmer et al., 2001). A 3 year study conducted in the US estimated the terrestrial flux to be comparable to the oceanic flux, with a contribution of 900 ± 1100 ng m^{-2} d^{-1} from the vegetation, and a contribution of 500 ± 400 ng m^{-2} d^{-1} from the soil (Sive et al., 2007). Yokouchi et al., 2012, reported that the long-term variation of atmospheric methyl iodide was link to global environmental changes like sea surface temperature. However, few abiotic mechanisms, which are probably of minor contribution, have been proposed for the formation of alkyl iodides in the environment. Photochemical formation of methyl iodide by sunlight was suggested to occur through the

1 formation of methyl radical and iodine (Moore and Zafiriou, 1994). An abiotic mechanism

2 was also proposed in soils and involved the oxidation of natural organic matter (NOM) by

3 ferric oxide, followed by nucleophilic substitution of iodide (Keppler et al., 2000). Formation

4 of methyl, ethyl, propyl and butyl iodides were observed from soils organic matter. Model

5 compounds such as guaiacol (2-methoxyphenol) and catechol (1,2-hydroquinone) are

6 oxidized by iron oxyhydroxide producing, in the presence of iodide, methyl iodide (Keppler

7 et al., 2003). Methoxy, ethoxy or propoxy groups within natural organic matter produce

8 methyl iodide, ethyl iodide and propyl iodide, respectively. A recent study showed the

9 formation of methyl iodide when iodide-containing waters are in contact with a natural

10 manganese oxide. Nevertheless, the mechanism of methyl iodide formation remains unclear

11 (Allard et al., 2010).

12

13 Manganese is the tenth most abundant element in the earth's crust and the second among the

14 heavy metals (after iron). Similar to iron oxides, manganese oxides are widely distributed as

15 suspended particles in surface waters, and constitute cements and coatings in soils and

16 sediments. In the ocean, they are present as ferromanganese nodules, the main Mn-bearing

17 phase being birnessite ($\delta-MnO_2$) (Burns and Burns, 1979). Manganese oxides contribute to

18 the oxidation of natural organic matter and xenobiotic organic compounds (Stone and

19 Morgan, 1984a; Stone and Morgan, 1984b; Wang and Burau, 1995). Oxidation of humic

20 substances by manganese oxides produces low molecular weight organic compounds such as

21 pyruvate, formaldehyde and acetaldehyde (Sunda and Kieber, 1994). In the presence of

22 iodide, manganese oxide could then catalyze the formation of alkyl-iodides through the

23 oxidation of NOM, as it was shown for acidic organic rich soils spiked with ferric iron

24 (Keppler et al., 2000).

1   The redox potential of manganese oxide is higher than that of ferric iron. The comparison of

2   the thermodynamic data of the manganese and iodide systems (see half-reactions and redox

3   potentials below) and recent studies (Allard et al., 2009; Fox et al., 2009) show that iodide is

4   oxidized by MnO_2 for pH values below $6.5 - 7.0$:

5   $$MnO_2 + 4H^+ + 2e^- \rightleftharpoons Mn^{2+} + 2 H_2O \qquad E^{\circ}_H = 1.23 \text{ V}$$

6   $$I_2 + 2e^- \rightleftharpoons 2I^- \qquad E^{\circ}_H = 0.615 \text{ V}$$

7   $$IO_3^- + 6H^+ + 5e^- \rightleftharpoons 3H_2O + \tfrac{1}{2} I_2 \qquad E^{\circ}_H = 1.196 \text{ V}$$

8

9   When MnO_2 is in excess, iodate is the final product. Iodine (I_2) at acidic pH and hypoiodous

10 acid (HOI) at mid alkaline pH values are well known halogenating agents which contribute to

11 the incorporation of iodine atoms within macromolecular organic matter, and to the formation

12 of specific iodinated compounds such as iodoform (Bichsel and von Gunten, 2000; Gallard et

13 al., 2009). One can assume that this reaction, which was not reported when the electron

14 acceptor was ferrihydrite, can also constitute a second mechanism and contributes to the

15 terrestrial emission of methyl iodide. Here, we report a mechanistic study where manganese

16 oxide catalyzes the production of methyl iodide at acidic pH through the oxidation of iodide

17 into iodine and the reaction of iodine with natural organic matter.

18

19 **2. Materials and methods**

20 *2.1 Materials*

21 A concentrated suspension of manganese oxide (18 g L^{-1}) was prepared according to Murray

22 (1973) (see (Gallard et al., 2009)). The concentration of the stock $\delta-MnO_2$ suspension was

23 measured by the spectrophotometric determination of manganous ion (Brewer and Spencer,

24 1971) after the total reduction of $\delta-MnO_2$ by ascorbic acid. The stoichiometry of the

25 manganese oxide determined by iodometric titration was $MnO_{1.89}$ (Murray et al., 1984). The

1   BET surface determined using N_2 as adsorbat was 140 m^2 g^{-1}. Using X-ray diffraction, the

2   following d-spacing: 7.14, 3.57 and 2.15 Å were all consistent with the mineral birnessite.

3   Stock solution of iodine (500 µM) was prepared from sublimated iodine and was standardized

4   by thiosulfate titration.

5   Suwannee River hydrophobic acid (SR HPOA) fraction was used as reference material for

6   natural organic matter. The hydrophobic acid fraction was chosen as a surrogate for NOM

7   because it is generally the largest fraction in natural waters. Five other NOM isolates were

8   extracted according to the XAD resins protocol (Leenheer and Croue, 2003) during previous

9   studies and were also tested for the formation of methyl iodide. The name, origin and specific

10   UV absorbance at 254 nm are given in Table 1. Hydrophobic to hydrophilic fractions with

11   different aromaticity were tested. The specific UV absorbance at 254 nm varied from 1.4 L

12   mgC^{-1} m^{-1} for Colorado River hydrophilic fraction to 4.6 L mgC^{-1} m^{-1} for Suwannee River

13   HPOA fraction.

14

15   Experiments were also conducted using three model compounds: phenol (pKa = 9.95), 2-

16   methoxyphenol (guaiacol) (pKa = 9.93) and pyruvic acid (pKa = 2.48). Phenolic compounds

17   are usually considered as monomeric constituents of humic materials. Pyruvic acid is

18   produced through the catalytic oxidation of NOM by metal oxides (Sunda and Kieber, 1994)

19   and is also released in sediments by biological activity (Sansone, 1986). Guaiacol was the

20   model compound used for the formation of methyl halide with ferrihydrite and iodide

21   (Keppler et al., 2000).

22

23   *2.2 Experimental procedures*

24   The reaction was initiated by the addition of a solution of iodide in a suspension of $\delta-MnO_2$

25   pre-equilibrated with organic matter fraction for 2-3 minutes. Initial concentrations of

1 δ–MnO$_2$, iodide and NOM varied in the range 0.01 – 15 g L^{-1}, 3.9 – 390 μM (0.5 – 50 mg/L)

2 and 0.5 – 50 mgC L^{-1}, respectively. The pH was controlled with NaOH and HClO$_4$ solutions

3 then 40 mL vials were filled without headspace to prevent the loss of volatile iodinated

4 organic compounds and sealed with PTFE-faced silicone septa. Vials were set on a rotary

5 tumbler for agitation at 25°C. Samples were withdrawn with a 50 mL gas syringe and filtered

6 using 0.2 μm membrane filter (Minisart, diameter 25 mm) to remove δ–MnO$_2$ before

7 analysis. Experiments were performed in perchlorate media because the perchlorate ion is less

8 likely than other ions to form complexes with metal surfaces and with iodine (Fox et al.,

9 2009). Adsorption of NOM was determined from the difference between DOC analysed in

10 NOM solutions before δ-MnO$_2$ addition and after filtration of δ–MnO$_2$ suspension.

11 Methyl halide formation from the three model compounds were conducted with the same

12 procedure but acetate buffer (10 mM) was used at pH 5.

13

14 *2.3 Analytical procedures*

15 Iodide analyses were carried out with an ion chromatography and conductimetric detection

16 after chemical suppression (Dionex AS3000). A Dionex® AS19 column (internal diameter: 4

17 mm; length: 250 mm) and a Dionex® AG19 guard column (internal diameter: 4 mm; length:

18 50 mm) was used with 50 mM NaOH as eluent at 30°C. The injection volume was 500 μL.

19 The detection limit was 5 μg L^{-1}. Error bars indicate the relative standard deviation (RSD) of

20 triplicate analysis.

21

22 Volatile alkyl-iodides were analysed using gas chromatography (model Varian 3300) with

23 headspace injection and electron capture detection. Separation of alkyl-iodides was carried

24 out on a J&W/DB 624 30 m x 0.53 mm. Nitrogen was used as carrier gas. The oven

25 temperature was set constant at 35°C for 20 min. Detector and injector temperatures were

1   300°C and 80°C, respectively. The headspace vials were equilibrated for 4 hours at 50°C

2   before injection. Methyl iodide was identified by comparison of the retention time from the

3   direct injection of a standard prepared in MeOH. Quantification of methyl iodide was

4   performed using external calibration standards. Stock standard solutions of methyl iodide

5   were prepared in methanol by introducing 100 µL of analyte into a 40 mL vial sealed with

6   PTFE-faced silicone septa and diluted to volume. Solutions were stored at -20°C in the dark.

7   Standard solutions were prepared in ultra-pure water. Detection limit for methyl iodide was

8   10 ng L^{-1}. The RSD for methyl iodide was 8% for 6 replicate experiments. The RSD was

9   calculated from standard experimental condition (i.e. $[I^-]_o = 7.87$ µM, $[MnO_2] = 0.5$ g L^{-1}, 5

10   mgC L^{-1} SR HPOA, $NaClO_4$ 10mM, pH 5, 24-hour contact time) used in 6 different sets of

11   experiments (i.e. influence of pH, iodide, MnO_2, NOM concentration and nature and ionic

12   strength). The same RSD of 8 % was considered for methyl iodide for all conditions.

13   Dissolved organic carbon (DOC) was analyzed in triplicate using a Shimadzu TOC Vcsh

14   analyzer. The detection limit was about 0.1 mgC L^{-1} and RSD was always below 3%.

15

16   **3. Results and discussion**

17   *3.1 Methyl iodide formation at acidic pH*

18   Kinetic experiments performed for an initial concentrations of iodide of 7.87 µM (1 mg L^{-1}), 5

19   mg C L^{-1} SR HPOA and 0.5 g L^{-1} (5.75 mM) δ–MnO_2 show that methyl iodide is formed at

20   pH 4.0 and pH 4.8 and no formation is observed at pH 6.8 (Figure 1a). Higher formation is

21   obtained at pH 4.0 compared to pH 4.8. Concentrations of methyl iodide range between 100

22   to 500 pmol L^{-1} (i.e. 20 to 75 ng L^{-1}) for contact times $\leq$ 7 hours. Methyl iodide is not detected

23   in absence of manganese oxides or in absence of iodide or natural organic matter. Ethyl iodide

24   and higher molecular weight iodoalcanes were also not detected in our conditions. At pH 4.8,

25   adsorption of organic carbon was about 3.0 mgC $gMnO_2^{-1}$ (Figure 1b). Similar results were

observed at pH 4.0. Equilibrium is immediately achieved because of the micrometric size of the manganese oxide particles. No significant adsorption is observed at pH 6.8 (Figure 1b), which was explained by electrostatic repulsions between negatively charged humic and fulvic acids (pKa value in the range 3-5) and manganese oxide surface (pH_{zpc} = 2.25, Murray (1973)).

Experiments performed in absence of NOM confirmed that iodide is rapidly oxidized to iodine and iodate by manganese oxide at pH range 5 - 6 (Allard et al., 2009; Fox et al., 2009). During iodide analysis, iodine rapidly hydrolyzes into iodide and hypoiodite in the 50 mM NaOH mobile phase. Disproportionation of hypoiodite being negligible, the analysis allowed the determination of the sum of iodide and reactive iodine species i.e. iodine at pH < 7 (see (Gallard et al., 2009)). At pH 4.8, iodide concentration decreased progressively as a function of reaction time, which indicates that iodide is oxidized to iodine and that iodine is converted to iodate and/or reacts with NOM by substitution reactions. At neutral pH, iodide oxidation is negligible because the values determined by ion chromatography remain almost constant after an immediate drop that is attributed to the rapid adsorption of iodide on manganese oxide.

The absence of NOM adsorption on synthetic birnessite and thus NOM oxidation explains the absence of methyl iodide formation at neutral pH according to the mechanism proposed by Keppler et al. (2000). However, the formation of methyl iodide at acidic pH when iodide is converted into iodine suggests that the formation of methyl iodide can also occur through the reaction of iodine with natural organic matter in presence of manganese oxide.

To validate the assumption that methyl iodide can be formed through the reaction of reactive iodine species with organic matter and to clarify the role of manganese oxide, iodine was directly added to a 5 mgC L^{-1} SR HPOA solution at pH 5.0 in the absence of $\delta-MnO_2$. For a low iodine concentration of 2 µM, no methyl iodide was detected after 24 hours contact time.

1 For the same conditions, methyl iodide formation was analysed at 250 pmol L^{-1} (about 35 ng

2 L^{-1}) for a high initial concentration of iodine of 80 μM, corresponding to a iodine residual

3 concentration of 60 μM after a contact time of 24 hours. Traces of methyl iodide can then be

4 formed through the direct reaction of iodine with NOM, but this formation is not

5 thermodynamically favoured because iodine is a poor electrophilic agent in absence of

6 catalyst and methyl iodide is not a good leaving group.

7

8 Experiments conducted in the same conditions showed that iodoform is formed at much

9 higher concentrations than methyl iodide (Gallard et al., 2009). Because thermal

10 decomposition of iodoform into methyl iodide and diiodomethane was observed during

11 SPME analyses for injection temperature $> 100°$ C (Frazey et al., 1998), it was then

12 hypothesized that low concentrations of methyl iodide could be formed during methyl iodide

13 analysis, even though the temperature of the transfer line and the injectors (80°C) are

14 relatively low. The analysis of 1 ppm aqueous iodoform standard did not allow the detection

15 of methyl iodide in our conditions, which confirmed that methyl iodide is not produced

16 through the decomposition of iodoform during analysis. We also verified that iodoform does

17 not decompose into methyl iodide when in contact with $\delta-MnO_2$. We, then, concluded that

18 manganese oxide catalyzes the reactions between NOM and iodine species resulting in the

19 formation of methyl iodide. Similar systems i.e. MnO_2/I^- or MnO_2/I_2 have been used for the

20 synthesis of iodinated organic compounds in organic chemistry (Le Bras et al., 2006).

21 Manganese oxide acts as a Lewis acid by receiving a pair of electron from iodine. This

22 electron withdrawing effect results of the polarization of the iodine molecule and favours the

23 electrophilic substitution. Active iodonium species I^+ i.e. HOI in aqueous solution could then

24 be produced as reactive intermediate that is further oxidized to iodate or reacts with natural

25 organic matter to produce iodinated organic compounds (Gallard et al., 2009). Activation of

1   iodine into iodine radical cation I_2^+ was also considered as possible reactive species in organic

2   synthesis (Stavber et al., 2008). Catalysts such as manganese oxide can also interact with

3   organic substrate (S-H) generating its radical cation (S-H$^+$), which after collapse with iodine

4   leads to iodinated substrate (S-I) (Stavber et al., 2008). Manganese oxide in excess also

5   continuously oxidises iodide released from oxidation reactions between reactive iodine

6   species and NOM. These different reactions show that the formation of iodinated organic

7   compounds in presence of catalyst can be a complex mechanism and that different pathways

8   can be considered for the formation of methyl iodide.

9

10 *3.2 Effect of iodide and $\delta-MnO_2$ concentrations*

11 Figure 2 and Figure 3 illustrate the influence of iodide and $\delta-MnO_2$ concentrations on the

12 production of methyl iodide, respectively. As expected, Figure 2 shows that the sum of iodide

13 and iodine analysed as iodide increases with increasing initial iodide concentration. It is

14 expected that reactive iodine species exposure is directly related to the initial concentration of

15 iodide, which explains that methyl iodide formation increases with the initial concentration of

16 iodide. Results in Figure 3 show that a different behaviour is observed when increasing

17 concentrations of $\delta-MnO_2$ are applied. Methyl iodide concentrations after 24 hours show a

18 maximum for $\delta-MnO_2$ concentrations of 0.5 and 1 g L^{-1} probably corresponding to the

19 highest reactive iodine exposure. Iodide analysis shows that the concentration of iodide +

20 iodine continuously decreased with increasing concentrations of $\delta-MnO_2$ because of the

21 conversion of iodide and iodine to iodate. For high concentrations of $\delta-MnO_2$ of 10 and 15 g

22 L^{-1}, iodide is rapidly oxidized to iodate (Allard al., 2009; Fox et al., 2009); only a small part

23 of reactive iodine species being converted to iodinated organic compounds. A similar

24 behaviour is observed for iodinated organic compounds formation with increasing chlorine

1 concentrations (Bichsel and von Gunten, 2000). Excess of chlorine oxidizes the reactive

2 iodine species into inactive iodate.

3

4 *3.3 Influence of concentrations and nature of natural organic matter*

5 Figure 4 illustrates the influence of organic matter concentrations on both methyl iodide

6 concentrations and the sum of iodide and iodine after 24-hour contact time. Results show

7 behaviour similar to the effect of $\delta-MnO_2$ concentrations i.e. that the methyl iodide

8 production exhibits a maximum (5 mgC L^{-1}) and then decreases when the concentration of

9 NOM increases. The concentration of I$^-$ + I$_2$ increases with increasing organic carbon

10 concentration for organic carbon concentration < 5 mgC L^{-1}. Adsorption of NOM on $\delta-MnO_2$

11 at acidic pH reduces the number of reactive sites for iodide and iodine oxidation into iodate.

12 For the same reason, it is expected that a very high concentration of NOM reduces the

13 adsorption i.e. the activation of iodine onto manganese oxide, which explains that the

14 concentration of methyl iodide decreases for organic carbon > 5 mgC L^{-1}. This results in

15 catalyst poisoning by natural organic matter.

16

17 Different NOM isolates were tested upon the production of methyl iodide. Results are

18 presented in Table 1 and methyl iodide concentration and organic carbon adsorption are

19 plotted in Figure 5 as a function of the specific UV absorbance at 254 nm. Results show that

20 the formation of methyl iodide increases slightly with increasing aromatic character of

21 organic matter isolates with a relatively good linear correlation (R^2 = 0.810). Organic carbon

22 adsorption also increases with the increasing aromatic character of NOM, which is in

23 agreement with the known reactivity of NOM with metal oxides (Gallard et al., 2009;

24 McKnight et al., 1992). For the two hydrophobic fractions, organic carbon adsorption is about

25 3.0 and 3.6 mgC gMnO$_2$$^{-1}$ whereas adsorption of the hydrophilic Colorado River fraction is

1   not significant. It is then interesting to notice that methyl iodide production per unit of

2   adsorbed organic carbon is much higher for the non aromatic, hydrophilic organic matter

3   fractions. The hydrophilic organic matter fraction is a better precursor for methyl iodide

4   formation. The high adsorption and subsequent oxidation of the hydrophobic fractions into

5   hydrophilic low molecular weight substrates (Sunda and Kieber, 1994) could then explain the

6   significant formation of methyl iodide from hydrophobic moieties. Residual iodide + iodine

7   species represents between 25 to 37% of the initial iodide concentrations and no correlation

8   has been determined with methyl iodide production or organic carbon adsorption. Iodide and

9   reactive iodine species concentration depends on the extent of NOM adsorption but also on

10   the oxidation and substitution reactions between reactive iodine species and NOM.

11

12   *3.4 Influence of ionic strength*

13   Figure 6 illustrates the effect of ionic strength (IS) on methyl iodide formation, organic

14   carbon adsorption and iodide residual. Ionic strength ranges from 0 (no $NaClO_4$ added) to 20

15   mM $NaClO_4$. Results show that methyl iodide concentrations analysed after 24-hour contact

16   time increases linearly with $I^{1/2}$. As expected, increasing ionic strength also strongly enhances

17   the adsorption of NOM on manganese oxide. Residual iodide concentration decreases with

18   increasing ionic strength, which can be attributed to the oxidation to iodate or the formation of

19   iodinated organic compounds. The second assumption is more likely because higher

20   formation of methyl iodide is observed. Moreover, the experiments conducted in absence of

21   organic matter showed that reactive iodine species were more stable and the rate of iodate

22   formation decreased when ionic strength increased (Allard et al., 2009). Calculation of mass

23   balance for the same experiments showed also that adsorption (i.e. activation) of reactive

24   iodine species on manganese oxide is enhanced when ionic strength increases. The increase of

1   both NOM and reactive iodine species adsorption on manganese oxide explained that methyl

2   iodide production increased with ionic strength.

3

4   *3.5 Formation of methyl iodide from model organic compounds*

5   The formation of methyl iodide from phenol, 2-methoxyphenol and pyruvic acid was studied

6   at pH 5.0 in acetate buffer (10 mM) for concentrations of model compounds, iodide and

7   manganese oxide of 0.5 mM, 1 mM and 5 mM, respectively. A blank experiment was also

8   carried out with acetate buffer in the same conditions but without model compound. After 24-

9   hour contact time, no significant formation of methyl iodide was observed for both phenol

10   and 2-methoxyphenol. High formation of about 7 nM (i.e. about 1 μg L^{-1}) of methyl iodide

11   was only analysed for pyruvic acid. The absence of methyl halide production from guaiacol

12   confirms that methyl halide production in presence of $\delta-MnO_2$ at pH 5.0 involves a different

13   mechanism than the mechanism proposed by Keppler et al. (2000) for ferric iron. The low

14   concentration of methyl iodide produced (~ 7 nM) compared to the high initial concentrations

15   of iodide and pyruvate indicates that the reaction is a minor pathway. Iodination of pyruvate

16   was shown to occur through the reaction of the enol form with iodine at the α position

17   (Albery et al., 1965). Hence, in basic conditions, halogenation of pyruvate leads to the

18   formation of trihalomethanes by the haloform reaction. In acidic conditions, it is known that

19   halogenation of carbonyl compounds yields monohalogenated α carbonyl compounds because

20   the electron density of the α carbon is reduced by the electron withdrawing effect of the

21   halogen atom (March, 1977). In our conditions, it is then expected that 1-iodopyruvate is

22   preferentially formed. Pyruvate was shown to be partially mineralized into acetic acid and

23   CO_2 by manganese oxides (Wang and Stone, 2006). Then, the main pathway for the oxidation

24   of 1-iodopyruvate would lead to the formation of iodoacetic acid. Alternative pathway is

25   proposed that would consist in the mineralization of iodopyruvate into CO_2, CO and methyl

1 iodide. The first step would be the formation of metal-organic complexes between Mn^{IV}

2 surface sites and both iodine and oxygen atom of iodopyruvate according to Figure 7.

3 Electron transfers between metal oxides and organic compounds would result of C-C bond

4 cleavage and release of methyl iodide.

5

6 The formation of methyl iodide from carbonyl compounds may also explain the relatively

7 high formation of methyl halide from the hydrophilic fractions of NOM compared to the

8 hydrophobic fractions, which are generally enriched in aromatic structures. However,

9 interpretations of methyl iodide formation from different NOM isolates are complicated by

10 the complex nature of NOM and the multitude of reactions that could occur on the manganese

11 oxide surface. For example, carbonyl compounds such as pyruvate can also be produced

12 through the oxidation of humic substances (rich in aromatic structures) by manganese oxide.

13 Further experiments with model compounds are required to clearly identify the pathways

14 leading to methyl iodide formation in presence of manganese oxide.

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18 **4. Conclusions**

19 In this study a new abiotic mechanism for the formation of methyl iodide is described. Unlike

20 previous research, we postulate that the mechanism involves the oxidation of iodide to iodine

21 by manganese oxide, followed by iodination of organic compounds and C-C bond cleavages

22 on the manganese oxide surface. Methyl iodide formation was investigated in suspensions of

23 manganese oxide, and was found to be highly dependent on the concentrations of manganese

24 oxide, iodide, organic carbon, as well as pH and ionic strength. Experiments with pyruvic acid

25 confirm the mechanism and suggest that methyl halide would be formed as a minor by-

1 product of the iodination reaction between methyl ketones and reactive iodine species. The

2 diverse functional group composition of different fractions of NOM and their varying

3 manganese oxide adsorption affinities also influence the extent of methyl iodide formation.

4 The process described in this study provides new insight into the terrestrial production of

5 methyl iodide by an abiotic mechanism. Given that manganese oxides are widespread in

6 soil/water and are powerful oxidants, they may contribute significantly to the methyl iodide

7 input from terrestrial sources and consequently to the pool of volatile halogenated organic

8 compounds in the atmosphere. Little is known about the relative proportions of methyl iodide

9 originating from biogenic processes and abiotic formation from soil or water. As a result, it is

10 difficult to extrapolate these findings to a quantitative flux of emission and associated field

11 measurements have to be performed to estimate the contribution of this chemical process to

12 the methyl iodide budget.

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1 **<u>Figure captions</u>**

2

3 Figure 1. Effect of pH on the formation of methyl iodide (a) and on the evolution of Corg and

4 iodine species (b) ($[I^-]_o$ = 7.87 µM, $[\delta-MnO_2]$ = 0.5 g L^{-1}, 5 mgC L^{-1} SR HPOA, $NaClO_4$ 10

5 mM)

6

7 Figure 2. Effect of iodide concentration on methyl iodide formation (5 mgC L^{-1} SR HPOA,

8 $[\delta-MnO_2]$ = 0.5 g L^{-1}, $NaClO_4$ 10 mM, pH 5.0, 24-hour contact time)

9

10 Figure 3. Effect of the concentration of manganese dioxide on methyl iodide formation

11 (5 mgC L^{-1} SR HPOA, $[I^-]_o$ = 7.87 µM, $NaClO_4$ 10 mM, pH 5.0, 24-hour contact time)

12

13 Figure 4. Effect of the concentration of NOM on methyl iodide formation

14 (SR HPOA isolate, $[I^-]_o$ = 7.87 µM, $[\delta-MnO_2]$ = 0.5 g L^{-1}, $NaClO_4$ 10 mM, pH 5.0, 24-hour

15 contact time)

16

17 Figure 5. Effect of aromaticity of NOM on methyl iodide formation and organic carbon

18 adsorption (5 mgC L^{-1}, $[I^-]_o$ = 78.7 µM, $[\delta-MnO_2]$ = 0.5 g L^{-1}, $NaClO_4$ 10 mM, 24-hour

19 contact time)

20

21 Figure 6. Effect of ionic strength on methyl iodide formation, carbon adsorption and the sum

22 of iodide and iodine species (5 mgC L^{-1}, $[I^-]_o$ = 7.87 µM, $[\delta-MnO_2]$ = 0.5 g L^{-1}, pH 5.0, 24-

23 hour contact time)

24

1   Figure 7. Proposed pathway for the iodination of pyruvate and formation of iodomethane
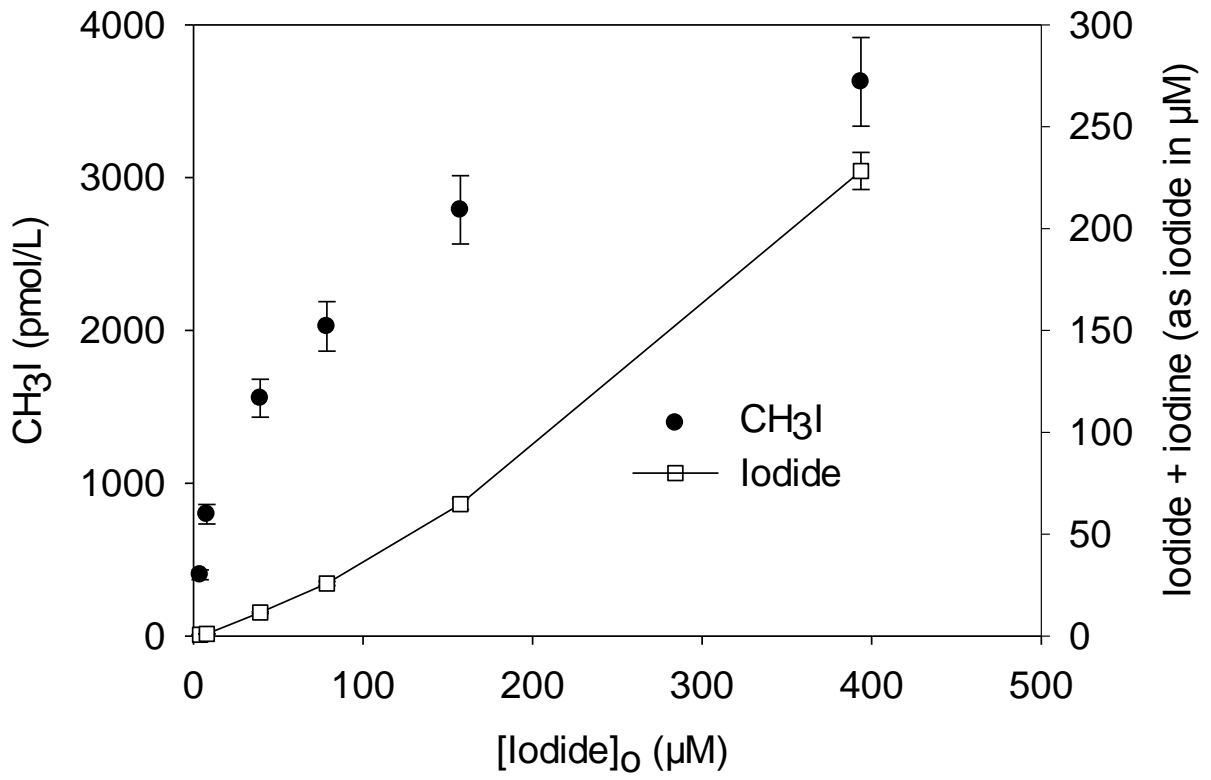
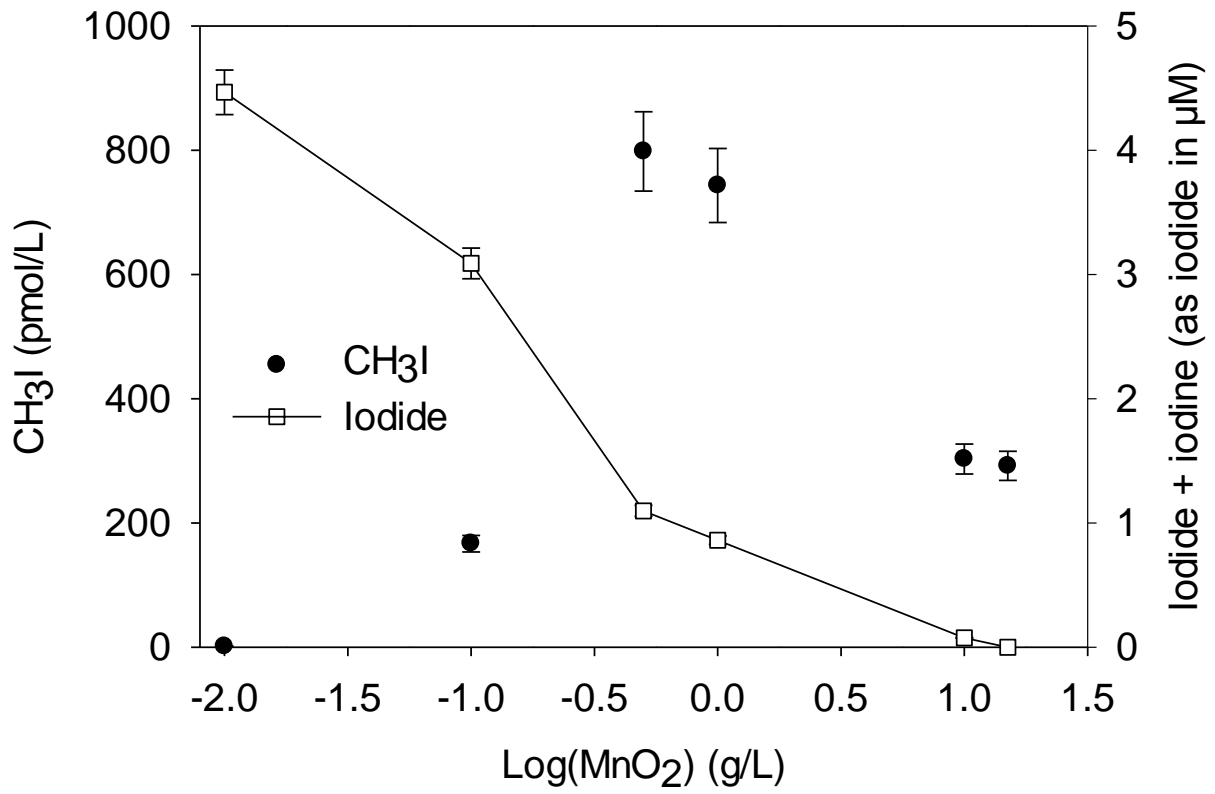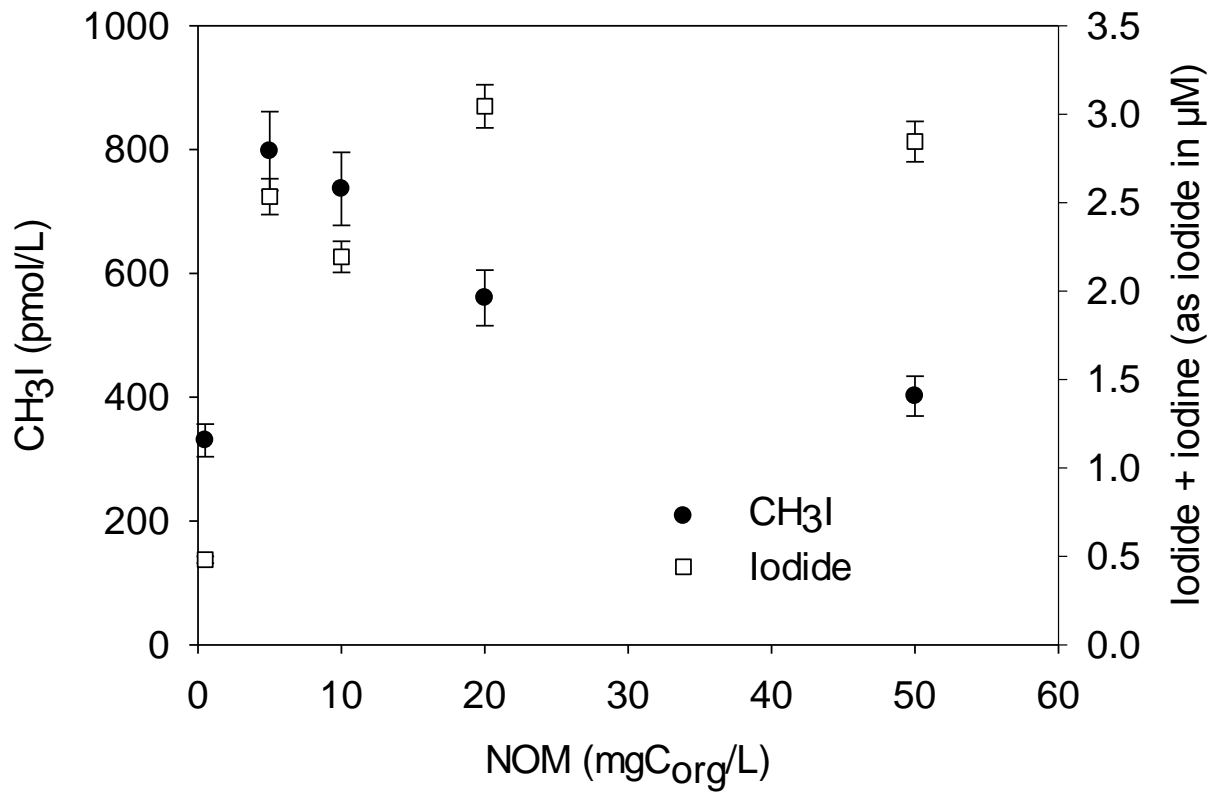2   catalyzed by MnO_2

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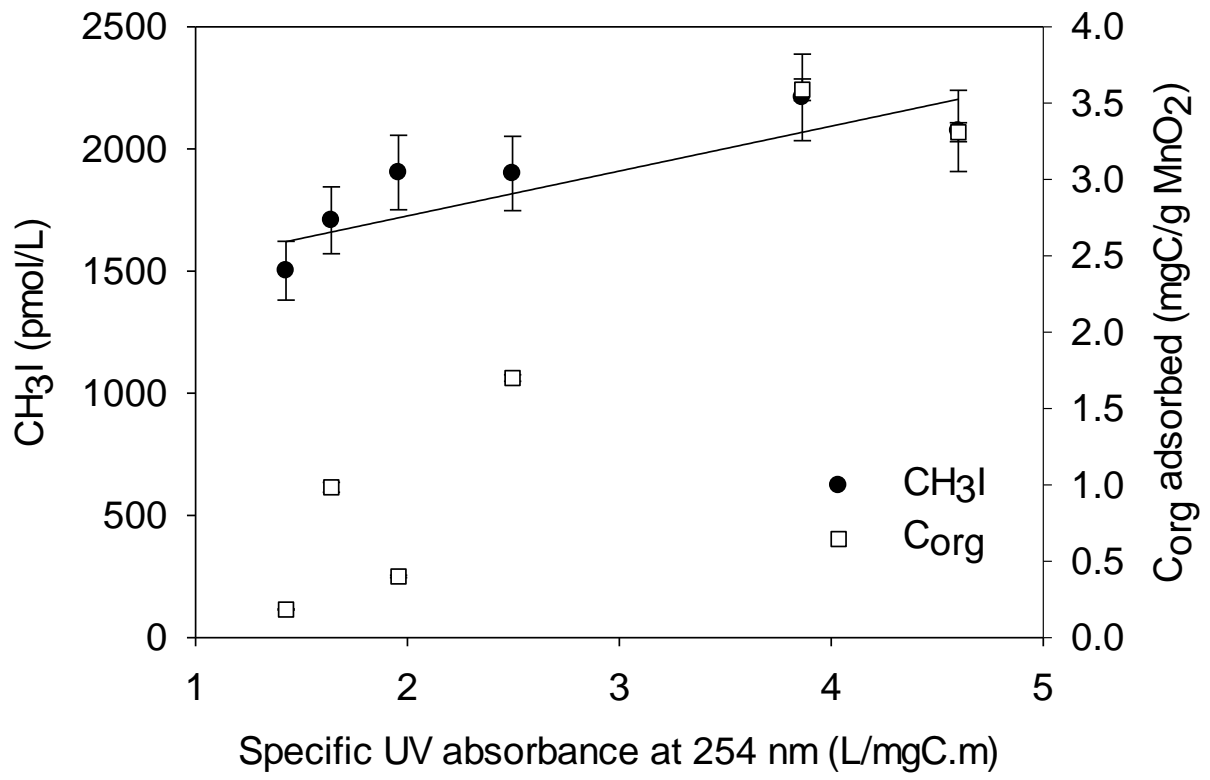1   Figure 1

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1   Figure 2
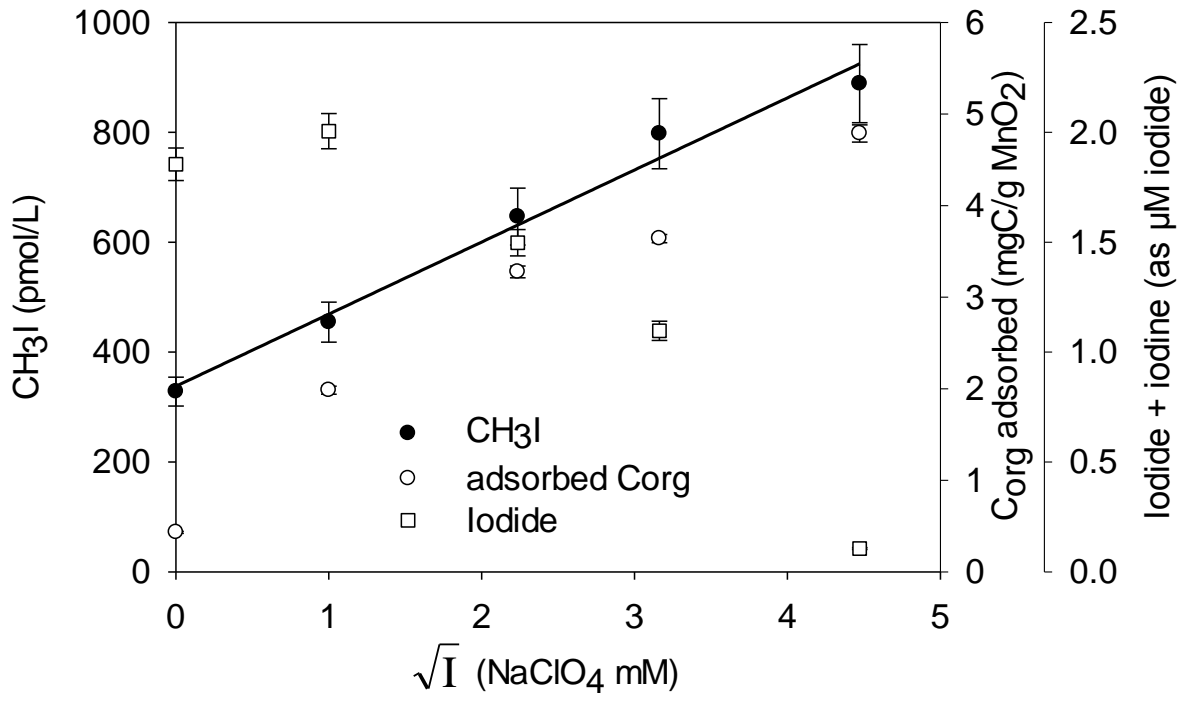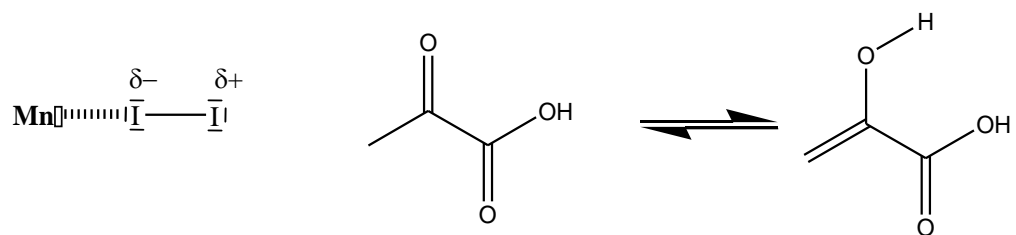
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1   Figure 3
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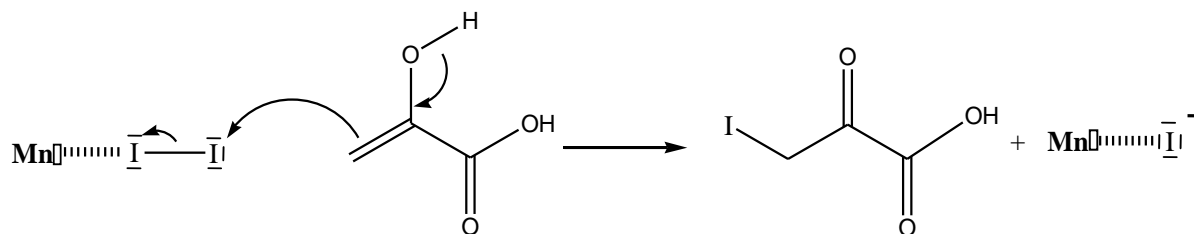

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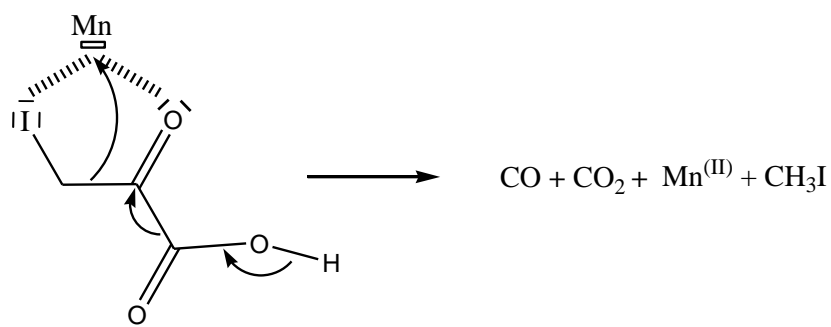1   Figure 4

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1   Figure 5
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1   Figure 7

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$$CO + CO_2 + Mn^{(II)} + CH_3I$$
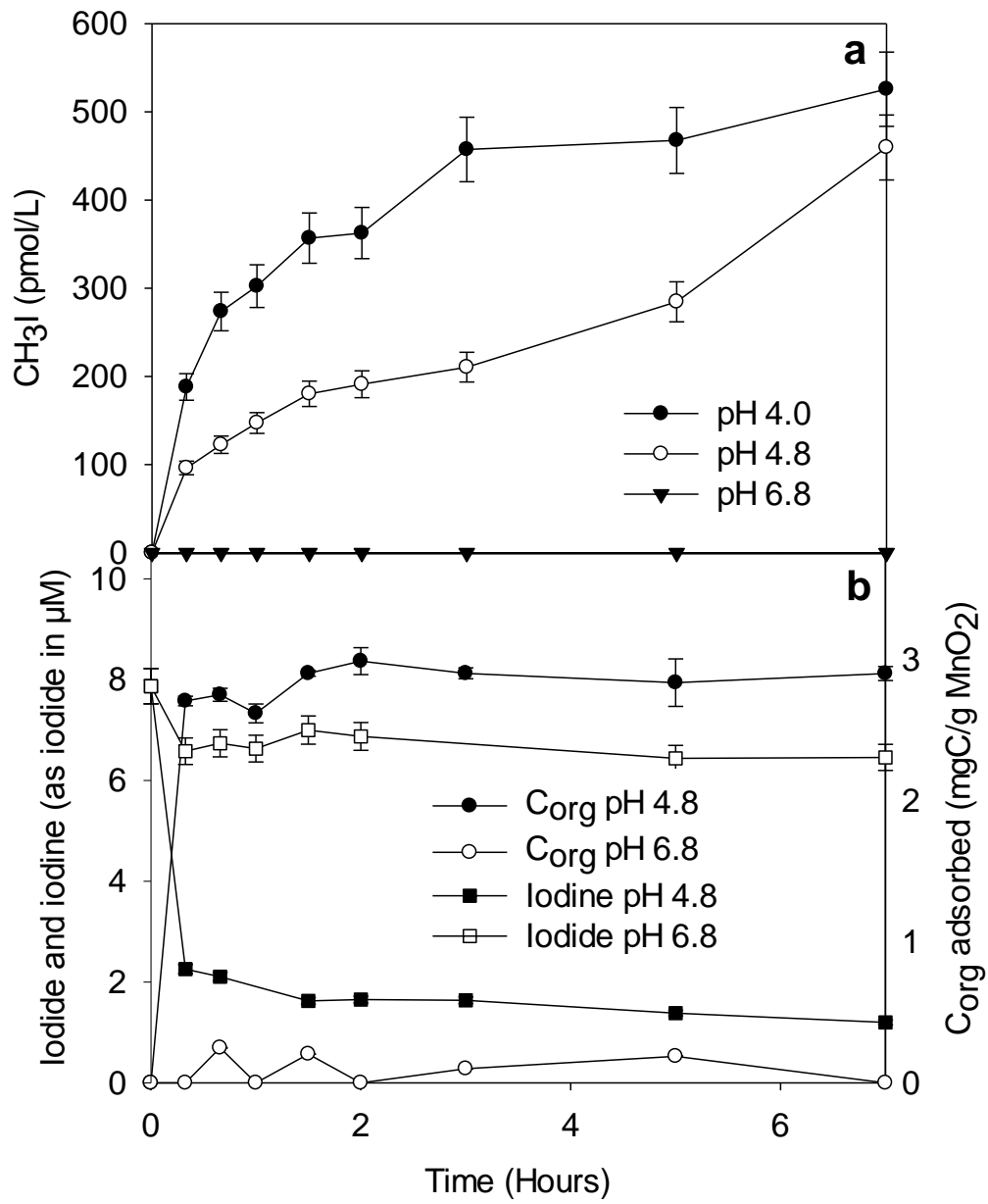
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5

1 Table 1. Characteristics of NOM fractions and methyl iodide formation, organic carbon

2 adsorption and residual I^- and I_2 species (5 mgC L^{-1}, $[I^-]_o$ = 78.7 μM,

3 $[\delta-MnO_2]$ = 0.5 g L^{-1}, NaClO$_4$ 10 mM, pH 5.0, 24-hour contact time)

Origin	Fraction	SUVA (L/m.mgC)	CH$_3$I (pmol/L)	I^- + I_2 (as μM I^-)	Corg ads. (mgC/g MnO$_2$)
Colorado River – US	HPI	1.4	1500	26.4	0.2
Loire River –France	HPI	1.6	1700	18.9	1.0
Loire River – France	TPI	2.0	1900	29.2	0.4
Moulin Papon Reservoir – France	HPOA	2.5	1900	22.0	1.7
Jau River – Brazil	HPO	3.9	2210	28.0	3.6
Suwannee River – US	HPOA	4.6	2070	25.7	3.0

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