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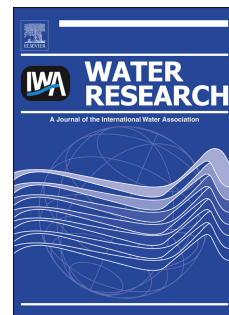
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Formation of methyl iodide on a natural manganese oxide**Sébastien Allard^a, Hervé Gallard^{a*}, Claude Fontaine^b, Jean-Philippe Croué^a****^a Laboratoire de Chimie et Microbiologie de l'Eau UMR CNRS 6008, ESIP – Université de Poitiers, 40 avenue du recteur Pineau 86 022 POITIERS Cedex****^b Laboratoire Hydrogéologie, Argiles, Sols et Altérations FRE CNRS 3114, Faculté des Sciences Fondamentales et Appliquées - Université de Poitiers, 40 avenue du recteur Pineau 86 022 POITIERS Cedex***** Corresponding author phone: (33) 5 49 45 44 31, email: herve.gallard@univ-poitiers.fr**

Abstract

This paper demonstrates that manganese oxides can initiate the formation of methyl iodide, a volatile compound that participates to the input of iodine into the atmosphere. The formation of methyl iodide was investigated using a natural manganese oxide in batch experiments for different conditions and concentrations of iodide, natural organic matter (NOM) and manganese oxide. Methyl iodide was formed at concentrations $\leq 1 \mu\text{g L}^{-1}$ for initial iodide concentrations ranging from 0.8 to 38.0 mg L⁻¹. The production of methyl iodide increased with increasing initial concentrations of iodide ion and Mn sand and when pH decreased from 7 to 5. The hydrophilic NOM isolate exhibited the lowest yield of methyl iodide whereas hydrophobic NOM isolates such as Suwannee River HPOA fraction produced the highest concentration of methyl iodide. The formation of methyl iodide could take place through the oxidation of NOM on manganese dioxide in the presence of iodide. However, the implication of elemental iodine cannot be excluded at acidic pH. Manganese oxides can then participate with ferric oxides to the formation of methyl iodide in soils and sediments. The formation of methyl iodide is unlikely in technical systems such as drinking water treatment i.e. for ppt levels of iodide and low contact times with manganese oxides.

Keywords: Manganese oxide, natural organic matter, iodide, methyl iodide

18

1 **1. Introduction**

2 Methyl iodide (CH₃I) was first analysed in seawater and air by Lovelock *et al.* (1973). In the
3 atmosphere, methyl iodide is photolysed to produce methyl radical (CH₃) and iodine atom (I),
4 which contributes to the natural iodine cycle. Methyl radical reacts with ozone and thus may
5 influence the ozone budget. The oceans would be the main source of methyl iodide through biotic
6 reactions mediated by microorganisms such as algae (Gschwend *et al.*, 1985). Laboratory studies
7 provided evidence that a wide variety of bacteria including terrestrial and marine bacteria are
8 capable of methylating low amount of iodide in the environment (Amachi *et al.*, 2001).

9 Only a few abiotic mechanisms have been proposed. An abiotic mechanism for the formation of
10 methyl iodide and other iodoalkanes (e.g. iodoethane, iodopropane,...) has been demonstrated in
11 soils and sediments containing natural organic matter (NOM), iodide (I⁻) and Fe(III) as electron
12 acceptor (Keppler *et al.*, 2000). Experiments conducted with model compounds gave evidence that
13 methoxy group could be responsible for the formation of methyl iodide. The mechanism involves
14 the oxidation of NOM by ferric iron followed almost simultaneously by the nucleophilic
15 substitution of the methyl group by iodide. The production of methyl iodide and other iodoalkanes
16 increases with the increase of iodide, NOM and ferric iron concentrations and when pH decreases.

17 Manganese oxides are widely distributed in the environment and participate with iron oxides to the
18 adsorption (Tipping and Heaton, 1983) and oxidation of NOM (Stone and Morgan, 1984; Chorover
19 and Amistadi, 2001). Manganese oxides are also known to oxidize phenols used as model
20 compound of complex NOM structures (Stone and Morgan, 1984). The oxidation of NOM by
21 manganese oxides results in the production of low molecular weight organic compounds e.g.
22 formaldehyde, acetaldehyde and pyruvate through adsorption and electron transfer (Sunda and
23 Kieber, 1994).

24 In ground waters, manganese is present as a form of soluble manganous ion species Mn^{II} at ppb to
25 ppm levels. Iodine can also be encountered in ground waters as iodide at ppt levels (about 0 to 100

1 $\mu\text{g L}^{-1}$) with increasing concentrations near sea coast (Fuge and Johnson, 1986). Manganese and
2 iodine are essential trace elements for human and small amounts from food or water is required to
3 stay healthy. However, manganese has to be removed from drinking water because its oxidation
4 products cause taste, odours and coloured water problems (Wong, 1984; Jaudon *et al.*, 1989).
5 Recent studies have reported links between excessive manganese exposure and neurologic
6 disorders in children (Bouchard *et al.*, 2007). The WHO guideline for this element in drinking
7 water is $400 \mu\text{g L}^{-1}$ (WHO, 2006) and a maximum concentration level of $50 \mu\text{g L}^{-1}$ in the European
8 Union. Manganous ion oxidation by oxygen is a slow process at neutral pH (Stumm and Morgan,
9 1996). Strong oxidants e.g. chlorine or ozone can be used but catalytic materials such as natural
10 manganese oxides or manganese oxide coated sands are preferred in some circumstances especially
11 for mineral waters when strong oxidants are prohibited. Removal of iron (White and Asfar-
12 Siddique 1997) and arsenic (Bissen and Frimmel, 2003; Ouyard *et al.*, 2005) can also be
13 performed with manganese oxides due to their relatively high redox potential. Manganese oxides
14 have also been proposed as an adsorbant for natural organic matter (NOM) (Bernard *et al.*, 1997)
15 and thus for the removal of DBP in drinking water production (Colthurst and Singer, 1982).
16 Manganese dioxide was recently shown to oxidize iodide to iodine and iodate (Fox *et al.*, 2009;
17 Allard *et al.*, 2009) as well as initiating the formation of iodinated organic compounds such as
18 iodoform (Gallard *et al.*, 2009). The use of manganese oxides for the treatment of iodide-
19 containing waters could also be responsible for the formation of iodoalkanes such as methyl iodide
20 in drinking waters. Even though methyl iodide has been recently approved as a soil fumigant by the
21 USEPA to control soils-borne diseases and pests, it is neurotoxic for humans and mutagenic to
22 bacteria and rats (IARC, 1999 and references therein). The International Agency for Research on
23 Cancer (IARC) classified methyl iodide in the group 3 (i.e. not classifiable as to its carcinogenicity
24 to humans) because there is no epidemiological data relevant to its carcinogenicity and there is
25 limited evidence for the carcinogenicity in experimental animals (IARC, 1999). However, methyl

1 iodide is considered to be a human carcinogen in Germany and California. To our knowledge,
2 methyl iodide has never been reported in drinking waters and no international guideline exists for
3 this compound in water.

4 The goal of this study was to demonstrate the possible formation of iodoalkanes mediated by
5 manganese dioxides. Because this study is of interest for both environmental and technical systems,
6 the experiments were carried out with a natural manganese oxide used in water treatment. The
7 kinetics formation of methyl iodide were followed using a variety of conditions to evaluate the
8 effect of different parameters e.g. pH, concentrations of reactants, nature of NOM.

10 **2. Material and methods**

11 *2.1 Manganese oxide*

12 The catalytic material was a natural manganese oxide (79% MnO₂) approved for drinking water
13 treatment. The material was rinsed with ultra pure water to eliminate the fines before experiments.
14 The selected size fraction was in the range of 300 – 700 μm. The specific density was 3.88.
15 Specific surface area determined by the BET method using N₂ as adsorbate was 26 m² g⁻¹.
16 Manganese sand was dry ground in an agate mortar before X-ray analysis. X-ray diffraction was
17 performed using a PANalytical Xpert Pro diffractometer operated under reflexion using a Cu
18 K_α radiation at a wavelength of 1,541838 Å. Three Mn minerals were identified: birnessite,
19 lithiophorite and cryptomelane (see X-ray diffractogram in Figure S1 in supplementary material).

20 *2.2 Natural Organic Matters (NOM)*

21 Six NOM isolates (Table 1) extracted and characterized from previous studies were used for
22 adsorption on manganese sand and formation of iodoalkanes. Details of the fractionation procedure
23 have been presented elsewhere (Leenheer, 1981; Croué *et al.*, 1999). The colloidal fraction was
24 isolated using 3,500 Da dialysis bag against HCl 0.1N and then HF 0.2N. The hydrophobic (HPO)
25 fractions refer to the NOM fractions recovered from the XAD-8 resin by elution with an

1 acetonitrile/water mixture; the hydrophobic acid (HPOA) and the transphilic (TPI) fractions refer
2 to the NOM fraction recovered by elution with NaOH from the XAD-8 and XAD-4 resins,
3 respectively. The hydrophilic fraction (HPI) refers to NOM fraction not adsorbed on both XAD-8
4 and XAD-4 resins. Solid samples of the NOM fractions were obtained by freeze-drying. The NOM
5 fractions were characterized by determination of their Specific UV Absorbance values at 254nm
6 (SUVA₂₅₄ = UV₂₅₄/mg/L of dissolved organic carbon (DOC)) and the % aromatic carbon content
7 determined using solid state ¹³C nuclear magnetic resonance (NMR) spectroscopy. ¹³C NMR
8 spectra of Jau River extracts were not determined but the origin and the specific UV absorbance
9 values of these extracts suggest that the aromatic carbon content was similar to the Suwannee River
10 HPOA fraction. The NOM extracts were chosen to describe a large range of properties from humic
11 like (hydrophobic with high aromatic carbon content e.g. Suwannee HPOA fraction) to non humic
12 like NOM (more hydrophilic with low aromatic carbon content e.g. Loire River HPI fraction).

13 *2.3 Experimental procedures*

14 The experiments were conducted at room temperature (20 ± 2°C) with solutions prepared with
15 ultrapure water produced with a Milli-Q water purification system (Millipore). All chemicals used
16 were reagent grade.

17 The reaction was initiated by the addition of a diluted solution containing NOM and/or iodide in 40
18 mL EPA vials sealed with PTFE-faced silicone septa containing a given mass of manganese sand.
19 Vials were filled without headspace to prevent the loss of volatile iodinated organic compounds
20 and were set on a rotary tumbler for agitation at 25°C in a thermostated room. At given time
21 intervals, a vial was taken and the solution was withdrawn with a 50 mL gas syringe and filtered
22 with 0.45µm membrane filter (Minisart, diameter 25 mm) before analysis. The use of the same
23 filtration procedure on standard solutions did not cause significant loss of iodoalkanes.
24 Experiments were performed in carbonate buffer at pH 7 and in perchlorate media at pH 5.

25 *2.4 Analytical procedures*

1 The identification of alkyl iodides was performed by using the headspace GC-MS technique on a
2 Varian CP3800 gas chromatograph coupled with a Varian 1200L mass spectrometer. The
3 separation was carried out on a VF5HS 30m x 0.25mm capillary column. Initial oven temperature
4 was set at 30°C for 5 minutes, then temperature increased to 150°C at 20°C min⁻¹. The vials were
5 shaken at 80°C with an incubation period of 10 minutes before injection.

6 Volatile alkyl iodides were analyzed using gas chromatography (model Varian 3300) with
7 headspace injection and electron capture detection. Separation of alkyl iodides was carried out on a
8 J&W/DB 624 30 m x 0.53 mm column. Nitrogen was used as carrier gas. The oven temperature
9 was set constant at 35°C for 20 min. Detector and injector temperatures were 300°C and 80°C,
10 respectively. The headspace vials were equilibrated for 4 hours at 50°C before injection.

11 Quantification of methyl iodide was performed using external calibration standards. Stock standard
12 solutions of methyl iodide were prepared in methanol by introducing 100 μ L of analyte into a 40
13 mL EPA vial sealed with PTFE-faced silicone septa and diluting to volume. Solutions were stored
14 at -20°C in the dark. Standard solutions were prepared in ultra pure water. Detection limit for
15 methyl iodide was 10 ng L⁻¹ and the relative standard deviations for 5 replicates were in the range
16 of 1 – 5%.

17 Iodide ion analyses were carried out with ion chromatography and conductometric detection after
18 chemical ion suppression (Dionex AS3000). A Dionex® AS19 column (internal diameter: 4 mm;
19 length: 250 mm) and a Dionex® AG19 guard column (internal diameter: 4 mm; length: 50 mm)
20 was used with 50 mM NaOH as mobile phase at 30°C. The injection volume was 500 μ L. The
21 detection limit was 5 μ g L⁻¹.

22 Dissolved organic carbon was analyzed using a Shimadzu TOC Vcsh analyzer. The detection limit
23 was about 0.1 mgC L⁻¹.

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3. Results and discussion

3.1 Identification of volatile iodoalkanes

Both methyl iodide and ethyl iodide were identified by GC/MS when manganese sand was added to solutions containing both NOM and iodide (see Figure S2). However, ethyl iodide was only detected at trace levels and was not quantified. Keppler *et al.* (2003) also reported that methyl iodide was the main iodoalkanes produced from humic acids and the formation of high molecular weight iodoalkanes such as propyl and butyl iodide was significant for soil organic matter only. The different nature of organic matter (i.e. solubility, molecular weight, aromatic content and concentration of methoxy aryl group) between soils and surface waters is probably responsible for this finding. Keppler *et al.* (2000) also observed the formation of methyl bromide and methyl chloride in presence of ferrihydrite. The formation of these compounds was not investigated in the present study but it can be expected that manganese oxides could also catalyse the production of these compounds.

3.2 Influence of NOM, manganese sand and iodide concentrations at pH 7

The Figure 1 illustrates the influence of NOM, manganese oxide and iodide concentrations on the formation kinetics of methyl iodide for reaction times up to 120 hours. Concentrations range of methyl iodide varied between a few ng L^{-1} to about $1 \mu\text{g L}^{-1}$. The rates of formation increased with increasing the initial concentrations of manganese sand and iodide. However, for reaction times higher than 60 hours, increasing Mn sand concentrations did not necessarily lead to an increase in methyl iodide formation (Figure 1a). Further experiments conducted with aqueous standard solutions showed that methyl iodide slowly disappears on Mn sand, which could explain the behaviour observed over a long time scale for high concentrations of Mn sand. Methyl iodide is a good methylating agent of carboxylic acids in alkaline solution where carboxylate acts as the

1 nucleophile in the S_N2 substitution reactions (Avila-Zarraga and Martinez, 2001). Same reactions
 2 occur with phenols. These reactions were identified as the predominant pathway through which
 3 methyl iodide was degraded in presence of organic matter in soils (Gan and Yates, 1996). The
 4 DOC analysed after filtration in the absence of SR HPOA was 2.05 ±0.37 mgC L⁻¹ i.e. 0.14 ±0.02
 5 mgC g⁻¹ MnO₂, which explain the significant formation of methyl iodide observed for this
 6 condition (Figure 1c). The formation of methyl iodide increased with increasing the concentrations
 7 of NOM from 0.5 to 20 mgC L⁻¹ but lower final yield was observed for high DOC of 50 mgC L⁻¹.
 8 Sunda and Kieber (1994) showed that a maximum in production rate of low molecular weight
 9 compounds by manganese oxides was also achieved when all of the adsorption sites are saturated.
 10 A decrease in production rate could even be expected at very high NOM concentrations through
 11 direct competition for active sites and pore blockage. These data support the model of Keppler *et*
 12 *al.* (2000) for the formation of iodoalkanes through the oxidation of NOM by an electron acceptor.
 13 The initial rates of methyl iodide production calculated from the first data point were found to be
 14 linearly proportional to the concentrations of iodide and Mn sand (Figure 2). The overall
 15 production rate for 5 mgC L⁻¹ of NOM was 8.62 x 10⁻⁴ nmol h⁻¹ g⁻¹ Mn sand mg⁻¹ I. A similar
 16 approach was used for the experiments performed with different NOM concentrations. As observed
 17 by Sunda and Kieber (1994), the initial rates of production followed a Monod kinetics equation:

$$\frac{dP}{dt} = \frac{V_{\max} [DOC]K}{[DOC]K + 1} \quad (1)$$

18
 19 where [DOC] is the concentration of dissolved organic carbon after filtration, K is a pseudo-
 20 equilibrium adsorption constant and V_{max} is the maximum reaction rate. The initial rates were
 21 found similar in the absence of NOM and in the presence of NOM at a concentration of 0.5 mg L⁻¹
 22 DOC. The isotherm was extrapolated to the origin. Values of 0.49 (±0.03) nM h⁻¹ for V_{max} and
 23 0.073 (±0.012) L mg⁻¹ for K were obtained from the nonlinear least-square regression of our data
 24 (Figure 3). The V_{max} value was 1 to 2 orders of magnitude lower than the values obtained for the

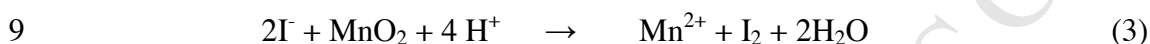
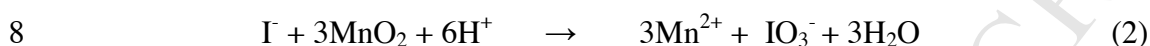
1 formation of acetaldehyde and pyruvate on synthetic Mn oxides (Sunda and Kieber, 1994). A lower
2 value for methyl iodide production was expected because the formation is also limited by the
3 concentration of iodide. The value of K is in the same range as those determined in Sunda and
4 Kieber (1994) and by Waite *et al.* (1988) for the rates of reduction of Mn oxides by Suwannee
5 River Fulvic acid in 50 mM NaCl (i.e. 0.16 and 0.023 L mg⁻¹ at pH 4.0 and 7.1, respectively).
6 For all experiments, the evolution of iodide was also analysed by ion chromatography. At pH 7.0,
7 the concentrations of iodide slowly decreased for 100 hours (see Figure 4), which can be attributed
8 either by diffusion-limited adsorption or slow oxidation on the manganese sand. Diffusion-limited
9 adsorption of inorganic anions was also observed for similar Mn product (Ouvrard *et al.*, 2002).
10 Results in Figure 4 show that the rate and extent of iodide disappearance decreased significantly
11 when NOM concentrations increase from 0 to 50 mgC L⁻¹, which can be explained by competition
12 mechanisms between negatively charged iodide and NOM.

13 3.3. Influence of electrolyte composition and pH

14 To evaluate the influence of electrolyte composition, 15 g L⁻¹ of Mn sand was added to ten
15 different mineral waters spiked with the SR HPOA fraction (5 mgC L⁻¹) and iodide (10 mg L⁻¹).
16 The alkalinity varied from 1.3 to 6.6 mM and the concentrations of calcium and sulphate varied
17 from 0.3 to 13.7 mM and 0 to 16 mM, respectively. The pH values of the solutions after the 24-
18 hour reaction time were in the range of 6.7 - 7.3. Linear negative correlations were only found with
19 both bicarbonate concentrations ($r^2 = 0.847$, $n = 10$) and final pH ($r^2 = 0.668$, $n = 10$). No clear
20 conclusion can be proposed because these two parameters are directly linked. Lower final pH of
21 6.7 was observed for low alkalinity of 1.3 mM. The role of pH is more likely to be of more
22 significant importance because adsorption of bicarbonate is very weak

23 To study the effect of pH, the formation of methyl iodide was compared at pH 7.0 (10 mM
24 carbonate buffer) and pH 5.0 (10 mM perchlorate media). Both the rates of methyl iodide
25 production (Figure 5a) and iodide decay (Figure 5b) increased by a factor of 5 from pH 7.0 to pH

1 5.0 conditions, which confirmed the role of pH in the formation of methyl iodide. According to the
2 model of Keppler (2003), the higher formation of iodoalkanes at acidic pH can be attributed to the
3 higher rate of NOM oxidation by metal oxides when pH decreases (Stone and Morgan, 1984). The
4 analysis of thermodynamic data of Mn and iodine species (Truesdale *et al.*, 2001) and recent
5 studies on iodide oxidation by MnO₂ (Allard *et al.*, 2009, Fox *et al.*, 2009) demonstrate that iodide
6 is readily oxidised to iodate (reaction 2) by manganese oxides for pH < 6.5 and reactive iodine
7 species (e.g. I₂) are produced as intermediate species (reaction 3).



10

11 The oxidation of iodide to iodine and iodate could then explain the quick disappearance of iodide at
12 pH 5.0 and the increase of the formation rate of methyl iodide through electrophilic iodination of
13 natural organic matter. However, assuming that methyl iodide could also be formed through the
14 monoiodination of a terminal methyl group, this reaction is not thermodynamically favoured
15 because iodine is a poor electrophilic oxidant and methyl iodide is not a good leaving group.
16 Manganese oxide might act as a catalyst of the reaction as it was suggested for iodoform formation
17 through the activation of the iodine molecule (Gallard *et al.*, 2009).

18 3.3.3. Effect of the nature of NOM

19 The kinetics of methyl iodide formation was studied for six different NOM isolates (colloid,
20 hydrophobic, transphilic and hydrophilic fractions) at pH 5.0 in 10 mM perchlorate solution (5
21 mgC L⁻¹ DOC, 10 mg L⁻¹ iodide and 15 g L⁻¹ Mn sand). Table 1 gives the concentrations of methyl
22 iodide analysed after a reaction time of 24 hours. The lowest formation of methyl iodide (i.e. 0.44
23 µg/L) was obtained for the Loire River hydrophilic fraction. Higher formation of methyl iodide
24 (i.e. 0.84 µg/L) was observed for the Suwannee and Jau River hydrophobic NOM fractions. This
25 result is in agreement with the study of Keppler *et al.* (2003) where the highest formation of methyl

1 iodide was obtained with organic matter extracted from peaty soil. These lignin-derived organic
2 matters are enriched in aryl methoxy groups that are responsible of the formation of methyl iodide
3 according to the mechanism proposed by Keppler et al. (2000). Even though higher formation was
4 observed for the hydrophobic fractions, no direct correlation could be obtained between methyl
5 iodide formation and global parameters such as the SUVA values or the aromatic content of NOM.
6 This can be explained by the fact that methyl iodide is produced at very low concentrations from
7 very specific sites within NOM. Further investigations and characterization of NOM are needed to
8 fully explain the role of the chemical composition of NOM.

10 **4. Conclusion**

11 This study shows that natural manganese sand can initiate the formation of methyl iodide in the
12 presence of iodide and natural organic matter.

- 13 ○ Low amount of methyl iodide ($<1\mu\text{g L}^{-1}$) was formed at pH 7 in carbonate buffer for
14 concentrations of iodide up to 38 mg L^{-1} . The initial rate of formation linearly increased
15 with the concentrations of iodide and Mn sand. The production of methyl iodide reached a
16 plateau when NOM concentration increased, which corresponds probably to the saturation
17 of the Mn sand. The formation of methyl iodide was lower for the hydrophilic fraction of
18 NOM compared to hydrophobic (i.e. humics) fractions. Decreasing the pH from 7.0 to 5.0
19 caused a strong increase in both rates of methyl iodide formation and iodide disappearance.
20 The formation of methyl iodide through the nucleophilic substitution of methyl group by
21 iodide or the electrophilic substitution of iodine could not be distinguished in this study.
22 Further experiments are needed to conclude about the mechanism controlling the formation
23 of methyl iodide by manganese oxide.
- 24 ○ Even though manganese oxides are less abundant than ferric oxides in the environment,
25 these results suggest that they can also contribute to the formation of methyl iodide in soils

1 and sediments. The experiments were carried out with high concentrations of iodide and
2 NOM, which allowed the formation of significant amount of methyl iodide. Much lower
3 formation is expected in the environment or in technical systems i.e. for lower iodide and
4 NOM concentrations. Also, only traces of methyl iodide are probably produced during the
5 filtration of iodide-containing waters on MnO₂ bed filters because the hydraulic retention
6 times are limited to 10-15 minutes compared to several hours for this study.

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22 addendum. Vol. 1, Recommendations. – 3rd ed.

1 Table 1. Characteristics of NOM isolates and methyl iodide formation (conditions: Mn sand 15
2 g/L; iodide 10 mg/L, DOC 5 mgC/L, pH 5, 10 mM perchlorate, reaction time 24 hours)

3

4 Figure 1. Effect of manganese sand, iodide and NOM concentrations on kinetic formation of
5 methyl iodide at pH 7.0 (carbonate buffer 10 mM)

6 Figure 2. Effect of Mn sand (closed symbols; Iodide 10 mg L⁻¹) and iodide (open symbols; Mn
7 sand 30 g L⁻¹) concentrations on the initial rate of methyl iodide production (NOM 5 mgC L⁻¹, pH
8 7.0, 10 mM carbonate buffer)

9 Figure 3. Influence of organic carbon concentration on the initial rate of methyl iodide production
10 (Mn sand 15 g L⁻¹, Iodide 10 mg L⁻¹, pH 7.0, 10 mM carbonate buffer)

11 Figure 4. Effect of NOM on loss of iodide (Mn sand 30 g L⁻¹, iodide 10 mg L⁻¹, pH 7.0, 10 mM
12 carbonate buffer)

13 Figure 5. Effect of pH on the formation of methyl iodide and iodide loss (Mn sand 15 g L⁻¹, SR
14 HPOA 5 mgC L⁻¹, Iodide 10 mg L⁻¹)

15

Figure 1

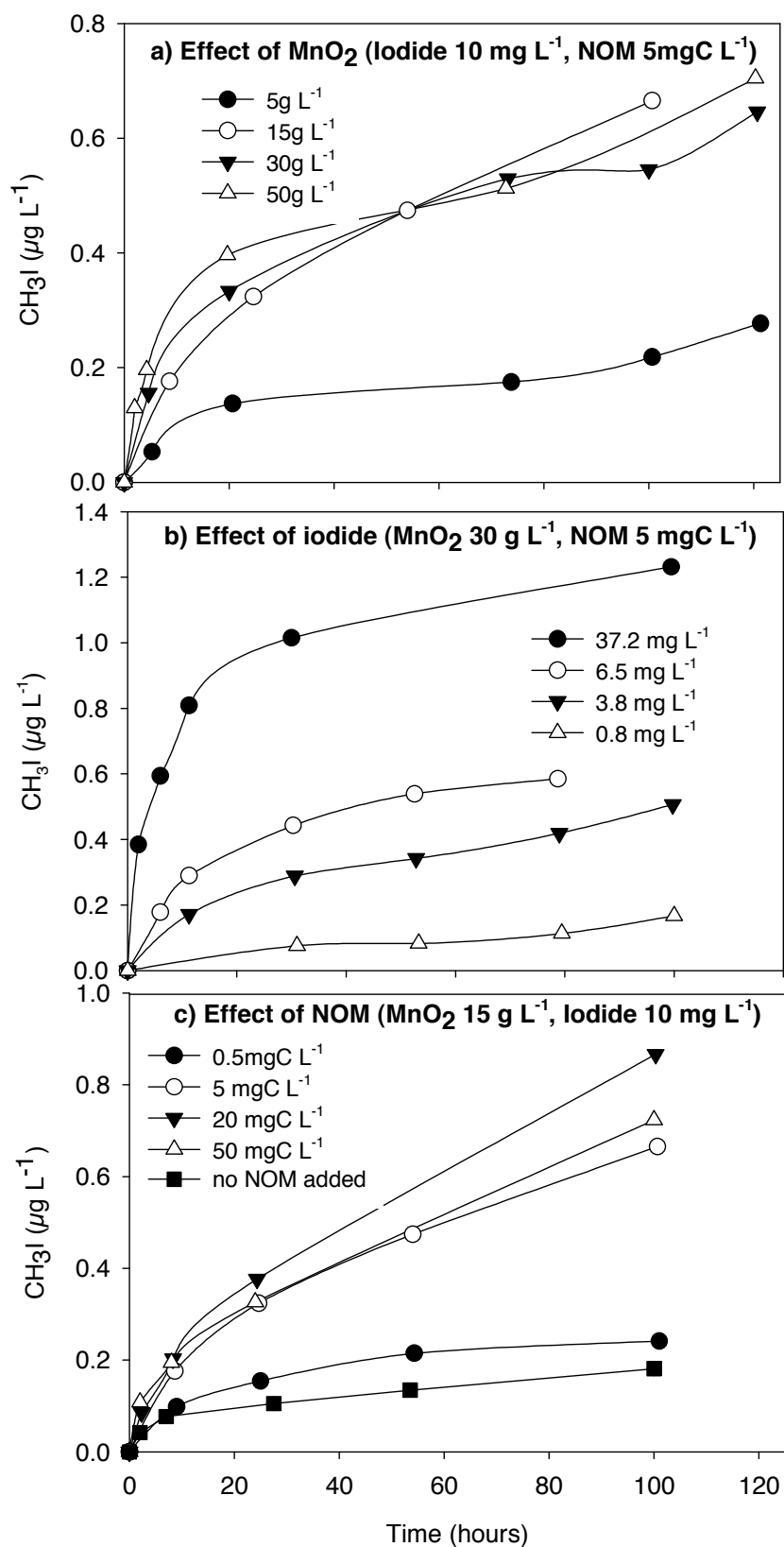


Figure 2

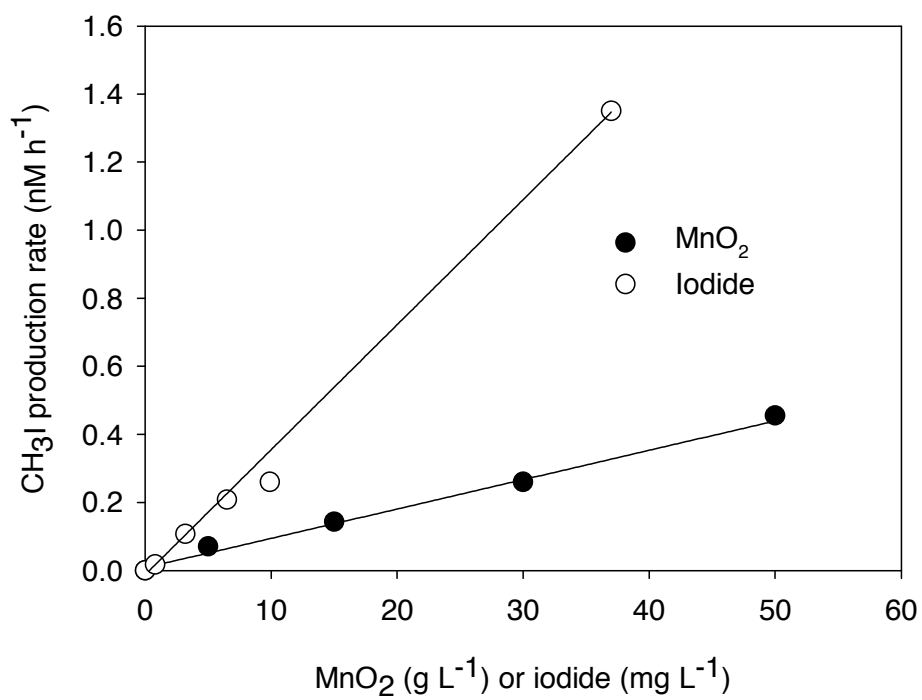


Figure 3.

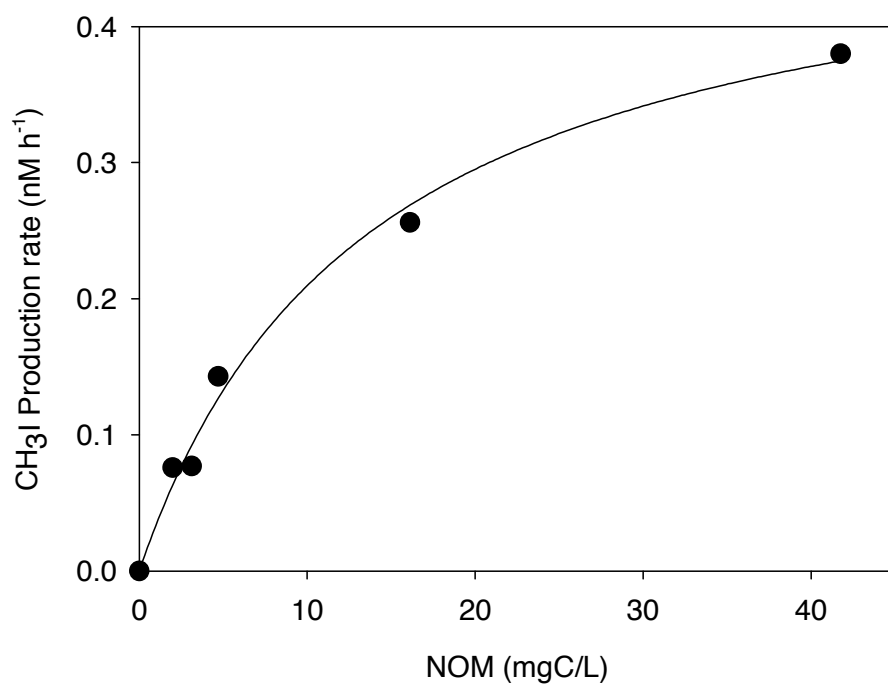


Figure 4.

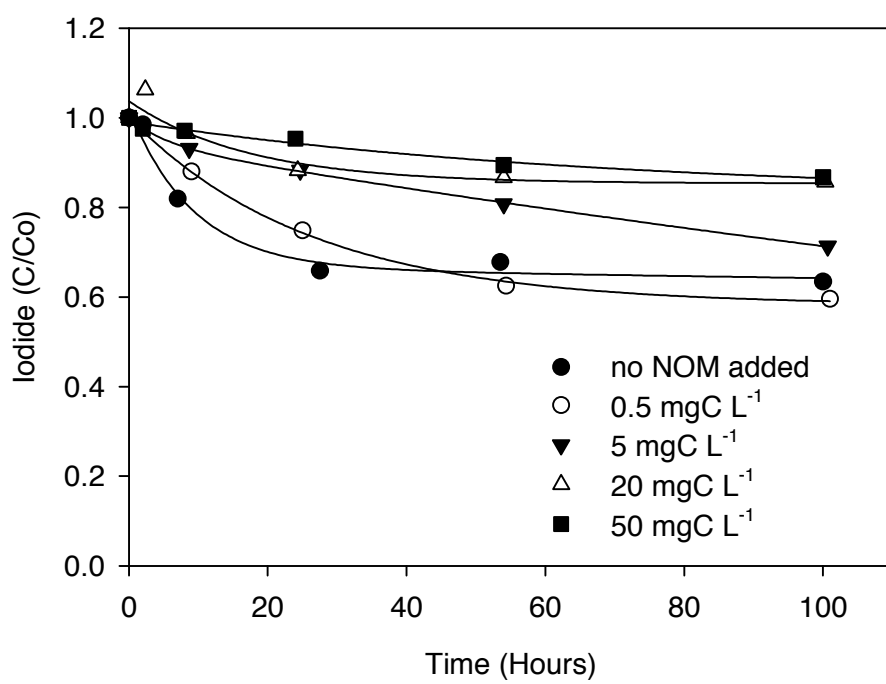


Figure 5.

