Article

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Introduction and removal of disinfection byproducts and mutagenic activity by chemical and photolytic treatments

Elimination des sous-produits organiques de désinfection et de leur activité mutagène, par photolyse

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RÉSUMÉ

La désinfection des eaux de consommation par chloration est connue comme étant à l'origine de la formation de sous-produits organo-chlorés. Certains de ces sous-produits présentent une activité mutagène. Les plus abondants produits organo-chlorés et les plus fréquemment présents dans les eaux sont les trihalométhanes, les haloacétonitriles, les acides haloacétiques, les chlorocétones et les chlorophénols. En 1981, Holmbom et al ont mentionné l'identification d'une hydroxyfuranone chlorée, le 3-chloro-4-(dichlorométhyl-5-hydroxy-2 (5H)-furanone (ou MX), dans des effluents de papeterie.

Puis, il a été montré que le MX est un des plus puissants mutagènes, en termes de génotoxicité mesurée par le test d'Ames, avec les souches TA 100. En 1985, le MX a été détecté dans des extraits d'eaux chlorées issues de Finlande. Un peu plus tard, il a été évalué que le MX contribue à plus de 57 % de la génotoxicité des eaux. Le MX a été de nouveau détecté dans des eaux chlorées aux USA, au Canada, au Royaume Uni, au Japon et en Chine.

Pendant les deux dernières décennies, les distributeurs d'eau potable ont fait des progrès significatifs dans la diminution des concentrations en organo-chlorés dans les eaux. Ces améliorations de la qualité des eaux passe par l'utilisation croissante d'eaux brutes de meilleure qualité (eaux souterraines), la supression de la pré-chloration et l'amélioration du traitement de la coagulation-floculation, de la filtration (en particulier, lente sur sable), de la pré-oxydation (avec d'autres réactifs désinfectants que le chlore) pour conduire à l'utilisation de faibles doses de chlore en désinfection finale. Cependant, il reste des préoccupations d'ordre génotoxique concernant la présence de sous-produits organochlorés dans les eaux de consommation. Cet article est une revue de certains de nos résultats sur la production et l'élimination des sous-produits de désinfection et l'activité

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mutagène qu'ils engendrent, après traitement de différentes eaux par le chlore, le dioxyde de chlore, la monochloramine, l'ozone, les radiations UV et différents traitements combinés.

L'allure de la réponse de mutagénicité et l'identification des sous-produits organo-chlorés ayant été trouvées similaires pour des solutions de substances humiques chlorées en laboratoire et des eaux potables chlorées, les eaux brutes contenant des substances humiques sont donc tout à fait adaptées aux études de laboratoires sur la formation des sous-produits de désinfection dans les eaux potables. Les eaux étudiées dans ce travail ont été collectées dans le lac Savojärvi situé au sud-ouest de la Finlande, dans l'eau souterraine de St Janskloster aux Pays Bas et dans les rivières Meuse et Rhin, également aux Pays-Bas. L'eau du lac Savojärvi et celle de St Janskloster sont des eaux fortement colorées de par la présence de concentrations élevées en substances humiques (COD de 20 mg/l et 6,5 mg/l, respectivement). Les teneurs en COD des eaux de la Meuse et du Rhin étaient de 3,8 mg/l et 4,2 mg/l, respectivement. Les prélèvements d'eau ont été filtrés (0,45 µm) et le pH a été ajusté à 7,0 (par une solution de soude et un tampon phosphate) avant toute expérimentation. Les désinfectants et les doses utilisées sont donnés dans le tableau 1.

La MX et autres composés mutagènes ont été extraits des eaux acidifiées (pH 2,1) par extraction liquide-liquide (en 4 fois) par de l'éther éthylique fraîchement distillé. La totalité des extraits ont été déshydratés par congélation à - 20°C. Une partie des extraits a été ensuite évaporée à sec et le résidu a été redissous dans du diméthyl sulfoxyde et l'activité mutagène a été testée. Une autre partie de l'extrait, dans laquelle a été ajouté l'acide mucobromique comme étalon interne, a été utilisée pour le dosage du MX. Cet extrait a été évaporé à sec, puis méthylé pendant 1 heure à 70 °C, avec du méthanol en présence de 2 % d'acide sulfurique. Après neutralisation avec 2 % de bicarbonate de sodium et extraction des dérivés methylés par le n-hexane, les extraits ont été analysés par CG/SM.

Les produits de réaction volatils, formés pendant l'irradiation UV ont été isolés par la technique de CLSA ("closed-loop stripping apparatus") décrite par Grob et Zurcher en 1976. Une série de 1-chloroalcanes ont été utilisés comme étalons internes.

Les acides carboxyliques ont été isolées par extraction liquide-liquide de l'eau acidifié (pH 1) et analyse après estérification par le butanol en milieu acide.

Le chloroforme a été extrait de 100 ml de chaque échantillon, par de l'éther de pétrole dopé avec du tetrachloroéthylène comme étalon interne.

Les tests de mutagénicité ont été effectués en accord avec la méthode de Ames *et al.*, utilisant la souche TA 100 *Salmonella typhimurium*, sans activation métabolique. Le 3-chloro-1,2-propanediol a été utilisé comme contrôle positif. La contribution du MX à la mutagénicité de la souche TA 100, a été calculée en multipliant la concentration molaire du MX par la mutagénicite spécifique du MX (5 600 revertants nets/nmol).

Le carbone organique dissous (COD) a été dosé par un analyseur de carbone Ionics 555 at la concentration en AOX, avec un analyseur Dohrmann DX 20.

L'identification du MX et des autres sous-produits acides a été réalisée par un détecteur de masse HP 5971 couplé à une chromatographie gazeuse HP 5980 (séries II) et un système de données Vectra 386/25. Les données sur le détermination du MX ont été acquises en mode SIM. L'identification a été basée sur la correspondance des temps de rétention et sur l'intensité relative des pics de fragmentation, en accord avec les données du tableau 2. Les données pour les autres acides ont été acquises en mode ionisation.

La séparation a été effectuée sur une colonne capillaire HP 1, de 25 m de longueur et de 20 µm de diamètre intérieur avec une épaisseur de phase

stationnaire de 0,33 µm La température du four de chromatographie a été programmée de 50 °C à 270 °C, à une vitesse de 8 °C/min. Le spectrophotomètre de masse a été réglé en mode impact électronique (70 eV) et la température de la source d'ions, à 140 °C. La quantification des acides carboxyliques a été effectuée à l'aide d'une chromatographie gazeuse Varian (modèle 3700) équipée d'un détecteur à ionisation de flamme et d'une station de travail Omega de Perkin Elmere. La quantification du chloroforme a été effectuée avec le même équipement. Les analyses ont été faites en isotherme (50 °C) et la détection, assurée par un détecteur à capture d'électrons. Les chlorites ont été déterminés par titrage à la DPD-FAS.

L'eau du lac riche en substances humiques qui a été traitée par le procédé d'oxydation combinée UV/chlore a été trouvée fortement mutagène et contenant des concentrations de MX et de chloroforme plus élevées que dans l'eau traitée au chlore seul.

La même observation a pu être faite concernant la mutagénicité et la concentration en chloroforme des eaux pré-traitées avec des faibles doses d'ozone et par UV/ozone, respectivement.

Quand des doses plus élevées de ces oxydants puissants ont été utilisées en pré-traitement, l'activité mutagène, les concentrations en MX et chloroforme ont été trouvées plus faibles que dans les eaux chlorées sans pré-traitement.

La combinaison UV/ozone a été trouvée être plus efficace que l'ozonation seule dans la destruction des composés précurseurs de mutagénicité et de chloroforme.

Plus la teneur en dioxyde de chlore est élevée dans la combinaison chlore/dioxyde de chlore, plus les niveaux de mutagénicité et les concentrations de MX, chloroforme et AOX sont faibles. La production de chlorites augmente avec la proportion de dioxyde de chlore.

Des aldéhydes, des n-alcanes et des acides carboxyliques de faible masse moléculaire ont été identifiés comme sous-produits du traitement par UV de l'eau de lac riche en substances humiques.

L'activité mutagène (rapportée au COD) est approximativement similaire après chloration de l'eau de surface et des eaux souterraines riches en substances humiques, qu'après chloration des eaux des rivières Meuse et Rhin, contenant des faibles teneurs de substances humiques. Toutefois, les précurseurs de MX ont été trouvés être plus abondants dans les eaux riches en substances humiques que dans les eaux de rivières.

Mots clés : *eau, désinfection, sous-produits, activité mutagène.*

SUMMARY

Samples from four different raw water sources were treated with various disinfectants and subjected to chemical analyses and mutagenicity assays. The following disinfectants were used: chlorine (Cl_2), chlorine dioxide (ClO_2), monochloramine (NH_2Cl), ozone (O_3), ultraviolet radiation (UV), and combinations of Cl_2/ClO_2, O_3/Cl_2, UV/Cl_2, and $UV/O_3/Cl_2$. The samples were analysed for adsorbable organic halogens (AOX), chloroform ($CHCl_3$), carboxylic acids, volatile organics, chlorite, the strong mutagen 3-chloro-4-(dichloromethyl)-5-hydroxy-2 (5H)-furanone (MX), and mutagenic activity (as detected by the Ames test).

Humic lake water which had been treated with the combination UV/Cl_2 exhibited a higher level of mutagenicity and higher concentrations of MX and $CHCl_3$ than

water treated with Cl_2 alone. The same observation was made for the mutagenicity and the $CHCl_3$ concentration in waters preoxidized with low doses of O_3 and UV/O_3, respectively. When higher doses of these powerful oxidants were used in the pretreatment step, the level of mutagenicity, MX and $CHCl_3$ were lower than in water chlorinated without pretreatment. The combination UV/O_3 was found to be more efficient than O_3 alone in destroying the precursor material to the mutagenic compounds and chloroform.

The higher the proportion of ClO_2 in the combined Cl_2/ClO_2 process, the lower the levels of mutagenicity, MX, $CHCl_3$, and AOX. The production of inorganic chlorite increased with a higher proportion of ClO_2.

Aldehydes, n-alkanes, and low molecular-weight carboxylic acids were identified as byproducts following UV treatment of humic lake water.

The mutagenic activity (per amount of DOC) was approximately similar after chlorination of humic rich surface- and ground waters as after chlorination of waters from the rivers Meuse and Rhine, containing relatively low amounts of humic matter. The precursors to MX were found to be more abundant in the humic waters than in the river waters.

Key-words : *water, disinfection, by-products, mutagenic activity.*

INTRODUCTION

Disinfection of drinking water with elemental chlorine is known to produce chlorinated organic byproducts, including mutagens (ROOK, 1974; DE LEER, 1987; LOPER, 1980; MEIER, 1988; NOOT and others, 1989). Dissolved organic matter (DOM) of natural origin has been proposed to be the main precursors to these byproducts (DE LEER, 1987; KOPFLER and others, 1985).

Principally, two main approaches could be chosen in the evaluation of the health hazards associated with disinfection byproducts: 1) A « total analysis » of the byproducts formed, i.e. identification of all the products formed, followed by biological testing of the identified compounds. This is, however, an impractical and economically questionable way to proceed because of the large diversity in extractability and concentrations of the individual compounds present in disinfected waters. In addition, a complete evaluation of the health effects of the several hundred compounds formed during disinfection is practically impossible; 2) The use of chemical mass parameters (like AOX) and/or mutagenicity-directed subfractionation (biological tests coupled with chromatographic techniques) to localize and purify fractions of interest from the bulk organic matter. The biologically active compound(s) in the purified fraction(s) can then be identified by mass spectrometry (MS) or nuclear magnetic resonance (NMR) spectroscopy. By using the first of these approaches the extremely potent bacterial mutagen 3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone (MX) was identified in pulp bleaching effluents in 1981 (Holmbom and others, 1981). The same compound was later found in chlorinated drinking waters in several countries (HEMMING and others, 1986; HORTH, 1989; MEIER and others, 1987; SUZUKI and NAKANISHI, 1990).

The mutagenicity response pattern and the identity of chlorinated organic byproducts have been found to be similar in humic waters chlorinated in the laboratory and in chlorinated drinking water derived from humic surface waters (KRONBERG and others, 1985; DE LEER, 1987). Humic raw waters are thus well suited for laboratory studies on the formation of disinfection byproducts in drinking waters.

During the last two decades, drinking water authorities have made substantial progress in decreasing the concentrations of chlorinated organic byproducts and the level of mutagenic activity in drinking water. Improvements include increased utilization of less contaminated raw water sources (e.g. ground waters), omission of prechlorination, improvements of the coagulation/flocculation technique, the use of slow sand filtration (e.g. artificial ground water), the use of oxidative pretreatment steps and alternative disinfection methods, and the use of « low-dose » postchlorination. However, there is still concern about chlorinated byproducts, as chlorinated drinking water still contains mutagenic compounds, and considerable concentrations of other chlorinated acids (e.g. chloroacetic acids) (PETERS, 1991).

This paper reviews some of our results on the production and removal of disinfection byproducts and mutagenic activity following treatment of various raw waters with chlorine, chlorine dioxide, monochloramine, ozone, ultraviolet radiation, and various combined treatment methods.

MATERIALS AND METHODS

Water samples

The water samples were collected from Lake Savojärvi which is situated in a marsh area in s.w. Finland, from St Jansklooster which is a ground water area in The Netherlands, and from the rivers Meuse and Rhine in the Netherlands. The Lake Savojärvi and St Jansklooster waters are highly coloured because of high contents of dissolved humic material (DOC values 20 mg/L and 6.5 mg/L, respectively). The DOC values of the waters from Meuse and Rhine were 3.8 mg/L and 4.2 mg/L, respectively. The water samples were filtered (Millipore HA 0.45 µm filters) and the pH was adjusted to 7.0 (NaOH solution and phosphate buffer) before the start of the experiments.

Disinfectants

Methods for the generation of chlorine, monochloramine, chlorine dioxide, and ozone, and a more detailed description of the methods of application and measurements of the disinfectant concentrations have been described elsewhere (BACKLUND, 1988; BACKLUND, 1994). The disinfectants and the doses used are listed in Table 1.

The UV-irradiation and the combined UV/ozone-treatment were carried out in a 24 mm x 380 mm quartz tube (Labor-UV-reaktorsystem 2/Heraeus Noblelight). The samples were stirred with a small magnet during treatment.

The irradiation was carried out with two 15-W low-pressure mercury discharge lamps (Phillips TUV) installed vertically in a reflector at a distance of 20 cm from the sample tube. According to the manufacturer, the power output of the lamps at the germicidal 253.7 nm wavelength is 4 W. The incident radiation flux was measured with a ferric oxalate actinometer (Hatchard and Parker 1956) under constant stirring.

Tableau 1 Désinfectants utilisés et leurs doses.

Table 1 *Disinfectants and disinfectant doses used.*

Disinfectant	Dose (Disinfectant/DOC)
Cl_2	1.0
ClO_2	1.0
O_3	0.50-1.50
$O_3 + Cl_2$	0.50+1.0
$Cl_2 + ClO_2$	0.75+0.25
	0.50+0.50
	0.25+0.75
NH_2Cl	0.5
UV	10-60 mWs/cm^2

Sample extraction and derivatization

MX and other mutagenic compounds were extracted from 900 ml of acidified (pH 2.1) water by liquid/liquid partitioning into four aliquots (150 + 50 + 50 + 50 mL) of freshly distilled diethylether. The combined extract was dried for 20 h at -20°C. Part of the extract was then evaporated to dryness, the residue was redissolved in dimethyl sulphoxide (2 µL DMSO/mL water equivalent), and tested for mutagenic activity. Part of the dry extract was subjected to MX analysis. Mucobromic acid (MBA) was added to the rest of the dried diethylether extract as standard (350 ng/L water equivalent), the diethylether was evaporated, and the residue was methylated for 1 h at 70°C, using 2% sulphuric acid in methanol. Following neutralisation with 2% $NaHCO_3$ and extraction of the methylated derivatives into n-hexane, the extracts were subjected to gas chromatographic/mass spectrometric analyses. A more detailed description of the methods used for concentration, derivatization, and analysis of MX have been described elsewhere (HEMMING and others, 1986).

The volatile reaction products formed during UV-irradiation were isolated from 2 L water by the closed-loop stripping technique described by Grob and Zurcher (1976). A series of even numbered 1-chloroalkanes (C_8-C_{14}) were added to the water in known amounts as internal standards.

The carboxylic acids were isolated by liquid-liquid extraction and analysed as butyl esters according to the method described previously (BACKLUND, 1992).

Chloroform was extracted from a 100-mL sample using 5 mL petroleum ether which was spiked with 30 ng/mL of tetrachloroethylene as internal standard.

Mutagenicity tests

The mutagenicity assays were performed by the plate incorporation method according to AMES and others (1975), using Salmonella typhimurium strain TA100 without metabolic activation. Duplicate plates and five dose levels per plate were used. The activity was calculated by least-squares regression analysis of the means of the dose/response values obtained from the two plates. The spontaneous revertants were subtracted from the experimental results before presenting the data. 3-Chloro-1,2-propanediol was used as positive control.

The mutagenicity contribution from MX to the observed TA100 activity was calculated by multiplying the molar MX concentration by the specific TA100 mutagenicity of MX (5600 net revertants/nmol) (KRONBERG and others, 1988).

Analytical procedures

Dissolved organic carbon (DOC) was measured with an Ionics 555 carbon analyzer and AOX with a Dohrmann DX 20 total organic halide analyzer. The identification of MX and other acidic byproducts was performed with a Hewlett Packard 5971A mass selective detector equipped with a Hewlett Packard 5890 Series II gas chromatograph (GC/MSD) and a Vectra 386/25 data system.

Data for the MX determinations were acquired in the selected ion monitoring (SIM) mode. Identification was based on positive matching of retention times and relative ion peak ratios *(tabl. 2)*. Data for the other acids were acquired in the total ionization mode. The separation was performed on a HP 1 capillary column of 25 m length and 0.20 mm i.d. with a stationary phase film thickness 0.33 µm. The GC oven temperature was programmed from 50°C (2 min) to 270°C at a rate of 8°C/min. The mass spectrometer was operated in the electron impact mode (70 eV) and the ion source temperature was 140°C.

Tableau 2 Ions enregistrés et rapport des surfaces des pics en fragmentométrie de masse pour le MX méthylé.

Table 2 *Ion peaks used and relative peak area ratios determined for SIM mode GC MS analyses of methylated MX.*

Compound	Frangment Ion	m/z	Rel. Peak Area Ratio
MX	M-OCH_3	198.912	0.54
		200.909	1.00
		202.906	0.62
MBA[a]	M-OCH_3	240.832	

[a] Mucobromic acid, used as standard.

The quantification of carboxylic acids was performed with a Varian Model 3700 gas chromatograph equipped with a flame ionization (FID) detector and a Perkin Elmer OMEGA Analytical Work station. The chromatographic conditions, as well as the separation column, were identical to the ones described above.

The quantification of chloroform was performed with the same GC equipment as above. The analyses were done isothermally at 50°C and the detection was done with an electron capture (EC) detector.

Chlorite was determined by the DPD-FAS titration method (APHA, 1985).

RESULTS AND DISCUSSION

Mutagenicity and MX

Figure 1 shows the mutagenic activity and the calculated mutagenicity contribution from MX in Lake Savojärvi water after treatment with various disinfectants. The mutagenicity and the MX concentration were highest in water treated with a combination of UV and chlorine (UV/Cl_2). When the UV preoxidation step before chlorination was omitted, a slight decrease was

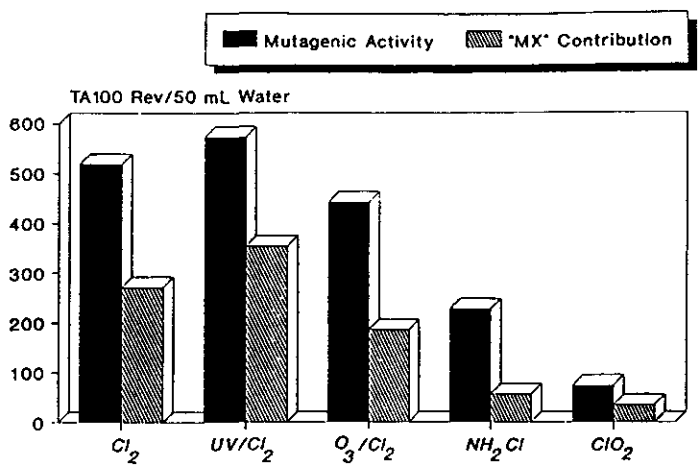

Figure 1 Activité mutagène (Rev./50 mL) et contribution du MX à la mutagénicité calculée dans l'eau du lac Savojärvi (COD: 20 mg/L) après traitement avec divers désinfectants.
Doses initiales des désinfectants: Cl_2 : 20 mg/L; UV/Cl_2 : 12 min/20 mg/L ; O_3/Cl_2 : 30 mg/L/20 mg/L ; NH_2Cl : 10 mg/L ; ClO_2 : 20 mg/L.

Mutagenic activity (Rev./50 mL) and calculated MX mutagenicity contribution in Lake Savojärvi water (DOC: 20 mg/L) after treatment with various disinfectants.
Initial disinfectant doses: Cl_2: 20 mg/L; UV/Cl_2: 12 min/20 mg/L; O_3/Cl_2: 30 mg/L/20 mg/L; NH_2Cl: 10 mg/L; ClO_2: 20 mg/L.

observed both in the mutagenicity and in the MX concentration. Thus, at the conditions used in this study, UV irradiation is capable of producing molecular sites in the DOM that, upon chlorination, will produce mutagenic compounds, including MX. The contributions from MX to the total TA100 mutagenicity in these waters were 50-60%, which corresponds to a concentration of 500-600 ng/L. These amounts correspond to approximately 0.003% of the total dissolved organic carbon content of the water, which demonstrates the extreme mutagenic potency of the compound.

Monochloramine treatment resulted in mutagenic activity which was approximately 40% of that in chlorinated water. The MX contribution to the total TA100 mutagenicity was only 20% which corresponds to a concentration of 47 ng/L.

Chlorine dioxide treatment resulted in mutagenic activity which was less than 15% of that in chlorinated water. The MX contribution to this activity was 45%, corresponding to 28 ng/L.

Treatment with UV radiation or O_3 alone did not produce mutagenic activity in strain TA100 (results not shown).

Preoxidation with O_3 or with a combination of UV/O_3 before chlorination resulted in a slight dose-dependent decline in mutagenic activity at the two highest doses *(fig. 2)*. Low pretreatment doses (2-min contact time) before chlorination gave a slightly higher activity as compared to that in chlorinated, nonpretreated water, while higher pretreatment doses (8-12 min) resulted in a dose-dependent decrease in mutagenicity. When higher doses were applied, the UV/O_3 system was found to be more effective in destroying the precursor material than was the O_3 system. A 12-min pretreatment time with O_3 and UV/O_3 resulted in a 20% and 33% loss of mutagenicity, respectively.

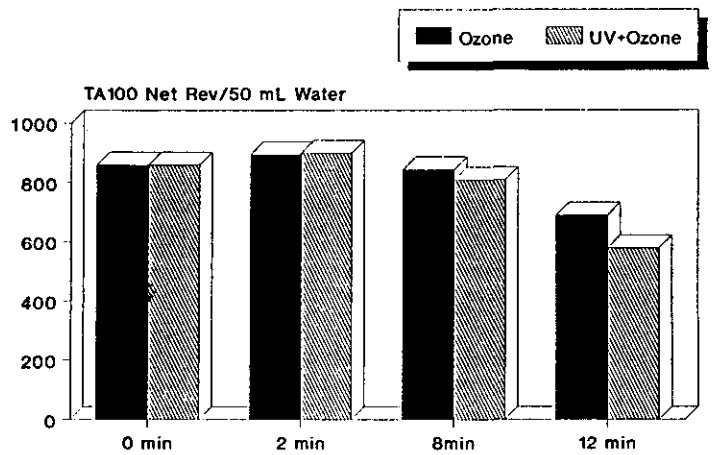

Figure 2 Activité mutagène (Rev./50 mL) dans l'eau du lac Savojärvi chlorée, prétraitée avec l'ozone et UV/ozone.
Chlore/COD : 1,0 et dose d' ozone: 10 mg/L. min.

Mutagenic activity (Rev./50 mL) in chlorinated Lake Savojärvi water pretreated with ozone and UV/ozone.
Chlorine/DOC-ratio: 1.0; Ozone-dose: 10 mg/L. min.

In contrast to the mutagenic activity, the MX concentration was found to decline rapidly over the full range of O_3- and UV/O_3-pretreatment doses *(fig. 3)*. A 12-min contact time with O_3 and UV/O_3 resulted in a 58% and 76% decrease in the MX concentrations, respectively. This indicates that the slight increase which was noted in the concentration levels of the overall mutagen precursors after low pretreatment doses with O_3 and UV/O_3 are not precursors to MX. Further it can be concluded that the precursors to MX are destroyed far more efficiently by O_3 and UV/O_3 than are the other TA100 mutagen precursors present in the original DOM.

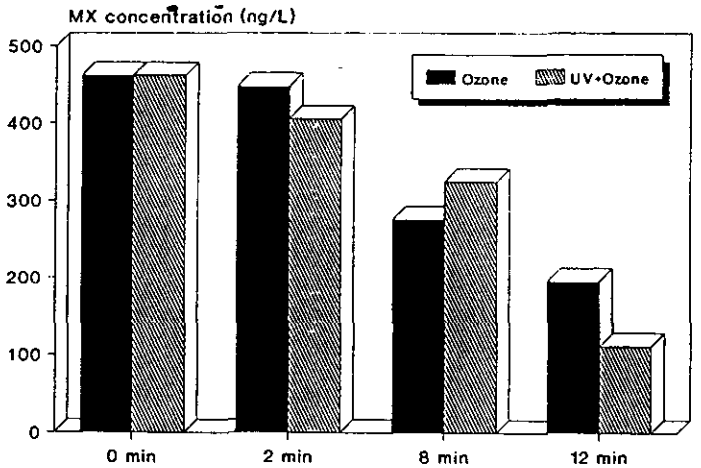

Figure 3 Concentration (ng/L) de MX dans l'eau du Lac Savojärvi traîtée avec l'ozone et UV ozone.
Chl ore/COD : 1,0 et dose d' ozone : 10 mg/L.min.

Concentration (ng/L) of MX in Lake Savojärvi water treated with ozone and UV/ozone.
Chlorine/DOC-ratio: 1.0; Ozone-dose: 10 mg/L. min.

Treatment with combinations of chlorine and chlorine dioxide (Cl_2/ClO_2) generated a substantially lower mutagenicity and lower MX concentrations than did disinfection with chlorine alone *(fig. 4)*. The higher the proportion of chlorine dioxide applied, the lower the mutagenicity and the amount of MX generated. One reason why the production of MX is so highly dependent on the presence of chlorine dioxide in the combined treatment process, might be that the compound is further oxidized by the action of chlorine dioxide. Such degradation products have, however, not yet been identified.

AOX, chloroform and chlorite in Lake Savojärvi water treated with Cl_2/ClO_2

In water treated with Cl_2/ClO_2, the concentrations of AOX and chloroform declined with the chlorine dose *(fig. 5)*, which is the same trend noted for mutagenicity and MX concentrations *(fig. 4)*. The highest concentrations of AOX and chloroform were found in water treated with chlorine alone *(fig. 5)*,

while only minor amounts of these compounds were detected in water treated with chlorine dioxide alone. The higher the proportion of chlorine in the Cl_2/ClO_2 treatment process, the higher the AOX and chloroform concentrations.

The production of inorganic chlorite followed an opposite trend to that of AOX and chloroform. The main reason for this is probably that chlorine dioxide is reduced to chlorite during the treatment process (NOACK and DOERR, 1978).

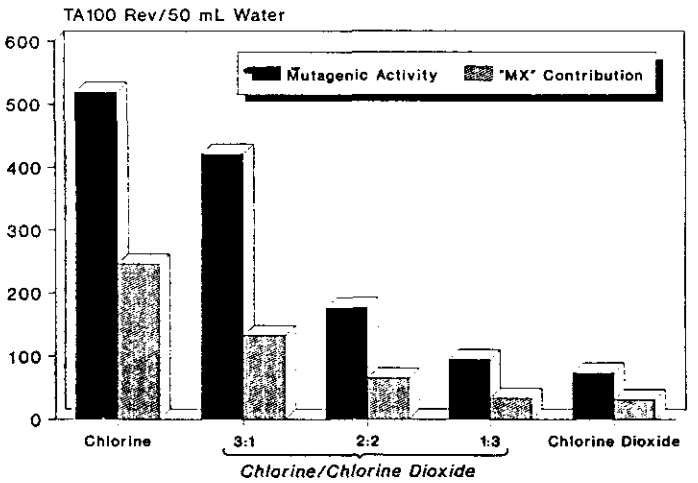

Figure 4 Activité mutagène (Rev./50 mL) et contribution du MX à la mutagénicité calculée dans l'eau du lac Savojärvi après traitement à différentes valeurs de chlore/dioxide de chlore. Concentration initiale de désinfectant : 20mg/l.

Mutagenic activity (Rev./50 mL) and calculated MX mutagenicity contribution in Lake Savojärvi water after treatment with various combinations of chlorine/chlorine dioxide. Total initial disinfectant dose: 20 mg/L.

Chlorine derived mutagenicity and MX in raw waters containing different types of DOM

A direct comparison of mutagenicity results obtained in different studies is often hampered by the lack of a standard method for extracting and concentrating samples. In addition, the treatment conditions, such as chlorination pH, chlorine dose, and contact time, may vary considerably. To enable a direct comparison of the results obtained by treatment of different water types, we collected water samples from four locations: Lake Savojärvi, Finland (Humic W, FIN), a ground water source at St Jansklooster, The Netherlands (Humic W, NL), and the rivers Rhine (River 1, NL) and Meuse (River 2, NL). The waters from Lake Savojärvi and St Jansklooster are rich in humic material, but relatively unaffected by industrial or municipal waste, while the waters from Meuse and Rhine contain only low amounts of humic material but are more polluted by industrial waste and effluents from sewage treatment plants.

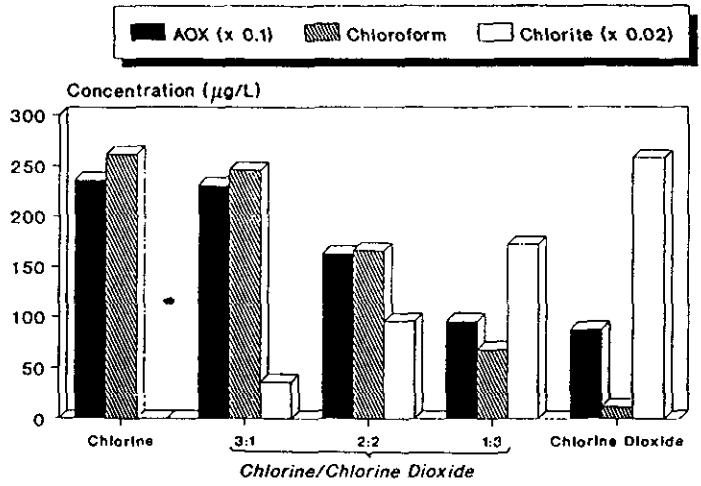

Figure 5 Concentrations en AOX, chloroforme, et chlorite (µg/L) dans l'eau du lac. Savojärvi après traitement à différentes valeurs de chlore//dioxide de chlore. Concentraion initiale de désinfectant : 20mg/l. (Les valeurs d'AOX sont à multiplier par 10 et celles de chlorite par 50 pour obtenir les valeurs réelles).

Concentration of AOX, chloroform, and chlorite (µg/L) in Lake Savojärvi water after treatment with various combinations of chlorine/chlorine dioxide. Total initial disinfectant dose: 20 mg/L. (The AOX values should be multiplied by a factor of 10, and the chlorite values by a factor of 50 to obtain the real values.)

All the waters were found to exhibit a considerable mutagenicity after chlorination *(fig. 6)*. The TA100 activity (expressed as net revertants/mg DOC) was slightly higher in chlorinated Lake Savojärvi water than in chlorinated St Janskloster water. The MX mutagenicity contribution in the same waters were 50% and 40%, respectively. Interestingly, the activities (per mg of DOC) after chlorination of waters from the Meuse and Rhine rivers were approximately the same as that after chlorination of the humic rich St Janskloster water. The activities of the chlorinated river waters (Rhine: 1500 net revertants/L and Meuse: 1580 net revertants/L) are 10-70 times higher than those found for the same waters by other groups (VAN DER GAAG and others, 1982; KOOL and HRUBEC, 1986), a discrepancy most probably due to the different sample preparation procedures used.

Although the overall mutagenic activity (Rev./mg DOC) was consistent in all of the natural waters studied, the MX concentrations were found to be substantially higher in the chlorinated humic waters than in the chlorinated river waters (MX activity contribution of 40-50% and 20-26%, respectively). This demonstrates that, in spite of the low humic contents of the waters of river Rhine and river Meuse, they do contain important precursors generating mutagenic compounds upon chlorination. Based on the observation that the mutagenic compounds could be extracted from the river waters only at acidic

pH (results not shown), we concluded that organic acids are responsible for a substantial part of the mutagenicity. The identities of the main mutagens in these waters are still unknown.

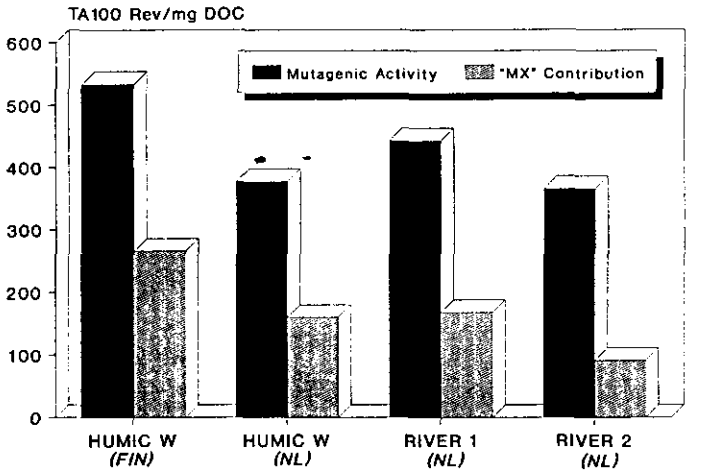

Figure 6 Activité mutagène (Rev./mg/COD) et contribution du MW à la mutagénicité calculée dans des eaux chlorées.
Humic W (FIN) : Eau du Lac Savojärvi, Finlande; Humic W (NL) : eau souterraine de St Jansklooster, Pays-Bas ; River 1 (NL) : Le Rhin, aux Pays-Bas ; River 2 (NL) : La Meuse, aux Pays-Bas.

Mutagenic activity (Rev./mg DOC) and calculated mutagenicity contribution from MX in chlorinated waters.
Humic W (FIN): Lake Savojärvi water, Finland; Humic W (NL): humic ground water from St Jansklooster, The Netherlands; River 1 (NL): River Rhine, The Netherlands; River 2 (NL): River Meuse, The Netherlands.

Degradation products identified in UV-treated Lake Savojärvi water

The main volatile aliphatic byproducts detected after UV irradiation of Lake Savojärvi water were low molecular-weight mono- and dicarboxylic acids (C_2-C_4) and aldehydes (C_8-C_{14}). In addition, a series of n-alkanes and a group of compounds tentatively identified as alcohols were detected.

The degradation of the relatively bioresistant humic material to compounds of lower molecular weight during UV-irradiation is likely to enhance the microbiological growth in the water. This means that UV-irradiation should not be used alone or as the last step in the treatment process, if the content of natural DOC in the water is high. Figure 7 shows a total ion chromatogram of volatile by products formed.

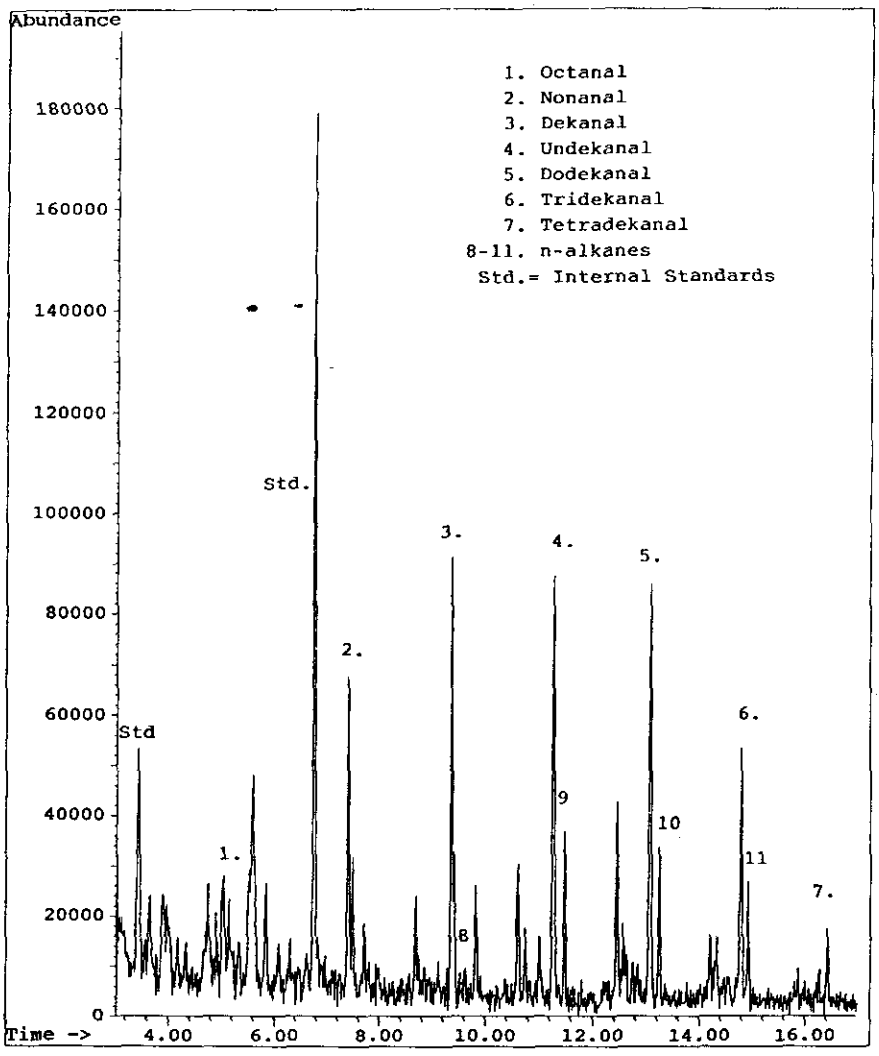

Figure 7 Chromatogramme des sous-produits organiques volatils formés lors d'une désinfection UV de l' au du lac Savojärvi
Temps d'irradiation : 6 heures.

Total ion chromatogram of volatile organic byproducts formed during UV disinfection of Lake Savojärvi water.
Irradiation time: 6 h.

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