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Impact of Chlorine, Chlorine Dioxide and Ozone on the Oxidation of NTA during Drinking Water Treatment

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The use, as it is proposed, of nitrilotriacetic acid (NTA) for phosphate replacement in detergents will lead to its discharge in surface water at relatively high concentrations. It has been predicted that NTA concentrations between 30 and 580 µg/l in the river Rhine will be reached after complete substitution of polyphosphate in detergents in the drainage area of the river (Salomons and Van Pagee 1981). Questions have been raised about potential health hazards related to the uptake and treatment of the NTA containing riverwater for drinking water supply. Literature information on the behaviour of NTA during water treatment processes is limited. Given the structure and chemical properties of NTA, it can be expected that the oxidation step can be a most effective water treatment process favouring its removal. On the other hand the potential hazard of the formation of toxic products during the reaction of NTA with the oxidants should be envisaged.

Degradation of NTA by biological oxidation in waste water treatment systems, soil and surface water under aerobic conditions has been demonstrated many times (Thompson and Duthie 1968, Shumate et al. 1970, Renn 1974, Woodiwiss et al. 1979, Tiedje and Mason 1974, Hrubec and Van Delft 1981, Warren and Malec 1972, Larson et al. 1981). However reports on degradation of NTA by chemical oxidation applied in water treatment processes are scarce. Games and Staubach 1980) investigated the reaction of NTA with ozone. A rapid and complete degradation of NTA and NTA metal complexes has been found under conditions simulating water treatment practice. The effect of chlorination on NTA degradation has been studied by Warren (1976). This study showed that no oxidation of NTA occurred in systems containing excess divalent metal ions or ammonia. In addition it has been concluded that the only chlorinated organic intermediate, having any likelihood of existance during the reaction, is N-chloroglycine.

Kain (1978) suggests that under potable water chlorine disinfection NTA removal up to 50% may be expected.

No data could be retrieved on the reaction of chlorine dioxide with NTA.

The aim of the present investigation was to determine:
- removal of nitrilotriacetic acid upon chlorine, chlorine dioxide and ozone treatment under conditions characteristic for drinking

water treatment practice;
- possible formation of mutagenic substances from the reaction of NTA with these oxidants;
- formation of halogenated reaction products of NTA with chlorine and chlorine dioxide, as far as analyses of the group parameters adsorbable organic halogens (AOX), extractable organic halogens (EOX) and volatile organic halogens (VOX) allow.

MATERIALS AND METHODS

NTA was determined by the method described by Reichert and Linckens (1980).
After evaporation of the aqueous sample to dryness, derivatization of NTA with propanol followed.
The formed tri-propylester was quantified by gaschromatography applying a Carlo Erba 4160 GC equipped with a nitrogen specific detector.
Residual chlorine was determined by amperometric titration with phenyl arsine oxide (American Public Health Service 1971a), ozone by iodometric titration (American Public Health Service 1971b) and chlorine dioxide by the diethyl-phenyl-diamine (DPD) method according to Palin (1974).
AOX response was generated after adsorption of compounds from the aqueous sample on activated carbon and pyrolysis by microcoulometric titration (Dressman et al. 1979). EOX values result from microcoulometry after extraction of the water sample with hexane (Wegman and Greve 1977). The VOX method consisted of purging the water sample with inert gas, trapping the purged compounds, followed by the coulometric determination of the halogens after pyrolysis (Wegman and Hofstee 1979).
Before testing, the water samples were concentrated by a factor of 200 through lyophilization. The concentrates were tested according to the procedure described by Ames et al. (1975). The strains which have been used in the tests were TA 98 and TA 100, with and without the rat liver S-9 homogenate (Mc Cann et al. 1975).
Most experiments were carried out with a solution of sodium nitrilotriacetate (E. Merck, Darmstadt, Fotopur) in distilled water or in tap water of the cities of Dordrecht and The Hague. Due to its high complexation ability, NTA is mainly present in tap water in the form of metal chelates (Lerman and Childs 1975). The complexation state in the used tap waters with 500 µg NTA/l, shown in Table 1, was calculated by Procter and Gamble Comp., Cincinnati, using a modification of the computer program of Mc Duff and Morel (1973).

For experiments with Cu^{2+}- and Ca^{2+} complexes of NTA the metals were added in excess to the aqueous solutions of NTA. The experiments with chlorine and chlorine dioxide were performed in 10 l dark glass flasks covered with aluminum foil. Aqueous solutions of sodium hypochlorite and chlorine dioxide were used. Chlorine dioxide was generated by the sodium chlorite acid activation technique (Valenta and Gahler 1975) in a commercial generator (Bello-Zon, Filter GmbH, Heidelberg).

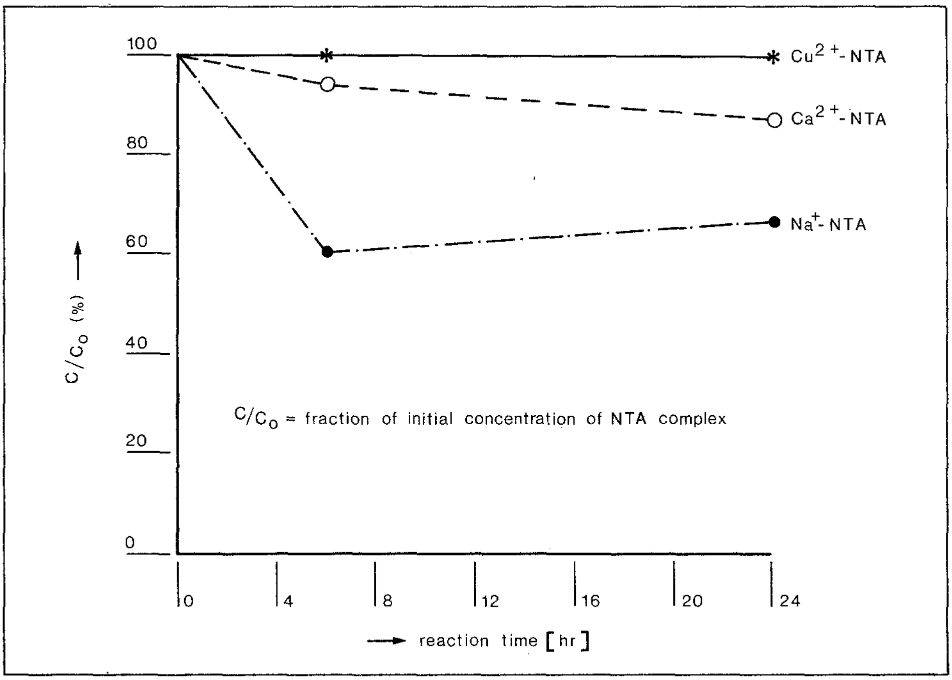

Fig. 1. Degradation of NTA complexes in distilled water by treatment with 10 mg Cl_2/l. (C_0= 500 µg NTA/l, pH 7, temp. 21 ° C).

Table 1. Concentration of NTA complexes in tap water at different pH (Concentrations calculated as percentages of the total NTA concentration).

	The Hague tap water			Dordrecht tap water		
pH	6	8	9	6	8	9
Ca-NTA	34.9	46.9	31.0	43.3	73.0	53.0
Mg-NTA	0.8	1.3	16.2	1.4	2.3	21.3
Fe-NTA	6.8	-	-	20.4	-	-
Cu-NTA	36.3	35.9	35.9	7.8	7.7	7.7
Zn-NTA	15.1	15.2	15.3	16.0	16.1	15.9
Mn-NTA	-	-	1.1	-	-	-
H -NTA	5.7	-	-	10.4	-	-

Prior to the oxidant dosing, pH adjustment took place by addition of phosphate or borax buffer in distilled water or by dosing of H_2SO_4 or NaOH for pH adjustment of the tap water. The oxidation reactions were stopped by addition of sodium thiosulphate.

The ozonation was carried out in a 10 l glass tube reactor. Ozone generated from a Walace & Tierman laboratory generator was fed into the reactor via an all-glass frit.

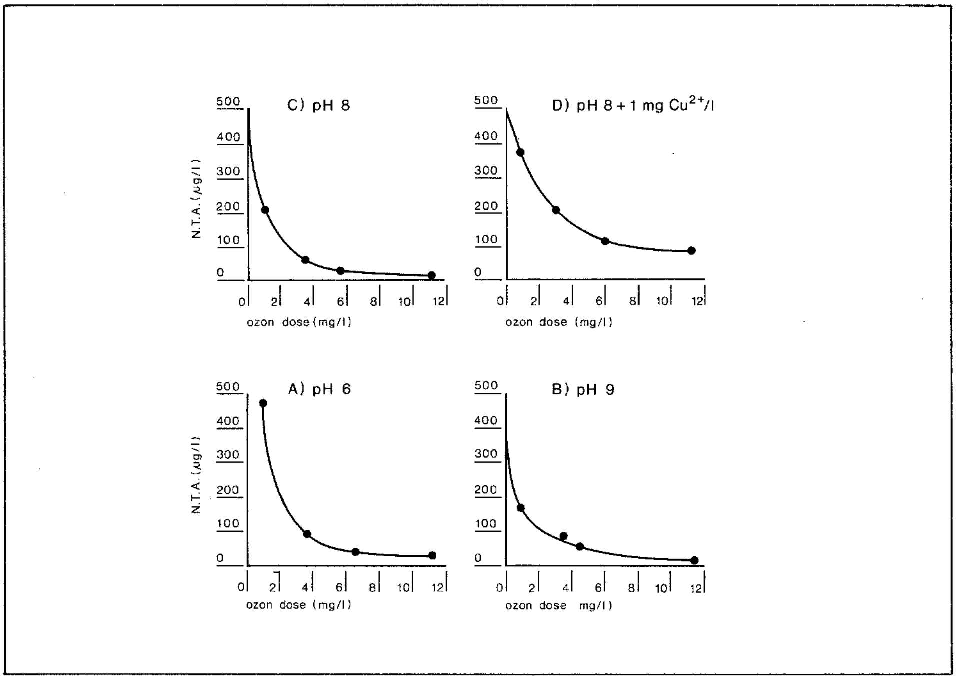

Fig. 2. Removal of NTA in tap water (Dordrecht) by ozonisation at different pH's.

RESULTS AND DISCUSSION

The treatment of 500 µg NTA/l in the form of Na^+, Ca^{2+} and Cu^{2+} complexes in separate experiments in distilled water with 2.5 and 10 mg Cl_2/l at pH 7 resulted, after a reaction time of 6 and 24 hours, in a slight degradation of Na^+-NTA and Ca^{2+}-NTA as is illustrated for 10 mg Cl_2/l in Figure 1. No removal of Cu^{2+}-NTA was found at the 10 mg Cl_2/l level.

No measurable degradation of NTA at the 500 µg/l level in tap water of the city of The Hague, treated under the same conditions as in the previous experiment, was observed. The reason for the low degradability of NTA in the tap water is likely the high degree of its complexation.
Another reason could be the relatively low molar ratio of Cl_2/NTA applied in our study. By a high Cl_2/NTA ratio which was applied by Kain (1978) a partial degradation of NTA metal complexes, with the exception of Ni-NTA, was observed.
Similar results as with chlorine have also been obtained by experiments with chlorine dioxide. The tests were conducted with 500 µg/l of Na^+-NTA, Ca^{2+}-NTA and Cu^{2+}-NTA in distilled water and in tap water of the city of Dordrecht. Chlorine dioxide was applied at doses of 1 and 2.5 mg per liter, at pH 6, 8 and 9. The reaction time was 4 and 24 hours. No degradation was found in the reaction with Ca^{2+}-NTA and Cu^{2+}-NTA complexes and with NTA in the tap water and

only a 10-30% removal was observed in the reaction with Na^+-NTA in distilled water.

The results of the tests with chlorine and with chlorine dioxide allow the conclusion that under typical conditions of the drinking water practice in The Netherlands, characterized by application of low doses of both oxidants, no or only a slight degradation of NTA can be expected.
The tests with ozone were conducted using tap water from the city of Dordrecht applying 500 µg NTA/l at pH 6, 8 and 9. The ozone doses were varied from 1 mg O_3/l up to 11 mg O_3/l. The reaction time was 30 minutes. The results (Figure 2) show a nearly complete destruction of NTA at doses of ozone above about 4 mg/l. The degradation was independent of the pH. The presence of Cu^{2+} at high concentration had a minor influence on the degradation at dosage levels of ozone encountered normally in the treatment of drinking water, i.e. lower than ca. 4 mg O_3/l.

To check whether NTA can act as a potential precursor of halogenated organics by reaction with chlorine, an orientation test with a high NTA concentration (5 mg NTA/l) in distilled water treated with 5 and 50 mg Cl_2/l at pH 6 and 9 was carried out.
After 5 hours of reaction time VOX, AOX and EOX were determined. In all samples the values for these parameters were below the detection limit of the analytical methods.
The results of the treatment of tap water of the city of The Hague with 500 µg NTA/l are shown in Table 2. No significant differences can be seen between the values of the measured parameters in water with and without NTA, treated at the same conditions.

Table 2. VOX, AOX and EOX of The Hague tap water with 500 µg NTA/l treated with 10 mg Cl_2/l at pH 6 and 9 (Reaction time 4 hours, temperature 22°C)

		pH = 6		pH = 9	
NTA concentration	(µg/l)	500	0	500	0
VOX	(µg Cl/l)	32	31	34	39
AOX	(µg Cl/l)	55	59	73	75
EOX	(µg Cl/l)	1.2	1.2	1.8	1.6
Residual chlorine	(mg/l)	8.8	9.1	9.1	9.3

The experiments with chlorine dioxide which were performed at the same conditions as those with chlorine, also gave no increase of halogenated organics after treatment of water containing NTA.
These results indicate that formation of halogenated organics, by reaction of NTA with chlorine and chlorine dioxide during water treatment, which can be detected with the used analytical methods, can be regarded as highly improbable.

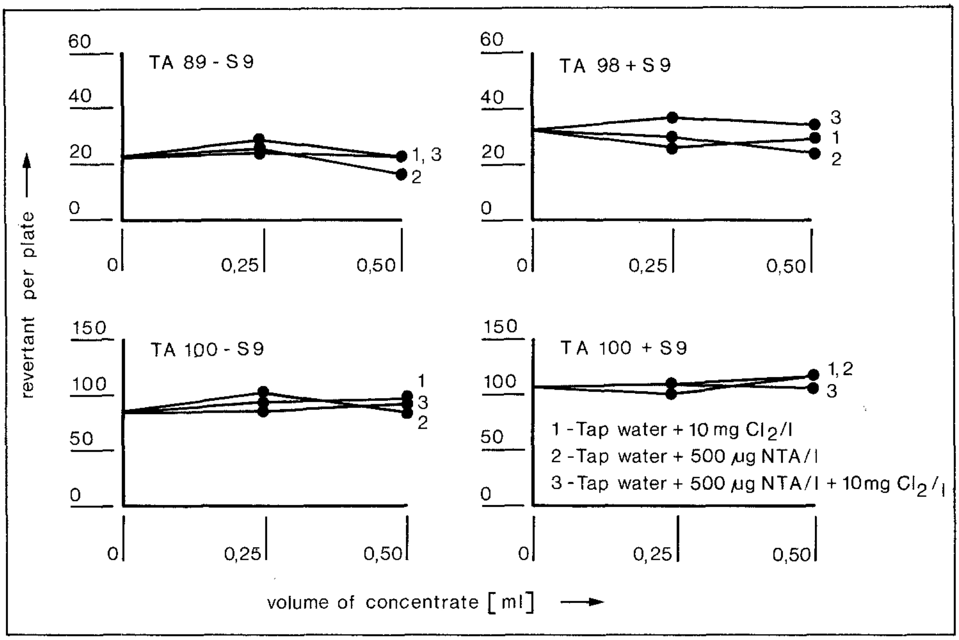

Fig. 3. Mutagenic activity of tap water containing NTA, treated with chlorine dioxide.

Mutagenicity tests have been performed with tap water of the city of The Hague, which proved to possess no mutagenic activity in itself. A solution of 500 µg NTA/l was treated with the three oxidants. Chlorine and chlorine dioxide were applied at a dose of 10 mg/l at pH = 7.9 The reaction time was 24 hours. The ozonation was performed at a dose of 6 mg O_3/l for 30 minutes.
The results of the tests with the concentrates of water (concentration factor 200 times) previously treated with chlorine dioxide are shown in Figure 3 for the strains TA 98 and TA 100, with and without S9 homogenate addition. From this Figure it can be seen that the concentrates of untreated water as well as these of water treated with NTA were non-mutagenic.

Also no increase of mutagenic activity was found in water with NTA addition treated with ozone and chlorine. Upon interpreting the results of the mutagenicity tests the relatively low preconcentration factor of 200 should be kept in mind.

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