Influence of nitrogen source on NDMA formation during chlorination of diuron

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ABSTRACT

N-Nitrosodimethylamine (NDMA) is formed during chlorination of water containing the herbicide diuron (N'-(3,4-dichlorophenyl)-N,N-dimethylurea) but formation is greatly enhanced in the presence of ammonia (chloramination). Groundwater impacted by agricultural runoff may contain diuron and relatively high total nitrogen concentrations; this study examines the impact of the nitrogen form (ammonium, nitrite or nitrate) on NDMA formation during chlorination of such waters. NDMA formation during chlorination of diuron increased in the order nitrite < nitrate < ammonium for a given chlorine, nitrogen, and diuron dose. Formation of dichloramine seemed to fully explain enhanced NDMA formation in the presence of ammonium. Nitrate unexpectedly enhanced nitrosation of diuron derivatives to form NDMA compared to the cases of no added nitrogen or nitrite addition. Nitrite addition is less effective because it consumes more chlorine and produces intermediates that react rapidly with diuron and its aromatic byproducts. Differences between surface water and groundwater in nitrogen forms and concentrations and disinfection approaches suggest strategies to reduce NDMA formation should vary with drinking water source.

1. Introduction

Concerns regarding N-nitrosodimethylamine (NDMA), classified as a probable human carcinogen by the U.S. Environmental Protection Agency (EPA), have been increasingly reported after its discovery in treated drinking waters and wastewaters in 1999. Many studies have identified NDMA as a byproduct of disinfection and it has been detected in many drinking water and wastewater treatment plants applying chlorination or chloramination. Currently, there is no national maximum contaminant level (MCL) established for NDMA in drinking water in the U.S., but other regulatory agencies have established NDMA guidelines. The California Department of Health Services (DHS), for example, has an interim action level of 10 ng/L for NDMA (Mitch et al., 2003b).

Although many studies have been conducted in response to the health concerns associated with NDMA, the exact precursors of NDMA and the associated formation pathways remain unclear. NDMA is known to be produced during chloramination when mono- and/or di-chloramines react with secondary amines, such as dimethylamine (DMA) (Choi et al., 2002; Mitch and Sedlak, 2002; Schreiber and Mitch, 2006). Another NDMA formation pathway involves the nitrosation of DMA in the presence of nitrite and free chlorine, with a mechanism that involves the formation of highly nitrosating intermediates such as dinitrogen tetroxide (N_2O_4) during the oxidation of nitrite to nitrate (Choi and Valentine, 2003). In most previous studies, DMA has served as the model precursor for NDMA; however, it is important to note that the formation of NDMA found in drinking water or wastewater

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typically cannot be completely accounted for by the known formation mechanisms and the amount of DMA present, indicating other possible precursors and/or formation pathways (Gerecke and Sedlak, 2003).

In our previous study, it was shown that diuron, a widely used substituted phenylurea herbicide that has been frequently detected in California source waters, is a potential precursor for NDMA formation during disinfection with chlorine or chloramines (Chen and Young, 2008). Although the yield of NDMA from diuron was lower than for some other nitrogen-containing precursors, particularly ranitidine (Schmidt et al., 2006), this formation pathway was notable because it could proceed without the addition of another nitrogen source such as ammonium or nitrite.

Based on previous research it is likely that the form and concentrations of additional nitrogen sources (such as ammonium and nitrite) will play a significant role in determining the exact NDMA formation mechanism, affecting the formation rate and yield of NDMA from its precursors. Ammonium, nitrite, and nitrate, from natural and anthropogenic sources, are three common nitrogen forms and the exact form present is strongly related to input form and redox status of the environment. In wastewater ammonium is ubiquitous, while nitrate (and nitrite at relatively lower concentrations) is possibly the most widespread contaminant in groundwater (Nolan et al., 2002). The disinfection process employed also varies depending on whether surface water or groundwater is being treated. For example, in California, chloramines and free chlorine are the typical disinfectants used to treat surface water and groundwater, respectively (USEPA, 2002). It is likely that NDMA formation from its precursors may be very different between drinking water treatment using surface water and groundwater due to the disinfectants selected and additional nitrogen-containing species involved.

The objective of this study was therefore to investigate the effect of these common nitrogen-containing species on the formation of NDMA from the herbicide diuron during disinfection applying chlorine or chloramines. An overall mechanism of NDMA formation from diuron when different nitrogen sources are present is proposed. While detailed mechanistic studies remain to be done, our results provide the ability to establish whether the amount of diuron and major nitrogen species typically present in surface water or groundwater could pose significant health risks with respect to NDMA formation during disinfection with free chlorine or chloramines.

2. Experimental section

2.1. Materials

Diuron (>98%; Sigma–Aldrich; CAS# 330-54-1; N′-(3,4-dichlorophenyl)-N,N-dimethylurea), NDMA, and NDMA-d_6 (internal standard; Chem Service) were used without further purification. 1,2-dichloro-4-nitrobenzene and 1,2-dichloro-4,5-dinitrobenzene (Sigma–Aldrich) were used to verify the presence of selected reaction intermediates and were diluted as necessary. Ammonium chloride, sodium nitrite, and potassium nitrate (Fisher Scientific) were used as initial N sources. All experiments were conducted using deionized water (Milli-Q; Millipore) buffered with sodium acetate (pH = 4), phosphate (pH = 6–8), or carbonate (pH = 10). Solution pH values were adjusted as needed using sodium hydroxide or sulfuric acid (0.2 N). Sodium hypochlorite (NaOCl, purified grade, 4–6%) and ascorbic acid (Spectrum Chemical) were used as the chlorination reagent and the chemical added to quench the chlorination, respectively. Ambersorb 572 beads (Sigma–Aldrich) were used to extract NDMA from aqueous solution. Ammonium iron (II) sulfate (98.5–101.5%, Alfa Aesar), N,N-diethyl-p-phenylenediamine sulfate (97%, Alfa Aesar), thioacetamide (0.25%, LabChem), disodium ethylenediamine tetraacetate, and potassium iodide were chemicals used in the DPD ferrous titrimetric method. All reagents not specified were obtained from Fisher Scientific.

2.2. Chloramine formation and analysis

Stock hypochlorite (OCl⁻) solutions were prepared by adding NaOCl to Milli-Q water. Monochloramine (NH$_2$Cl) solutions were prepared fresh daily by slowly adding NaOCl to a rapidly stirred ammonium chloride (NH$_4$Cl) solution at a Cl:N molar ratio of at least 1:1.2 to reduce breakpoint chlorination resulting from local excesses of OCl⁻. The pH was maintained at 8.5 to minimize the disproportionation of NH$_2$Cl to dichloramine (NHCl$_2$) (Mitch and Sedlak, 2002).

$$2NH_2Cl + H^+ = NHCl_2 + NH_4^+ \tag{1}$$

When chloramines were prepared at Cl:N molar ratios below 1.5:1, NH$_2$Cl and NHCl$_2$ coexist without the presence of free chlorine following eq. (1) with an equilibrium constant of 6.7×10^5 at 25 °C (Deinzer et al., 1978; Schreiber and Mitch, 2005). Stock NHCl$_2$ solution was prepared by lowering the pH of stock NH$_2$Cl solution to 3.7 and aging for 1 h. Concentrations of all chlorinated compound stock solutions were standardized by using the DPD ferrous titrimetric method (Eaton et al., 1998).

2.3. NDMA formation assays

NDMA formation potential was assessed by varying doses of reagents, pH values, or contact times during chlorination of aqueous diuron solutions. Prior to experiments, all glassware was washed and baked at 450 °C for at least 3 h. Batch experiments were conducted at room temperature (23 °C ± 3 °C) in 1 L sealed amber jars under dark conditions to avoid NDMA photolysis. Diuron solution was prepared by fully dissolving a pre-determined amount of diuron in 1 L of Milli-Q water, and chlorine and selected reagents were added to simulate the condition of chlorination or chloramination. Dependence of NDMA formation on system conditions was assessed by varying initial diuron concentrations, the form and concentration of chlorine and nitrogen-containing species, contact time, and solution pH. All experiments were at least duplicated to assess reproducibility.

2.4. Analytical methods

Concentrations of NDMA and other possible reaction intermediates including 1,2-dichloro-4-nitrobenzene and 1,2-dichloro-4,5-dinitrobenzene were determined by an isotope dilution GC–MS method after extraction (Choi and Valentine, 2002a; Schreiber and Mitch, 2005). NDMA-d_6 (50 μL of a 10 mg/L stock solution in methanol) was added to each 1 L sample as an internal standard and the reaction was quenched with 500 mg ascorbic acid at the end of the selected contact time. Samples were extracted by adding Ambersorb 572 carbonaceous beads (2.5 g, baked at 300 °C for >3 h) to the solutions and shaking for at least 1 h at 200 rpm. Prior to extraction with 6 ml of methylene chloride in 16 ml amber vials overnight, carbonaceous beads were recovered by vacuum filtration (Whatman paper fiber filter 2, >8 μm) followed by air drying for at least 3 h. After extraction, methylene chloride was decanted and concentrated to 0.5 ml using a rotary evaporator. Although NDMA recoveries from spiked deionized water samples were low (average 40% ± 7% (average ± SD)) compared to those for other organic chemicals, they were precisely known by use of the deuterated internal standard. Analyses for 1,2-dichloro-4-nitrobenzene and 1,2-dichloro-4,5-dinitrobenzene were conducted to determine the occurrence of these potential intermediates rather than to quantify their formation, so no internal standards were used.

An Agilent 6890 Gas Chromatograph with an Agilent 5973 mass spectrometer (splitless 2 μL injection at 220 °C, 240 °C transfer line, Agilent Technology DB-624 capillary column 30 m by 0.25 mm internal diameter and 1.4 m thickness, initial oven 35 °C ramped at 10 °C/min to 120 °C, then 30 °C/min to 220 °C, hold 2 min) was used to analyze extracts for NDMA and other selected compounds with mass spectrometry being performed in electron ionization mode. Target ions were 74 and 80 m/z for NDMA and NDMA-d_6, respectively, and quantitation ions were 43 and 42 m/z for NDMA, and 46 and 30 m/z for NDMA-d_6. Concentrations of NDMA were corrected for extraction efficiencies using NDMA-d_6 as a surrogate standard, with the detection limit of this NDMA analysis at the 99% confidence level being determined to be 2.3 ng/L. For 1,2-dichloro-4-nitrobenzene and 1,2-dichloro-4,5-dinitrobenzene, the target ions were 191 and 236 m/z, respectively. Quantitation ions were 145 and 109 m/z for 1,2-dichloro-4-nitrobenzene and 97 and 238 m/z for 1,2-dichloro-4,5-dinitrobenzene.

3. Results and discussion

The initial experiments employed high concentrations of diuron (0.09 mM) and nitrite or nitrate (0.36 mM) during chlorination (3.45 mM) for a contact time of 24 h to investigate the effect of these additional nitrogen sources on NDMA formation from diuron (Table 1). Chlorine was in excess compared to diuron as expected in typical chlorination scenarios. The initial concentration of nitrate and nitrite was selected to be 5 mg/L as N considering that the U.S. federal MCL is 10 mg/L as N for nitrate (USEPA, 1995) and 9% of domestic wells sampled by the U.S. Geological Survey's National Water-Quality Assessment (NAWQA) program

Table 1 – NDMA formation from the reaction between diuron and NaOCl with or without the addition of nitrite or nitrate for 24 h contact time.

Initial N concentrations		Final NDMA concentration			
NO_2^- (mg/L as N)	NO_3^- (mg/L as N)	Mean (ng/L)	STD (ng/L)	Mean (nM)	STD (nM)
0	0	46.2	5.5	0.6	0.1
0	5	398.5	13.6	5.4	0.2
5	0	399.9	15.7	5.4	0.2
5	5	395.2	9.0	5.3	0.1

STD represents one standard deviation.
The initial concentrations of diuron and NaOCl were 0.09 mM (20 mg/L) and 3.45 mM (245 mg/L as Cl_2), respectively.
The initial concentration of nitrate and nitrite applied was 0.36 mM (5 mg/L as N).

during 1993–2000 had nitrate concentrations exceeding this limit (Nolan et al., 2002). In a typical groundwater, nitrite might be detected occasionally at a concentration lower than that of nitrate; however, the same nitrite and nitrate concentrations were employed to compare the effects more easily. Addition of nitrite or nitrate greatly enhanced (by almost 10-fold) the production of NDMA during chlorination of diuron compared to the case with no additional N source (Table 1). However, no significant difference was observed in NDMA formation between the two nitrogen forms. Further, when both nitrate and nitrite were added, NDMA formation was almost identical to that observed in the experiments with only nitrate or nitrite.

To examine the reaction kinetics and further compare the influence of nitrite and nitrate on NDMA formation during chlorination, experiments were conducted with nitrite or nitrate at a lower chlorine concentration (0.07 mM) for various contact times (Fig. 1). NDMA formed rapidly at the beginning of both experiments and continued to form over 24 h. However, NDMA formation was slower in the presence of nitrite than in the presence of nitrate, an unexpected result. NDMA formation in all of the experiments was far lower than that observed by Choi and Valentine, who found, for example, more than 200 nM of NDMA was produced in 24 h experiments with nitrite (0.5 mM), DMA (0.1 mM) and HOCl (0.1 mM), concentrations similar to those used here for nitrite (0.36 mM), diuron (0.09 mM) and NaOCl (0.07 mM) (Choi and Valentine, 2003). Probably the most significant difference between these two studies is the different reactivity imparted by the aromatic ring of diuron and its byproducts compared with the simpler amine structure of DMA used as the precursor in Choi and Valentine (2003). To our knowledge the direct effect of nitrate on NDMA formation has not been investigated previously.

The significant difference in NDMA formation caused by nitrite and nitrate addition under a lower free chlorine concentration indicated the role of the Cl/N ratio in the process. This effect was investigated by changing the Cl/N molar ratio during chlorination of diuron in solutions containing either added nitrite or nitrate. Significant differences were observed in NDMA formation between the experiments with nitrite and nitrate addition at Cl/N molar ratios below 5,
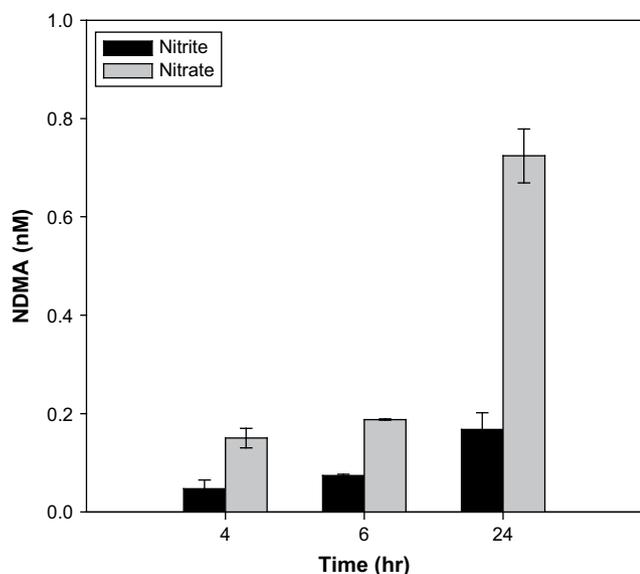
Fig. 1 – NDMA formation during chlorination of diuron in the presence of nitrate or nitrite. NaOCl (0.07 mM; 5 mg/L as Cl$_2$) was added to aqueous diuron solutions (0.09 mM; 20 mg/L) containing either nitrite or nitrate (0.36 mM; 5 mg/L as N). The experiments were controlled at pH 8 ± 0.2 by using 10 mM phosphate buffer. The bar and error bar represent the mean and the difference between the maximum and minimum values.
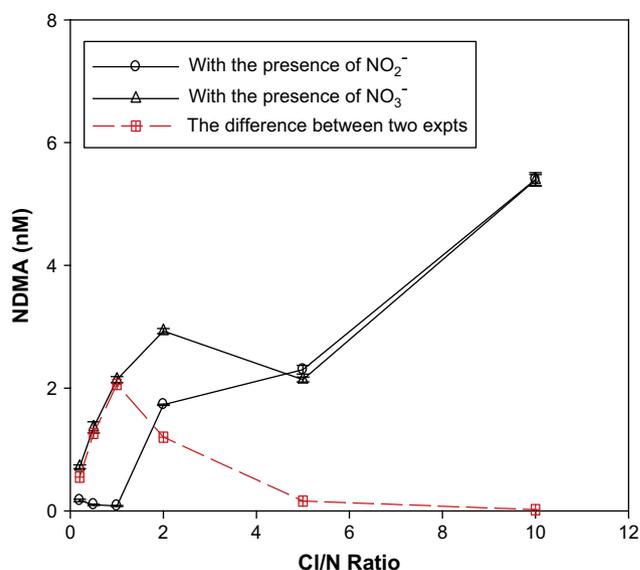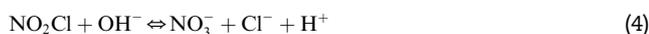

Fig. 2 – NDMA formation during chlorination of diuron in the presence of either nitrite or nitrate under various Cl/N molar ratios. Different NaOCl concentrations were added to aqueous diuron solutions (0.09 mM; 20 mg/L) containing either nitrite or nitrate (0.36 mM; 5 mg/L as N). The experiments were controlled at pH 8 ± 0.2 by using 10 mM phosphate buffer for 24 h. The point and error bar represent the mean and the difference between the maximum and minimum values.

with a maximum difference at Cl/N = 1. No difference was observed between the nitrate and nitrite experiments for Cl/N = 5 or 10 (Fig. 2). Essentially no NDMA was produced in the nitrite experiments until Cl/N exceeded 1, while NDMA formation occurred for all Cl/N ratios tested with nitrate. One possibility is that chlorine added was consumed by the reaction with nitrite to form nitryl chloride and ultimately nitrate, as shown in eqs. (2)–(4) (Choi and Valentine, 2003).

$$HOCl + NO_2^- \Leftrightarrow NO_2Cl + OH^- \tag{2}$$

$$NO_2Cl + NO_2^- \Leftrightarrow N_2O_4 + Cl^- \tag{3}$$

$$NO_2Cl + OH^- \Leftrightarrow NO_3^- + Cl^- + H^+ \tag{4}$$

As the Cl/N ratio exceeded 1 in the experiment with nitrite present, the excess free chlorine was thus available to react with diuron to form NDMA and the effects of further chlorine addition were similar to those in which the initial form of N was nitrate. These results are in direct contrast to the results of Choi and Valentine, who observed a maximum in NDMA formation at Cl/N ~1 and suggested that extra nitrite might be required beyond that which reacted with HOCl to form NO$_2$Cl. This difference likely results from consumption of nitryl chloride and/or dinitrogen tetroxide with aromatic carbon to form nitro-aromatic byproducts at lower Cl/N ratios, a pathway unavailable in Choi and Valentine (2002a). This probably accounts for the far lower NDMA yields observed in our experiments.

Our previous study focused on the influence of another nitrogen-containing species, ammonium, on NDMA

formation by the reaction of diuron with free chlorine (Chen and Young, 2008). Ammonium significantly enhanced the yield of NDMA in aqueous diuron solutions during chlorination. To investigate the relative health risks posed by NDMA formation from these nitrogen species (nitrite, nitrate, or ammonium) to determine diuron concentration thresholds for concern in the presence of each N form, experiments were conducted with each species in solutions containing various initial diuron concentrations. For a given chlorine and diuron dose, NDMA formation was greatest in the experiments with ammonium added (Fig. 3a). An NDMA yield of 0.2 nM (15 ng/L), above the California DHS interim NDMA action level of 10 ng/L, was detected when the initial diuron concentration was raised to 0.7 μM (0.16 mg/L) in the presence of ammonium. In the presence of nitrite and nitrate, NDMA yields were 0.07 nM (5.2 ng/L) and 0.14 nM (10.4 ng/L), respectively, when diuron concentration was increased to 17.2 μM (0.8 mg/L). The formation of NDMA was not detected in any experiment employing an initial diuron concentration of 0.1 μM (0.02 mg/L). This diuron concentration was selected to represent the upper end of those detected in California source waters of 20 μg/L in surface water (CDPR) and 5 μg/L in groundwater (USEPA, 1992; USGS). Therefore it appears that typical diuron concentrations in California source waters may not pose significant health threats with respect to NDMA formation during chlorination. However, it is important to note that the conditions in these experiments were simplified by solely involving free chlorine and three nitrogen-containing species (ammonium, nitrite, and nitrate) at a specific pH value. Higher yields of NDMA may
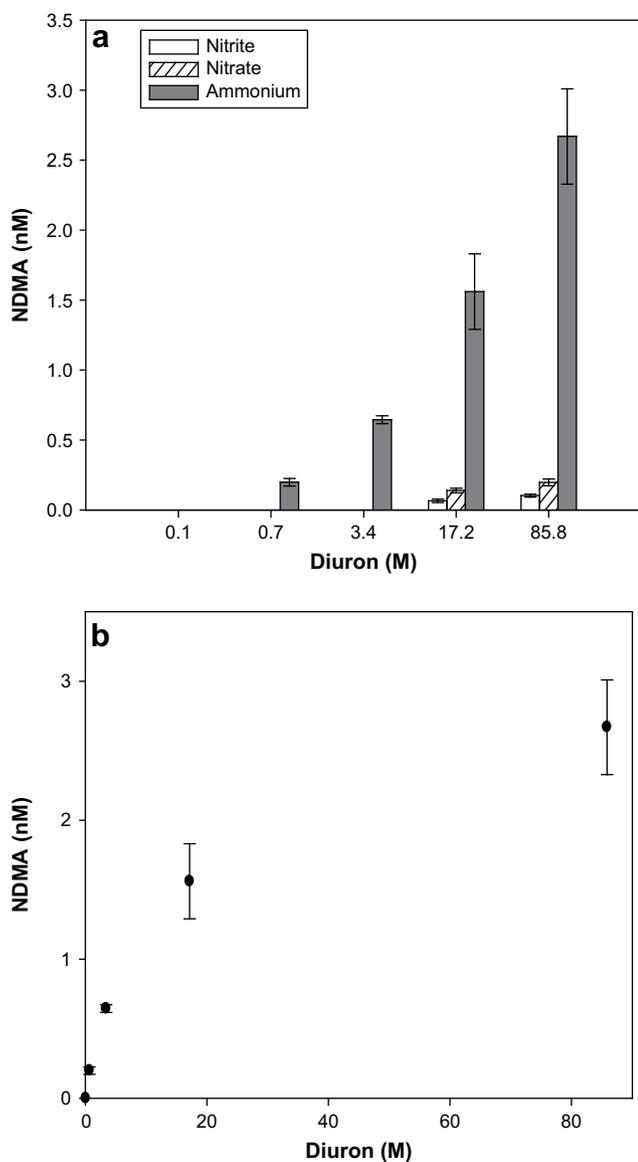
Fig. 3 – NDMA formation in solutions of various diuron concentrations during chlorination in the presence of ammonium, nitrate, or nitrate. (a) 0.07 mM (5 mg/L as Cl_2) NaOCl was added to diuron solutions containing 0.36 mM (5 mg/L as N) ammonium, nitrite, or nitrate. (b) 0.07 mM (5 mg/L as Cl_2) NaOCl was added to diuron solutions containing 0.36 mM (5 mg/L as N) ammonium. The experiments were controlled at pH 8 ± 0.2 with 10 mM phosphate buffer for 2 h. The bar in figure (a) and point in figure (b) and error bar represent the mean value and difference between the maximum and minimum values.

during chlorination, and to further elucidate reaction pathways, experiments were conducted by adding nitrite or nitrate to aqueous diuron solutions containing pre-determined amounts of ammonium. The initial concentrations of ammonium, nitrite, and nitrate were equal (0.36 mM or 5 mg/L as N). The formation of NDMA was thus measured as a function of time under three different conditions: (1) only ammonium was present, (2) ammonium and nitrite coexist, and (3) ammonium and nitrate coexist. The addition of nitrite suppressed NDMA formation compared to the case when only ammonium was present (Fig. 4). Presumably the inhibition of NDMA formation by adding nitrite resulted from chlorine consumption by nitrite via free chlorine reaction with nitrite to form nitryl chloride as shown in eq. (2) or chloramination of nitrite to ammonium and nitrate as shown in eq. (5) (Choi and Valentine, 2003; Margerum et al., 1994):

$$NH_2Cl + NO_2 + H_2O \Leftrightarrow NH_4 + NO_3 + Cl^- \qquad (5)$$

These chlorine consumption reactions associated with the presence of nitrite will be most significant at low Cl/N ratios as in this experiment (Cl/N = 0.2).

NDMA yields with ammonium and nitrate were very similar to those with only ammonium present. Nitrate presumably did not inhibit NDMA formation because it imposed a far smaller chlorine demand than nitrite, while the failure of nitrate to measurably add to NDMA formation is likely a result of the much lower efficiency of the nitrosation pathway compared with the UDMH pathway (e.g., Fig. 3a and Choi and Valentine, 2003).

The larger NDMA yields from various precursors during chloramination have focused research attention on various chlorinated nitrogen species present in such processes (Choi
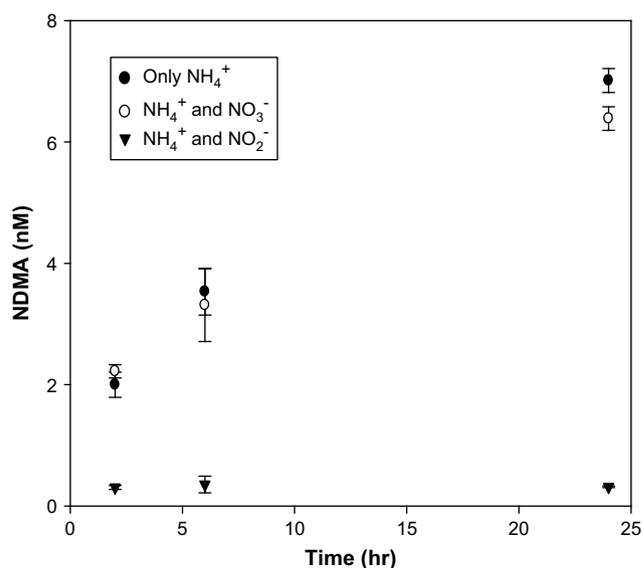
Fig. 4 – The yield of NDMA in aqueous diuron solutions during free chlorine application. The initial concentrations of diuron and free chlorine were 0.09 mM (20 mg/L) and 0.07 mM (5 mg/L as Cl_2), respectively. Ammonium, nitrite, and nitrate were added in the beginning of the experiments at 0.36 mM (5 mg/L as N). The pH was controlled at 8 ± 0.1 by using 10 mM phosphate buffer.

be possible under other realistic conditions. In Fig. 3b, the yield of NDMA decreased as the diuron concentration increased, possibly because of reductions in chlorinated or nitrated diuron intermediates as diuron concentrations increased relative to nitrogen and chlorine.

Many source waters contain nitrogen in a mixture of forms. To investigate the effect of coexistence of these additional nitrogen sources on NDMA formation from diuron

and Valentine, 2002b, 2003; Mitch et al., 2003a; Mitch and Sedlak, 2002; Schreiber and Mitch, 2006). Depending on the pH and chlorine to nitrogen ratio ammonium can react with free chlorine to form inorganic chloramines, NH_2Cl, $NHCl_2$, and NCl_3. Our previous study indicated that for a given chlorine and diuron dose at neutral pH NDMA formation increased in the order $OCl^- < NH_2Cl < NHCl_2$ (Chen and Young, 2008). To further investigate the relationship among these oxidants and NDMA formation, and also to determine whether nitrogen trichloride (NCl_3) is a significant contributor to NDMA formation from diuron during chloramination, experiments were conducted by adding preformed chloramine solutions prepared at various pH values to aqueous diuron solutions controlled at pH 8 for a contact time of 0.5 h. The purpose of preparing chloramine solutions at different pH values was to vary the concentration ratio among each chloramine species, which can then be compared with the yield of NDMA. NDMA formation varied significantly when chloramine solutions prepared at various pH values were added to solutions with a common diuron concentration (Fig. 5a). NDMA formation in aqueous diuron solution was highest and lowest when the chloramine solution added was prepared at pH 6.7 and 9.3, respectively.

To assess the relative importance of the three chloramine species, their relative concentrations were estimated in the solutions prepared at three pH values. As the pH decreases, $NHCl_2$ and NCl_3 become predominant forms as described in eqs. (1) and (6).

$$3NHCl_2 + H^+ = 2NCl_3 + NH_4^+ \qquad (6)$$

The Gibbs energies of formation (ΔG_f^o) of H^+, NH_4^+, $NHCl_2$, and NCl_3, as listed in Table 2, were used to estimate the equilibrium constant of eq. (6). Two Gibbs energies of formation for NCl_3 are available in the literature, so an average value was used. By applying the Gibbs free energy values of these chemicals, the equilibrium constant of eq. (6) was determined ($K = 16.7$).

Two equations (eqs. (1) and (6)) and the associated equilibrium constants were thus used to estimate the concentrations of NH_2Cl, $NHCl_2$, and NCl_3 in the chloramine solutions prepared at three pH values (Fig. 5b). The predicted concentrations of $NHCl_2$ at pH 2, 6.7, and 9.7 were 0.18, 0.38, and 0.01 mM, while the final NDMA concentrations were 11.0, 35.5, and 2.1 nM, respectively. There is a strong linear relationship ($[NDMA] = 8.76 \times 10^{-5}$ $[NHCl_2]$; $R^2 = 0.98$) between the predicted $NHCl_2$ concentration in these experiments and the resulting NDMA concentration, suggesting that $NHCl_2$ was the primary NDMA-forming oxidant in these three experiments. This finding also indicates that in our previous study (Chen and Young, 2008), NDMA formation in aqueous diuron solutions during NH_2Cl application may have resulted from the reaction between diuron and $NHCl_2$, which might be formed by transformation or self-disproportionation of NH_2Cl. It is important to note, however, that $NHCl_2$ is not stable at the pH values investigated here, so the possible involvement of intermediates from the decay of $NHCl_2$ cannot be ruled out as opposed to a direct reaction of $NHCl_2$.

To follow up on the results presented in Fig. 5, the influence of pH on NDMA formation from diuron during dichloramination
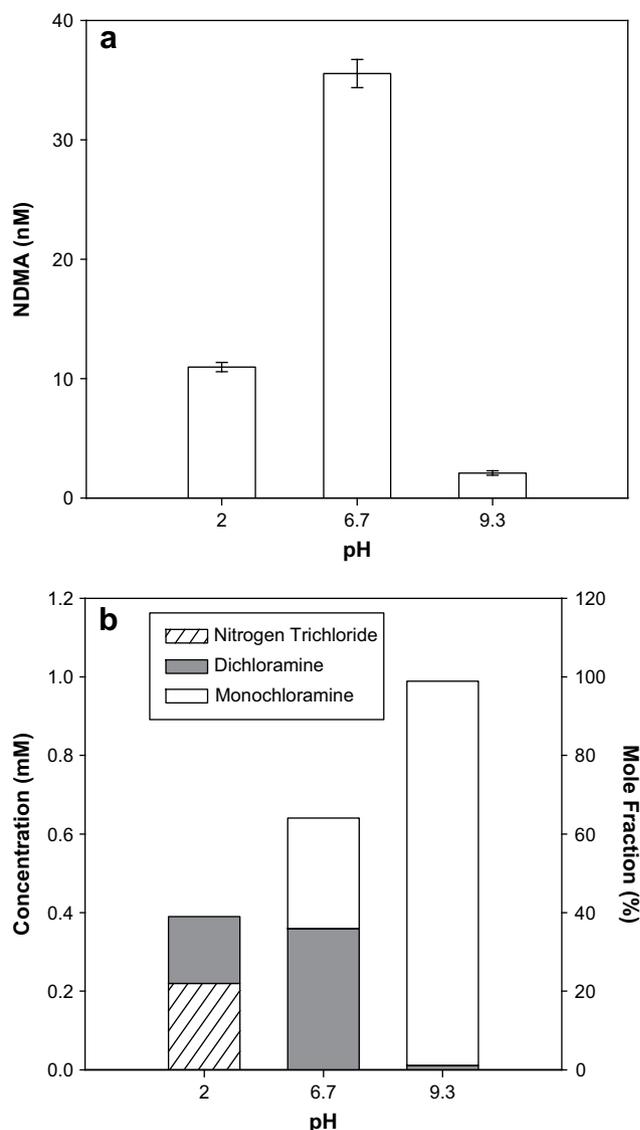

Fig. 5 – (a) Concentration of NDMA produced after 0.5 h contact time during diuron chloramination using chloramine solutions prepared at various pH values. The initial concentration of diuron was 0.09 mM (20 mg/L). (b) Molar fraction and concentration of three nitrogen species (NH_2Cl, $NHCl_2$, and NCl_3) at various pH values after aging 1 h. The concentration of total chlorine and NH_4Cl used to prepare the chloramine solutions at various pH values were 1.05 mM (74.34 mg/L as Cl) and 1.43 mM (76.51 mg/L), respectively. The reaction was buffered using acetate buffer for pH 2, phosphate buffer for pH 6.7, and carbonate buffer for pH 9.3. The bar and error bar represent the mean value and one standard deviation, respectively.

was studied by varying the solution pH (Fig. 6). Preformed $NHCl_2$ solutions were added to aqueous diuron solutions controlled at three pH values and NDMA formation was measured after various contact times. Previous research indicated that $NHCl_2$ became dominant as the pH ranged approximately from 2.5 to 5.5 (Palin, 1950), indicating that NDMA formation in aqueous diuron solution during dichloramination may be maximized

Table 2 – Standard state Gibbs free energies of formation from the elements for selected compounds.

Substance	State	ΔG_f^o at 25 °C (kJ/mol)	Reference
H^+	Aqueous	0	Thauer et al. (1977)
NH_4^+	Aqueous	−79.37	Thauer et al. (1977)
$NHCl_2$	Aqueous	209.2	Soulard et al. (1981)
NCl_3	Aqueous	341.4, 362.1	Soulard et al. (1981), Wrona (1998)

over this pH range. Similar results were found in Fig. 6; NDMA formation from diuron at pH 4 was relatively higher than at pH 7 or 10 throughout the time scale of the experiments. For shorter contact time (i.e., 0.5 h), the similarly high yield of NDMA from diuron detected at the end of experiments conducted at pH 4 and 10 was possibly attributable to the enhanced hydrolysis of diuron. Previous studies have shown that diuron is stable toward hydrolysis at neutral pH values; however, the hydrolysis rate sharply increases at lower or higher pH values releasing additional DMA (Giacomazzi and Cochet, 2004; Salvestrini et al., 2002). It is worth noting that in Fig. 6 as the contact time increased, the NDMA yield from diuron at pH 10 became relatively less than those measured at pH 4, which possibly resulted from the self-disproportionation of $NHCl_2$ producing NH_2Cl, which was found to be a less reactive form for producing NDMA.

A schematic of the potential reaction pathways for NDMA formation in aqueous diuron solution during chlorination or chloramination is shown in Fig. 7. In this proposed mechanism, diuron is initially oxidized by OCl^- to produce
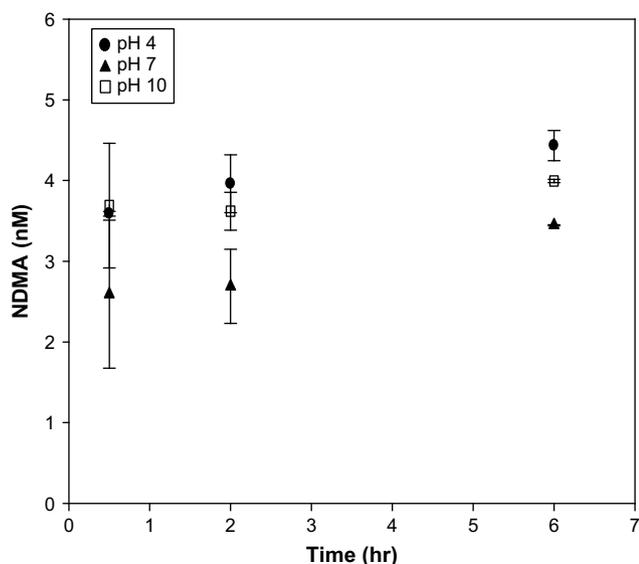

Fig. 6 – Concentration of NDMA produced in aqueous diuron solutions at various pH values after various contact times. The initial concentrations of diuron and $NHCl_2$ were 0.09 mM (20 mg/L) and 0.6 mM (40 mg/L as Cl_2), respectively. The reaction was buffered by using acetate buffer for pH 4; phosphate buffer for pH 7; and carbonate buffer for pH 10. The point and error bar represent the mean value and one standard deviation, respectively.

phenylisocyanate and DMA, which can be further transformed to DCA and chlorinated DMA (CDMA). It is known that primary aromatic amines can be oxidized to form nitroso compounds, while aromatic nitroso compounds are easily oxidized to nitro compounds by many oxidizing agents (Boyer, 1980; Hedayatu, 1972). Therefore, one potential oxidation product from DCA is 1,2-dichloro-4-nitrobenzene. This compound and other chloro-, nitrobenzene species such as 1,2-dichloro-4,5-dinitrobenzene were observed during chlorination of diuron (data not shown). Formation of inorganic chloramines was monitored during the chlorination of phenylisocyanate or DCA to investigate whether chloramines were involved at this stage to form NDMA; no inorganic chloramines were detected.

When ammonium is present NDMA formation occurs via the UDMH pathway, initially by the combination of DMA or CDMA and $NHCl_2$, which appears to be the single most important NDMA-forming nitrogen species commonly found in water treatment operations. Although $NHCl_2$ is only a trace chloramine species under typical chloramination conditions, a strong correlation was observed between its concentration and NDMA formation in this study. Although the NDMA formation pathway involving ammonium is expected to increase at lower and higher pH values because of enhanced hydrolysis of diuron, higher pH values over a longer contact time did not favor this pathway due to the potential self-disproportionation of $NHCl_2$.

Addition of nitrite and free chlorine was expected to produce significant enhancement of NDMA formation from diuron following the pathway proposed by Choi and Valentine (2003). However, NDMA yields were far lower than in their study. Although experimental conditions differed slightly between the two studies, the key difference is probably the presence of the aromatic rings in diuron, phenylisocyanate, DCA, and 1,2-dichloro-4-nitrobenzene. Each of these provides an attractive target for nitrosation or nitration by nitryl chloride (NO_2Cl), the key intermediate in nitrite chlorination (Johnson and Margerum, 1991), producing various potential nitro-, chloro-benzene derivatives. Rates of these reactions could easily exceed those for nitrosation of DMA and the absolute number of non-DMA nitrosation targets is clearly larger. When Cl/N was large, virtually all nitrite would be quickly chlorinated to form NO_2Cl, which in turn was converted to various nitro-aromatic compounds. Consumption of nitrite and chlorine by these processes probably accounts for the relative ineffectiveness of nitrite as an NDMA-forming reagent with diuron compared to results for DMA (Choi and Valentine, 2003).

Although our experiments do not indicate a precise reaction mechanism, one possibility is that nitrate enhanced NDMA formation by increasing N_2O_4 concentration via the reaction between NO^+ and NO_3^- (Fig. 10, Choi and Valentine, 2003). Rapid reaction of nitryl chloride with aromatic diuron derivatives may have suppressed N_2O_4 production in the case of nitrite addition accounting for the greater formation of NDMA in the nitrate case. The additionally formed nitrosating agent when nitrate was added must have been reactive enough to nitrosate DMA but not so reactive that it was rapidly consumed by reactions with diuron and its other aromatic byproducts. Once sufficient chlorine was present to convert

Fig. 7 – Proposed NDMA formation pathway in aqueous diuron solutions during chlorination or chloramination.

the nitrite to nitrate, the nitrite and nitrate pathways converged so that NDMA yields were similar (Fig. 2).

4.   Conclusion

In summary, the reaction pathway for NDMA formation in aqueous diuron solution during chlorination is a multi-step process that proceeds through the formation of various intermediates. Additional nitrogen sources including ammonium, nitrite, and nitrate are able to significantly enhance NDMA formation, with the yields increasing in the order of nitrite < nitrate < ammonium for a given chlorine, nitrogen, and diuron dose. Dichloramine, $NHCl_2$, appears to be the most efficient NDMA-forming oxidant for diuron. By employing representative concentrations of chlorine and nitrogen,

NDMA formation was not detected during chlorination of a diuron concentration at the upper end of typically detected concentrations in California source waters regardless of the form of the added nitrogen. Inhibition of NDMA formation during chlorination of diuron was observed in the experiments with coexistence of nitrite and ammonium as compared to those measured when ammonium was solely present, with only a slight difference being shown between NDMA yields in the presence of ammonium and both ammonium and nitrate. The pH affected the yield of NDMA from chlorination of diuron in the presence of additional nitrogen-containing species. Although the exact effect from pH became more complex because many intermediates and reactions were involved, the enhanced hydrolysis of diuron, which was kinetically favorable at lower and higher pH values releasing additional amounts of DMA, and formation of

$NHCl_2$, which was more stable at moderately lower pH values, were likely to be the major factors contributing to the enhancement of NDMA formation at low pH.

Results from this study suggest that diuron may pose greater health risks with respect to NDMA formation during chloramination of surface water as compared to chlorination of groundwater containing nitrate (or nitrite). Although the concentrations of diuron detected in groundwater are generally lower than those found in surface water (CDPR; USEPA, 2003; USGS), the typically less intensive treatment before disinfection of groundwater, which is often subjected only to disinfection before use (USEPA, 2002), increases the chance that more diuron will reach the chlorine contact chamber. This study showed that the risks posed by representative concentrations of diuron and other reagents with respect to NDMA formation during chlorine-based disinfection may be limited even in the presence of multiple nitrogen species, the proposed reaction mechanism provides insight into the potential influences of additional nitrogen-containing species on NDMA formation.

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R E F E R E N C E S

Boyer, J.H., 1980. Increasing the index of covalent oxygen bonding at nitrogen attached to carbon. Chemical Reviews 80 (6), 495–561.

CDPR. Surface Water Data Base. California Department of Pesticide Regulation, Sacramento, CA.

Chen, W.H., Young, T.M., 2008. NDMA formation during chlorination and chloramination of aqueous diuron solutions. Environmental Science & Technology 42 (4), 1072–1077.

Choi, J., Duirk, S.E., Valentine, R.L., 2002. Mechanistic studies of N-nitrosodimethylamine (NDMA) formation in chlorinated drinking water. Journal of Environmental Monitoring 4 (2), 249–252.

Choi, J., Valentine, R.L., 2002a. A kinetic model of N-nitrosodimethylamine (NDMA) formation during water chlorination/chloramination. Water Science and Technology 46 (3), 65–71.

Choi, J.H., Valentine, R.L., 2002b. Formation of N-nitrosodimethylamine (NDMA) from reaction of monochloramine: a new disinfection by-product. Water Research 36 (4), 817–824.

Choi, J.H., Valentine, R.L., 2003. N-Nitrosodimethylamine formation by free-chlorine-enhanced nitrosation of dimethylamine. Environmental Science & Technology 37 (21), 4871–4876.

Deinzer, M., Schaumburg, F., Klein, E., 1978 JUN. Environmental-health sciences center task-force review on halogenated organics in drinking-water. Environmental Health Perspectives 24, 209–239.

Eaton, A.D., Clesceri, L.S., Greenberg, A.E., 1998. Standard Methods for the Examination of Water and Wastewater. American Public Health Association, American Water Works Association, Water Environmental Federation Publishers, Washington, DC.

Gerecke, A.C., Sedlak, D.L., 2003. Precursors of N-nitrosodimethylamine in natural waters. Environmental Science & Technology 37 (7), 1331–1336.

Giacomazzi, S., Cochet, N., 2004. Environmental impact of diuron transformation: a review. Chemosphere 56 (11), 1021–1032.

Hedayatullah, M., 1972. Oxidation of primary aromatic-amines – review. Bulletin De La Societe Chimique De France (7), 2957.

Johnson, D.W., Margerum, D.W., 1991. Non-metal redox kinetics: a reexamination of the mechanism of the reaction between hypochlorite and nitrite ions. Inorganic Chemistry 30, 4845–4851.

Margerum, D.W., Schurter, L.M., Hobson, J., Moore, E.E., 1994. Water chlorination chemistry – nonmetal redox kinetics of chloramine and nitrite ion. Environmental Science & Technology 28 (2), 331–337.

Mitch, W.A., Sedlak, D.L., 2002. Formation of N-nitrosodimethylamine (NDMA) from dimethylamine during chlorination. Environmental Science & Technology 36 (4), 588–595.

Mitch, W.A., Gerecke, A.C., Sedlak, D.L., 2003a. A N-nitrosodimethylamine (NDMA) precursor analysis for chlorination of water and wastewater. Water Research 37 (15), 3733–3741.

Mitch, W.A., Sharp, J.O., Trussell, R.R., Valentine, R.L., Alvarez-Cohen, L., Sedlak, D.L., 2003b. N-Nitrosodimethylamine (NDMA) as a drinking water contaminant: a review. Environmental Engineering Science 20 (5), 389–404.

Nolan, B.T., Hitt, K.J., Ruddy, B.C., 2002. Probability of nitrate contamination of recently recharged groundwaters in the conterminous United States. Environmental Science & Technology 36 (10), 2138–2145.

Palin, A., 1950. A study of the chloro derivatives of ammonia. Water and Water Engineering (54), 248–258.

Salvestrini, S., Di Cerbo, P., Capasso, S., 2002. Kinetics of the chemical degradation of diuron. Chemosphere 48 (1), 69–73.

Schmidt, C.K., Sacher, F., Brauch, H., 2006. Strategies for minimizing formation of NDMA and other nitrosamines during disinfection of drinking waters.

Schreiber, I.M., Mitch, W.A., 2005. Influence of chloramine speciation on NDMA formation: implications for NDMA formation pathways. Abstracts of Papers of the American Chemical Society 230, U1503–U1504.

Schreiber, I.M., Mitch, W.A., 2006. Nitrosamine formation pathway revisited: the importance of chloramine speciation and dissolved oxygen. Environmental Science & Technology 40 (19), 6007–6014.

Soulard, M., Bloc, F., Hatterer, A., 1981. Diagrams of existence of chloramines and bromamines in aqueous-solution. Journal of the Chemical Society-Dalton Transactions 12, 2300–2310.

Thauer, R.K., Jungermann, K., Decker, K., 1977. Energy-conservation in chemotropic anaerobic bacteria. Bacteriological Reviews 41 (1), 100–180.

USEPA, 1992. Pesticide in Ground Water Database – a Compilation of Monitoring Studies: 1971–1991. Office of Prevention, Pesticides, and Toxic Substances. EPA 734-12-92-001.

USEPA, 1995. Drinking Water Regulations and Health Advisories. Office of Water, Washington, DC.

USEPA, 2002. Community Water System Survey 2000. Office of Water, U.S. Environmental Protection Agency. EPA 815-R-02–005A.

USEPA, 2003. Environmental Risk Assessment for the Reregistration of Diuron. Office of Prevention, Pesticides, and Toxic Substances, U.S. Environmental Protection Agency.

USGS. National Water Quality Assessment (NAWQA), Pesticides National Synthesis Project. The U. S. Geological Survey.

Wrona, P.K., 1998. Electrode processes of chloramines in aqueous solutions. Journal of Electroanalytical Chemistry 453 (1–2), 197–204.