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NDMA Formation during Chlorination and Chloramination of Aqueous Diuron Solutions

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Abstract

Formation of the potent carcinogen *N*-nitrosodimethylamine (NDMA) during chlorine disinfection of water containing secondary amines is now generally acknowledged. The phenylurea herbicide diuron is one of the most widely used herbicides in California, has been frequently detected in California's water sources with a transient nature of appearance, and has a structure that suggests it might be an NDMA precursor. This study sought to quantify the potential for NDMA formation from aqueous diuron solutions under varied chlorine and chloramine conditions. NDMA formation was consistently observed even in the absence of added ammonia, which has usually been the source of the nitroso-nitrogen during chloramination of other precursors. It appears that both nitrogen atoms in NDMA are donated by diuron during chlorination in the absence of added ammonia. For a given chlorine and diuron dose, NDMA formation increased in the order $OCl^-<NH_2Cl<NHCl_2$, a result consistent with previous NDMA formation studies. Significant quantities of NDMA (170 ng/L) were produced during dichloramination of diuron using a low dichloramine concentration and a diuron concentration at the upper end of typically detected concentrations in California (20 μg/L), suggesting a need for further investigation to accurately assess the human health risks posed by diuron with respect to NDMA formation potential. A reaction pathway is proposed to provide a possible explanation for NDMA formation from diuron during chlorination or chloramination. The findings in this study identify a specific potential precursor of NDMA formation, one that arises from non-point sources. This further highlights the difficulties associated with determining the environmental safety of chemicals and their associated byproducts.

Introduction and Problem Statement

Diuron (CAS# 330-54-1, *N'*- (3,4-dichlorophenyl)-*N, N*-dimethylurea), a substituted phenylurea herbicide belonging to the family of phenylamides, is registered for pre- and early post-emergent control of broad leaf and annual grassy weeds for agricultural and nonagricultural uses. Concerns regarding diuron have been frequently reported worldwide. For example, in France, diuron was found to be one of the most used and contaminating products in urbanized catchments *(1)*. In Germany, recurring detection of diuron residues in drinking water supplies has led to the prohibition of diuron usage in confined areas where excess water can flow into drainage pipes and sewers *(2)*. Around the United States, diuron is notably used as an algicide or herbicide. In California, diuron is one of the most heavily used herbicides with over 600,000 kg (~1.4 million pounds) applied statewide in 2004; almost 50% of the total usage was applied to rights-of-way, e.g., along power lines and roadways *(3)*. Nearly 95% of diuron in California is applied from November through March, with a peak in December *(4)*.

Diuron can degrade by various biotic and abiotic pathways producing dimethylamine (DMA) and dichloroaniline (DCA) via one such pathway.

N'-(3,4-dichlorophenyl)-N,N-dimethylurea (Diuron) → Dichloroaniline (DCA) + Dimethylamine (DMA)
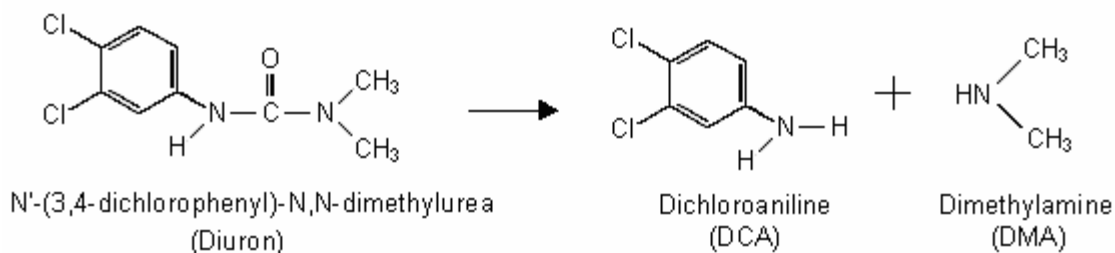
However, it is moderately persistent *(5)* and has been widely detected in California surface water *(6)* and groundwater supplies *(7, 8)* and in the State Water Project, which serves as a drinking water supply for millions of southern California residents *(9)*. Nearly all detections of diuron, especially those of high concentrations, occurred between December and March, which coincided with both the rainy season and the peak diuron application season *(10)*. The concentration observed was usually above 1 µg/L *(6)*, which is the concentration of acute toxicity (the concentration exhibiting effects on 50% of test organisms from a single exposure in a short space of time) for algae *(11)*, and some of the observations exceeded 10 µg/L *(6)*. Diuron's wide occurrence in water results from its high use and combination of moderate aqueous solubility (42 mg/L at 20 $^{\circ}$C), low Henry's law constant (0.051 mPa·m^3/mol), low to moderate hydrophobicity (log K_{OW} = 2.6), modest sorption coefficient (K_{OC} ~ 500 L/kg), slow hydrolysis under neutral conditions *(10)*, negligible photolytic breakdown, and limited biotransformation, which primarily involves *N*-demethylation reactions *(12, 13)*.

Diuron is of concern in drinking water supplies for two main reasons. First, diuron is classified as a "known/likely" human carcinogen and is consequently on the U.S. EPA's "2nd Contaminant Candidate List" *(14)*. The second concern is that diuron may be transformed to other, possibly more potent, byproducts during water treatment operations. Associated with the infrequent testing by water utilities for diuron, it is possible that risks posed by potential byproducts of diuron go undetected or are underestimated. For example, the California Department of Water Resources (DWR) has monitored the State Water Project for a variety of organic contaminants 2-3 times per year, and diuron is one of the most frequently observed compounds and nearly always at the spring check date that falls around March *(9)*.

This research was particularly motivated by the well documented formation of N-nitrosodimethylamine (NDMA) from secondary amines *(15, 16)*.

Dimethylamine (DMA) + Cl—NH₂ → N-Nitrosodimethylamine (NDMA)
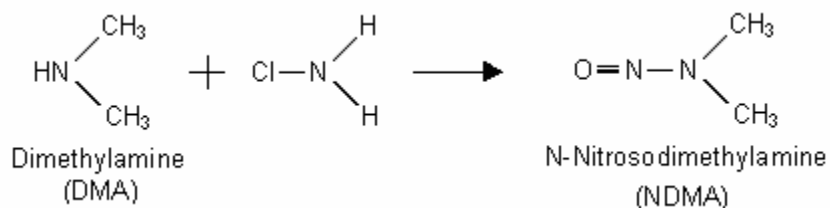
Although a federal maximum contamination level (MCL) has not been established for NDMA in drinking waters, EPA has established a clean up level of 0.7 ng/L for NDMA, and other regulatory agencies have established their own NDMA guidelines. For example, the California Department of Health Service (DHS) set an interim action level of 10 ng/L. Dimethylamine has served as the "model" NDMA precursor in most studies, but the formation of NDMA typically cannot be fully accounted for by known formation mechanisms and the amounts of DMA present *(17)*. It appears that other precursors are present in drinking waters, and diuron might be one of them. This study was therefore intended to quantify NDMA formation from diuron during chlorination or chloramination, and thereby to estimate whether typical diuron concentrations in drinking water sources are of concern because of NDMA formation.

Objectives

(1) Determine if diuron is a precursor of NDMA formation, and quantify the potential for NDMA formation during chlorination or chloramination of aqueous diuron solutions.

(2) Investigate the NDMA formation pathway from diuron during chlorination or chloramination and the possible significant factors, and further estimate if there is a risk posed by diuron in drinking waters with respect to NDMA formation.

Procedures

Materials. All experiments were conducted using deionized water (Milli-Q; Millipore) buffered with sodium acetate (pH = 4), phosphate (pH = 6 to 8), or carbonate (pH = 10). Solution pH values were adjusted as needed using sodium hydroxide or sulfuric acid (0.2 N). Diuron (>98%; Sigma-Aldrich), NDMA and NDMA-d_6 (internal standard; Chem Service) were used without further purification. Sodium hypochlorite (NaOCl, purified grade, 4-6%) and ammonium chloride were used as chlorination reagents. Ambersorb 572 beads (Sigma-Aldrich) were used to extract NDMA from aqueous solution. All reagents were obtained from Fisher Scientific unless otherwise noted.

Chloramine Formation and Analysis. Stock hypochlorite (OCl⁻) solutions were prepared by adding NaOCl to MilliQ water. Monochloramine (NH₂Cl) solutions were prepared fresh daily by slowly adding NaOCl to a rapidly stirred ammonium chloride (NH₄Cl) 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 NH₂Cl to dichloramine (NHCl₂) *(18)*.

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

When chloramines are prepared at Cl/N molar ratio <1.5:1, NH₂Cl and NHCl₂ coexist without the presence of free chlorine following eq. 1 with an equilibrium constant $K = 6.7 \times 10^5$ at 25 °C *(19, 20)*. Stock NHCl₂ solution was prepared by lowering the pH of stock NH₂Cl solution below 3.7 and aging for 1 h. Concentrations of all chlorinated compound stock solutions were standardized by using the DPD ferrous titrimetric method *(21)*.

NDMA Formation Assays. NDMA formation potential was assessed by applying relatively high doses of chlorine or chloramines to aqueous diuron solutions for different contact times. All glassware used in this study were washed and baked at 450 °C for at least 3 h prior to use. 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 was fully dissolved in 1 L MilliQ water at predetermined concentrations, and chorine or chloramine solutions were added. Dependence of NDMA formation on system conditions was assessed by varying initial diuron concentrations,

the form and concentration of chlorine species, and the solution pH. Final chlorine species concentrations were measured using the DPD ferrous titrimetric method *(21)*. All experiments were at least triplicated to ensure the reproducibility of the results and the quality of the experiments.

Analytical Methods.　NDMA was determined by an isotope dilution GC-MS method *(16, 19)*. Prior to extraction, the reaction was quenched with 600 mg ascorbic acid. NDMA-*d6* (50 μL of a 10 mg/L stock solution in methanol) was added to each 1 L sample as an internal standard. Ambersorb 572 carbonaceous beads (2.5 g, baked at 300 ^{o}C for >3 h) were added and the solutions were shaken for >1 h at 200 rpm to extract NDMA. Carbonaceous beads were recovered by vacuum filtration (Whatman paper fiber filter 2, >8 μm), air-dried for >3 h, and extracted with 6 ml of methylene chloride for 1 hour in 16 mL amber vials. Methylene chloride was decanted and concentrated to 0.5 mL by nitrogen (99.999%) blow down. NDMA recoveries from spiked deionized water samples averaged 40% ± 7% (average ± SD), which are low compared to those for other organic chemicals but which are precisely known because of the deuterated internal standard.

　　　Extracts were analyzed for NDMA using an Agilent 6890 gas chromatography with an Agilent 5973 mass spectrometer (splitless 2 μL injection at 220 ^{o}C, 240 ^{o}C transfer line, Agilent Technology DB-624 capillary column 30 m by 0.25 mm i.d. and 1.4 μm thickness, initial oven 35 ^{o}C ramped at 10 ^{o}C/min to 120 ^{o}C, then 30 ^{o}C/min to 220 ^{o}C, hold 2 min). Mass spectrometry was performed in electron ionization mode. Target ions were 74 and 80 *m/z* for NDMA and NDMA-*d$_6$*, respectively. 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. The detection limit of this NDMA analysis at the 99% confidence level was determined to be 2.0 ng/L.

　　　Diuron analyses followed published approaches *(5)* using a high-pressure liquid chromatograph (Hewlett-Packard 1100 series, Wilmington, DE; Prodigy reverse-phase column, 100 mm x 2.00 mm, 5 μm ODS, 100 Å Phenomenex, Torrance, CA; 0.5 mL/min 70/30 v/v water/acetonitrile linear gradient to 90/10 v/v over 10 min) with a diode array detector at 252 nm (HP G1315A).

NDMA Control Experiment.　NDMA is a relatively volatile compound *(22)*, and its measured concentration might be reduced by volatilization over long contact times. Control experiments were conducted to determine whether estimates of NDMA formation in the system were affected

by decomposition or volatilization. A known concentration of NDMA (1.35 nM or 100 ng/L) was added to an identical system as the reactors used for diuron chlorination experiments. The solution was kept in the dark at room temperature for 10 days. NDMA remaining in solution was analyzed after 2, 5, and 10 days contact time, and showed that NDMA was not removed from the system by volatilization or degradation (Figure 1).
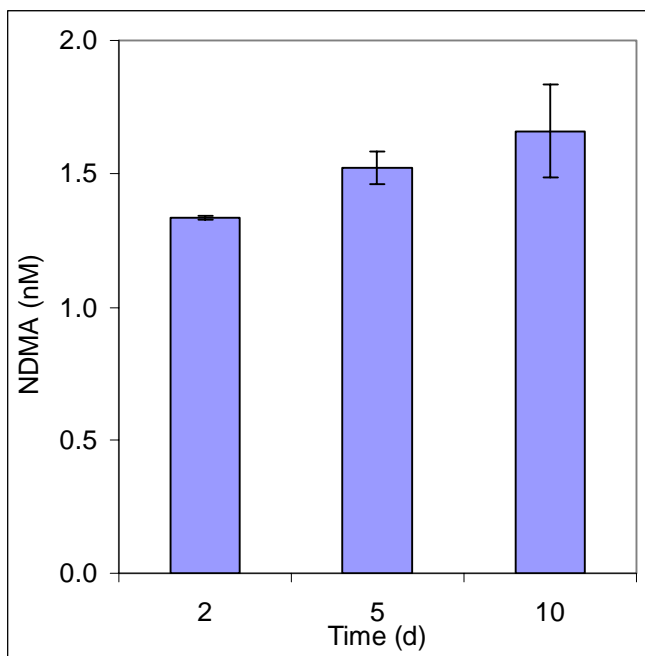
Figure 1: NDMA concentrations remaining over time in control experiments. The initial NDMA concentration was 1.35 nM (100 ng/L). The value and bar represent the mean value and one standard deviation, respectively.

Results and Discussion

The potential for NDMA formation during the reaction between diuron and NaOCl was determined in experiments employing high concentrations of diuron and NaOCl. Chlorine was in excess compared to diuron as anticipated for chlorine compared to diuron under typical disinfection conditions. NDMA formation was measured for various contact times up to 10 days to allow the reaction to reach completion *(15)* (Figure 2).

NDMA concentrations increased rapidly at the beginning of the reaction and continued increasing, reaching an apparent plateau after 5 days. This potential maximum yield of NDMA was explained by measuring diuron residual in the system in the duplicate experiments (Table 1). The concentrations of diuron was below 1 mg/L after 1 day indicating that almost 98% of diuron

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was rapidly oxidized in 1 day; the plateaus of NDMA formation in Figure 1 therefore seem to be caused by the shortage of diuron. A similar experiment was conducted at a higher free chlorine concentration (6.9 mM or 490 mg/L as Cl_2), and the results indicate that higher free chlorine concentrations slightly decreased NDMA formation rather than increasing it (Table 2). This finding of no enhancement of NDMA formation in samples can also be attributed to the complete consumption of diuron and is consistent with the early finding in Table 1. The rapid consumption of diuron (i.e., < 1 day) but slow appearance of maximum NDMA formation (i.e., > 5 days) implies that NDMA formation from diuron is likely a complex reaction pathway involving other intermediates, which potentially delays ultimate NDMA formation.
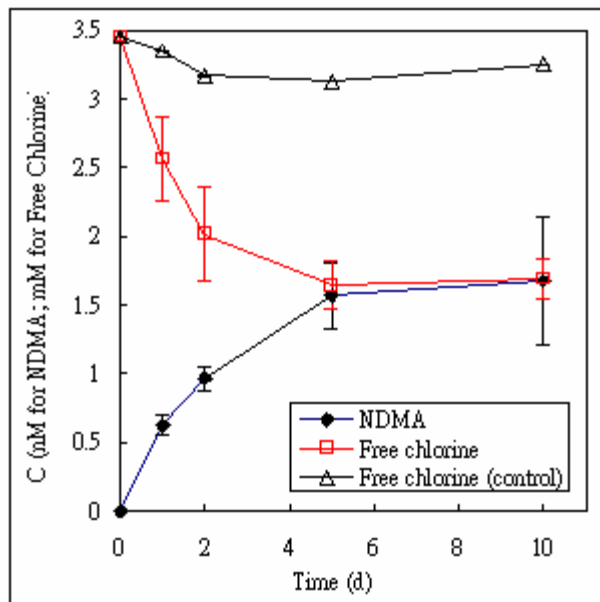
Table 1: Diuron concentrations measured in samples at the end of the chlorination reaction. The initial diuron and NaOCl concentration were 0.09 mM (20 mg/L) and 3.45 mM (245 mg/L as Cl_2), respectively. The pH was controlled at 8 ($\pm$ 0.2) with 10 mM phosphate buffer.

Time (day)	Diuron (μM) (Average $\pm$ SD)
1	3.91 $\pm$ 0.04
2	0.13 $\pm$ 0.17

Table 2: Concentration of NDMA measured after 5 days in diuron free chlorine application experiments. The initial diuron concentration was 2.15 μM (500 μg/L), and two different chlorine concentrations were applied. The pH was controlled at 8 ($\pm$ 0.2) with 10 mM phosphate buffer.
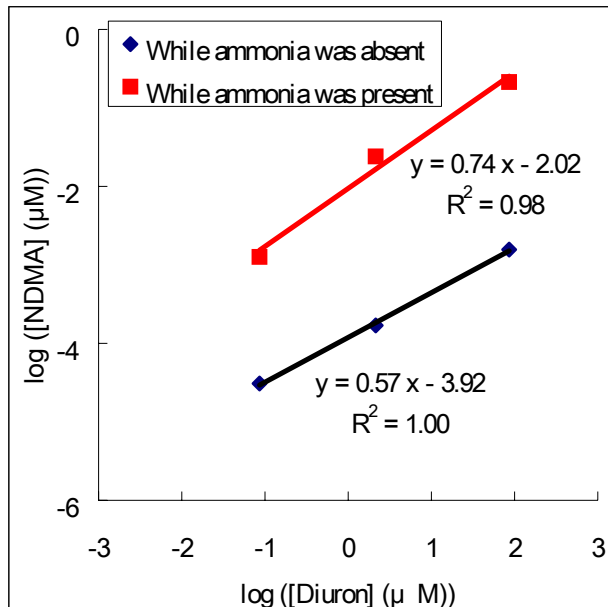
Initial OCl^- concentration (mM)	NDMA formation (nM) (Average $\pm$ SD)
3.5	0.15 $\pm$ 0.03
6.9	0.11 $\pm$ 0.01

Concentrations of free chlorine residuals in samples at the end of the reaction were also measured, and the trend of free chlorine depletion was consistent with NDMA formation. However, approximately 1.3 mmol of chlorine is consumed for each nmol of NDMA formed, indicating that chlorine decayed by some mechanism besides reacting with diuron. A control experiment showed that self-decomposition of free chlorine is negligible (Figure 1), so it is clear that many chlorination products of diuron such as chlorinated diuron, chlorinated DMA, or more highly chlorinated DCA derivatives must be formed in addition to NDMA. It is still unknown how or whether these byproducts participate in the formation of NDMA from diuron.

Figure 2: NDMA and free chlorine residual concentrations during the reaction between diuron and NaOCl at pH 8 ± 0.2, and free chlorine residual concentrations in control experiments using diuron-free solutions. The initial concentrations of diuron and free chlorine were 0.09 mM (20 mg/L) and 3.45 mM (245 mg/L as Cl₂), respectively. The point and error bar depict the mean value and one standard deviation, respectively.

The effect of diuron concentrations on NDMA formation was studied by conducting experiments applying different initial diuron concentrations. The initial diuron concentration was lowered from 20 mg/L (0.09 mM) to 20 μg/L (0.09 μM), which represents the upper end of concentrations typically detected in California. As shown in Figure 3, the decrease of initial diuron concentration greatly reduced NDMA formation. The results indicate that under typical conditions in California, diuron may not be a concern with respect to NDMA formation during chlorination using free chlorine, even under very high free chlorine concentrations. A nonlinear relationship between diuron concentration and NDMA formation was observed, which was presumably due to complex reactions involving other intermediates or byproducts in the NDMA formation pathway from diuron such as chain reactions, competitive reactions, or branching pathways.

Figure 3: NDMA formation under different initial diuron concentrations at pH = 8 ± 0.2 after 5 days contact time while NH₃ was either present or absent in the system. The initial concentration of NaOCl in each experiment was 3.45 mM (245 mg/L as Cl₂). The value and bar depict the mean value and one standard deviation, respectively.

The influence of pH on NDMA formation from diuron during chlorination was studied by varying the solution pH (Figure 4). Previous studies demonstrated that NDMA formation during chloramination of DMA and wastewater effluent is affected by pH with a maximum formation rate occurring between pH 6 and 9 *(15, 18, 23)*. Similar results were observed when pH was varied between 6 and 10 during chlorination of diuron. The pH dependence of NDMA formation during diuron chlorination between pH 6 and 10 seems to be consistent with that of NDMA formation from DMA suggesting that DMA may be involved in NDMA formation over that pH range.

The much higher yield of NDMA at pH 4 may be attributable to enhanced hydrolysis of diuron releasing additional DMA. Diuron is stable toward hydrolysis under neutral conditions but at lower and higher pH values the hydrolysis rate sharply increases *(12, 24)*. Enhanced NDMA formation at pH 4 may therefore be attributed to the greater availability of DMA under this condition.
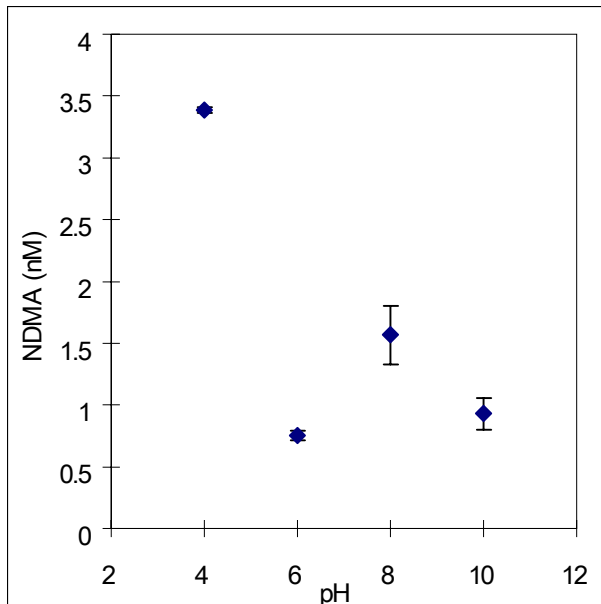
Figure 4: Concentration of NDMA produced at various pH values after 5 days contact time. The initial concentration of diuron and NaOCl were 0.09 mM (20 mg/L) and 3.45 mM (245 mg/L as Cl_2), respectively. The reaction was buffered by using acetate buffer for pH 4; phosphate buffer for pH 6 and 8; and carbonate buffer for pH 10. The point and bar represent the mean value and one standard deviation, respectively.

Previous studies have focused on NDMA formation during chloramination *(15, 18, 23, 25, 26)*. Results from these studies have shown that ammonia (NH_3) or chloramines, such as NH_2Cl and $NHCl_2$, can enhance the yield of NDMA compared to chlorination. To determine if NDMA formation from diuron is affected by these factors, experiments were conducted by adding NH_3 to diuron aqueous solution before chlorination. A slight excess of NH_3 over free chlorine was employed to prevent breakpoint chlorination and to mimic typical drinking water chloramination conditions *(19)* The concentrations of chlorine species were measured before the experiment to ensure that no free chlorine was present initially in the system, and NDMA formation was monitored over 10 days (Figure 5). NDMA formation was greatly increased by the presence of NH_3, and no apparent maximum was observed over 10 days; longer contact times may produce even more NDMA in this experiment. Enhanced NDMA formation may be attributable to the capability of NH_3 to provide another, more efficient nitrogen source for one of the nitrogen atoms in the nitroso group in NDMA *(27)*.
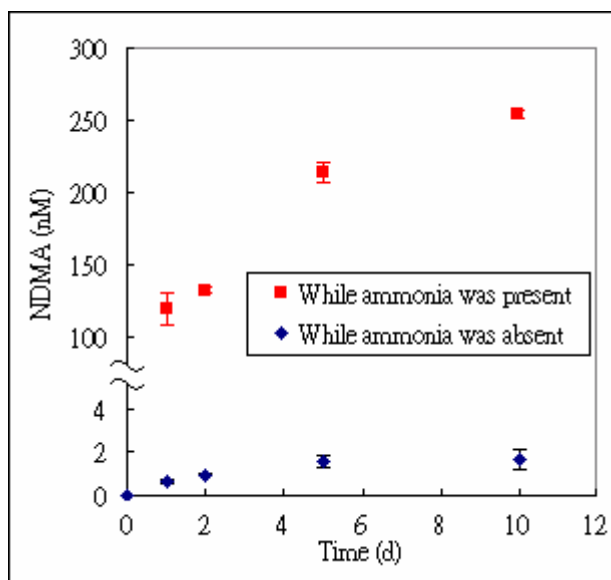
Figure 5: NDMA formation in aqueous diuron solutions (pH 8 ± 0.2) during chlorination for different contact times with or without NH₃ added. The initial concentrations were as follows: [diuron] = 0.09 mM (20 mg/L), [NaOCl] = 3.45 mM, and [NH₃] = 4.1 mM. The point and bar depict the mean value and one standard deviation, respectively.

The effect of diuron concentration on NDMA formation during chlorination in the presence of NH_3 was investigated (Figure 3). As expected, NDMA formation decreased significantly when the diuron concentration was lowered. However, the final NDMA concentration when diuron was

20 μg/L (0.09 μM) was 93.37 ng/L (1.26 nM), which is still an order of magnitude above the

California DHS interim action level of 10 ng/L, but these experiments were still conducted under a very high chlorine concentration.

The influence of the order of reagent addition involving organic nitrogen precursors, chlorine, and NH_3 on NDMA formation has been described previously *(19)*. To determine if NDMA formation from diuron exhibits similar behavior, experiments were conducted with varied order of reagent addition. Two scenarios were examined: (1) NaOCl was added to a well-mixed solution containing diuron and NH_3. In this case, diuron and NH_3 may compete with each other for reaction with free chlorine forming chlorinated diuron and inorganic chloramines, respectively. Partial $NHCl_2$ formation was hypothesized in this scenario due to the high Cl/N ratio at the point of reagent addition *(19)*. Meanwhile, due to partial consumption of free chlorine by reacting with diuron, less inorganic chloramine formation was anticipated in this scenario. (2) Diuron was added to a well-mixed solution containing NH_3 and OCl^-. In this case, inorganic chloramines were completely preformed before reacting with diuron to form NDMA. In both scenarios, the same initial reagent concentrations were applied ([NaOCl] =3.45 mM, [diuron] =

0.086 mM, and $[NH_3] = 4.1$ mM).

More NDMA was formed in scenario 2 (22.1 ± 0.2 µg/L or 298.5 ± 2.2 nM) than in scenario 1 (15.8 ± 0.5 µg/L or 205.4 ± 6.8 nM) as expected, although the effect was small. Reduced NDMA yields in scenario 1 may occur either because of the decreased concentration of the more efficient oxidant (inorganic chloramines) *(18, 27)* or the increased concentrations of less efficient oxidation targets (chlorinated diuron and derivatives). The latter appears more plausible based on the low ratio of diuron to OCl^- at the beginning of the experiment. It is noteworthy that under scenario 1, diuron successfully competed with NH_3 for free chlorine, even though the concentration applied was almost 40 times less than NH_3.

Previous studies have shown that $NHCl_2$ is a more potent NDMA-forming oxidant toward DMA than NH_2Cl *(19, 26)*. Similar to the results of Schreiber and Mitch, NDMA formation from the reaction between diuron and $NHCl_2$ was much higher than that from the reaction between diuron and NH_2Cl or free chlorine (Figure 6). Experiments were repeated with less concentrated NH_2Cl and $NHCl_2$ solutions (0.345 mM or 24.5 mg/L as Cl_2) to investigate the effect of chloramine concentration (Figure 6). One order of magnitude lower chloramine concentration resulted in approximately 24-37 times less NDMA formation.
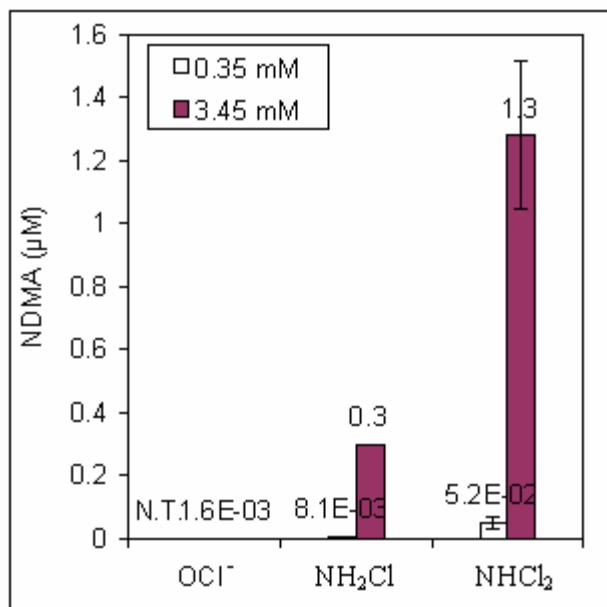
Figure 6: NDMA formation in samples after 5 days following addition of various forms of chlorine to 0.09 mM (20 mg/L) of diuron solution. The initial concentration of each chlorine species was 0.35 or 3.45 mM (24.5 or 245 mg/L as Cl_2), and the pH was controlled at 8 ± 0.2. The value and bar represent the mean value and one standard deviation, respectively. N.T. represents not tested.

Concentrations of chlorine residuals were monitored during diuron chloramination

experiments with less concentrated NH_2Cl and $NHCl_2$ solutions (Figure 7). Compared to the results from the control experiments using diuron-free samples, most of the inorganic chloramine consumption in Figure 7 was probably caused by self-disproportionation instead of reactions with diuron based on the similarity of chlorine species destruction between experiments with and without diuron. However, partial consumption of NH_2Cl (~0.04 mM or 2.84 mg/L as Cl_2) was still observed during the monochloramination experiment, which could result from reactions with diuron. During the dichloramination of diuron, no $NHCl_2$ was detected at the end of experiment but an appreciable amount of NH_2Cl was formed probably because $NHCl_2$ was transformed to NH_2Cl under the pH 8 conditions of the experiment. Characteristic times of chloramine formation reactions are rapid *(28)*, so enhanced NDMA formation during dichloramination of diuron may result only from the short period at the beginning of the experiments (i.e., in the first hour of reaction) when $NHCl_2$ was present.
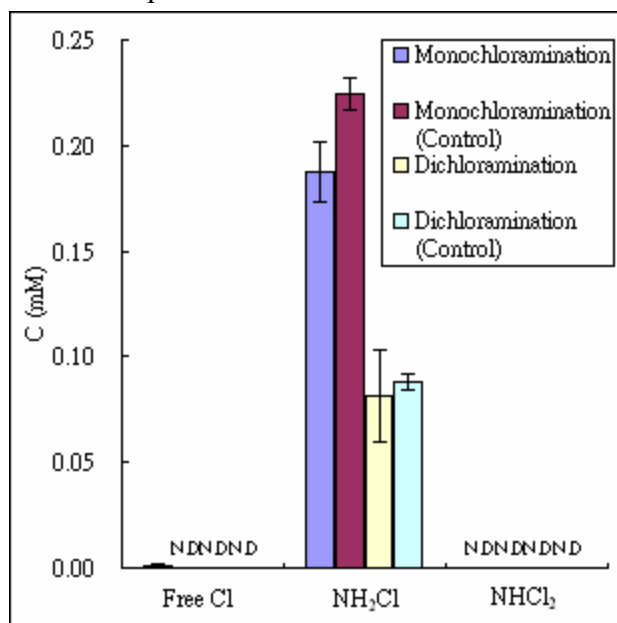
Figure 7: Concentrations of chlorine residuals in samples after 5 days from the reaction of 0.35 mM (24.5 mg/L as Cl_2) of NH_2Cl, or $NHCl_2$ with 0.09 mM (20 mg/L) aqueous diuron solution or diuron-free solution (control experiments) buffered at pH 8 (±0.2). The value and bar represent the mean value and one standard deviation, respectively (N.D. represents nondetected).

To investigate this assumption, NDMA formation in aqueous diuron solutions during dichloramination at different pH values for shorter contact times was investigated (Figure 8). As expected, NDMA formation increased rapidly in the first half hour following the addition of $NHCl_2$ in all experiments conducted at different pH values, proving that the enhanced NDMA formation during dichloramination of diuron is a rapid reaction. In the first half hour, the higher

yield of NDMA measured in the experiments at pH 4 and 10 presumably resulted from the enhanced hydrolysis of diuron releasing additional DMA under the more extreme pH conditions. However, as the contact time increased, dichloramine added in the experiments at pH 10 was transformed to NH_2Cl, causing NDMA formation at pH 10 to decrease beyond the 1 hour time point.
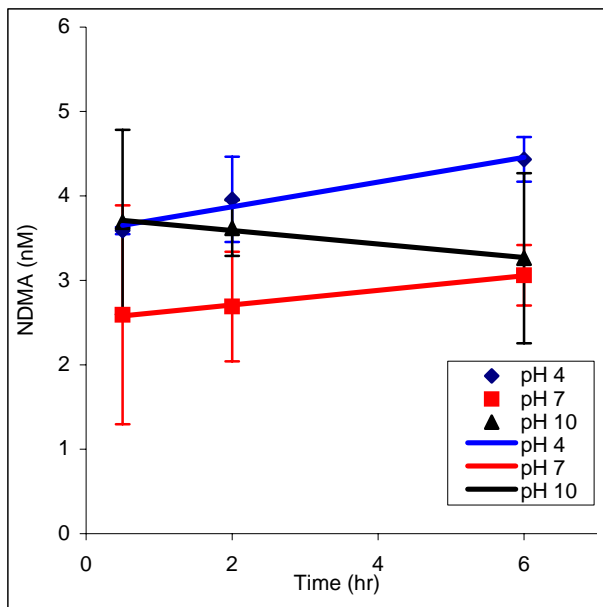
Figure 8: NDMA formation in aqueous diuron solutions at different pH values during dichloramination for various contact times. The initial concentrations of diuron and dichloramine were 0.09 mM (20 mg/L) and 0.56 mM (40 mg/L as Cl_2), respectively. The value and bar represent the mean value and one standard deviation, respectively.

The relationship between the yield of NDMA from diuron and the presence of $NHCl_2$ in the system was further investigated (Figure 9). Experiments were initiated by preparing preformed $NHCl_2$ solutions at different pH values. Each chloramine solution contains the same total chlorine concentration but at different concentration fractions of $NHCl_2$ depending on the pH during the preparation of the solutions. NDMA formation in aqueous diuron solutions was analyzed for thirty minutes contact time following addition of the chloramine solutions (Figure 9A).

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

When chloramines are prepared at Cl/N molar ratio <1.5:1 and the pH is above 3.7, NH_2Cl and $NHCl_2$ coexist following eq. 1 with an equilibrium constant $K = 6.7 \times 10^5$ at 25 ^oC *(19, 20)* and the presence of NCl_3 is negligible. However, when the pH is lowered below 3.2, $NHCl_2$ begins to transform to NCl_3 following eq. 2; the associated equilibrium constant was estimated using the thermodynamic data listed in Table 3. By applying the conditions of experiments and

the equilibrium constants of eq. 1 and 2, the concentration fraction of $NHCl_2$ in each chloramine solution prepared at different pH values was estimated (Figure 9B).

Table 3: Gibbs free energies of formation from the elements for various species of interest at 25 °C.

Species	ΔG_f^o(KJ/mol)
H^+ (aq)	0 [1]
NH_4^+ (aq)	-79.37 [1]
NCl_3 (aq)	351.75 [2]
$NHCl_2$(aq)	209.2 [2]
1. Reported by Thauer et al. in 1977 *(29)*. 2. Reported by Wrona et al. in 1998 *(30)*.	

(A)

(B)
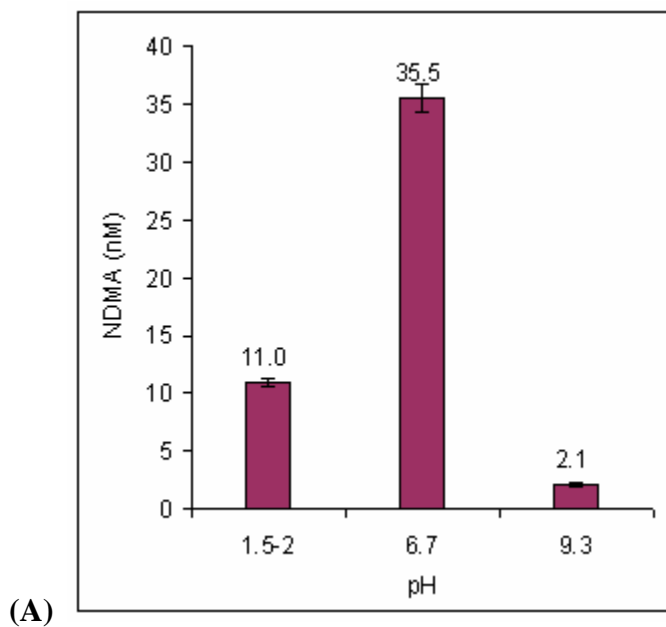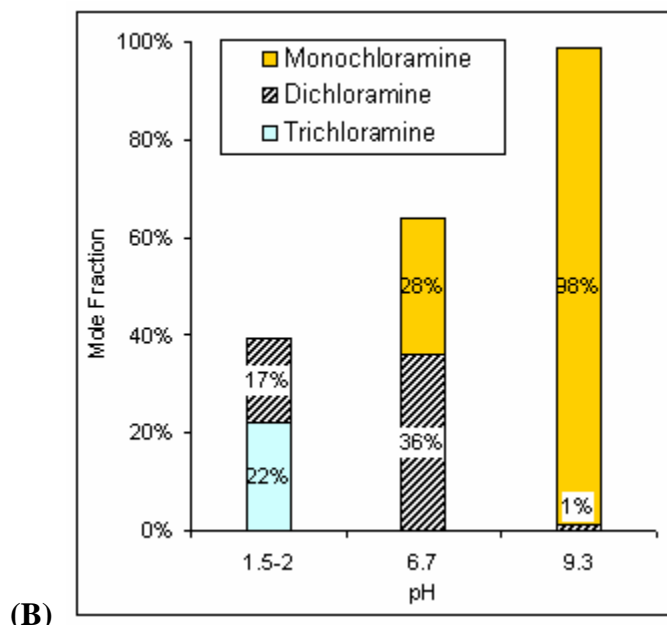
Figure 9: Effect of NHCl$_2$ fraction under the same total chlorine concentration on NDMA formation in aqueous diuron solutions. The initial concentration of diuron and total chlorine was 0.09 mM (20 μg/L) and 1.05 mM (74.34 mg/L as Cl$_2$), respectively. The pH of the experiments was controlled at 8 (± 0.2). (A) Concentration of NDMA produced in aqueous diuron solutions after 30 minutes following addition of NHCl$_2$ prepared at various pH values. The point and bar depict the mean value and standard deviation, respectively. (B) Estimated mole fraction of various forms of chlorine in NHCl$_2$ solutions prepared at various pH values for diuron dichloramination experiments. The concentration of NH$_4^+$ in the system was 29.5 mM.

The trend of NDMA formation in aqueous diuron solutions during chloramination was consistent with the fraction of chlorine present as NHCl$_2$ in each experiment, suggesting that NHCl$_2$ plays a significant role in the formation pathway of NDMA from diuron during chloramination. When the chloramine solution was prepared at pH 9.3, the yield of NDMA from diuron did not increase because of the presence of the larger fraction of NH$_2$Cl, but on the contrary agrees with the percentage of NHCl$_2$ in the system, suggesting that it is likely that NDMA formation detected in aqueous diuron solutions during monochloramination primarily resulted from the reaction with the small fraction of chlorine present as NHCl$_2$ in the system. The finding of lower NDMA formation from diuron in the experiments for pH .1.5-2 suggests that NCl$_3$ is not an effective NDMA-forming oxidant, consistent with suggestions in previous studies *(19)*.

NDMA formation during chloramination of diuron under reactant concentrations more

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representative of water treatment operations (initial concentration of diuron 0.09 μM or 20 μg/L, and chlorine dose 0.03 mM or 2 mg/L as Cl_2, pH = 8 ± 0.2, 5 day contact time) was investigated. The reaction of diuron with free chlorine at this concentration was not considered due to the much lower potential of forming appreciable amounts of NDMA under more realistic reactant concentrations. No NDMA formation was detected during the monochloramination experiment, but the NDMA concentration formed from $NHCl_2$ and diuron was 170 ng/L (2.30 nM), more than an order of magnitude above the California DHS interim NDMA action level of 10 ng/L.

A possible formation pathway for NDMA during chlorination or chloramination of diuron is proposed here. During chlorination or chloramination, diuron could be oxidized releasing two primary molecular fragments, DMA and DCA, by breaking the two carbon-nitrogen bonds in diuron. Each of these two fragment compounds could be further chlorinated or not. The presence of DMA and CDMA during the reaction has been demonstrated by mass spectrometry in our laboratory. The reaction between DMA or chlorinated DMA and DCA or more highly chlorinated anilines may form NDMA. In this possible NDMA formation pathway, the two nitrogen atoms in diuron can serve as a source for the two nitrogen atoms in the N-nitroso group in NDMA. This explains NDMA formation during chlorination of diuron when NH_3 or chloramines were not present. During diuron chloramination or chlorination in the presence of NH_3, chloramines or NH_3 can serve as the other nitrogen source, and the greater efficiency of this process probably results in the higher yield of NDMA during chloramination compared to reactions among DCA, DMA, and their chlorinated analogs.

Compared to chlorination or monochloramination that show negligible or low yield efficiency of NDMA from diuron at environmentally relevant concentrations, dichloramination exhibited much greater potential for NDMA formation, suggesting that the presence of $NHCl_2$ might be a primary determinant of whether a particular treatment system was at risk for significant NDMA formation if diuron was present in the source water. Although $NHCl_2$ is not intentionally used for disinfection, it will be present to some extent in systems using chloramination; its concentration will be highest when pH decreases or Cl/N molar ratios increase toward the breakpoint *(19)*. To take a particular (but randomly chosen) treatment system as an example, the San Francisco Public Utilities Commission (SFPUC) currently uses a chloramine target concentration of 2.1 mg/L as Cl_2 in plant effluent and slightly less in the distribution system. Chloramine is formed at the SFPUC treatment plants by combining chlorine and ammonia at a weight ratio of 5:1 or slightly less *(31)*. Applying the conditions given above (assuming that essentially all of the chlorine is present as NH_2Cl and the chlorine to ammonia ratio is between 5:1 and 1:1) the reaction shown in eq.1 will yield equilibrium $NHCl_2$ concentrations of 0.2 mg/L as Cl_2 (2.82×10^{-3} mM) between pH 6.9 and 7.6. This amount of $NHCl_2$ may be sufficient to produce a significant amount of NDMA since NDMA more than an

order of magnitude above the interim California DHS action level was formed by the reaction between 2 mg/L $NHCl_2$ as Cl_2 (0.03 mM) and 20 μg/L (0.09 μM) diuron. Typical chloramination pH values are above 7.6, but in some cases not far above. The current pH value in the SFPUC drinking water system varies between 8.6 and 9.4, depending on the water source, and given the alkalinity of such supply, a pH decrease to 7.6 or less is unlikely at SFPUC. However, other treatment plants may be operating closer to the "edge". In such systems, a relatively modest decrease in pH, combined with the presence of diuron, may produce NDMA levels of concern. The choice of a disinfectant and its dosage is becoming ever more complicated because of greater demands on inactivation of a broader spectrum of microorganisms and the avoidance of disinfection byproducts including NDMA. Although the particular risk identified here is likely small in comparison with the whole spectrum of risks associated with disinfection (or lack of it), avoiding this particular risk involves the avoidance of chloramines (e.g., by nitrification prior to free chlorine application for wastewaters or breakpoint chlorination for source waters containing NH_3) or, if chloramination is desired, the addition of free chlorine prior to NH_3, the avoidance of low pH, and the control of the Cl/N ratio.

Obviously, it is important to distinguish between diuron concentrations in source waters and those in disinfection processes. Diuron can be removed by varied treatment mechanisms in conventional drinking water or wastewater treatment facilities. For example, granular activated carbon can provide high removal efficiency for well-adsorbed compounds like diuron *(32)*. Another effective removal technique for diuron is membrane filtration, notably nanofiltration, which can achieve 43-87% removal of diuron *(33)*. To correctly determine the health risk posed by diuron in terms of NDMA formation to downstream water users, these potential removals of diuron must be taken into account. However, most water treatment facilities do not have these treatment systems. Even with effective treatment, some diuron may pass through the treatment processes and reach the disinfection chambers. Further studies are needed to better define the pathway and kinetics of NDMA formation from diuron chlorination or chloramination to support accurate assessment of the human health risks posed by diuron in water sources. Understanding the NDMA formation pathway from diuron will also support the broader goal of developing effective strategies for minimizing NDMA formation during disinfection operations.

Conclusion

NDMA formation was consistently detected in aqueous diuron solutions during chlorination

or chloramination in this study. Compared to free chlorine and NH_2Cl, the commonly used disinfectants in conventional water treatment plants, $NHCl_2$ exhibits much higher potentials for being a more effective NDMA-forming oxidant from diuron at environmentally relevant concentrations, suggesting that the presence of $NHCl_2$ might be a good indicator of whether a risk of a significant human health risk exists in a water treatment system by the formation of NDMA if diuron is present in the source waters. Although $NHCl_2$ is not intentionally used for disinfection, its presence is possible in systems with source waters that contain diuron and that disinfect using chloramination.   In these (likely very limited) cases human health risks with respect to NDMA formation may be present.

The current concerns about diuron focus on its wide occurrence in surface water and groundwater resulting from heavy use and persistence. This study reports that diuron may represent a possible nonpoint source precursor for NDMA formation.   Most previous research regarding NDMA formation has focused on loading of precursors from municipal wastewater effluents or in drinking water supplies from waters affected by point sources. The yield efficiency of diuron to form NDMA during chlorination or chloramination probably does not account for a significant fraction of the unknown precursors of NDMA formation in the environment, but diuron may be an important contributor under certain circumstances.   For example, Schmidt et al. *(34)* presented results indicating much higher yields for NDMA formation from other compounds including rantidine; nevertheless, diuron's heavy use in both agriculture and other applications and its frequent detection in water sources may partially compensate for its lower efficiency of NDMA formation.

In addition, the findings from this research provide insight regarding the difficulties associated with the current regulations for compounds that have not been recently detected or that do not have established MCLs with respect to byproducts formation, especially those with a transient nature. In the case of diuron, infrequent monitoring may make it possible that the human health risks posed by diuron may be underestimated, and more importantly, more significant threats from the formation of more toxic byproducts (such as NDMA in this case) may go undetected. Broader knowledge and more detailed studies regarding the characteristics of compounds and byproducts formation will be required to design appropriate regulations to ensure the safety of delivered water.

List of Publications

1. Chen, W. H. and Young, T. M. **(2007).** NDMA Formation during Chlorination and Chloramination of Aqueous Diuron Solutions. Accepted for publication. *Environ. Sci. Technol.*

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