Formation and degradation of dichloroacetonitrile in drinking waters

David A. Reckhow, Teresa L. Platt, Andrew L. MacNeill and John N. McClellan

ABSTRACT

Dichloroacetonitrile (DCAN) is an important example of a reactive disinfection by-product for which a large body of occurrence data exists. Although it is known to undergo base-catalysed hydrolysis, DCAN's peculiar dependence on reaction time, chlorine dose and pH has never been fully reconciled with expectations based on its presumed precursor (i.e. amino acid residues). The purpose of this research was to improve existing models for DCAN degradation and to use this information for interpretation of DCAN concentration profiles.

Laboratory studies were performed using buffered solutions of DCAN, natural organic matter (NOM) and treated drinking waters, both with and without free residual chlorine. DCAN concentrations were measured as a function of reaction time. Results indicate a decomposition scheme encompassing three pathways of hydrolysis: attack by hydroxide, hypochlorite and water. Any one of the three pathways may predominate in drinking water systems, depending on the pH and chlorine residual. The resulting chemical kinetic model was used to show that the DCAN formed (and subsequently decomposed) was often many times the actual measured DCAN concentration. DCAN formation was found to agree with expectations based on the underlying chemistry of chlorine attack on proteinaceous material.

Key words | chlorine, dichloroacetonitrile, disinfection by-products, hydrolysis, kinetics, precursors

David A. Reckhow (corresponding author)
Andrew L. MacNeill
Department of Civil & Environmental Engineering,
University of Massachusetts,
Amherst, MA 01003, USA
Tel: 413-545-5392
Fax: 413-545-2202
E-mail: *reckhow@ecs.umass.edu*

Teresa L. Platt
Department of Civil & Environmental Engineering,
University of Massachusetts,
Amherst, MA 01003, USA
and
Seattle Public Utilities,
Water Engineering Division,
Seattle, Washington

John N. McClellan
Department of Civil & Environmental Engineering,
University of Massachusetts,
Amherst, MA 01003, USA
and
Tighe & Bond Consulting Engineers,
Westfield, Massachusetts

INTRODUCTION

Addition of chemical disinfectants to drinking water produces a wide range of unwanted organic disinfection by-products. When chlorine or chloramines are used, a certain fraction of the disinfection by-products (DBPs) will contain halogen atoms. Human health concerns have led to regulations in the USA for two groups of these compounds: the trihalomethanes (THMs) and the haloacetic acids (HAAs) (Pontius 1999). While many other halogenated by-products have been identified in chlorinated waters (e.g. Richardson 1998), most have not been widely quantified in actual drinking waters. The only two non-regulated compound groups that have been widely measured are the haloacetonitriles and the haloketones. The haloacetonitriles (HANs) include dichloroacetontrile (DCAN), trichloroacetonitrile and their brominated analogues.

BACKGROUND

HAN in drinking water

Dichloroacetonitrile was detected in US tap water in the mid-1970s (McKinney *et al*. 1976) although its origin was unknown at the time. Later work by Trehy and Bieber (1981) showed that this compound and its brominated analogues were formed from the reaction of chlorine with

natural organic matter (NOM). Through numerous studies in the early to late 1980s, it was learned that the HANs were nearly ubiquitous contaminants in chlorinated drinking waters although the levels were lower that those of the THMs or HAAs (e.g. Oliver 1983; Krasner *et al*. 1989; Peters *et al*. 1990*b*)

Chemistry of HAN formation

Trehy & Bieber (1981), and later Ueno and co-workers (1996) showed that DCAN could be produced from the chlorination of many common amino acids. These first authors also recognized from earlier chemical literature (e.g. Dakin 1916) that nitriles are major by-products of the chlorination of amino acids when chlorine is in excess (aldehydes may predominate under conditions of chlorine limitation).

Free amino acids are probably not the primary dihaloacetonitrile (DHAN) precursors, because the actual concentration of these compounds in drinking waters is generally quite low (Peake *et al*. 1972; Lytle & Perdue 1981). Much of the amino nitrogen in natural waters is present in proteinaceous material or bound to humic structures (e.g. Tuschall & Brezonik 1980). Empirical studies have shown a strong positive correlation between the overall nitrogen content of aquatic humic substances and their tendency to form DCAN (Reckhow *et al*. 1990). Algal suspensions, rich in proteinaceous material, have also been shown to readily form DHANs (Oliver 1983; Plummer & Edzwald 1998). In addition, the basic fractions of extracted NOM have been found to produce the highest levels of DCAN upon chlorination (Reckhow *et al*. 2000). Thus, it seems that proteinaceous material is the most likely precursor for DHANs in drinking waters.

The attack of chlorine on proteins can be viewed as a two-step process. First is a series of rapid reactions with reactive side groups. This gives rise to fast chlorine demand and formation of THMs and total organic halide (TOX) (Hureiki *et al*. 1994), but probably not much DHAN (although some side groups contain nitrogen, they do not appear to be the centre of DHAN formation; e.g. Trehy & Bieber 1981). Then, the polypeptide backbone undergoes a slow degradation. Although many have shown that amino acids within proteins are relatively unreactive (e.g. Pereira *et al*. 1973), the polypeptide linkages will degrade in a slow stepwise fashion in the presence of chlorine (e.g. Goldschmidt *et al*. 1927; Fox *et al*. 1997). This is a base-catalysed process that has been interpreted in terms of HAN formation by Bieber & Trehy (1983). These authors also pointed out that data from Helz *et al*. (1983) indicate that certain reactive amino acids (e.g. tyrosine) will undergo ring cleavage and further accelerate protein degradation. Scully & co-workers (1988) presented empirical evidence that the degradation of total dissolved amino nitrogen (i.e. the protein backbone) occurs only after many days and in the presence of a long-lasting chlorine residual.

Based on the protein-chlorine reactions, DHAN should be characterized by slow chlorine-dependent formation, which occurs at higher rates as the pH increases. Actual observations with natural waters and NOM extracts, however, show a very different pattern (e.g. Reckhow & Singer 1985). DHAN concentrations are almost always lower when chlorination is conducted at higher pHs. In addition, their concentrations accumulate rapidly to a maximum and either level off, or sometimes even decrease. A decrease in concentration is clear evidence of decomposition. However it is not clear if the discrepancy between expected DHAN formation and observed concentrations can be attributed to this decomposition phenomenon.

HAN degradation

Unlike the THMs, DCAN is susceptible to chemical degradation in treated waters. Trehy & Bieber (1981) showed that haloacetonitriles undergo a base-catalysed decomposition that is dependent on the nature of the bound halogens. Oliver (1983) recognized that DHAN degradation was accelerated at pH 7 and pH 8 by the presence of free chlorine. This did not seem to be the case at pH 6. Peters & co-workers (1990*a*) substantiated the accelerated loss of DCAN in the presence of free chlorine.

Most recently, Glezer & co-workers (1999) studied the hydrolysis and chlorination kinetics of all nine bromine and chlorine-containing HANs. For each HAN, they

developed separate rate constants for the three pHs examined. They observed highest rates of hydrolysis for the trihaloacetonitriles (THANs), followed by the DHANs and finally the monohalogenated forms. This is consistent with the known activating effect of electron withdrawing substituents on nitrile hydrolysis (Schaefer 1970). Reaction rates with chlorine followed a similar trend. All degradation rates increased with increasing pH. These authors proposed that degradation produced almost exclusively the corresponding haloacetamide. They found that degradation of the nine compounds both with and without chlorine could be fit to a LFER (linear free energy relationship) model comprising standard polar and steric substituent constants. The two models representing hydrolysis and chlorination were similar in terms of the impacts of the polar and steric properties of the DHAN. The authors viewed this as an indication that the two reactions proceed by similar pathways.

Despite the existence in the literature of data from several teams of researchers, HAN degradation reactions have not been adequately characterized to allow for quantitative predictions under a range of pH and temperatures. This is because the studies were either focused on qualitative effects (e.g. Trehy & Bieber 1981; Oliver 1983), or they were focused on the development of LFER models (Glezer *et al*. 1999). A more detailed level of kinetic analysis is necessary if we are to understand and adequately describe DBP reactions in drinking water distribution systems. This is especially important if we are to continue to use and develop kinetic-based DBP formation models (e.g. McClellan *et al*. 2000).

OBJECTIVES

The purpose of this research was to quantitatively define the decomposition kinetics of DCAN with respect to pH and chlorine dose; and to use this information to characterize the overall formation of DCAN and daughter products expected from the chlorination of drinking waters and NOM. This study represents the latest addition to our long-term work on DBP decomposition (e.g. Reckhow & Singer 1985; Croué & Reckhow 1989; Xie & Reckhow 1993, 1994, 1996). Information of this sort will help with the following:

- development of mathematical models for predicting DBP concentrations
- understanding of the nature and lifetime of intermediate products which might be susceptible to removal by treatment processes immediately following disinfectant addition
- understanding of the role of metastable DBPs in the formation of subsequent, secondary DBPs
- more fundamental understanding of disinfectant reactions and DBP formation.

Dichloroacetonitrile is of special interest, because it is one of only a few metastable DBPs that are routinely measured in treated drinking waters. The NOM and drinking water chlorination data are taken from typical examples collected over the past 15 years at the University of Massachusetts. This paper represents an attempt to summarize our findings with regard to one of the by-products that has been systematically analysed over this period.

MATERIALS AND METHODS

All reaction solutions were prepared in buffers containing 0.01 M sodium phosphate and adjusted to the desired pH with sodium hydroxide or sulphuric acid. The pH 7 buffer prepared in this way had an ionic strength of about 0.018. Small volumes of a secondary dichloroacetonitrile stock (20 mg l^{-1}) were typically introduced at the start of each experiment so that the initial concentration was about 50 μg l^{-1}. Samples were partitioned off into identical 40-ml amber septum-capped vials. These were placed in a dark 20°C constant temperature chamber, and periodically sacrificed for immediate analysis.

PTFE gas sampling bags (Berghof/America, Concord, CA) were used in the preliminary DCAN experiments in place of the separate vials. These were sampled at intervals over the course of the reactions. Because of the flexible nature of these bags, the internal volume was reduced after each sampling, such that they remained headspace-free (MacNeill 1994).

Primary stock DCAN solution was prepared from the commercially available pure compound (Pfaltz & Bauer). About 10 μl of DCAN was added to a 25 ml volumetric flask containing some stock solvent (acetone for the hydrolysis experiments and methanol for the chlorination experiments). The exact amount of DCAN transferred was determined by gravimetry using an analytical balance. This was then used to prepare a secondary stock of 20 mg l^{-1} by use of graduated volumetric syringes and a volumetric flask.

DBP analysis was conducted according to a widely accepted LLE/GC/ECD method (*Standard Methods for the Examination of Water & Wastewater* 1992). Samples containing free residual chlorine were quenched prior to analysis with ammonium chloride. A capillary GC (Hewlett Packard 5890, Hewlett Packard Corporation, Menlo Park, CA) was used with a linearized electron capture detector. Zero grade nitrogen was used as the carrier gas. Concentrations were assessed from peak area ratios to the internal standard. Residual chlorine measurement was made by the DPD colorimetric method (*Standard Methods for the Examination of Water & Wastewater* 1992).

Aquatic fulvic acid was extracted from Thousand Acre Reservoir (Athol, MA) by the method of Thurman & Malcolm (1981) with minor modifications (Wacks 1987). Treated drinking water was collected from a utility in Connecticut (Nov 1997). This was a filter effluent from a direct filtration plant. The effluent had a 2.11 mg l^{-1} TOC and a UV absorbance of 0.067 cm^{-1}.

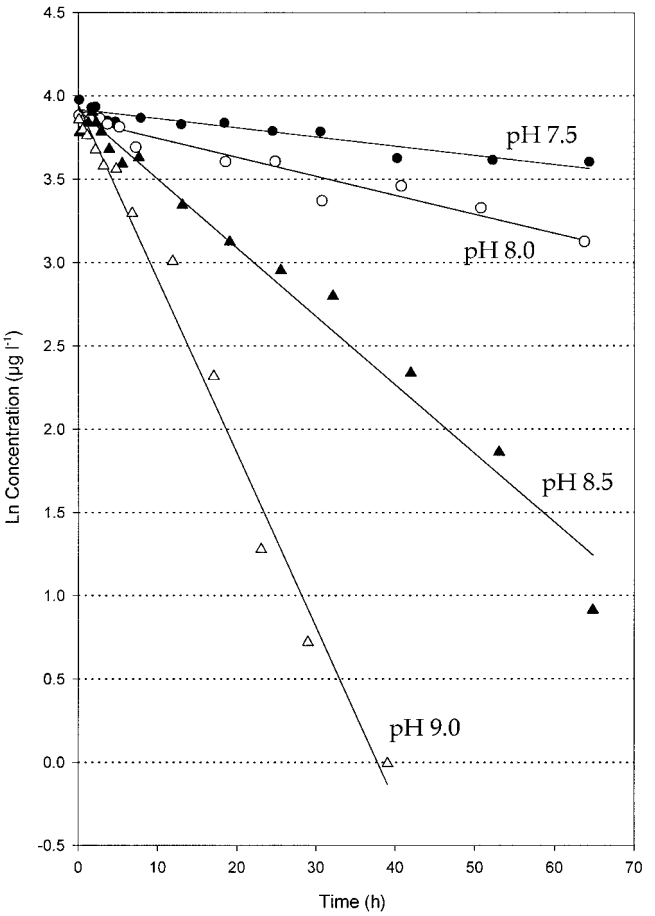

Figure 1 | Kinetic analysis of DCAN degradation experiments in the absence of free chlorine (20°C).

RESULTS

Kinetic studies with DCAN solutions

Preliminary tests were run as part of a larger study aimed at developing mechanistic DBP formation models (MacNeill 1994). These results (data not shown) indicated that there is a substantial rate of decomposition at neutral pH as reported by Trehy and Bieber, and that this rate was greater in the presence of 10 mg l^{-1} free chlorine. These tests also showed that little or no decomposition occurs under slightly acidic conditions (i.e. pH 5), even in the presence of a substantial concentration of free chlorine. Based on these data it was decided that careful hydrolysis experiments should be conducted over the range of pH and chlorine doses relevant to drinking water treatment.

Several series of controlled laboratory experiments were conducted with pure solutions of DCAN. These were incubated at varying pH both with and without chlorine and analysed periodically for residual DCAN. Figure 1 shows the semi-log plots of DCAN concentration versus time at four different pHs in the absence of chlorine. The data support a rate law that is first order in DCAN (linear response in a semi-log plot). They also show an increasing rate of loss with increasing pH.

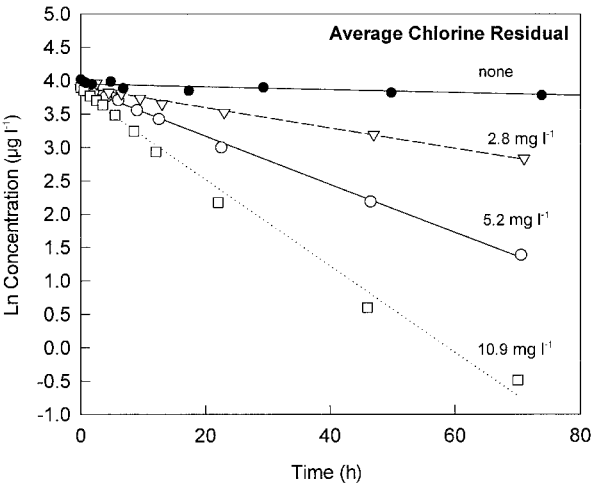

Figure 2 | Kinetic analysis of DCAN degradation experiments in the presence of free chlorine at pH 7 (20°C).

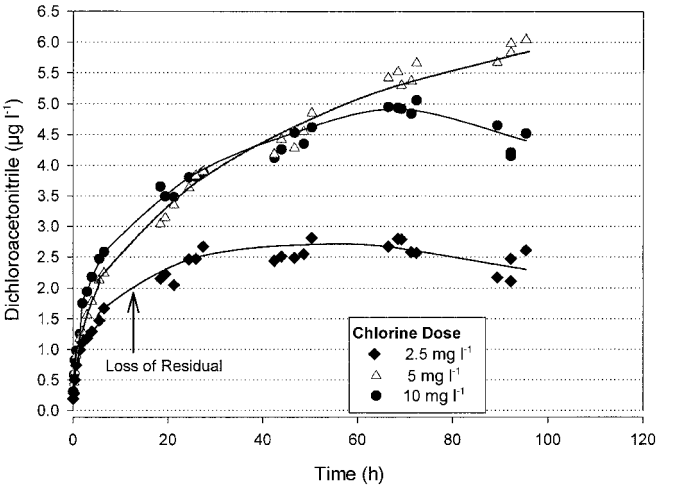

Figure 3 | DCAN concentration versus reaction time for the chlorination of thousand acre fulvic acid (2.8 mg l^{-1} TOC) at three different chlorine doses (pH 7; 21°C).

Figure 2 shows the results of experiments conducted with varying chlorine doses, and in the absence of light. Analysis of free chlorine residual (data not shown) revealed an immediate drop, followed by a relatively stable residual (± 10%). The chlorine residuals indicated in Figure 2 are averages of these measurements. All curves still show good first order behaviour. It is also clear that the rate of DCAN degradation increases with chlorine concentration.

Chlorination of NOM

To evaluate the impact of DCAN degradation on observed DCAN concentrations, several typical data sets were selected. One of these is a long-term, high chlorine dose study from the published literature (Reckhow & Singer 1985). The second is a variable chlorine dose study using an extracted NOM fraction (Thousand Acre Fulvic Acid, or TAFA). The third is a variable pH study using a filter effluent (CT utility). All were conducted in the laboratory under well-controlled conditions of pH, temperature and chlorine dose. Figure 3 shows DCAN data from the TAFA study. Three separate timed experiments were run at chlorine doses of 2.5, 5 and 10 mg l^{-1}. Complete loss of chlorine residual was noted toward the end of the first day in the 2.5 mg l^{-1} dose test, whereas the others maintained a measurable chlorine residual throughout.

THM data (not shown) indicated an initial rapid formation that slowed to a gradual increase over a period of days. TTHM concentration also increased with increasing chlorine dose. When chlorine became exhausted, TTHM formation nearly stopped. The same general characteristics applied for chlorine demand (not shown). However, DCAN showed a different behaviour (Figure 3). First, an actual drop in concentration was observed in two of the three tests at longer contact times. This is clear evidence of chemical decomposition. Second, the relationship between observed concentration and chlorine dose was a complicated one. We will try to show that the dual dependence of DCAN formation and degradation on chlorine concentration is responsible for this.

The third data set will only be represented by its DCAN concentrations in the interest of brevity (Figure 4). Here the three tests were run at the same chlorine dose (2.7 mg l^{-1}), but at different pH. As with most data sets of this type, increasing pH leads to increasing TTHM concentration (data not shown). However, Figure 4 shows that the trends for DCAN are again more complicated. Not only are there clear losses at the highest pH, but it is the intermediate pH conditions that lead to the highest DCAN concentrations.

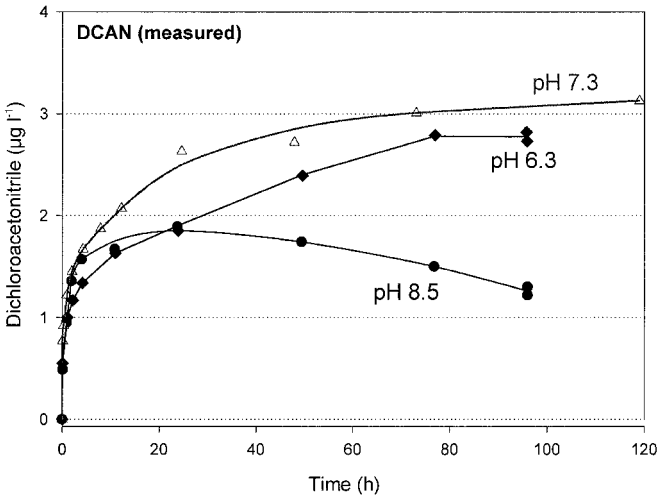

Figure 4 | DCAN concentrations measured in water from CT utility (11/97) chlorinated at three different pHs (2.7 mg l^{-1} dose, 15°C).

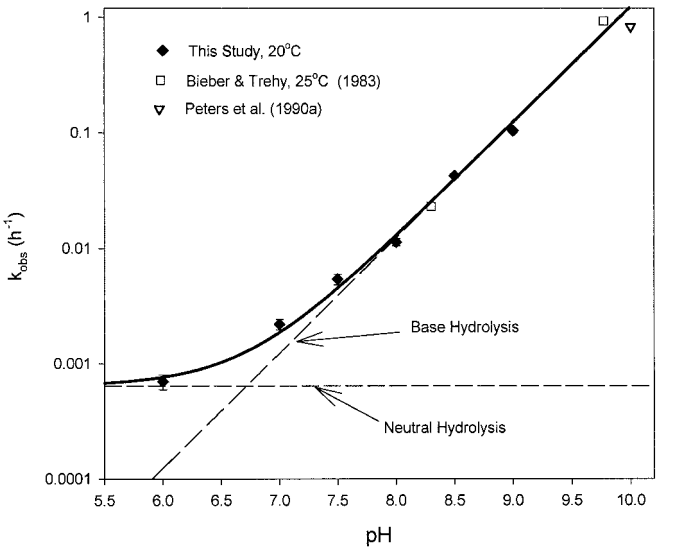

Figure 5 | Relationship between pH and first order decomposition rate of DCAN in the absence of chlorine.

DISCUSSION

Decomposition kinetics

Figure 5 shows the observed first order rate constants for the hydrolysis experiments plotted against pH. Also plotted on this figure are two rate constants reported by Bieber & Trehy (1983) at 25°C. In addition, we have calculated an observed rate constant from the pH 10 data of Peters & co-workers (1990*a*; temperature not reported). Data from their tests at pH 7 and 4 are not shown, because they were of too short a duration to record any significant compound loss.

Of the work reported here, the data sets at pH 8.0, 8.5 and 9.0 were considered the most reliable, because of the extensive degradation of DCAN. If these three are subjected to linear regression on a scale of Log K_{obs} vs. pH, a line of slope 0.96 is obtained. This is a good indication that the hydrolysis can be treated as first order in hydroxide.

The lower pH data show substantial positive deviation from the predicted rate based on base-catalysed hydrolysis. This is suggestive of a neutral hydrolysis pathway; presumably involving attack by an uncharged water molecule. To investigate this possibility, the full data set was analysed by non-linear least-squares regression whereby the k_{obs} was treated as a function of hydroxide concentration plus a constant. The constant term was found to be statistically significant ($\alpha = 0.05$) and, as a result, the final model includes a neutral hydrolysis term.

$$\frac{dC}{dt} = -\{k_1 + k_2[OH^-]\}C \quad (1)$$

While there are other sources of data on the decomposition of DCAN in water (e.g. Oliver 1983; Croue & Reckhow 1989), these are from studies that were not designed to address DCAN kinetics. As a result, the data from these sources are limited and not as appropriate for quantitative kinetic analysis as those already cited.

Figure 6 shows the first order observed degradation rates for the three tests run in the presence of chlorine. Also included is the rate for pH 7 degradation without chlorine. A good linear relationship is observed, with a slope of 0.0066 mg-Cl_2 l^{-1} h^{-1} (or 0.13 M^{-1} s^{-1}). This is indicative of a second order rate limiting step which involves some form of aqueous chlorine.

Based on the data presented, the following rate law can be proposed.

$$\frac{dC}{dt} = -\{k_1 + k_2[OH^-] + k_3[FRC]\}C \quad (2)$$

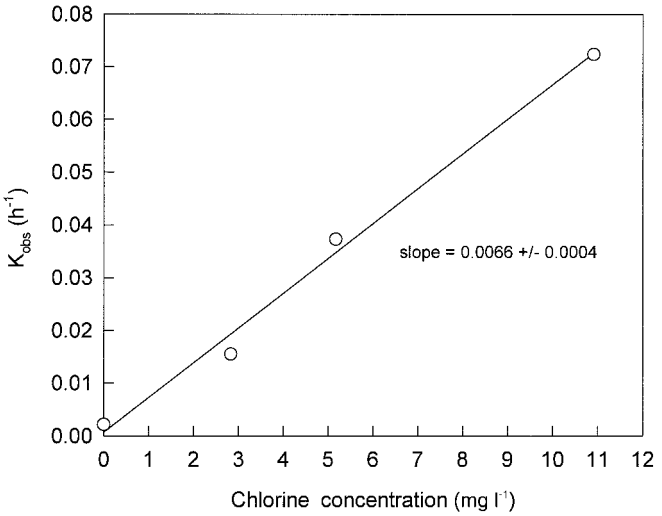

Figure 6 | Effect of chlorine concentration on observed first-order degradation rate of DCAN (20°C).

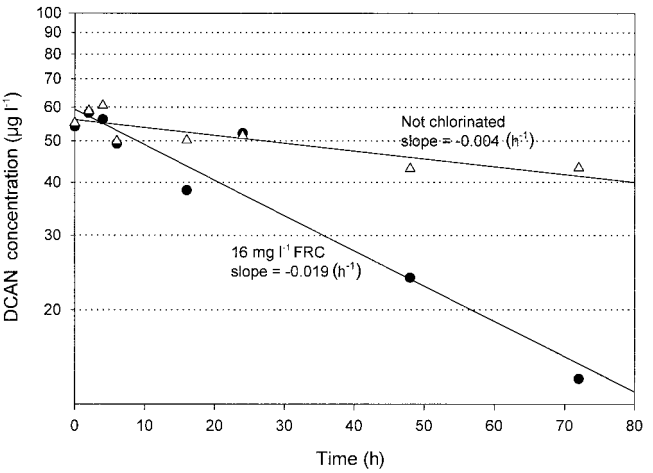

Figure 7 | Results of validation test run at pH 6.15 and 20°C.

where:

$k_1 = 1.78 \times 10^{-7} \pm 0.35 \times 10^{-7}$ (s^{-1})
$k_2 = 3.42 \pm 0.31$ ($M^{-1}\ s^{-1}$)
$k_3 = 1.30 \times 10^{-1} \pm 0.08 \times 10^{-1}$ ($M^{-1}\ s^{-1}$)
$[FRC]$ = free residual chlorine concentration without regard to $HOCl/OCl^-$ speciation.

Although the data in Figure 6 were all collected at the same pH, it is clear from other information that the reactive form of chlorine in DCAN degradation is hypochlorite. This is evident in the preliminary data, which showed no measurable degradation at pH 5 in the presence of 10 mg l^{-1} free chlorine. This is also in agreement with the hydrolysis mechanism, which indicates that the anionic form of the attacking nucleophile (i.e. hydroxide) is about nine orders of magnitude more reactive than the fully protonated form (i.e. water). In this way Equation (2) can be reformulated to reflect the specific participation of hypochlorite, and the rate constant can be recalculated using a pKa for hypochlorous acid of 7.58 at 20°C (Morris 1966).

$$\frac{dC}{dt} = -\{k_1 + k_2[OH^-] + k_4[OCl^-]\}C \qquad (3)$$

where $k_4 = 0.62 \pm 0.04$ ($M^{-1}\ s^{-1}$).

As a test of this model, a single DCAN decomposition experiment was run under conditions outside of those used to develop and calibrate the model (i.e. acidic pH, in presence of residual chlorine). In addition, a different group of researchers was asked to perform these tests, without prior knowledge of the decomposition model. The results show a small, but measurable decomposition rate in the presence of 16 mg l^{-1} free chlorine residual (average throughout the reaction period), but almost no loss without chlorine (Figure 7). At pH 6.15, the model predicts an apparent first order loss rate of 0.019 h^{-1} in the presence of 16 mg l^{-1} chlorine residual, and 0.001 h^{-1} in its absence. This compares very well with the data in Figure 7. Had the chlorine-induced decomposition shown in Figure 6 been due to reaction with HOCl, the expected degradation rate for Figure 7 would have been 0.130 h^{-1}. The slightly higher than expected control degradation rate may be attributable to other losses. During the model development and calibration runs (e.g. those represented in Figure 5), it was found that extreme care had to be exercised for low pH runs in order to avoid losses to volatilization and other 'bottle-effects'.

Decomposition pathways

Whenever a chemically based kinetic model is proposed for reactants of known structure, it is important that there

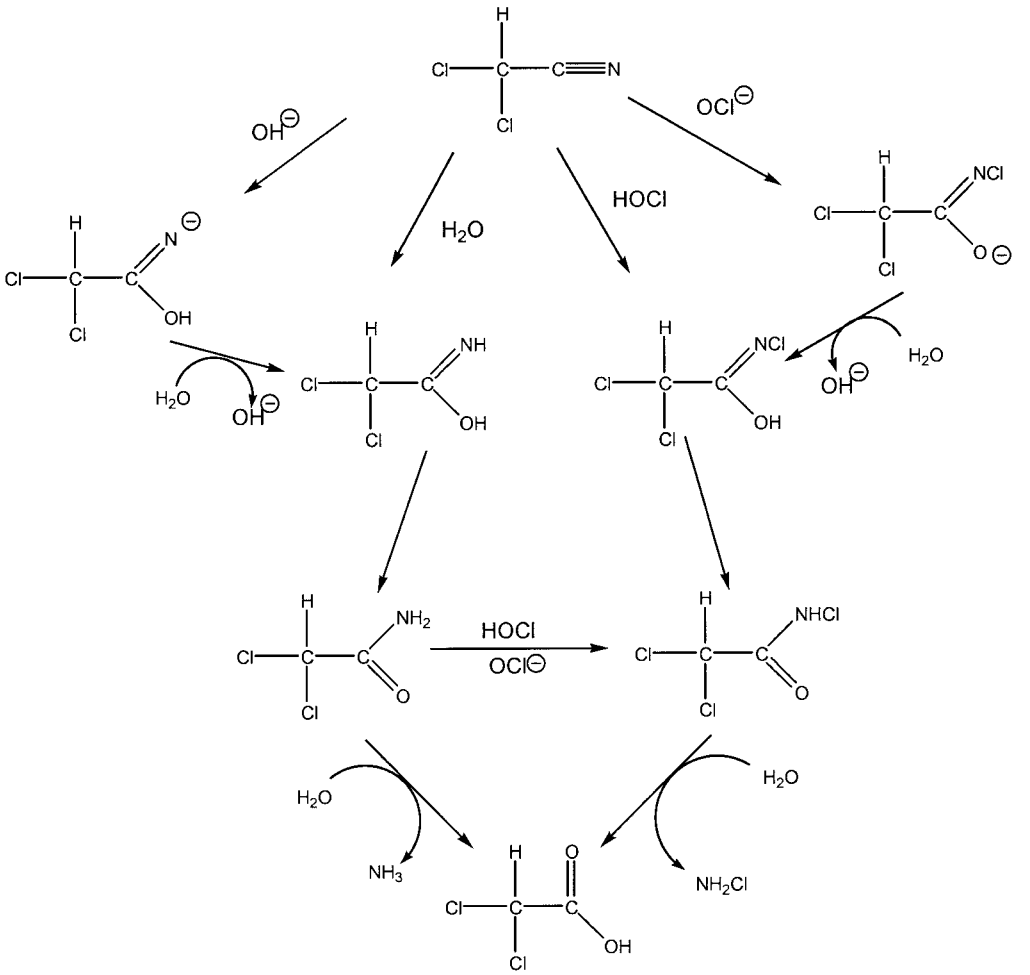

Figure 8 | Proposed mechanisms for the degradation of DCAN (summarized from Le Cloirec and Martin (1985) and Peters *et al.* (1990*a*)).

be a reasonable mechanistic rationale. Figure 8 shows a summary of degradation pathways that have been proposed in the literature. The base and neutral hydrolysis pathways can be seen on the left. Our kinetics suggest that the first step is rate limiting for base hydrolysis. Furthermore, we propose that the two pathways on the right are relatively unimportant under the conditions tested here. Instead, the hypochlorite-induced degradation follows a pathway analogous to that of hydroxide. This is consistent with our observation that degradation by HOCl is much slower that by OCl^-, and with the conclusions of Glezer & co-workers (1999) that the base-catalysed and chlorine degradation reactions give similar LFERs. Nucleophilic attack by hypochlorite has been cited in the hydrolysis pathway for another chlorination by-product, 1,1,1-trichloropropanone (Reckhow & Singer 1985).

Although not the focus of this kinetic study, it is helpful to consider the possible end products of these reactions. Most of the relevant literature confirms that DCAN will degrade to form dichloroacetamide, which can then hydrolyse to form dichloroacetic acid (DCAA). However, it is not at all clear as to which of these two products will predominate under typical drinking water treatment conditions. Exner & co-workers (1973) presented data that suggest rapid hydrolysis of dibromoacetamide to dibromoacetic acid, in the absence of free chlorine. However, it is difficult to interpret their work as

pH was allowed to drift, and many tests were conducted in strong sodium hydroxide solutions. Nevertheless, they cite Krieble & Noll (1939) and Hammett (1940) in support of rapid hydrolysis of amides versus nitriles. Later, Peters & co-workers (1990*a*) reported that dichloroacetamide was rapidly converted into the N-chloroamide form in the presence of free chlorine. This compound was found to be stable over a range of pH in the absence of free chlorine. In the presence of free chlorine it underwent rapid hydrolysis to DCAA at pH 4 and 7, but a slower hydrolysis (8 h half-life) at pH 10. However, these rates may be high due to the very high chlorine concentrations used (about 4,000 mg l^{-1}).

Glezer & co-workers (1999) showed that trichloroacetamide hydrolyses to trichloroacetic acid (TCAA) at pH 8.7 with a half-life of many days. This was done in the absence of free chlorine. They claim that other tests (data was not shown) indicated none of the di- or trihaloacetamides showed any detectable hydrolysis at neutral or acidic pH. They did not comment on the hydrolysis rates in the presence of free chlorine.

Implications with respect to chlorination of drinking waters

Figure 9 presents a summary of the DCAN degradation half-lives over the range of pH and chlorine residuals that one might encounter in drinking water systems. These were all calculated from Equation (3). Also shown on this figure are regions where each of the three potential reactants predominates. For example, at a chlorine concentration of 1 mg l^{-1}, the neutral hydrolysis will predominate below pH 5.8, the hypochlorite pathway will predominate between pH 5.8 and 8.3, and above 8.3 the hydroxide-catalysed reaction becomes most important. Thus, at high pH sometimes employed for corrosion control or precipitative softening, the DCAN half life becomes so short that chlorine concentration does not play an important role.

Because of continuous decomposition, the total amount of DCAN formed [DCAN-F] may be substantially greater than the actual 'instantaneous' DCAN measured [DCAN-M] in chlorinated waters. Using actual measured

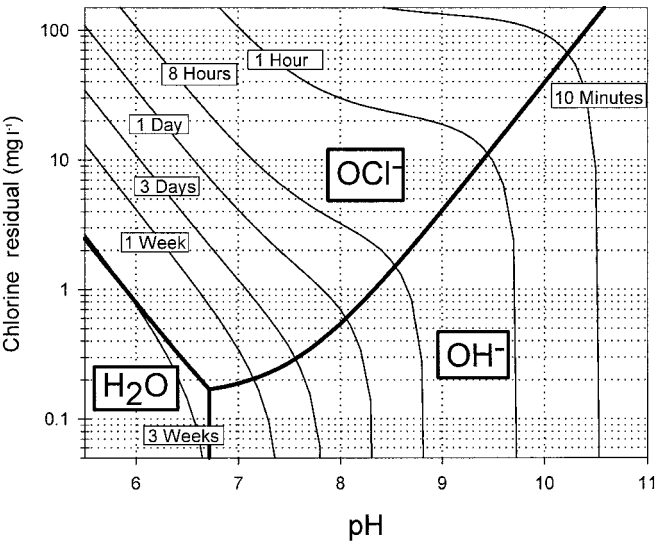

Figure 9 | DCAN degradation: zones for the predominant pathway and half-lives at 20°C.

data, the DCAN formed can be back calculated by augmenting the measured data with the amount decomposed in a discretized timestep,

$$[DCAN\text{-}F_{t+1}] = [DCAN\text{-}F_t] + ([DCAN\text{-}M_{t+1}] - [DCAN\text{-}M_t]) + r_{DCAN\text{-}decomp}{}^{\Delta}t \quad (4)$$

where the subscripts represent the timestep 't' and 't + 1'. The decomposition rate is based on the measured DCAN concentration and the measured free residual chlorine (FRC) concentration (multiplied by α_1, the fraction of FRC that is in the form of OCl^- at any given pH).

$$r_{DCAN-decomp} = (k_1 + k_2[OH^-] + k_4\alpha_1[FRC_t]) \times \left(\frac{[DCAN-M_t] + [DCAN-M_{t+1}]}{2} \right) \quad (5)$$

Actual DCAN and FRC data must be collected over time. These values may need some smoothing, and then intermediate concentrations are obtained by linear interpolation. Timesteps are chosen to match the rate of observed change in the reactants (e.g. 0.1 hours early in the reaction to 1 hour later).

Figure 10 presents the results of this calculation based on data previously reported in the literature (Reckhow & Singer 1985). In this and subsequent figures, both

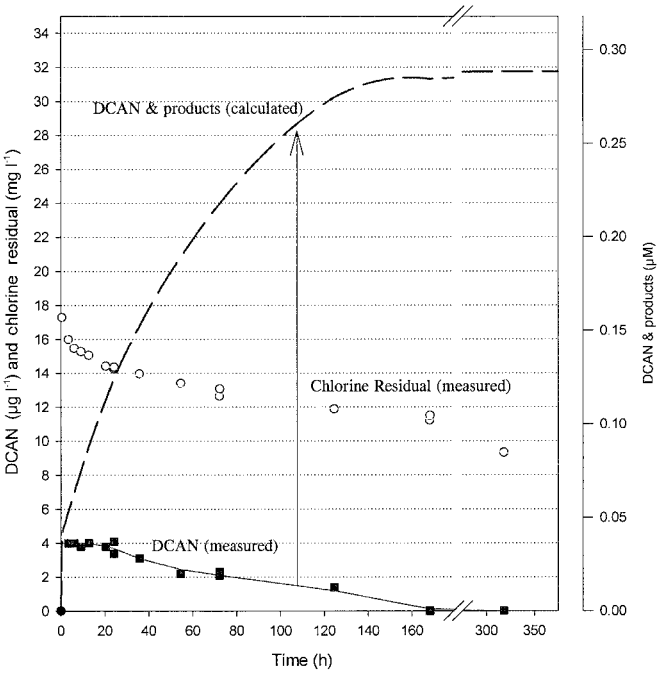

Figure 10 | Calculated DCAN formation (labelled: DCAN & products) for the chlorination of Black Lake Fulvic Acid (4.2 mg l^{-1} TOC, pH 7, 20°C).

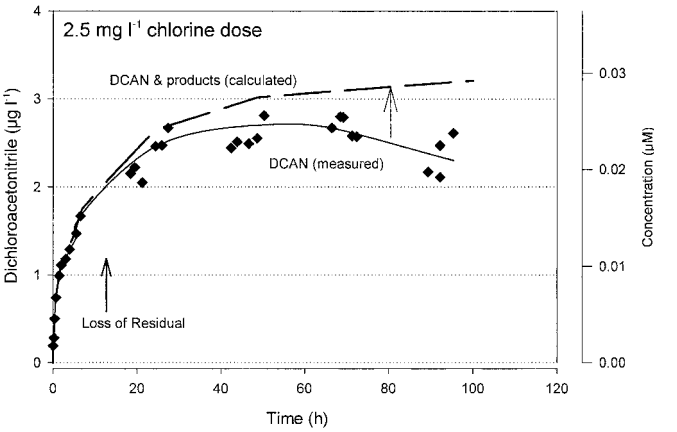

Figure 11 | Calculated DCAN formation (labelled: DCAN & products) for the chlorination of Thousand Acre Fulvic Acid (2.8 mg l^{-1} TOC) at a chlorine dose of 2.5 mg l^{-1} (pH 7; 21°C).

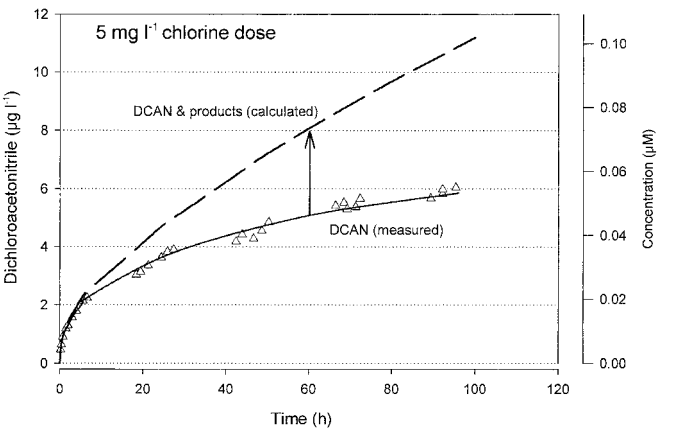

Figure 12 | Calculated DCAN formation (labelled: DCAN & products) for the chlorination of Thousand Acre Fulvic Acid (2.8 mg l^{-1} TOC) at a chlorine dose of 5 mg l^{-1} (pH 7; 21°C).

DCAN-M (labelled DCAN) and DCAN-F (labelled DCAN & products) are shown in μM units (right axis) and μg l^{-1} units as DCAN (left axis). Figure 10 shows that when high doses of chlorine (20 mg l^{-1} in this case) are used over long periods of time, relatively large amounts of DCAN can be formed and subsequently decomposed. The production is about 0.25 μM after about 100 h. This compares with about 0.70 μM DCAA, 1.5 μM TCAA, 2.0 μM TTHM and 25 μM TOX formed after the same reaction time (see: Reckhow & Singer 1985).

The Black Lake Fulvic Acid used in this experiment has been measured to contain about 1.16% N and 55.0% C (Reckhow *et al.* 1990). With a TOC of 4.2 mg l^{-1}, the organic N content would have been about 7 μM or 0.1 mg l^{-1} as N. Therefore, the DCAN pathway represents about 4% of the total organic nitrogen after a reaction of 140 h under these conditions. It is clear from this figure that the DCAN pathway is slowing down at this point in the reaction. However, there is probably a small amount of DCAN (i.e. near the detection limit) which persists, and signals a slow but continued DCAN formation. Oliver (1983) found that about 1.3% of the nitrogen in his fulvic acid was converted to DHAN after 24 h (pH 7). Of course, he did not consider the DHAN decomposition, which would tend to elevate this estimate.

Figures 11 to 13 show the individual measured DCAN profiles from the three TAFA chlorination experiments (from Figure 3). These also show the DCAN-F values that were calculated with Equations (4) and (5). These figures show a strong dependence of DCAN formation on chlorine dose. This is in contrast to most chlorinated DBPs

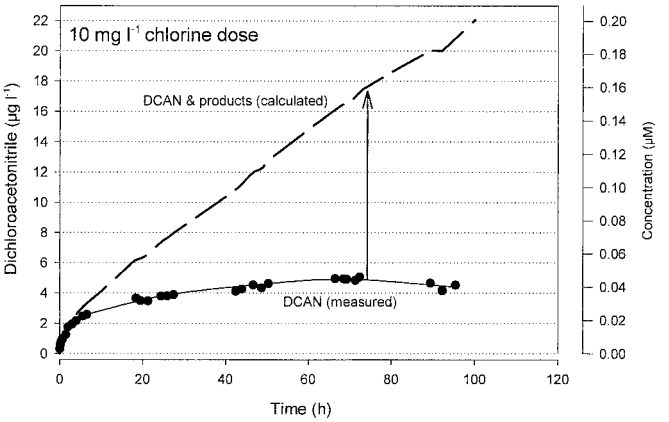

Figure 13 | Calculated DCAN formation (labelled: DCAN & products) for the chlorination of Thousand Acre Fulvic Acid (2.8 mg l^{-1} TOC) at a chlorine dose of 10 mg l^{-1} (pH 7; 21°C).

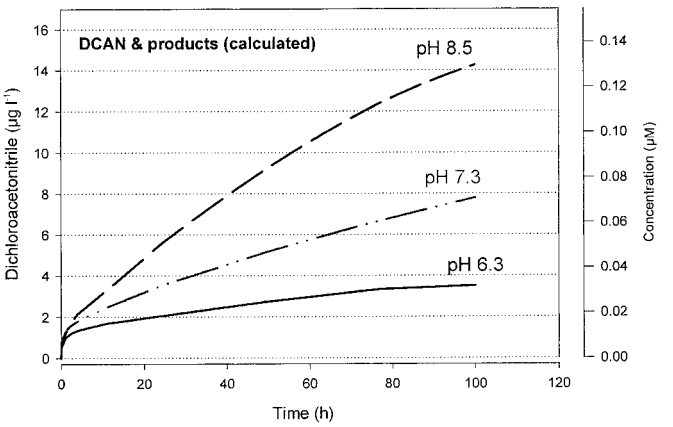

Figure 14 | Predicted DCAN formation in water from CT utility (11/97) chlorinated at three different pHs.

that tend to show only modest increases in formation with increasing chlorine dose.

Differences in the chlorine dependence of DCAN formation versus that of other DBPs may be attributed to fundamental differences in the precursor material. As proposed in the literature (e.g. Rook 1976), major DBPs such as the THMs and HAAs are largely derived from activated aromatic centres in NOM. These may include phenolic structures and aromatic amines (Reckhow *et al*. 1990). Such precursor structures react on a timescale of seconds to minutes and the reactions proceed rapidly to completion as long as there is some chlorine present. As each precursor-chlorine reaction nears completion, it loses its apparent dependency on chlorine concentration. This is a necessary result of the mismatch that exists between the reaction timescale and the observation timescale.

In contrast, the DHANs are thought to be derived from amino acids in NOM. Some are in a free form, but most are probably bound to humic substances or incorporated into proteins. Free amino acids react quickly with excess chlorine leading to very rapid nitrile formation (e.g. Alouini & Seux 1987). If they contain activating groups, DHANs may be formed. The bulk of the precursor material, combined amino acids, will react more slowly. For example, most polypeptide bonds are only slowly degraded under conditions typical of drinking water treatment. Many polypeptide bonds are not degraded at all under these conditions (e.g. Pereira *et al*. 1973), or they are very slowly degraded in a stepwise fashion (Goldschmidt *et al*. 1927; Fox *et al*. 1997). Chlorine reactions with proteinaceous material are, therefore, slow and do not reach completion under drinking water treatment conditions. Thus, the timescales of reaction and observation are more closely matched. This makes the dependence of DHAN formation on chlorine concentration much more evident in chlorination tests.

Figure 14 shows predicted DCAN formed (DCAN-F) from the CT utility experiments conducted at three different pHs (see Figure 4 for measured DCAN data). Despite lower measured DCAN concentrations at high pH, the amount of DCAN formed is greater. The difference is attributed to a higher degradation rate. This is in agreement with the expected pH-dependence of chlorine-induced degradation of proteins. These reactions are thought to be subject to base catalysis (e.g. Bieber & Trehy 1983).

CONCLUSIONS

DCAN degrades in the absence of chlorine by base-catalysed and neutral pathways. The former dominates above pH 7, and the latter below pH 6.5. In the presence

of free chlorine, DCAN degradation can be much faster. This third degradation pathway probably involves hypochlorite as a catalyst. The acceleration due to chlorine is observed from a pH of about 6–8.5 under low to moderate chlorine residuals.

The features of dichloracetonitrile formation are consistent with expectations based on a presumed proteinaceous precursor. This by-product is slowly formed over a period of hours to days. Its formation is strongly dependent on the chlorine concentration. The reactions are faster at higher pH, and continue at a nearly constant rate long after the THM and HAA forming reactions have become essentially exhausted.

ACKNOWLEDGEMENTS

The authors wish to thank the National Science Foundation for financial support through the Research Experiences for Undergraduates Program (Platt) and through research grant BCS-8958392 (MacNeill). The assistance of Caroline von Stechow and Tianjie Wu in conducting the model validation run is also acknowledged.

REFERENCES

Alouini, Z. & Seux, R. 1987 Kinetics and mechanisms of hypochlorite oxidation of α-amino acids at the time of water disinfection. *Wat. Res.* **21**(3), 335–343.

Bieber, T. I. & Trehy, M. L. 1983 Dihaloacetonitriles in chlorinated natural waters. In *Water Chlorination: Environmental Impact and Health Effects*. Vol 4, Book 1, *Chemistry and Water Treatment*. Proceedings of the Fourth Conference on Water Chlorination (ed. R. L. Jolley, W. A. Brungs, J. A. Cotruvo, R. B. Cumming, J. S. Mattice, & V. A. Jacobs), pp. 85–96. Ann Arbor Science, Ann Arbor, Michigan.

Croué, J. & Reckhow, D. A. 1989 The destruction of chlorination byproducts with sulfite. *Eviron. Sci. Technol.* **23**(11), 1412–1419.

Dakin, H. D. 1916 Oxidation of amino acids to cyanides. *J. Biochem. Tokyo* **10**, 319–323.

Exner, J. H., Burk, G. A. & Kyriacou, D. 1973 Rates and products of decomposition of 2,2-dibromo-3-nitrilopropionamide. *J. Agr. Food Chem.* **21**(5), 838–842.

Fox, T. C., Keefe, D. J., Scully, F. E. Jr & Laikhter, A. 1997 Chloramines VII: chlorination of alanylphenylalanine in model solutions and in a wastewater. *Environ. Sci. Technol.* **31**(7), 1979–1984.

Glezer, V., Harris, B., Tal, N., Iosefzon, B. & Lev, O. 1999 Hydrolysis of haloacetonitriles: linear free energy relationship, kinetics and products. *Wat. Res.* **33**(8), 1938–1948.

Goldschmidt, S., Wiberg, E., Nagel, F. & Martin, K. 1927 About proteins. *Justus Liebigs Ann. Chem.* **456**, 1–38.

Hammett, L. P. 1940 *Physical Organic Chemistry*, 1st edition. McGraw-Hill, New York.

Helz, G. R., Dotson, D. A. & Sigleo, A. C. 1983 Chlorine demand: studies concerning its chemical basis. In *Water Chlorination: Environmental Impact and Health Effects*. Vol 4, Book 1, *Chemistry and Water Treatment*. Proceedings of the Fourth Conference on Water Chlorination (ed. R. L. Jolley, W. A. Brungs, J. A. Cotruvo, R. B. Cumming, J. S. Mattice & V. A. Jacobs), pp. 181–190. Ann Arbor Science, Ann Arbor, Michigan.

Hureiki, L., Croué, J. & Legube, B. 1994 Chlorination studies of free and combined amino acids. *Wat. Res.* **28**(12), 2521–2531.

Krasner, S. W., McGuire, M. J., Jacangelo, J. G., Patania, N. L., Reagan, K. M. & Aieta, E. M. 1989 The occurrence of disinfection by-products in US drinking water. *J. Am. Wat. Wks Assoc.* **81**(8), 41–53.

Krieble, V. K. & Knoll, C. I. 1939 The hydrolysis of nitriles with acids. *J. Am. Chem. Soc.* **61**, 560–563.

Le Cloirec, C. & Martin, G. 1985 Evolution of amino acids in water treatment plants and the effect of chlorination on amino acids. In *Water Chlorination: Environmental Impact and Health Effects*. Vol 4, Book 1, *Chemistry and Water Treatment*. Proceedings of the Fourth Conference on Water Chlorination (ed. R. L. Jolley, R. J. Bull, W. P. David, S. Katz, M. H. Roberts, Jr & V. A. Jacobs), pp. 821–834. Ann Arbor Science, Ann Arbor, Michigan.

Lytle, C. R. & Perdue, E. M. 1981 Free, proteinaceous and humic-bound amino acids in river water containing high concentrations of aquatic humus. *Environ. Sci. Technol.* **15**(2), 224–228.

McClellan, J. N., Reckhow, D. A., Tobiason, J. E., Edzwald, J. K. & Smith, D. B. 2000 A comprehensive kinetic model for chlorine decay and chlorination byproduct formation. In *Natural Organic Matter and Disinfection Byproducts: Characterization and Control in Drinking Water* (ed. S. Barrett, S. Krasner & G. Amy). American Chemical Society, Washington, DC.

McKinney, J. D., Mauer, R. R., Hass, J. R. & Thomas, R. O. 1976 Possible factors in the drinking water of laboratory animals causing reproductive failure. In *Identification and Analysis of Organic Pollutants in Water* (ed. L. H. Keith), vol 1. pp. 417–432. Ann Arbor Science, Ann Arbor, Michigan.

MacNeill, A. L. 1994 Mechanistic Modeling of Trihalomethanes and Other Neutral Chlorination Byproducts. MS thesis, University of Massachusetts, Amherst.

Morris, J. C. 1966 The acid ionization constant of HOCl from 5 to 35 C. *J. Phys. Chem.* **70**(12), 3798–3805.

Oliver, B. G. 1983 Dihaloacetonitriles in drinking water: algae and fulvic acid as precursors. *Eviron. Sci. Technol.* **17**(2), 80–83.

Peake, E., Baker, B. L. & Hodgson, G. W. 1972 Hydrogeochemistry of the surface waters of the Mackenzie river drainage basin, Canada—II. The contribution of amino acids, hydrocarbons and chlorins to the Beaufort Sea by the Mackenzie river system. *Geochim. Cosmochim. Acta* **36**(8), 867–883.

Pereira, W. E., Hoyano, Y., Summons, R. E., Bacon, V. A. & Duffield, A. M. 1973 Chlorination studies. II. The reaction of aqueous hypochlorous acid with alpha-amino acids and dipeptides. *Biochim. Biophys. Acta* **313**, 170–180.

Peters, R. J. B., de Leer, E. W. B. & de Galan, L. 1990*a* Chlorination of cyanoethanoic acid in aqueous medium. *Eviron. Sci. Technol.* **24**(1), 81–86.

Peters, R. J. B., de Leer, E. W. B. & de Galan, L. 1990*b* Dihaloacetonitriles in Dutch drinking waters. *Wat. Res.* **24**(6), 797–800.

Plummer, J. D. & Edzwald, J. K. 1998 Effect of ozone on disinfection by-product formation of algae. *Wat. Sci. Technol.* **37**(2), 49–55.

Pontius, F. W. 1999 Complying with the Stage 1 D/DBP Rule. *J. Am. Wat. Wks Assoc.* **91**(3), 16–32.

Reckhow, D. A., MacNeill, A. L. & McClellan, J. N. 2000 DBP formation from contrasting NOM fractions. Unpublished manuscript.

Reckhow, D. A. & Singer, P. C. 1985 Mechanisms of organic halide formation during fulvic acid chlorination and implications with respect to preozonation. In *Water Chlorination: Environmental Impact and Health Effects* (ed. R. L. Jolley, R. J. Bull, W. P. David, S. Katz, M. H. Roberts, Jr & V. A. Jacobs), vol. 5. pp. 1229–1257. Lewis Publishers, Chelsea, Michigan.

Reckhow, D. A., Singer, P. C. & Malcolm, R. L. 1990 Chlorination of humic materials. Byproduct formation and chemical interpretations. *Eviron. Sci. Technol.* **24**(22), 1655–1664.

Richardson, S. D. 1998 Drinking water disinfection byproducts. In *Encyclopedia of Environmental Analysis and Remediation* (ed. R. A. Meyers), pp. 1398–1421. John Wiley & Sons, New York.

Rook, J. J. 1976 Haloforms in drinking water. *J. Am. Wat. Wks Assoc.* **68**(3), 168–172.

Schaefer, F. C. 1970 Nitrile reactivity. In *The Chemistry of the Cyano Group* (ed. Z. Rappoport). Wiley Interscience, New York.

Scully, F. E. Jr, Howell, G. D., Kravitz, R., Jewell, J. T., Hahn, V. & Speek, M. 1988 Proteins in natural waters and their relation to the formation of chlorinated organics during water disinfection. *Environ. Sci. Technol.* **22**(5), 537–542.

Standard Methods for the Examination of Water And Wastewater 1992 18th edition, American Public Health Association/ American Water Works Association/Water Environment Federation: Washington, DC.

Thurman, E. M. & Malcolm R. L. 1981 Preparative isolation of aquatic humic substances. *Environ. Sci. Technol.* **15**(4), 463–466.

Trehy, M. L. & Bieber, T. I. 1981 Detection, identification, and quantitative analysis of dihaloacetonitriles in chlorinated natural waters. In *Advances in the Identification and Analysis of Organic Pollutants in Water* (ed. L. H. Keith), vol 2. pp. 941–975. Ann Arbor Science, Ann Arbor, Michigan.

Tuschall, J. R. Jr & Brezonik, P. L. 1980 Characterization of organic nitrogen in natural waters: its molecular size, protein content, and interactions with heavy metals. *Limnol. Oceanogr.* **25**(3), 495–504.

Ueno, H., Moto, T., Sayato, Y. & Nakamuro, K. 1996 Disinfection by-products in the chlorination of organic nitrogen compounds: by-products from kynurenine. *Chemosphere* **33**(8), 1425–1433.

Wacks, M. J. 1987 The Formation and Decomposition of Halogenated Organics During Chlorination of a Drinking Water. MS thesis, University of Massachusetts, Amherst.

Xie, Y. & Reckhow, D. A. 1993 Stability of cyanogen chloride in the presence of sulfite and chlorine. In *Proceedings Water Quality Technology Conference, Toronto, Ontario, Canada*, pp. 1761–1777. American Water Works Association, Denver, Colorado.

Xie, Y. & Reckhow, D. A. 1994 Formation and degradation of dichloromalonic acid in chlorinated drinking water. In *Proceedings 1994 Water Quality Technology Conference*, pp. 857–869. American Water Works Association, Denver, Colorado.

Xie, Y. & Reckhow, D. A. 1996 Hydrolysis and dehalogenation of trihaloacetaldehydes. In *Disinfection By-Products in Water Treatment: The Chemistry of Their Formation and Control* (ed. R. A. Minear & G. L. Amy), pp. 283–291. Lewis Publishers, Boca Raton, Florida.