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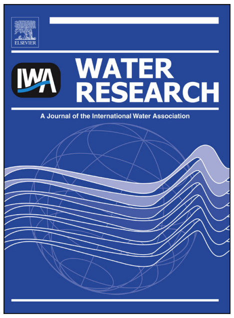

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Formation of methyl iodide on a natural manganese oxide

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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 ≤ 1 μg 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

1. Introduction

Methyl iodide (CH_3I) was first analysed in seawater and air by Lovelock *et al*. (1973). In the atmosphere, methyl iodide is photolysed to produce methyl radical (CH_3) and iodine atom (I), which contributes to the natural iodine cycle. Methyl radical reacts with ozone and thus may influence the ozone budget. The oceans would be the main source of methyl iodide through biotic reactions mediated by microorganisms such as algae (Gschwend *et al*., 1985). Laboratory studies provided evidence that a wide variety of bacteria including terrestrial and marine bacteria are capable of methylating low amount of iodide in the environment (Amachi *et al*., 2001).

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

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

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

μg L^{-1}) with increasing concentrations near sea coast (Fuge and Johnson, 1986). Manganese and iodine are essential trace elements for human and small amounts from food or water is required to stay healthy. However, manganese has to be removed from drinking water because its oxidation products cause taste, odours and coloured water problems (Wong, 1984; Jaudon *et al.,* 1989). Recent studies have reported links between excessive manganese exposure and neurologic disorders in children (Bouchard *et al*., 2007). The WHO guideline for this element in drinking water is 400 μg L^{-1} (WHO, 2006) and a maximum concentration level of 50 μg L^{-1} in the European Union. Manganous ion oxidation by oxygen is a slow process at neutral pH (Stumm and Morgan, 1996). Strong oxidants e.g. chlorine or ozone can be used but catalytic materials such as natural manganese oxides or manganese oxide coated sands are preferred in some circumstances especially for mineral waters when strong oxidants are prohibited. Removal of iron (White and Asfar-Siddique 1997) and arsenic (Bissen and Frimmel, 2003; Ouvrard *et al.,* 2005) can also be performed with manganese oxides due to their relatively high redox potential. Manganese oxides have also been proposed as an adsorbant for natural organic matter (NOM) (Bernard *et al.,* 1997) and thus for the removal of DBP in drinking water production (Colthurst and Singer, 1982). Manganese dioxide was recently shown to oxidize iodide to iodine and iodate (Fox *et al*., 2009; Allard *et al*., 2009) as well as initiating the formation of iodinated organic compounds such as iodoform (Gallard *et al*., 2009). The use of manganese oxides for the treatment of iodide-containing waters could also be responsible for the formation of iodoalkanes such as methyl iodide in drinking waters. Even though methyl iodide has been recently approved as a soil fumigant by the USEPA to control soils-borne diseases and pests, it is neurotoxic for humans and mutagenic to bacteria and rats (IARC, 1999 and references therein). The International Agency for Research on Cancer (IARC) classified methyl iodide in the group 3 (i.e. not classifiable as to its carcinogenicity to humans) because there is no epidemiological data relevant to its carcinogenicity and there is limited evidence for the carcinogenicity in experimental animals (IARC, 1999). However, methyl iodide is considered to be a human carcinogen in Germany and California. To our knowledge, methyl iodide has never been reported in drinking waters and no international guideline exists for this compound in water.

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

2. Material and methods

2.1 Manganese oxide

The catalytic material was a natural manganese oxide (79% MnO_2) approved for drinking water treatment. The material was rinsed with ultra pure water to eliminate the fines before experiments. The selected size fraction was in the range of 300 – 700 μm. The specific density was 3.88. Specific surface area determined by the BET method using N_2 as adsorbate was 26 m^2 g^{-1}. Manganese sand was dry ground in an agate mortar before X-ray analysis. X-ray diffraction was performed using a PANalytical Xpert Pro diffractometer operated under reflexion using a Cu K_α radiation at a wavelength of 1,541838 Å. Three Mn minerals were identified: birnessite, lithiophorite and cryptomelane (see X-ray diffractogram in Figure S1 in supplementary material).

2.2 Natural Organic Matters (NOM)

Six NOM isolates (Table 1) extracted and characterized from previous studies were used for adsorption on manganese sand and formation of iodoalkanes. Details of the fractionation procedure have been presented elsewhere (Leenheer, 1981; Croué *et al.,* 1999). The colloidal fraction was isolated using 3,500 Da dialysis bag against HCl 0.1N and then HF 0.2N. The hydrophobic (HPO) fractions refer to the NOM fractions recovered from the XAD-8 resin by elution with an acetonitrile/water mixture; the hydrophobic acid (HPOA) and the transphilic (TPI) fractions refer to the NOM fraction recovered by elution with NaOH from the XAD-8 and XAD-4 resins, respectively. The hydrophilic fraction (HPI) refers to NOM fraction not adsorbed on both XAD-8 and XAD-4 resins. Solid samples of the NOM fractions were obtained by freeze-drying. The NOM fractions were characterized by determination of their Specific UV Absorbance values at 254nm (SUVA254 = UV254/mg/L of dissolved organic carbon (DOC)) and the % aromatic carbon content determined using solid state ^{13}C nuclear magnetic resonance (NMR) spectroscopy. ^{13}C NMR spectra of Jau River extracts were not determined but the origin and the specific UV absorbance values of these extracts suggest that the aromatic carbon content was similar to the Suwannee River HPOA fraction. The NOM extracts were chosen to describe a large range of properties from humic like (hydrophobic with high aromatic carbon content e.g. Suwannee HPOA fraction) to non humic like NOM (more hydrophilic with low aromatic carbon content e.g. Loire River HPI fraction).

2.3 Experimental procedures

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

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

2.4 Analytical procedures

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

Volatile alkyl iodides were analyzed using gas chromatography (model Varian 3300) with headspace injection and electron capture detection. Separation of alkyl iodides was carried out on a J&W/DB 624 30 m x 0.53 mm column. Nitrogen was used as carrier gas. The oven temperature was set constant at 35°C for 20 min. Detector and injector temperatures were 300°C and 80°C, respectively. The headspace vials were equilibrated for 4 hours at 50°C before injection. Quantification of methyl iodide was performed using external calibration standards. Stock standard solutions of methyl iodide were prepared in methanol by introducing 100 μL of analyte into a 40 mL EPA vial sealed with PTFE-faced silicone septa and diluting to volume. Solutions were stored at -20°C in the dark. Standard solutions were prepared in ultra pure water. Detection limit for methyl iodide was 10 ng L^{-1} and the relative standard deviations for 5 replicates were in the range of 1 – 5%.

Iodide ion analyses were carried out with ion chromatography and conductometric detection after chemical ion suppression (Dionex AS3000). A Dionex® AS19 column (internal diameter: 4 mm; length: 250 mm) and a Dionex® AG19 guard column (internal diameter: 4 mm; length: 50 mm) was used with 50 mM NaOH as mobile phase at 30°C. The injection volume was 500 μL. The detection limit was 5 μg L^{-1}.

Dissolved organic carbon was analyzed using a Shimadzu TOC Vcsh analyzer. The detection limit was about 0.1 mgC L^{-1}.

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 $\mu g\ L^{-1}$. 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 nucleophile in the S_N2 substitution reactions (Avila-Zarraga and Martinez, 2001). Same reactions occur with phenols. These reactions were identified as the predominant pathway through which methyl iodide was degraded in presence of organic matter in soils (Gan and Yates, 1996). The DOC analysed after filtration in the absence of SR HPOA was 2.05 ±0.37 mgC L^{-1} i.e. 0.14 ±0.02 mgC g^{-1} MnO_2, which explain the significant formation of methyl iodide observed for this condition (Figure 1c). The formation of methyl iodide increased with increasing the concentrations of NOM from 0.5 to 20 mgC L^{-1} but lower final yield was observed for high DOC of 50 mgC L^{-1}. Sunda and Kieber (1994) showed that a maximum in production rate of low molecular weight compounds by manganese oxides was also achieved when all of the adsorption sites are saturated. A decrease in production rate could even be expected at very high NOM concentrations through direct competition for active sites and pore blockage. These data support the model of Keppler *et al*. (2000) for the formation of iodoalkanes through the oxidation of NOM by an electron acceptor.

The initial rates of methyl iodide production calculated from the first data point were found to be linearly proportional to the concentrations of iodide and Mn sand (Figure 2). The overall 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 approach was used for the experiments performed with different NOM concentrations. As observed by Sunda and Kieber (1994), the initial rates of production followed a Monod kinetics equation:

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

where [DOC] is the concentration of dissolved organic carbon after filtration, K is a pseudo-equilibrium adsorption constant and V_{max} is the maximum reaction rate. The initial rates were found similar in the absence of NOM and in the presence of NOM at a concentration of 0.5 mg L^{-1} DOC. The isotherm was extrapolated to the origin. Values of 0.49 (±0.03) nM h^{-1} for V_{max} and 0.073 (±0.012) L mg^{-1} for K were obtained from the nonlinear least-square regression of our data (Figure 3). The V_{max} value was 1 to 2 orders of magnitude lower than the values obtained for the formation of acetaldehyde and pyruvate on synthetic Mn oxides (Sunda and Kieber, 1994). A lower value for methyl iodide production was expected because the formation is also limited by the concentration of iodide. The value of K is in the same range as those determined in Sunda and Kieber (1994) and by Waite *et al*. (1988) for the rates of reduction of Mn oxides by Suwannee 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).

For all experiments, the evolution of iodide was also analysed by ion chromatography. At pH 7.0, the concentrations of iodide slowly decreased for 100 hours (see Figure 4), which can be attributed either by diffusion-limited adsorption or slow oxidation on the manganese sand. Diffusion-limited adsorption of inorganic anions was also observed for similar Mn product (Ouvrard et al., 2002). Results in Figure 4 show that the rate and extent of iodide disappearance decreased significantly when NOM concentrations increase from 0 to 50 mgC L^{-1}, which can be explained by competition mechanisms between negatively charged iodide and NOM.

3.3. Influence of electrolyte composition and pH

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

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

5.0 conditions, which confirmed the role of pH in the formation of methyl iodide. According to the model of Keppler (2003), the higher formation of iodoalkanes at acidic pH can be attributed to the higher rate of NOM oxidation by metal oxides when pH decreases (Stone and Morgan, 1984). The analysis of thermodynamic data of Mn and iodine species (Truesdale *et al*., 2001) and recent studies on iodide oxidation by MnO_2 (Allard *et al*., 2009, Fox *et al*., 2009) demonstrate that iodide is readily oxidised to iodate (reaction 2) by manganese oxides for pH < 6.5 and reactive iodine species (e.g. I_2) are produced as intermediate species (reaction 3).

$$I^- + 3MnO_2 + 6H^+ \rightarrow 3Mn^{2+} + IO_3^- + 3H_2O \quad (2)$$

$$2I^- + MnO_2 + 4\,H^+ \rightarrow Mn^{2+} + I_2 + 2H_2O \quad (3)$$

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

3.3.3. Effect of the nature of NOM

The kinetics of methyl iodide formation was studied for six different NOM isolates (colloid, hydrophobic, transphilic and hydrophilic fractions) at pH 5.0 in 10 mM perchlorate solution (5 mgC L^{-1} DOC, 10 mg L^{-1} iodide and 15 g L^{-1} Mn sand). Table 1 gives the concentrations of methyl iodide analysed after a reaction time of 24 hours. The lowest formation of methyl iodide (i.e. 0.44 μg/L) was obtained for the Loire River hydrophilic fraction. Higher formation of methyl iodide (i.e. 0.84 μg/L) was observed for the Suwannee and Jau River hydrophobic NOM fractions. This result is in agreement with the study of Keppler et al. (2003) where the highest formation of methyl iodide was obtained with organic matter extracted from peaty soil. These lignin-derived organic matters are enriched in aryl methoxy groups that are responsible of the formation of methyl iodide according to the mechanism proposed by Keppler et al. (2000). Even though higher formation was observed for the hydrophobic fractions, no direct correlation could be obtained between methyl iodide formation and global parameters such as the SUVA values or the aromatic content of NOM. This can be explained by the fact that methyl iodide is produced at very low concentrations from very specific sites within NOM. Further investigations and characterization of NOM are needed to fully explain the role of the chemical composition of NOM.

4. Conclusion

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

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

and sediments. The experiments were carried out with high concentrations of iodide and NOM, which allowed the formation of significant amount of methyl iodide. Much lower formation is expected in the environment or in technical systems i.e. for lower iodide and NOM concentrations. Also, only traces of methyl iodide are probably produced during the filtration of iodide-containing waters on MnO_2 bed filters because the hydraulic retention times are limited to 10-15 minutes compared to several hours for this study.

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

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

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

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

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 carbonate buffer)

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

Figure 1

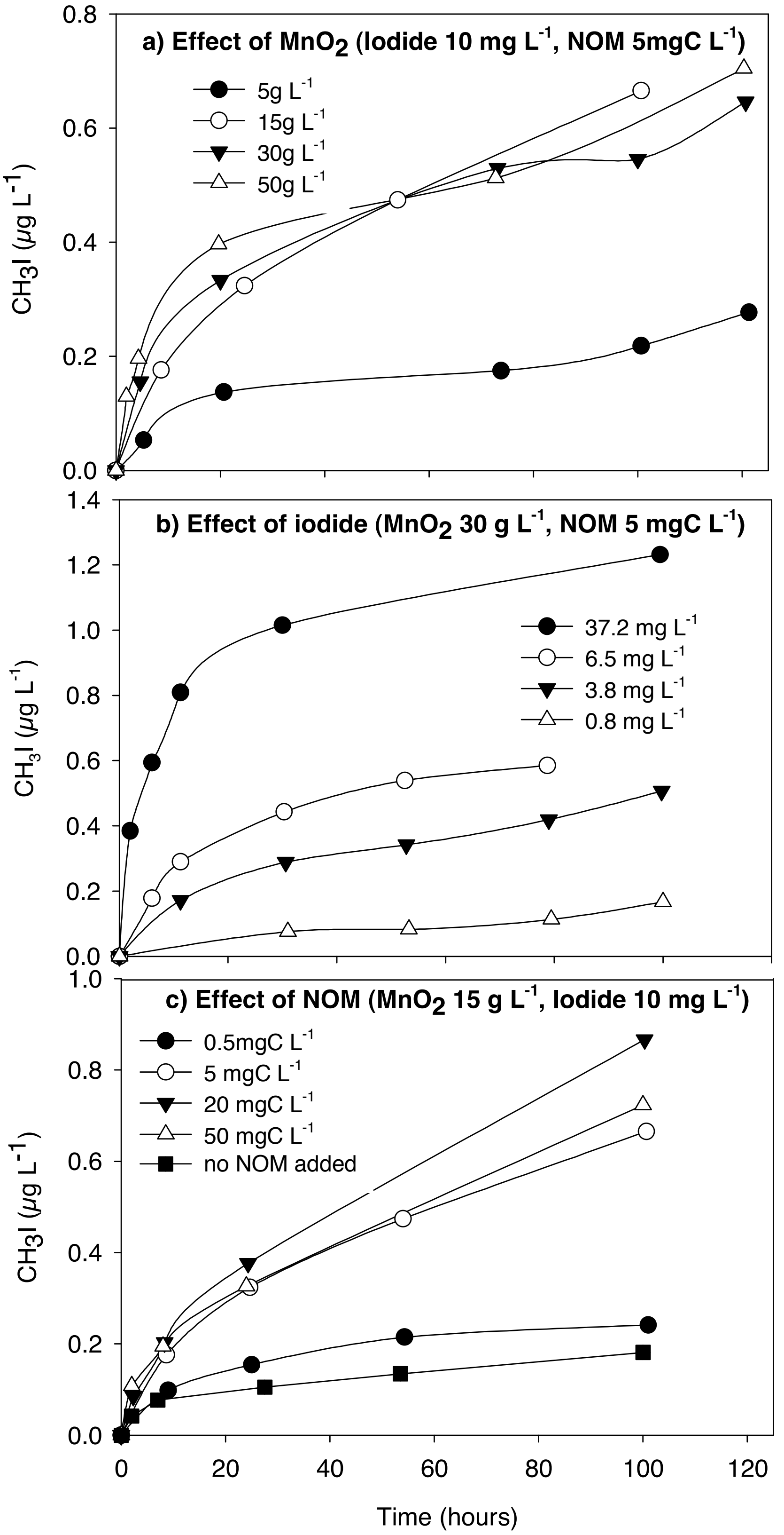

a) Effect of MnO2 (Iodide 10 mg L-1, NOM 5mgC L-1)
5g L-1
15g L-1
30g L-1
50g L-1
CH3I (μg L-1)
0.0
0.2
0.4
0.6
0.8
b) Effect of iodide (MnO2 30 g L-1, NOM 5 mgC L-1)
37.2 mg L-1
6.5 mg L-1
3.8 mg L-1
0.8 mg L-1
CH3I (μg L-1)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
c) Effect of NOM (MnO2 15 g L-1, Iodide 10 mg L-1)
0.5mgC L-1
5 mgC L-1
20 mgC L-1
50 mgC L-1
no NOM added
CH3I (μg L-1)
0.0
0.2
0.4
0.6
0.8
1.0
0
20
40
60
80
100
120
Time (hours)

Figure 2

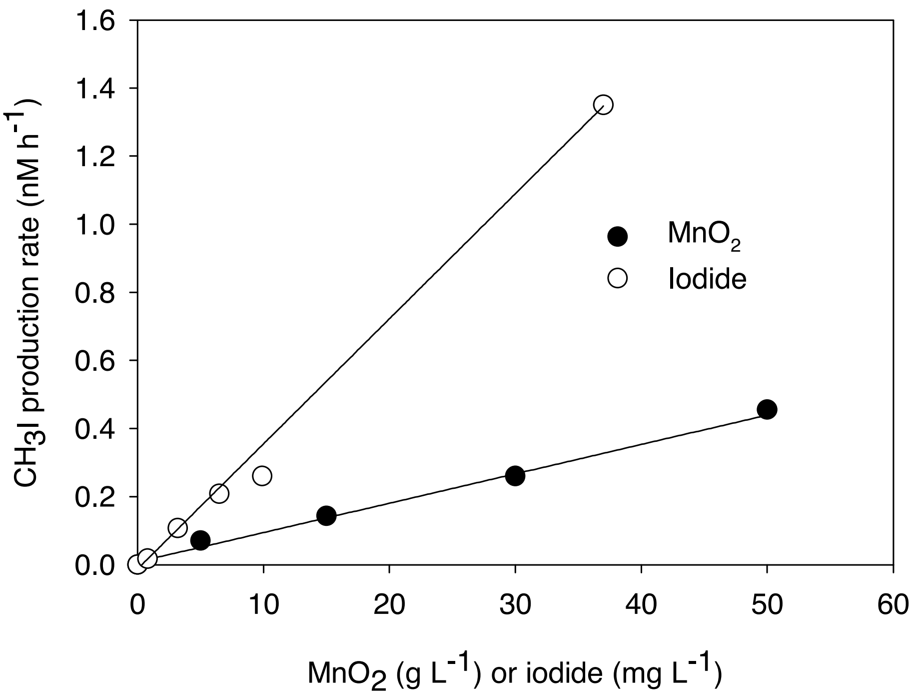

1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
10
20
30
40
50
60
CH3I production rate (nM h-1)
MnO2 (g L-1) or iodide (mg L-1)
MnO2
Iodide

Figure 3.

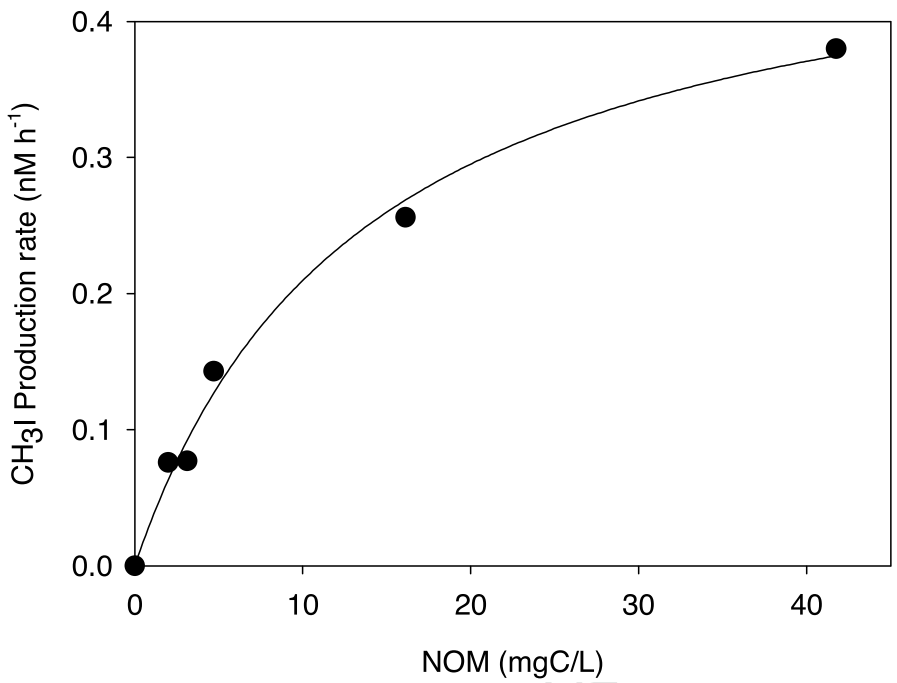


Figure 4.

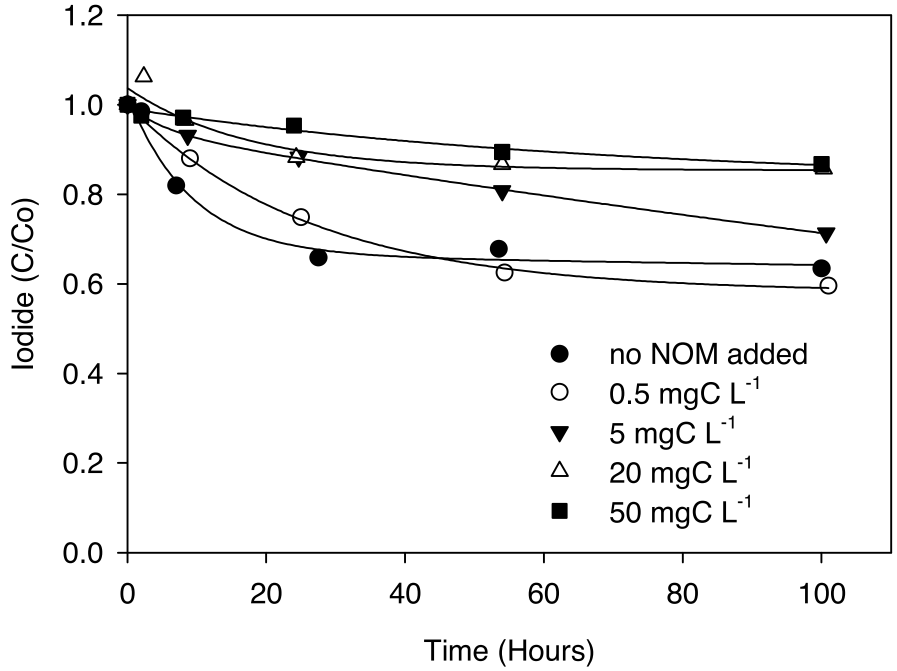
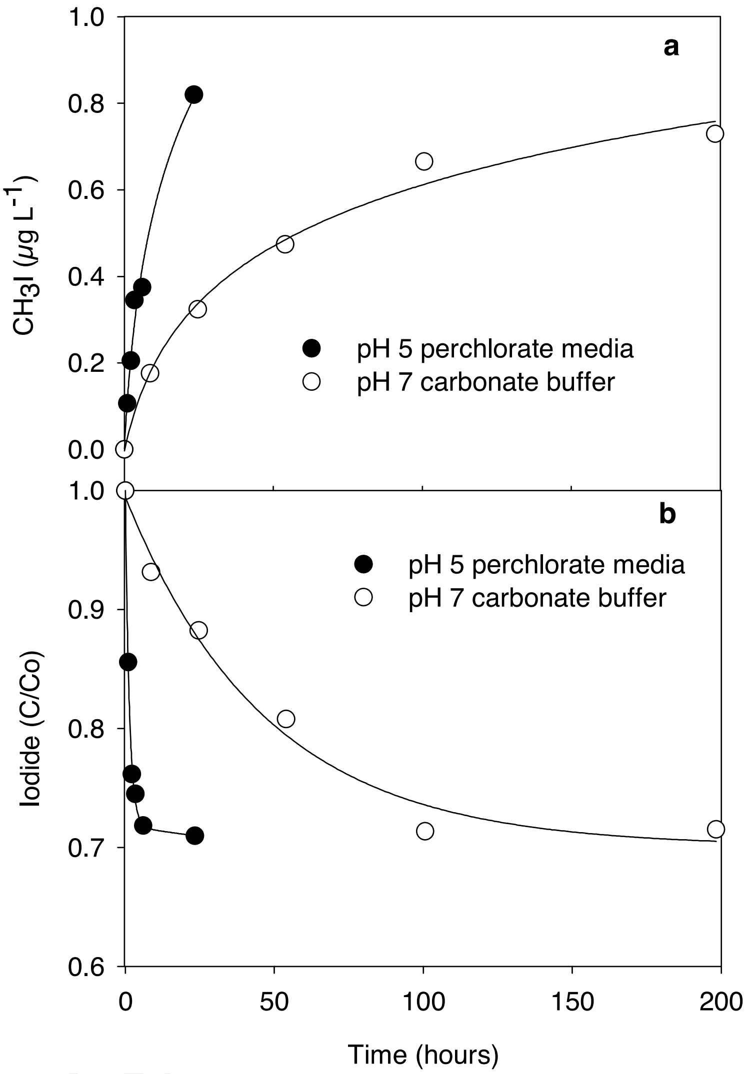

1.2
1.0
0.8
0.6
0.4
0.2
0.0
Iodide (C/Co)
0
20
40
60
80
100
Time (Hours)
no NOM added
0.5 mgC L-1
5 mgC L-1
20 mgC L-1
50 mgC L-1

Figure 5.


a
b
CH3I (μg L-1)
Iodide (C/Co)
Time (hours)
pH 5 perchlorate media
pH 7 carbonate buffer
pH 5 perchlorate media
pH 7 carbonate buffer
1.0
0.8
0.6
0.4
0.2
0.0
1.0
0.9
0.8
0.7
0.6
0
50
100
150
200