Kinetics and mechanism of dimethoate chlorination during drinking water treatment

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HIGHLIGHTS

- The reaction of DMT with chlorine was of first-order in each reactant.
- The observed rate constant of DMT degradation was strongly pH dependent.
- Both bromide and humic acid promoted but ammonium inhibited the degradation of DMT.
- Three organic byproducts were detected in DMT degradation by chlorine.
- The toxicity of DMT solution obviously increased after chlorination.

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ABSTRACT

Dimethoate (DMT), a commonly used organophosphorus pesticide, is of great concern because of its toxicity and potentially harmful effects on water sources. The elimination of DMT as well as the toxicity and persistence of the byproducts formed during DMT degradation is most important for the safety of drinking water. This study first determined the reaction kinetics of DMT with free chlorine (FC) under typical water treatment conditions. The reaction between DMT and FC proceeded rapidly, exhibiting first-order with respect to each reactant. The degradation of DMT by FC was highly pH dependent, and the pseudo-first-order rate constant decreased obviously from 0.13 to 0.02 s⁻¹ with an increase in pH from 7.0 to 8.3. Bromide ion accelerated the reaction by acting as a catalyst, and the accelerated reaction rate was linearly proportional to the bromide concentration. As a ubiquitous component in natural waters, humic acid also increased the reaction rate. However, the presence of ammonium inhibited the degradation of DMT due to its rapid converting FC to chloramines. Omethoate (OMT) was identified as an important byproduct of DMT chlorination, but only accounted for ca. 28% of the DMT degraded; and other two organic byproducts were also identified. The acute toxicity of DMT solution increased after treatment with FC due to the formation of more toxic byproducts (e.g. OMT).

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1. Introduction

Dimethoate (O,O-dimethyl-S-methylcarbamoyl methylphosphorothioate) (DMT) is widely used as an insecticide on crops (e.g., wheat, alfalfa, corn, and cotton), orchards, and vegetables; in forestry; and for residential purposes (Pappas and Kyriakidis, 2003; USEPA, 2011; Catalá-Icardo et al., 2012). Its moderate persistence coupled with its frequent applications can result in chronic surface water contamination. DMT has been detected in water samples collected from the Rosetta and Damiatta branches with concentrations ranging from 0.17 to 0.34 µg L⁻¹ during the

summer and autumn seasons of 1995–1997 (Abbassy et al., 1999). DMT was also found to be one of the main organophosphorus pesticide pollutants in water from the Jiulong River Estuary in China (Zhang et al., 2002). The DMT concentration could reach up to 11.31 µg L⁻¹ in California's surface water (Lisker et al., 2011). DMT is classified as “moderately hazardous” by the World Health Organization (WHO, 2009). In studies with human volunteers, DMT has been shown to be a cholinesterase inhibitor and a skin irritant (WHO, 2011). In a multigenerational study of reproductive toxicity in rats, the no-observed-adverse-effect level (NOAEL) appeared to be 1.2 mg kg⁻¹ body weight (bw) per day, but there was some indication that the reproductive performance might have been affected at lower doses (WHO, 2011). DMT could also pose an important ecological risk to the entire ecosystem (Qu

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et al., 2011). Because of its potentially dangerous effects on human health, DMT is listed on the third contaminant candidate list (CCL3) by the United States Environmental Protection Agency (USEPA) (USEPA, 2009), and a guideline value of $6 \mu\text{g L}^{-1}$ has been set for DMT in drinking water by the WHO (WHO, 2011). It is of great importance to control DMT residue in waters for minimizing its risks to human beings. Many methods have been attempted for removing DMT from water, such as nanofiltration (Ahmad et al., 2009), ultrasonication (Liu et al., 2008; Yao et al., 2011), microwave irradiation (Zhang et al., 2007), photo-Fenton oxidation (Evgenidou et al., 2007; Martín et al., 2008, 2009), and biological oxidation (Martín et al., 2008, 2009). However, toxic byproducts, such as omethoate (OMT), were formed during DMT oxidation. The oral LD50 values of DMT and OMT were reported to be 310 and 25 mg/kg bw in rats, indicating that the degradation byproduct (OMT) was much more toxic than DMT (FAO and WHO, 1996). Therefore, studies on the formation of byproducts and the variation of toxicity during DMT oxidation need to be done.

Free chlorine (FC) is the most commonly used chemical disinfectant for community water systems (USEPA, 1999). It is very effective against a wide range of pathogens, including bacteria and viruses. Chlorination is also a highly economical process. FC is stable and is capable of providing necessary residual protection in water distribution systems. For these reasons, chlorination will continue to be a commonly used disinfection method for the foreseeable future, despite the formation of harmful byproducts during chlorination. FC is known to react with numerous pesticides. For example, carbamate pesticides were found to react with FC to produce sulfoxides or sulfones (Mason et al., 1990; Miles, 1991). Isoproturon was also found to be degraded by FC (Lopez et al., 2001; Mascolo et al., 2001). Moreover, some organophosphate pesticides have been shown to react with FC to produce stable oxons or other oxidation analogues (Kamel et al., 2009; Duirk et al., 2009). DMT has the potential for exposure in drinking water and reaction with FC, but data for assessing its persistence and toxicity in finished drinking water are lacking.

The purpose of the current research is to determine the effectiveness of DMT degradation by FC under common conditions applied in drinking water treatment plants; to analyze the effects of pH, ammonium, bromide, and humic acid (HA) on the reaction kinetics of DMT with FC; to identify and quantify the byproducts formed during the reaction; and to assess the toxicity change of the DMT solution treated by FC. The results will provide useful information for water treatment workers when micro-pollution by DMT occurs.

2. Materials and methods

2.1. Chemicals

DMT (98.5%) and OMT (98%) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). The standards of sulfate ($1000 \mu\text{g mL}^{-1}$) and nitrate ($1000 \mu\text{g mL}^{-1}$) were obtained from the National Institute of Metrology (Beijing, China), and the phosphate standard (500 mg L^{-1}) was from the Institute for Environmental Reference Materials, Ministry of Environmental Protection (Beijing, China). High performance liquid chromatography (HPLC) grade methanol was obtained from Fisher Scientific (Fair Lawn, NJ, USA). Other chemicals were of at least analytical grade and used without further purification.

The stock solution of DMT was prepared in ultrapure water with a concentration of approximately 1 mM. All the reaction solutions were buffered with 20 mM phosphate in a pH range of 7.0–8.3. Ultrapure water, produced by a Milli-Q Integral 3 Water Purification System, was used to prepare the aqueous solutions.

2.2. Analysis methods

DMT and OMT were quantified by HPLC coupled with a diode array detector (DAD) (Agilent 1260, Infinity) and an Atlantis C18 column ($150 \text{ mm} \times 2.1 \text{ mm}$, $3 \mu\text{m}$) at 210 nm. Methanol and water (40/60 for DMT, 25/75 for OMT) were used as mobile phases at a flow rate of 0.2 mL min^{-1} under a constant temperature of 40°C . The retention times of DMT and OMT were 6.25 and 4.25 min, respectively.

The organic byproducts produced during DMT chlorination were concentrated by an Auto Trace 280 Solid-Phase Extraction Instrument (Dionex) with Oasis HLB cartridges ($500 \text{ mg}/6 \text{ mL}$, Waters, Milliford, MA) and then identified by gas chromatography/mass spectrometry (GC/MS) equipped with an HP-5 capillary column ($30 \text{ m} \times 0.25 \text{ mm}$, $0.25 \mu\text{m}$). The analysis procedures are detailed as follows: (1) adjust the sample (100 mL) pH to about 2.0 with $2.0 \text{ M H}_2\text{SO}_4$; (2) precondition an Oasis HLB cartridge with 5 mL of methanol/ethyl acetate mixture (1:1, v/v) and 5 mL of $0.01 \text{ M H}_2\text{SO}_4$ sequentially; (3) extract the sample with the HLB cartridge at a flow rate of 1 mL min^{-1} ; (4) elute the byproducts with 5 mL of methanol/ethyl acetate mixture (1:1, v/v); (5) blow the extract to about 1 mL under a gentle stream of N_2 ; and (6) analyze the final solution with GC/MS. The following operation conditions of GC/MS were adopted: the injection temperature was 300°C ; the oven temperature started at 40°C and held for 2 min, ramped at $10^\circ\text{C min}^{-1}$ to 300°C , and then held for 3 min; and helium gas was used as carrier gas at a flow rate of 1 mL min^{-1} .

An ion chromatograph (Dionex, ICS 3000) equipped with an IonPac AS19 analytical column ($4 \text{ mm} \times 250 \text{ mm}$) was used to detect inorganic anions formed during DMT chlorination. The following gradient elution was used: started with 20 mM KOH and held for 20 min, increased to 35 mM KOH over 0.1 min and held for 10 min, and then decreased to 20 mM over 0.1 min and held for 5 min. The retention times of sulfate and phosphate were 12.2 and 22.2 min, respectively.

The total organic carbon (TOC) was determined with a Shimadzu TOC-V_{CPH} analyzer. The concentrations of FC and total chlorine were measured with a Hach Pocket Colorimeter II (58700-00).

2.3. Dimethoate degradation kinetics

The reaction solutions of DMT were freshly prepared by spiking DMT stock solution to 20 mM KH_2PO_4 solution with or without additives (e.g., bromide, HA, and ammonium) in 250-mL brown glass reactors to prevent DMT hydrolysis and exclude potential light influence. After adjusting the solution pH to a desired value, 5 mL of the solution was transferred into a 10-mL colorimetric cylinder; then, 50 μL of NaOCl solution (5.4–22.3 mM according to the target reaction concentration) was added to initiate the reaction. After the NaOCl injection, the solution was vigorously stirred by vortex mixer. At a pre-selected reaction time, 50 μL of Na_2SO_3 solution (with a double concentration of NaOCl) was immediately added to quench the FC residue. The remaining concentration of DMT was analyzed by HPLC/DAD. All experiments were conducted in duplicate, and the relative standard deviations of all data points were determined to be below 5%.

2.4. Toxicity assessment

The toxicity change of the DMT solution after treatment with FC was measured using *Daphnia magna* following the national standards of China (MEPC, 1991). *D. magna* was obtained from the Chinese Research Academy of Environmental Sciences and was cultured in the laboratory for more than three generations. The oxidation of DMT by FC was conducted at 26°C and pH 7.62

(20 mM phosphate buffer) with initial concentrations of 7.9 and 211 μM for DMT and FC, respectively. Under these conditions, 98.3% of DMT was degraded within 1 min. After the residual FC was quenched by sulfite, the sample for testing (20 mL) was added to a 100 mL beaker with 20 mL synthetic natural water and 10 *D. magna*. Next, all the test beakers were incubated for 24 h at 26 °C. Acute toxicity was evaluated by monitoring the mobility of *D. magna*. The neonates were considered immobile if they remained at the bottom of the test beaker and did not resume swimming within a 15 s observation period. A preliminary experiment had shown that the presence of quenched FC and sulfite had a negligible effect on the test result. All the toxicity tests were performed in triplicate.

3. Results and discussion

3.1. Determination of reaction order for dimethoate degradation by chlorine

For the reaction of FC with an organic compound, first-order kinetics was generally observed with respect to each reactant (Pappas and Kyriakidis, 2003; Duirk and Collette, 2006). However, in some cases, the decay of FC may follow reaction orders that vary with pH (Mason et al., 1990). Fig. 1a shows the pseudo-first-order kinetic simulation of DMT degradation with various initial FC concentrations at pH 8.18 by Eq. (1). The good linearity of the fitting

Fig. 1. Determination of the reaction order for DMT degradation by FC: (a) plot of $\ln(C/C_0)$ vs. reaction time at different initial FC concentrations; and (b) plot of $\ln k'$ vs. $\ln([FC]_0)$. $[DMT]_0 = 2 \mu\text{M}$, 20 mM phosphate buffer, pH = 8.18, $T = 26^\circ\text{C}$.

curves clearly indicates that DMT was a first-order reactant in this reaction:

$$\ln(C/C_0) = -k't \quad (1)$$

where C_0 and C represent the initial and reacting (time = t) concentrations of DMT; and k' is the pseudo-first-order reaction rate constant of DMT degradation by FC.

To determine the reaction order of FC, the degradation rate of DMT can be expressed by the following equation:

$$dC/dt = -k''([FC]_0)^m C \quad (2)$$

where k'' is the second-order reaction rate constant; $[FC]_0$ is the initial concentration of FC; and m is the reaction order with respect to FC. When a large excess of FC is applied, Eq. (2) can be rearranged as follows:

$$\ln k' = m \ln([FC]_0) + \ln k'' \quad (3)$$

Fig. 1b shows the plot of $\ln k'$ vs. $\ln([FC]_0)$ at pH 8.18. The results indicate that FC was also a first-order reactant in the degradation of DMT. Thus, the overall reaction followed second-order kinetics, and the value of k'' was calculated to be $107 \text{ M}^{-1} \text{ s}^{-1}$ at pH 8.18 and 26 °C.

3.2. Effect of pH

As described above, the reaction of DMT with FC can be described by a second-order rate expression:

$$dC/dt = -k'C = -k''[FC]C \quad (4)$$

The kinetic results shown in Fig. 2a demonstrate a marked dependence of k' on pH. The degradation rate of DMT increased with a decrease in pH. The k' value was 0.13 s^{-1} at pH 7.01 but only 0.02 s^{-1} at pH 8.28. The large variation in k' from pH 7.0–8.3 could be attributed to the varying reactivity of the individual acid–base species of FC. The speciation of FC is shown as follows:

$$[\text{HOCl}] = \frac{[\text{H}^+]}{[\text{H}^+] + K_{a,\text{Cl}}} [\text{FC}] \quad (6)$$

where $K_{a,\text{Cl}} = 10^{-7.5}$ at 25 °C (Morris, 1966). Usually the contribution of OCl^- to the degradation of an organic compound can be neglected due to its much weaker oxidation potential than HOCl (Qiang and Adams, 2004). Hence, the degradation rate of DMT can be expressed as follows:

$$\frac{dC}{dt} = -k''_{\text{HOCl,DMT}} [\text{HOCl}]C = -k''_{\text{HOCl,DMT}} \frac{[\text{H}^+]}{[\text{H}^+] + K_{a,\text{Cl}}} [\text{FC}]C \quad (7)$$

where $k''_{\text{HOCl,DMT}}$ is the specific second-order rate constant for the reaction of DMT with HOCl, the neutral species of FC in aqueous solution. Thus, one has,

$$k' = \frac{[\text{H}^+]}{[\text{H}^+] + K_{a,\text{Cl}}} k''_{\text{HOCl,DMT}} \quad (8)$$

The plot of k' vs. $[\text{H}^+]/([\text{H}^+] + K_{a,\text{Cl}})$ exhibits a linear relationship (Fig. 2b), which implies that OCl^- indeed played a negligible role in the degradation of DMT. The linear slope yielded the value of $k''_{\text{HOCl,DMT}}$, i.e., $785 \text{ M}^{-1} \text{ s}^{-1}$.

3.3. Effect of bromide concentration

Bromide is present in many water sources. Westerhoff et al. (1994) conducted a nationwide survey of 101 drinking water sources in the United States and found an average bromide concentration of

Fig. 2. Effect of pH on DMT degradation by FC: (a) plot of $\ln(C/C_0)$ vs. reaction time under different pH conditions; and (b) plot of k' vs. $[H^+]/([H^+]+K_{a,Cl})$. $[DMT]_0 = 8 \mu M$, $[FC]_0 = 200 \mu M$, 20 mM phosphate buffer, $T = 26^\circ C$.

approximately $100 \mu g L^{-1}$. Bromide was also detected in the Qingcaosha Reservoir and the Huangpu River in China with a concentration ranging from 200 to $600 \mu g L^{-1}$ (Huang et al., 2010; Lu et al., 2011). Because bromide is quite ubiquitous and 90% of drinking water systems use FC for disinfection in China, the presence of bromide in source waters can affect the transformation rate of organophosphorus pesticides in chlorinated potable water (Duirk et al., 2008). In the presence of aqueous FC, bromide can be easily oxidized into hypobromous acid (HOBr), which was found to oxidize organics at a much faster rate than HOCl (Kumar and Margerum, 1987; Duirk et al., 2008).

Experiments to determine whether bromide accelerates the rate of DMT degradation were conducted at pH 8.29 with increasing bromide concentrations from 0 to $5 mg L^{-1}$ (Fig. 3a). Fig. 3b shows that the observed pseudo-first-order rate (k') increased linearly with an increasing bromide concentration. Similar results were also observed in chlorpyrifos transformation by FC in the presence of bromide (Duirk et al., 2008). In the presence of excessive FC, bromide would be oxidized to its active form (HOBr) with priority over DMT because the reaction rate constant for HOCl with bromide ($k_{HOCl,Br} = 7.2 \times 10^3 M^{-1} s^{-1}$) is approximately 10 times that for HOCl with DMT at $28^\circ C$ (Bousher et al., 1986). The degradation rate of DMT by native bromine was also found to be far higher than by HOCl and was hardly determined by conventional methods. The oxidation of DMT was carried out by both HOCl and HOBr in the presence of bromide. Furthermore, HOBr may be reverted to bromide after reaction with DMT. The regenerated

Fig. 3. Effect of bromide concentration on DMT degradation by FC: (a) plot of $\ln(C/C_0)$ vs. reaction time under different bromide concentrations; and (b) plot of k' vs. bromide concentration. $[DMT]_0 = 8 \mu M$, $[FC]_0 = 200 \mu M$, 20 mM phosphate buffer, pH = 8.29, $T = 28^\circ C$.

bromide could be oxidized by HOCl again and participate in additional reactions with DMT. Therefore, bromide tended to act as a catalyst in the reaction of DMT with HOCl. Under our experimental conditions, the addition of $1 mg L^{-1}$ bromide induced more than twofold increases in k' , which implies that the contribution of HOBr was likely to exceed that of HOCl.

3.4. Effect of ammonium concentration

Ammonium (NH_4^+) is universally present in source waters. The concentration of NH_4^+-N can reach up to $15 mg L^{-1}$ in some surface waters according to the monthly reports on surface water quality by the National Environmental Monitoring Centre of China. When FC is used in water treatment, NH_4^+ will quickly react with FC to produce monochloramine (MCA), dichloramine, trichloramine, nitrogen gas, nitrate, nitrogen chloride, and other compounds, depending on the pH and the FC to ammonia–nitrogen ($Cl_2:N$) ratio (Qiang and Adams, 2004). MCA is predominantly formed at $Cl_2:N$ molar ratios of less than 1:1 and in the pH range of 6.5–8.5, so the presence of NH_4^+ will significantly affect the reactivity of FC. The degradation rates of DMT at different NH_4^+ concentrations are shown in Fig. 4. The results show that the presence of NH_4^+ greatly inhibited the degradation of DMT. When the $Cl_2:N$ molar ratio decreased to 0.5 or less, the DMT concentration remained constant, indicating that DMT was resistant to MCA oxidation. An independent experiment with preformed MCA confirmed this inference.

Fig. 4. Effect of NH_4^+ concentration on DMT degradation by FC. $[\text{DMT}]_0 = 1 \mu\text{M}$, $[\text{FC}]_0 = 212 \mu\text{M}$, 20 mM phosphate buffer, pH = 8.29, $T = 27^\circ\text{C}$.

3.5. Effect of HA concentration

Dissolved humic substances are known to affect the transformation of pollutants either directly or indirectly (Huang and Weber, 2004; Georgi et al., 2007, 2008; Duirk et al., 2008). The chlorination of fluoranthene and naphthalene was found to be accelerated by addition of HA (Georgi et al., 2007). However, HA has little effect on the degradation of chlorpyrifos by FC (Duirk et al., 2008). To examine the effect of HA on the degradation of DMT, experiments were conducted under different HA concentrations in the presence of 200 μM FC.

Fig. 5a shows that the pseudo-first-order degradation rate of DMT increased with an increasing concentration of HA. The observed second-order rate constant (k''_{obs}) as a function of the total organic carbon (TOC) concentration, an indicator of the HA concentration, is plotted in Fig. 5b. The results show that the k''_{obs} increased from 85 to 131 $\text{M}^{-1}\text{s}^{-1}$ as the TOC concentration was raised from 0.77 to 15.52 mg L^{-1} . The addition of HA accelerated DMT degradation, similar to the results found in chlorination of fluoranthene and naphthalene (Georgi et al., 2007). The catalytic effect of HA could probably be attributed to its special micro-environment. The large HA molecules, due to their electronegativity and low polarity natures, were expected to have a high affinity for H^+ (through electrostatic attraction force) and DMT (through complexation), which caused a relatively lower pH condition and a relatively higher DMT concentration in the vicinity of HA molecules than in the bulk solution. As a result, these micro-environmental changes would favor the degradation of DMT by FC.

3.6. Byproducts formation

The inorganic and organic byproducts produced during the chlorination of DMT were detected by IC and GC/MS, respectively. The results show that sulfate was the only detected inorganic anion, and neither phosphate nor nitrate was detected by IC. Three organic byproducts were detected by GC/MS and then identified either according to the NIST library or by comparing their mass spectra with previously reported ones. The mass spectra and chemical structures of DMT and its organic degradation byproducts (C1–C3) are shown in Fig. S1 (Supplementary material). DMT exhibited a molecular ion at m/z 229, and the m/z 125 and 93 ions could probably correspond to $[(\text{CH}_3\text{O})_2\text{P}(\text{S})]^+$ and $[(\text{CH}_3\text{O})_2\text{P}]^+$, respectively.

Compound 1 (C1) was likely to be phosphorothioic acid, with a 93% matching probability with the NIST library. The fragment ions

Fig. 5. Effect of HA concentration on DMT degradation by FC: (a) plot of $\ln(C/C_0)$ vs. reaction time under different HA concentrations; and (b) plot of k''_{obs} vs. HA concentration. $[\text{DMT}]_0 = 8 \mu\text{M}$, $[\text{FC}]_0 = 200 \mu\text{M}$, 20 mM phosphate buffer, pH = 8.30, $T = 27^\circ\text{C}$.

at m/z 141 and 125 could arise from its molecular ion (m/z 156) by the loss of CH_3- and $\text{CH}_3\text{O}-$, respectively. Phosphorothioic acid was reported as a byproduct in the photodegradation of DMT catalyzed by TiO_2 and in the catalytic ozonation of OMT with Fe(III)-loaded activated carbon (Evgenidou et al., 2006; Qiang et al., 2013).

Compound 2 (C2), with a molecular ion of m/z 119, could correspond to *N*-methyl-2-(methylthio) acetamide by comparing its mass spectrum with that reported in the literature (Evgenidou et al., 2006; Qiang et al., 2013), which was also detected during DMT degradation by photocatalysis and OMT degradation by catalytic ozonation (Evgenidou et al., 2006; Qiang et al., 2013).

Compound 3 (C3) was identified as OMT by comparison with the spectrum of an authentic standard. The molecular ion of m/z 213 tended to yield the m/z 156 ion by the migration of hydrogen to the phosphoryl oxygen accompanied by the loss of the neutral *N*-methyl isocyanate, and the m/z 110 ion through α -cleavage accompanied by the rearrangement of hydrogen. OMT was formed because organophosphorus pesticides containing a $\text{P}=\text{S}$ bond could be oxidized to their corresponding oxons (with $\text{P}=\text{O}$) by chlorination (Duirk and Collette, 2006; Kamel et al., 2009; Duirk et al., 2009).

The formation of OMT and sulfate along with DMT degradation was determined, as shown in Fig. 6. Both OMT and sulfate accumulated with reaction time. The concentrations of OMT and sulfate were 1.5 and 7.4 μM , respectively, at the reaction time of 1 min. Native OMT was found to be stable in chlorinated water during

Fig. 6. Formation of OMT and sulfate along with DMT degradation by FC. [DMT]₀ = 8.8 μM, [FC]₀ = 204 μM, 20 mM borate buffer, pH = 8.26, T = 27 °C.

1 min reaction time. However, the amount of OMT formed in DMT chlorination only accounted for ca. 28% of the degraded DMT, implying that 72% of DMT was degraded through other pathways. Hence, the degradation mechanism of DMT by FC seemed more complicated than that of most organophosphorus pesticides containing the thiophosphate moiety (Duirk and Collette, 2006; Kamel et al., 2009; Duirk et al., 2009). The mass balance on the sulfur atom (i.e., the total S in DMT, OMT, and sulfate) reveals a deficiency of approximately 12% after 1 min chlorination, which means that some organic byproducts containing sulfur were not identified. More work needs to be performed to clarify the detailed pathways of DMT degradation in the presence of FC.

3.7. Toxicity assessment

The toxicity change of the DMT solution after 1 min chlorination was examined by the *D. magna* bioassay (see Section 2.4 for detailed experimental conditions). The inhibition values of the initial and treated DMT solutions were measured to be 6.7% and 100%, respectively. It indicates that chlorination greatly increased the DMT solution toxicity, which was most probably due to the formation of more toxic organic byproducts. As described above, OMT could accumulate with reaction time in the working solution, and was stable in chlorinated water. This highly toxic compound would certainly cause a marked increase in the DMT solution toxicity. This fact raises a serious concern about the toxicity of the degradation byproducts formed during DMT chlorination. To safeguard the drinking water quality, additional research concerning the chronic dietary risks of DMT degradates to human health should be undertaken in the future.

4. Conclusions

The reaction kinetics and mechanism of DMT with FC were investigated under typical water treatment conditions. DMT reacted rapidly with FC, and the reaction followed second-order kinetics. HOCl was the dominant reacting species accounting for DMT degradation, whereas OCl[−] could be neglected due to its much weaker oxidation potential. The specific rate constant for DMT reacting with FC ($k''_{\text{HOCl,DMT}}$) was determined to be 785 M^{−1} s^{−1}, which was independent of solution pH. Both bromide and HA were found to accelerate the reaction; however, ammonium decreased the degradation rate of DMT. Phosphorothioic acid, N-methyl-2-(methylthio) acetamide, and omethoate were identified

as possible degradation byproducts during DMT chlorination. The reaction mechanism of DMT with FC seemed more complicated than most organophosphorus pesticides containing the thiophosphate moiety, because OMT only accounted for ca. 28% of the DMT degraded. The acute toxicity of the DMT solution greatly increased after reacting with FC, most likely due to the formation of more toxic organic byproducts (e.g. OMT). It is necessary to control the toxic byproducts formed during DMT chlorination when DMT is present in source waters as a micropollutant. Additional research is needed to identify and quantify the unknown phosphorus-containing byproducts.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemosphere.2013.11.061>.

References

- Abbassy, M.S., Ibrahim, H.Z., El-Amayem, M.M.A., 1999. Occurrence of pesticides and polychlorinated biphenyls in water of the Nile river at the estuaries of Rosetta and Damietta branches, north of delta, Egypt. *J. Environ. Sci. Heal. B* 34, 255267.
- Ahmad, A.L., Tan, L.S., Shukor, S.R.A., 2009. Modeling of the retention of atrazine and dimethoate with nanofiltration. *Chem. Eng. J.* 147, 280286.
- Bousher, A., Brimblecombe, P., Midgley, D., 1986. Rate of hypobromite formation in chlorinated seawater. *Water Res.* 20, 865870.
- Catalá-Icardo, M., López-Paz, J.L., Choves-Barón, C., Peña-Bádena, A., 2012. Native vs photoinduced chemiluminescence in dimethoate determination. *Anal. Chim. Acta* 710, 8187.
- Duirk, S.E., Collette, T.W., 2006. Degradation of chlorpyrifos in aqueous chlorine solutions: Pathways, kinetics, and modeling. *Environ. Sci. Technol.* 40, 546551.
- Duirk, S.E., Desetto, L.M., Davis, G.M., 2009. Transformation of organophosphorus pesticides in the presence of aqueous chlorine: Kinetics, pathways, and structure-activity relationships. *Environ. Sci. Technol.* 43, 23352340.
- Duirk, S.E., Tarr, J.C., Collette, T.W., 2008. Chlorpyrifos transformation by aqueous chlorine in the presence of bromide and natural organic matter. *J. Agric. Food Chem.* 56, 13281335.
- Evgenidou, E., Konstantinou, I., Fytianos, K., Albanis, T., 2006. Study of the removal of dichlorovos and dimethoate in a titanium dioxide mediated photocatalytic process through the examination of intermediates and the reaction mechanism. *J. Hazard. Mater.* 137, 10561064.
- Evgenidou, E., Konstantinou, I., Fytianos, K., Poullos, I., 2007. Oxidation of two organophosphorus insecticides by the photo-assisted Fenton reaction. *Water Res.* 41, 20152027.
- FAO (Food and Agricultural Organization of the United Nations) and WHO (World Health Organization), 1996. Pesticide Residues in Food – 1996, Report of the Joint Meeting of the FAO Panel of Experts on Pesticide Residues in Food and the Environment and the WHO Expert Group on Pesticide Residues. Rome, Italy, 1625 September 1996.
- Georgi, A., Reichl, A., Trommler, U., Kopinke, F.D., 2007. Influence of sorption to dissolved humic substances on transformation reactions of hydrophobic organic compounds in water. I. Chlorination of PAHs. *Environ. Sci. Technol.* 41, 70037009.
- Georgi, A., Trommler, U., Reichl, A., Kopinke, F.D., 2008. Influence of sorption to dissolved humic substances on transformation reactions of hydrophobic organic compounds in water, Part II: Hydrolysis reactions. *Chemosphere* 71, 14521460.
- Huang, Q.G., Weber, W.J., 2004. Interactions of soil-derived dissolved organic matter with phenol in peroxidase-catalyzed oxidative coupling reactions. *Environ. Sci. Technol.* 38, 338344.
- Huang, X., Mei, H., Ding, G., Lu, N., 2010. Bromate formation during ozonation in bromide-containing Huangpu River water. *J. Shanghai Univ.* 16, 498502.
- Kamel, A., Byrne, C., Vigo, C., Ferrario, J., Stafford, C., Verdin, G., Siegelman, F., Knizner, S., Hetrick, J., 2009. Oxidation of selected organophosphate pesticides during chlorination of simulated drinking water. *Water Res.* 43, 522534.

- Kumar, K., Margerum, D.W., 1987. Kinetics and mechanism of general-acid-assisted oxidation of bromide by hypochlorite and hypochlorous acid. *Inorg. Chem.* 26, 27062711.
- Lisker, E.B., Ensminger, M.P., Gill, S.L., Goh, K.S., 2011. Detections of eleven organophosphorus insecticides and one herbicide threatening Pacific Salmonids, *Oncorhynchus spp.*, in California, 1991–2010. *Bull. Environ. Contam. Toxicol.* 87, 355360.
- Liu, Y.N., Jin, D., Lu, X.P., Han, P.F., 2008. Study on degradation of dimethoate solution in ultrasonic airlift loop reactor. *Ultrason. Sonochem.* 15, 755760.
- Lopez, A., Mascolo, G., Ciannarella, R., Tiravanti, G., 2001. Formation of volatile halogenated by-products during chlorination of isoproturon aqueous solutions. *Chemosphere* 45, 269274.
- Lu, N., Huang, X., Gao, N.Y., Liu, H., Zhang, D., 2011. Bromonium ion and its bromate formation potential in raw water of Qingcaosha Reservoir. *Water Purif. Technol.* 30 (1012), 19.
- Martín, M.M.B., Pérez, J.A.S., Fernández, F.G.A., López, J.L.C., García-Ripoll, A.M., Arques, A., Oller, I., Rodríguez, S.M., 2008. Combined photo-Fenton and biological oxidation for pesticide degradation: effect of photo-treated intermediates on biodegradation kinetics. *Chemosphere* 70, 14761483.
- Martín, M.M.B., Pérez, J.A.S., López, J.L.C., Oller, I., Rodríguez, S.M., 2009. Degradation of a four-pesticide mixture by combined photo-Fenton and biological oxidation. *Water Res.* 43, 653660.
- Mascolo, G., Lopez, A., James, H., Fielding, M., 2001. By-products formation during degradation of isoproturon in aqueous solution. II: Chlorination. *Water Res.* 35, 17051713.
- Mason, Y.Z., Choshen, E., Rav-Acha, C., 1990. Carbamate insecticides: Removal from water by chlorination and ozonation. *Water Res.* 24, 1121.
- MEPC (Ministry of Environmental Protection of China), 1991. Water quality-Determination of the acute toxicity of a substance to *Daphnia* (*Daphnia magna* Straus). Beijing.
- Miles, C.J., 1991. Degradation of aldicarb, aldicarb sulfoxide, and aldicarb sulfone in chlorinated water. *Environ. Sci. Technol.* 25, 17741779.
- Morris, J.C., 1966. The acid ionization constant of HOCl from 5 to 35 °C. *J. Phys. Chem.* 70, 37983805.
- Pappas, C.J., Kyriakidis, N.V., 2003. A comparison of dimethoate degradation in lemons and mandarins on the trees with two GC systems. *Food Chem.* 80, 23–28.
- Qiang, Z., Adams, C.D., 2004. Determination of monochloramine formation rate constants with stopped-flow spectrophotometry. *Environ. Sci. Technol.* 38, 14351444.
- Qiang, Z., Ling, W., Tian, F., 2013. Kinetics and mechanism for omethoate degradation by catalytic ozonation with Fe(III)-loaded activated carbon in water. *Chemosphere* 90, 19661972.
- Qu, C.S., Chen, W., Bi, J., Huang, L., Li, F.Y., 2011. Ecological risk assessment of pesticide residues in Taihu Lake wetland. *China. Ecol. Model.* 222, 287292.
- USEPA, 1999. Alternative Disinfectants and Oxidants Guidance Manual. US EPA 815-R-99-014. United States Environmental Protection Agency, Office of Water, Washington, DC.
- USEPA, 2009. Contaminant Candidate List 3 - CCL. United States Environmental Protection Agency, Office of Ground Water and Drinking Water, Washington, DC.
- USEPA, 2011. Regulatory Determinations for the Third Drinking Water Contaminant Candidate List. United States Environmental Protection Agency, Office of Ground Water and Drinking Water, Washington, DC.
- Westerhoff, P., Siddiqui, M.S., Debroux, J., Zhai, W., Ozekin, K., Amy, G., 1994. Nation-wide bromide occurrence and bromate formation potential in drinking water supplies. In: Ryan, J.N., Edwards, M. (Eds.), *Critical Issues in Water and Wastewater Treatment*. American Society of Civil Engineers, New York, p. 670677.
- WHO (World Health Organization), 2009. The WHO Recommended Classification of Pesticides by Hazard and Guidelines to Classification 2009.
- WHO (World Health Organization), 2011. Guidelines for Drinking-water Quality, 4th edition.
- Yao, J.J., Hoffmann, M.R., Gao, N.Y., Zhang, Z., Li, L., 2011. Sonolytic degradation of dimethoate: Kinetics, mechanisms and toxic intermediates controlling. *Water Res.* 45, 58865894.
- Zhang, L., Guo, X., Yan, F., Su, M., Li, Y., 2007. Study of the degradation behaviour of dimethoate under microwave irradiation. *J. Hazard. Mater.* 149, 675–679.
- Zhang, Z.L., Hong, H.S., Wang, X.H., Lin, J.Q., Chen, W.Q., Xu, L., 2002. Determination and load of organophosphorus and organochlorine pesticides at water from Jiulong River Estuary, China. *Mar. Pollut. Bull.* 45, 397–402.