



New Trends in Disinfection By-Products Formation upon Water Treatment

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Received date: 13 May 2014; Accepted date: 7 July 2014; Published date: 9 July 2015

Academic Editor: Miray Bekbolet

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Abstract

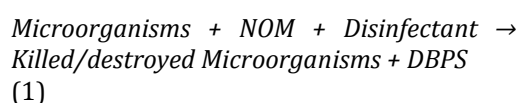
This review paper deals with the formation of disinfection by-products (DBPs). Water basin remains a wonderful chemical reactor that allows the occurrence of intricate secondary disinfection chemical reactions, forming several hundreds of DBPs at the same time with microorganisms killing. The kinetics of DBPs formation is tightly dependent on water physicochemical characteristics such as temperature, hydrophobic/hydrophilic fractions in natural organic matter (NOM), pH, and pretreatment. Reducing DBPs levels in drinking water is not a relevant measure as the newly-developed analytical techniques and the health-related research reveal that the tolerable DBPs' levels must be further decreased and would be detected at ng L⁻¹ instead of µg L⁻¹ scale. Furthermore, because of the fact that man is being exposed to DBPs concentrations in drinking water in his lifetime, there will be a cumulative effect of these toxic chemical products even at their more reduced concentrations. Hence, the removal of these chemical products is sought for and is considered a real challenge and the main objective of water treatment technology for mankind survival.

Keywords: Chlorination; Chloramination; Disinfection by-products (DBPs); Dissolved organic matter (DOM); Natural organic matter (NOM); Oxidation.

Cite this Article as: Ahmed Boucherit, Saâd Moulay, Djamel Ghernaout, Abdulaziz Ibraheem Al-Ghonamy, Badiaa Ghernaout, Mohamed Wahib Naceur, Nouredine Ait Messaoudene, Mohamed Aichouni, Ammar Abdallah Mahjoubi, Nouredine Ali Elboughdiri (2015), "New Trends in Disinfection By-Products Formation upon Water Treatment," Journal of Research & Developments in Chemistry, Vol. 2015 (2015), Article ID 628833, DOI: 10.5171/2015.628833

Introduction

Man's safety requires stringent measures. To live safely and lively, man has to be nurtured with contaminant-free food and beverages. Nowadays, water, being essential for man's survival, could be even a conflicting issue between people and between nations. Water is a sustainable substance for a sustainable life. As the world population grows, the need for potable water, among other vital items, becomes tight and acute. In our modern times, the use of chemicals to decontaminate and disinfect water remains an inevitable process, affording drinkable water. A concomitant fact concerns disinfecting chemical's reaction with the organic matter (OM), both of them the artificial and the natural organic matter (NOM), yielding by-products (see Eq. (1)), commonly called "disinfection by-products" (DBPs). These highly complicated chemical products are very toxic. Our potable water has been in an alarming state since decades (Nikolaou et al. (1999)). As a matter of fact, DBPs such as *N*-nitrosamines are reputed for their mutagenic properties with non-negligible cancer risk rate, *N*-nitrosodimethylamine (NDMA) being the most serious case (Agency for Toxic Substances (1989)). It was demonstrated that DBP formation is affected by the pH of treated water, its turbidity, its ambient temperature, the NOM concentration, the nature of disinfectant and its concentration.



Disinfection with halogens, namely chlorine, proved to engender reactions with NOM and algae, giving halogenated by-products (Rook (1974)), Bellar et al. (1974), Yang et al. (2011), Reckhow et al. (1990), Richardson et al. (2003), Richardson (2003), Richardson (2005), Roccaro et al. (2008), Hoffman et al. (2008), Ghernaout and Naceur (2011)). Of the several classes of DBPs (600-700) reported in the literature, trihalomethanes (THMs), in the first position, and haloacetic acids (HAAs), in the second position, ranked among the most studied ones (Krasner et al.

(2006), Simmons (2011), Ghernaout et al. (2011a), Amjad et al. (2013)). In addition, the halogenated DBPs (X-DBPs) production depended on the halide levels, the NOM level and reactivity, the pH of the treated water, and the temperature and the time of disinfection processing (Ghernaout et al. (2011b), Tian et al. (2013)). Because of the intricacy of NOM halogenation modeling, surrogate analytical methods were employed, such as the follow-up of the UV light absorbance decrease at $\lambda = 254 \text{ nm}$ (UV_{254}) upon chlorination and the measurement of the specific UV absorbance at $\lambda = 254 \text{ nm}$, SUVA_{254} , of dissolved organic matter (DOM), mainly dissolved organic carbon (DOC) (Korshin et al. (1997), Croué et al. (2000), Kitis et al. (2002), Ghernaout et al. (2009)); SUVA is calculated as the report of ultraviolet (UV) light absorbance of wavelength λ (usually 254 nm) to the DOC content in water. Other means are focused on the changes of NOM absorbance and fluorescence (Korshin et al. (1997), Korshin et al. (2002)). With phenolic-based NOMs, absorbance changes upon halogenation can be specifically monitored through $\lambda = 280 \text{ nm}$ of $\pi\text{-}\pi^*$ electronic transitions (Roccaro et al. (2008), Croué et al. (2000)). That is, absorbance alteration at 280 nm strongly indicates the formation of X-DBPs such as THM and HAA, and provides an indirect quantification of their formation potentials (FPs), all hinting at the aromatic nature of NOMs (Roccaro et al. (2008)). The link between the fluorescence of NOMs and their properties was advantageously explored (Croué et al. (2000), Korshin et al. (2002), Kumke et al. (2001)). McKnight et al. (2001) set mathematical "Power Function Models" to predict DBP FPs (DBPFP), providing the parameters DOC, UVA_{254} , bromides and nitrogenous species levels; carbonaceous DBPs FPs (C-DBP-FP) extents were predicted more accurately than nitrogenous DBPs FPs (N-DBP-FP) levels.

As far as NOMs' removal is concerned, water treatment technology has unequivocally gained a foothold during the last three decades (Chen and Westerhoff (2010)), with a special emphasis on the application of activated carbon adsorption and membrane processes. Yet, some unresolved issues and

some unanswered questions are pending: 1) How to assess the threshold concentration of NOMs at the water surface in order to avoid DBPs formation? 2) If the types of organic functional groups in NOMs of the aquatic environment, such as hydroxyl, carboxylic, and aromatic, are by now known, the parameters of the DBPs formation reactions, such as kinetics and stoichiometry, however, are by far unsettled.

It is within this framework that the present review sheds light on the outcomes of the DBPs formation reactions.

DBPs and their Precursors

The content of a DBP precursor in NOM and its characteristics have a great effect on the DBP formation course. DBP precursors have been commonly quantified from NOMs extracted via resin-based separation methods. Methodologies of estimation of DBPs precursors contents and their parameters were critically surveyed by Badawy et al. (2012), highlighting the differences between hydrophobic, hydrophilic and transphilic NOMs. Two main DBP precursors were of interest to many workers: the amine-/halogen-based precursors.

Amine-based DBPs (N-DBPs)

A class of N-DBPs is nitrosamines (Fig. 1). If we consider the most significant one present in potable water is NDMA, stemming from the chloramination of amine-based precursors upon water treatment with a chlorine/ammonia disinfecting system, via nitrosation/oxidation mechanism (Reckhow et al. (2008), Sharma (2012), Selbes et al. (2013), Bond et al. (2012)). NDMA, a very suspecting cancer compound, is a ubiquitous nitrosamine in all kinds of water, and originates from different sources of life, from wastes arising from animals (urine, faeces, etc.) to living comfort items

(cosmetics, rubber, plastics, etc.) (Fujioka et al. (2012)). As reviewed (Fujioka et al. (2012)), the removal of NDMA by reverse osmosis technique, a physical separative means, was inefficient as 86% of the nitrosamine was rejected. In view of eliminating NDMA precursors, and thus controlling NDMA formation, pre-oxidation such as prechlorination has been considered the most effective operation. Recently, Shen and Andrews (2013) investigated the prechlorination of water contaminated with amine-based pharmaceuticals. Their results were that, in the presence of NOM, the prechlorination for longer time induced a breakdown of NOM into smaller species that could bind to the pharmaceuticals, inhibiting the NDMA formation. However, in contrast to other amine-based pharmaceuticals, the prolonged chlorination of sumatriptan-contaminated and NOM-free water brought about an increase in NDMA formation. In another place (Shen and Andrews (2011)), the same authors studied the NDMA formation precursor propensity of twenty pharmaceuticals and personal care products, including tetracycline, tramadol, venlaxine, lidocaine, ranitidine, sumatriptan, and others, all having dimethylamine (DMA)/diethylamine (DEA). The highest conversion into NDMA was ranitidine-contaminated tap water that is 89.9-94.2%. A feature that emerged from this study was that the chemical structures of the pharmaceuticals that gave greater NDMA FPs have DMA groups attached to an electron-rich site. To appreciate mechanistically the NDMA formation/inhibition, the interaction between DMA precursor and water NOM was commonly taken as a reaction model. Also, tertiary amines with DMA functional groups and dimethylamides were attempted as model precursors and formed substantial NDMA concentrations upon chloramination (Mitch and Sedlak (2004)). The work undertaken by Chen and Valentine (2007) demonstrated that humic acids (HAs) could be also precursors of NDMA formation.

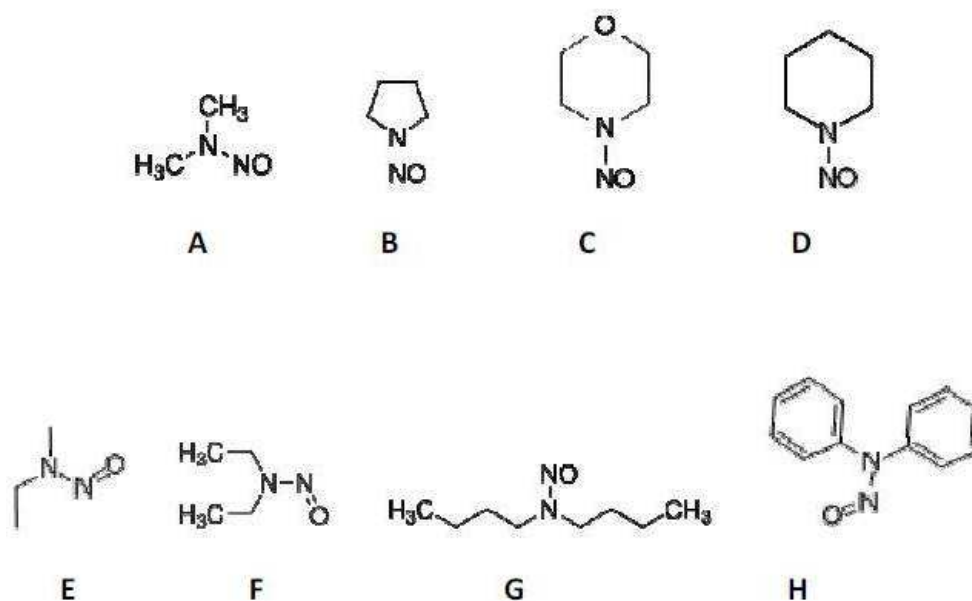


Fig. 1. A set of N-nitrosamines as DBPs encountered in disinfected waters: A, N-nitrosodimethylamine (NDMA); B N-nitrosopyrrolidine (NPYR); C, N-nitrosomorpholine (NMOR); D, N-nitrosopiperidine (NPIP); E, nitrosomethylethylamine (NMEA); F, nitrosodiethylamine (NDEA); G, nitrosodi-n-propylamine (NDPA); H nitrosodiphenylamine (NDPHA).

Other *N*-nitrosamines whose precursors belong to DOM were found in raw water (Bond et al. (2012), Luo et al. (2012), Wagner et al. (2012), Wang et al. (2013)). Recently, Wang *et al.* (2013) characterized DOM from a river water using Amberlite XAD resins and UF methods and investigated *N*-nitrosamine FPs. The extent of DOM fraction (molecular weight (MW) < 1 kDa) was ~ 47% of the total DOC, and that below 3 kDa was nearly 74%. In their work (Wang et al. (2013)), NDMA, *N*-nitrosopyrrolidine (NPYR), *N*-nitrosomorpholine (NMOR), and *N*-nitrosopiperidine (NPIP) were formed in a varying extent depending on the DOM fraction; yet, the NDMA FP was the highest in every fraction and elevated as MW diminished. The NDMA yields in the hydrophilic portion was 27.2 ng mg⁻¹-DOC against 17 and 25 ng mg⁻¹-DOC for hydrophobic and transphilic ones, respectively.

Luo and his co-workers (2012) detected in raw and finished waters, in some Chinese cities in varying extents, nine nitrosamines: NDMA, nitrosomethylethylamine (NMEA),

nitrosodiethylamine, nitrosodi-*n*-propylamine, nitrosodi-*n*-butylamine, nitrosodiphenylamine, NPYR, NPIP and NMOR. The global concentrations of these nitrosamines could reach values as high as 43.45 ng L⁻¹. NDMA was the one that existed in every kind of water.

Spanish investigators (Jurado-Sánchez et al. (2012)) detected twenty four amines (nitrosamines and aromatic amines) in the wake of chloramination treatment of Spanish drinking water treatment plants, including aniline, 3-chloroaniline, 3,4-dichloroaniline and NDMA. These workers observed that *N*-nitrosamines concentrations were higher in winter.

Earlier, Ueno et al. (1996) investigated the urinary components, found as contaminants in wastewaters, as potential precursors for DBPs upon chlorination with aqueous sodium hypochlorite. In this report, chlorination of kynurenine (a urinary component) generated about 81.8 μg L⁻¹ of dichloroacetonitrile (DCAN) and that of glutamic acid and histidine (other possible urinary components) resulted in a relatively

high formation of DCAN, 13.2 and 15.2 $\mu\text{g L}^{-1}$, respectively; that of wastewater HA gave only 3 $\mu\text{g L}^{-1}$ of DCAN.

Halogen-based DBPs (X-DBPs)

As stated above, halogenated DBPs (X-DBPs, X = halogen) stand as a prevailing class of by-products from water treatment (Fig. 2). Chlorination was the method of choice, particularly for a cost-effectiveness aspect, for treating saline sewage effluents. Because bromides are omnipresent in seawater (65 mg L^{-1}), hence in sewage effluents ($\sim 32 \text{ mg L}^{-1}$), such treatment may effectively induce their oxidation to hypobromous acid (HBrO) which may, in turn, partially dissociate into proton and hypobromite ion (BrO^-) in aqueous medium. Both of HBrO and BrO^- will be in reaction with the OM present in the effluents forming brominated DBPs (Br-DBPs). The OM covers non-decomposed and decomposed organic molecules from our daily consumed produced food, soaps,

detergents, etc. Ding *et al.*'s research results (Ding *et al.* (2013)) were that, upon chlorination of primary and secondary saline sewage effluents at different chlorine doses, fifty four polar Br-DBPs were detected, including, besides the different HAAs, bromomaleic acid, 5-bromosalicylic acid, 3,5-dibromo-4-hydroxybenzaldehyde, 3,5-dibromo-4-hydroxybenzoic acid, 2,6-dibromo-4-nitrophenol, and 2,4,6-tribromophenol. For the secondary saline effluent, the extent of the formed Br-DBPs reached a plateau at higher chlorine doses, whereas it kept rising for the primary saline effluent. As compared with the secondary saline effluent, the primary saline effluent was found to generate less Br-DBPs and fewer nitrogenous Br-DBPs. Elsewhere Zhang *et al.* (2012), the presence of several species with unknown structures such as $\text{C}_{11}\text{H}_9\text{Cl}_2\text{O}_6$, $\text{C}_{12}\text{H}_{13}\text{Cl}_2\text{O}_5$, $\text{C}_{11}\text{H}_{12}\text{ClO}_8$, and $\text{C}_{12}\text{H}_{16}\text{ClO}_7$ in chlorinated waters was confirmed.

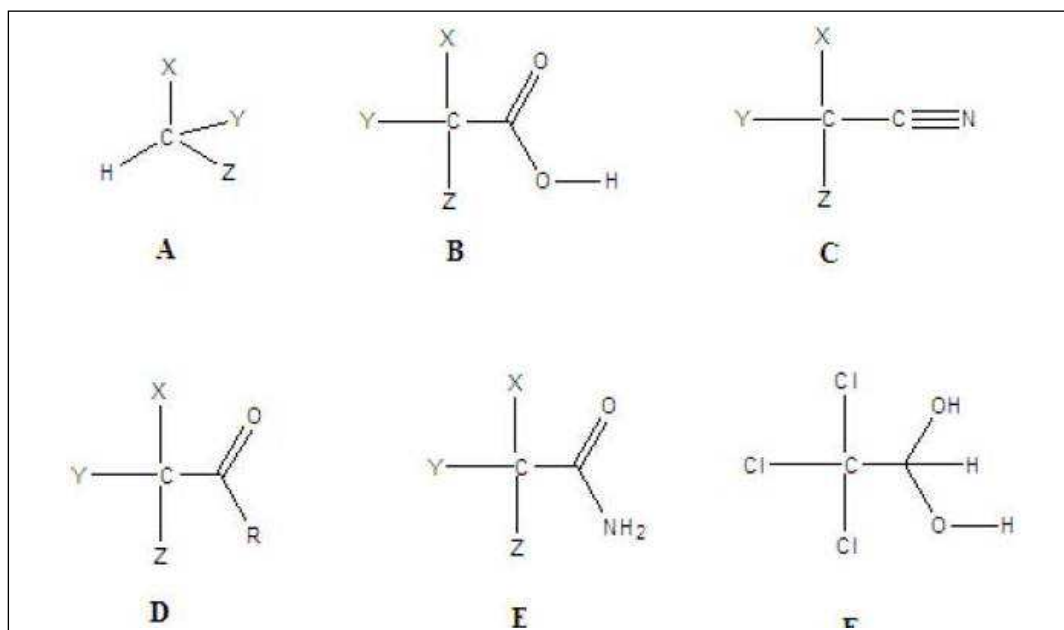


Fig. 2. A set of common X-DBPs encountered in disinfected waters: A, trihalomethanes (THMs); B, haloacetic acids (HAAs); C, haloacetonitriles (HANs); D, halo ketones (HKs); E, haloacetamides (HAcAms); F, chloral hydrate (CH). X, Y, Z = Cl, Br, I, H.

Gan *et al.* (2013) measured DBPs levels in the potable water, from water treatment plants in China. The outcome was the existence of a range of X-DBPs such as THMs

and HAAs in extents that are season-dependent; winter time favored their formation. Of these X-DBPs were the THMs group: chloroform, dichlorobromomethane,

dibromochloromethane, and bromoform as THMs, and the HAAs group: monochloroacetic acid, dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid, dibromoacetic acid, tribromoacetic acid, bromochloroacetic acid, bromodichloroacetic acid, and dibromochloroacetic acid, and the haloacetonitriles (HANs) group: trichloroacetonitrile, DCAN, bromochloroacetonitrile, and dibromoacetonitrile, and haloketones (HKs) group: 1,1-dichloropropanone and 1,1,1-trichloropropanone, and another group containing chloral hydrate and trichloronitromethane (TCNM). The levels of THMs and HAAs were measured in the range of 0.7-62.7 and 0.3-81.3 $\mu\text{g L}^{-1}$, respectively, and those of HANs, HKs, chloral hydrate, and TCNM were found in traces, that is < 0.2 to $12.2 \mu\text{g L}^{-1}$. Of the tested THMs, dichlorobromomethane and chloroform were found to be the most suspecting cancer agents in terms of cancer risk rate, the former acting through ingestion track and the latter through inhalation one.

It is worth noting the prediction of the formation of THMs during chlorination employing chemometric modeling as mathematical analysis (Platikanov et al. (2012), Singh and Gupta (2012)). Singh and Gupta (2012) disclosed that pH, residence time, and temperature were the most influential factors for the THM formation following chlorine adding. Platikanov and his co-workers (2012) employed some linear and non-linear regression methods, for the THMs formation in Barcelona's water treatment plant.

Sakai *et al.* (2013) launched an investigation on amino acids, namely leucine and serine, and resorcinol taken as HAAs precursor models. Their expectation was that the UV and UV/H₂O₂ treatment of these akin HAAs precursors would be destroyed and vanished before HAAs formation. The concentrations of all models were nearly unaltered upon UV irradiation, but decreased enormously upon oxidation by UV/H₂O₂ at a varying degradation rate (1.2×10^{10} for resorcinol, 3.2×10^8 for serine,

and $1.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for leucine). Moreover, HO[•] stemming from H₂O₂ was supposed to have a crucial contribution in the degradation mechanism. The species HO[•] was thought to destroy the benzene ring of the resorcinol molecule, leading to the succinic acid formation. However, in the case of the amino acids, the degradation could have been initiated by abstraction of their labile protons by hydroxyl species. HAA FPs (formation of DCAA and TCAA), from UV/H₂O₂ treatment, were seen to decrease in the case of resorcinol, slightly increase in the case of serine, and importantly increase in the case of leucine. This would suggest that leucine might be a serious HAAs precursor, as the action of hydroxyl radical species on this amino acid would have shortened its carbon chain, affording a β -carbonyl structure.

Besides the seasonal dependence of the DBPs formation extent, other natural events such as storming would have also a certain impact. In a recent report, Nguyen and his collaborators (2013) presented results on the variations in DOM spectroscopic properties and DBP FPs upon chlorination of the river water (from a basin located in a Korean province) samples collected during summer and fall. The chlorination of the water samples was affected by the addition of Cl₂/NaClO. Four THMs (CHCl₃, CHBr₃, CHClBr₂, and CHBrCl₂) and six HAAs (ClCH₂COOH, Cl₂CHCOOH, Cl₃CCOOH, ClBrC₂COOH, BrCH₂COOH) were detected by gas chromatography. The amounts of detected THMs are classified from 55.3 to 98.1 ppb and from 43.4 to 55.9 ppb for summer storm and fall storm, respectively, chloroform being the dominant THM. Whereas, those of HAAs were bigger than THMs', classifying from 78.2 to 158.6 ppb for summer storm and from 61.2 to 70.0 ppb for fall storm, bromochloroacetic acid and DCAA were the major ones. These differences in the THMs and HAAs contents were imputed to different structures of the precursors which are responsible for the two types of DBPs. The performed analysis suggested the fluorophore groups' presence and also the occurrence of humic-type DBPs. Such fluorophore groups were divided into two classes C1 and C2; the latter has a great

chance to contain less conjugated and less condensed structures with more functional groups of carbonyl, hydroxyl and amine compared to the former one. The class C2 contained less humic-like substances. Other findings were that SUVA values varied from 1.92 to 2.74 L mg⁻¹ C m⁻¹ during the summer storm event, and from 1.65 to 1.89 L mg⁻¹ C m⁻¹ during the fall storm event. Overall, good correlation between DBP FPs and the DOM parameters for the two storm events was observed, with correlation coefficients of 0.952 and 0.986 for THM and HAA FPs, respectively.

Iodine species in forms of iodide ions (I⁻) are present in about 0.5-10 µg L⁻¹ in freshwaters and 45-65 µg L⁻¹ in seawaters. Iodine ion is claimed to be the source of iodoorganic compounds as DBPs, namely iodoform (CHI₃), upon water disinfection. Hypoiodous acid (HOI), the product of the oxidation of iodine ion, is prone to react with NOM to generate iodo compounds. However, its oxidative transformation to iodate ion (IO₃⁻), a less toxic species, is highly coveted. Yet, the fate of iodine was found to be related to the employed oxidant (Bichsel and von Gunten (1999)). In fact, with chlorine and ozone as disinfectants for aquacultures, iodine ion can be first converted to hypoiodous acid (HOI) which is oxidized to iodate ion. However, in the case of seawaters, the treatment with ozone limited the oxidation to HOI. Kinetic study showed that the probability of formation of iodo compounds depended on the oxidant used and was in the following order: O₃ < Cl₂ < NH₂Cl.

Iodine-based DBPs (I-DBPs) were formed during water treatment with iodine tincture (aqueous solution of I₂/KI) or iodine tablets as disinfectant (Smith et al. (2010)). The detected I-DBPs were iodoform, chlorodiiodomethane, dichloriodomethane, iodoacetic acid (IAA), bromiodoacetic acid, diiodoacetic acid (DIAA), (E)-3-bromo-3-iodopropenoic acid, and (E)-2-iodo-3-methylbutenedioic acid. The concentrations of chlorodiiodomethane, dichloriodomethane were more than an order of magnitude lower than for iodoform, and those of IAA and DIAA were <11% of iodoform.

Halo-benzoquinones (HBQs) as DBPs found in drinking water were first reported in 2010 (Qin et al. (2010)). Five HBQs (Zhao et al. (2010), Zhao et al. (2012)), 2,6-dichloro-1,4-benzoquinone (DCBQ), 2,6-dibromo-1,4-benzoquinone (2,6-DBBQ), 2,6-dichloro-3-methyl-1,4-benzoquinone (DCMBQ), 2,3,6-trichloro-1,4-benzoquinone (TCBQ), and 2,5-dibromo-1,4-benzoquinone (2,5-DBBQ), were detected in chlorinated water. Chlorination treatment was found to generally favor DCBQ formation, but a coagulation pretreatment with alum reduced it (Diemert et al. (2013)); some species of NOM seemed to be recalcitrant to coagulation, contributing to DCBQ formation. These precursors may comprise smaller MW humics, or low MW neutral organics such as phenol as depicted in Fig. 3. These HBQs were found in concentrations of 165.1, 37.9, 1.3, 9.1, and 0.5 ng L⁻¹, respectively.

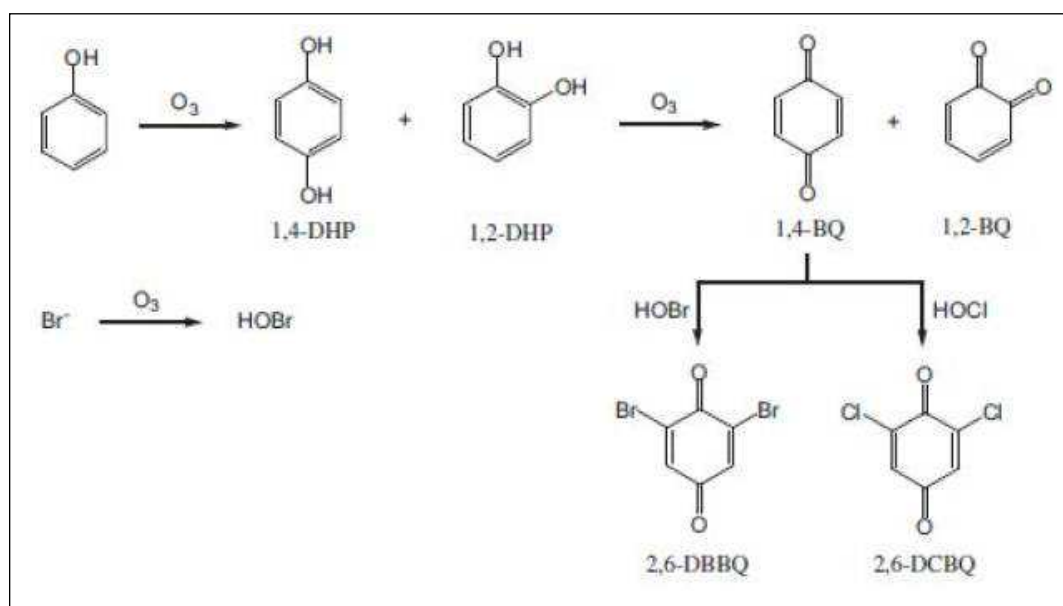


Fig. 3. Proposed Mechanism for the DBBQ and DCBQ Formation (Qin et al. (2010))

Factors Affecting DBPs Formation

Several parameters that related to DBPs precursors were reported to affect the course of their formation. Of these factors are the following: type of chromophore present in the precursor chemical structure, hydrophilicity/hydrophobicity ratio of the precursor, MW of the precursor, type of disinfecting agent, and pretreatment.

Chromophores

Korshin and Chang (2008) chlorinated several waters from different locations in the United States of America with HClO, and analyzed the output using the method of differential absorbance spectroscopy. In the experimental work, two distinct groups of chromophores during the ensued chlorination of NOM were detected: those, which reacted slowly, and those which reacted rapidly. In addition, the fast chromophores in all water sources exhibited identical spectroscopic characteristics while the properties of the slow chromophores showed some variability. Indeed, the fast chromophores were consumed at the onset of NOM chlorination, and their breakage seemed not to be related to a significant release of total

THMs and HAAs. However, the decomposition of slow ones was closely related to their formation, as revealed by the good correlations between the concentrations of these DBPs and the measured differential absorbances.

Organic Matters (OMs)

Hydrophilicity/Hydrophobicity Ratio

NOM and DOM (DOC; dissolved organic nitrogen, DON) are generally composed of hydrophobic and hydrophilic species. For example, it is well known that HA (Fig. 4A) can be fractionated into hydrophobic, transphilic, and hydrophilic mixtures. The hydrophobic fraction mainly contains phenolic hydroxyl and conjugated double bonds, the transphilic fraction contains more carbonyls, and the hydrophilic one may contain more amino, carboxyl and alcoholic hydroxyl groups. As to their separation, resin fractionation remains the mostly used technique for isolation of the hydrophobic and hydrophilic fractions, which may enable to set the appropriate treatment. Yet, the time consuming facet of this separative technique is considered a major drawback. Alternatively, Xing and his collaborators (2012) quantified the

hydrophobic and hydrophilic fractions of NOMs. In addition, the decrease in the total RP-HPLC peak area was found to be in a good correlation with DOC and UV₂₅₄ removal performance. DOMs in forms of DOC and DON revealed to be sources of carbon and nitrogen for C-DBPs and N-DBPs. Tung's research team (Chuang et al. (2013)) evaluated the impact of DOM composition on the formation of these DBPs upon chloramination. The outcome of this research was the formation of THMs, dihaloacetic acids, and dihaloacetoneitriles, during chloramination; they derived mainly from similar precursors, the organic compounds having β -dicarbonyl moieties within aromatic and aliphatic groupings. And, the NDMA FP was related to DON/DOC in hydrophilic and transphilic fractions, and the nitroso group of the constituted NDMA originated mostly from chloramines. The impact of hydrophilicity/hydrophobicity ratio extents of the precursors was reported to affect the formation of haloacetamides (HAcAms), an emerging class of N-DBPs, and their precursors (Chu et al. (2010b), Chu et al. (2010a). This work (Chu et al. (2010b)) focused on the precursors of dichloroacetamide (DCAcAm), stemming from chlorinated/chloraminated drinking water. FPs of DCAcAm upon chlorination of raw water samples, were determined to be the highest in summer take-up. Six fractions of DOM were separated in hydrophilic and hydrophobic groups: hydrophilic acid, hydrophilic base, hydrophilic neutral, hydrophobic acid, hydrophobic base, and hydrophobic neutral. These fractions were in turn gathered into main classes: DON compounds and DOC compounds. Excitation-emission matrix fluorescence spectrometry analysis revealed the plausible precursors of DCAcAm, including aromatic proteins, HA-like, and fulvic acid (FA)-like. Hydrophobic acid consisted primarily of HAs and FAs (Fig. 4), and hydrophilic acid was composed of a mass of protein-like substances. Acid fractions (hydrophilic acid and hydrophobic acid)

contributed to DOC by 59.1% and to DON by 68.2%. However, the hydrophobic fractions contributed to 57.1% of DOC, and the hydrophilic fractions to 60.5% of DON. In addition, hydrophilic acid DOM presented the maximum FP of DCAcAm, followed by hydrophilic bases and hydrophobic acids. To confirm the role of protein-like substances in hydrophilic acid fraction in the DCAcAm formation, seven amino acids were demonstrated to be precursors for DCAcAm during chlorination, in the order of increasing DCAcAm yield: aspartic acid, histidine, tyrosine, tryptophan, glutamine, asparagine, and phenylalanine. As early as 1986, Trehy and his co-workers (1986) demonstrated the formation of chloral and DCAN upon chlorination of aspartic acid, tyrosine, and tryptophan; these BDPs were detected in significant amounts in chlorinated waters from natural lake and wastewater treatment plant. The formation of chloral was observed to be pH-dependent; the yield of chloral rose by elevating pH from 7 to 8. Chlorination and chloramination of tyrosine under UV irradiation at pH 7-8 and 23°C was carried out by Gao and his colleagues (Chu et al. (2012)). During chlorine adding, the yields of different C-DBPs and N-DBPs (chloroform, DCAA, TCAA, 1,1-dichloro-2-propanone, 1,1,1-trichloropropanone, chloral hydrate, DCAN, trichloroacetoneitrile, TCNM, DCAcAm, trichloroacetamide, cyanogen chloride, and 4-chlorophenol) were contact time- and $[Cl_2]/[tyrosine]$ dependent. The highest contents of four detected C-DBPs (chloroform, DCAA, TCAA, and chloral hydrate) were 4.0, 2.4, 2.9 and 0.46%, respectively, after a contact time of 168 h and with $[Cl_2]/[tyrosine] = 15$. These C-DBPs were seen to increase with increasing $[Cl_2]/[tyrosine]$ molar ratio and peaked at the ratio of 25. DCAN and DCAcAm were the most detected N-DBPs for both variables, the first one being the highest; they reached maxima for $[Cl_2]/[tyrosine]$ of 15 at a contact time of 24 h and a pH of 7.

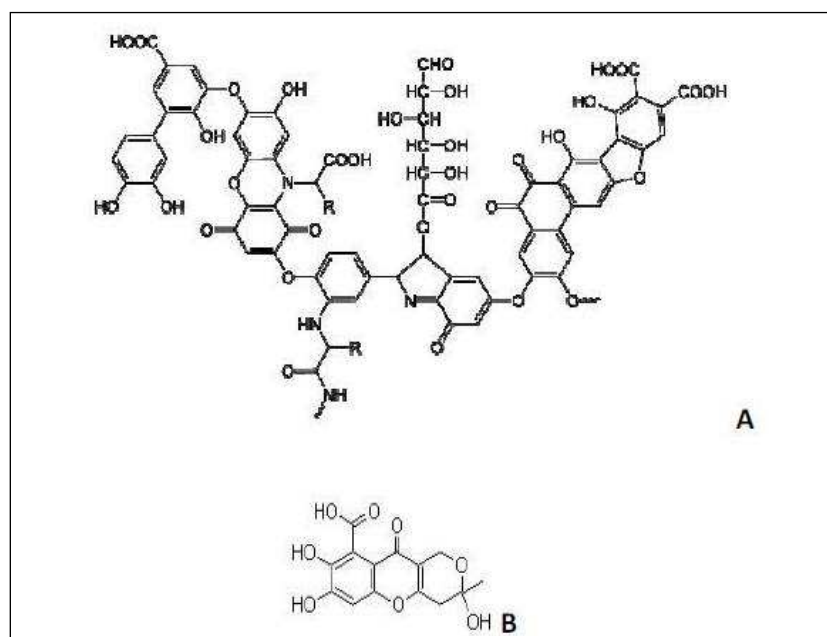


Fig. 4. Typical Structures of: A, HA; B, FA.

The proposed mechanism for the production of HANs and HAcAms as N-DBPs during chlorination of amino acids, taking aspartic acid as representative, is traced in Fig. 5. At this pH and $[Cl_2]/[ammonia] = 1$, chloramination of tyrosine showed that C-

DBPs were found to augment by prolonging the contact time and N-DBPs increased to some levels and dropped beyond. No change of the yields of the detected DBPs was observed after exposure of tyrosine to UV irradiation, followed by chlorination.

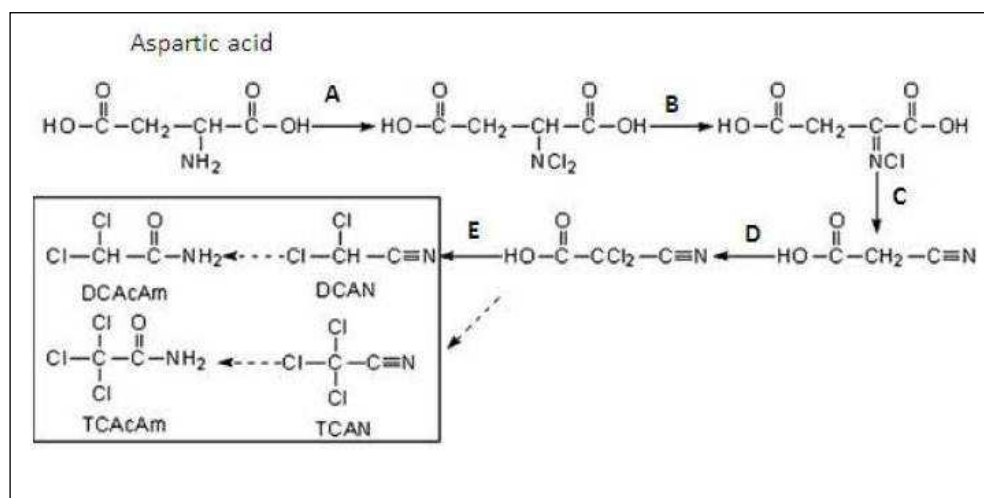


Fig. 5. Proposed formation pathway of HANs (DCAN and TCAN) and HAcAms (DCAcAm, TCACAm) during aspartic acid chlorination (Chu et al. (2010a): A, substitution; B, elimination; C, decarboxylation; D, substitution; E: Hydrolysis.

Recently, Chang and his collaborators (2013) employed the DON fractionation

method to assess C- and N-DBPs and their FPs (DBP-FPs) in two sources of treated

wastewater, waters from Neihu wastewater treatment plant (Taipei City) and from Tai Lake water treatment plant (Kinmen). Results showed that hydrophobic acids and hydrophilic acids/neutrals were the main contributors to C-DBP-FPs (up to 75%), and amphiphilic bases/neutrals were the ones for N-DBP-FPs (up to 94%).

Lu *et al.* (2009) discovered that precursors of THMs and HAAs in DOM isolates from filtered river water were either hydrophilic/hydrophobic acids, hydrophilic/hydrophobic bases, or hydrophilic/hydrophobic neutrals in nature. The THMs and HAAs species detected after chlorination (with sodium hypochlorite) and chloramination (with monochloramine) of the river water were CHCl_3 , CHBrCl_2 , Cl_2CHCOOH and Cl_3CHCOOH . For both chlorination and chloramination, hydrophilic/hydrophobic acids, hydrophilic base and hydrophobic neutral were the main precursors of the mentioned DBPs. Moreover, good correlations between DBPs FP and SUVA_{254} of these DOM fractions were observed. Overall, it was claimed that aromatic species present in DOM fractions played a significant role in the production of these DBPs without taking into account their hydrophobic or hydrophilic nature. In case of chlorination, hydrophobic acid had the highest FP and contributed by 43% to DOC. However, with chloramination, these DBPs were significantly reduced, about 9-13% of those in chlorination. Chloroform was produced in a mass much higher than that of dibromochloromethane in both treatments, and more DCAA was formed than TCAA. Nevertheless, HAAs were generally formed in higher quantities than THMs. In addition, the formation of these DBPs increased by increasing the disinfecting agent concentration, increasing the DOC, and prolonging time up to 48 h. As to the pH influence, more THMs were formed upon increasing the pH from 6 to 9 in chlorination process, and more HAAs was obtained as pH increased from 6 to 7, but decreased beyond. Overall, elevating these parameters had practically no contribution in DBPs formation upon chloramination.

The chlorination of sediment elutriate from South China generated THMs and HAAs. The NOM from this source was found to be composed of 50.7% hydrophilic OM, 34.2% hydrophobic OM, and 15.2% in transphilic OM (Hong *et al.* (2013)). The hydrophobic fractions were the major chloroform (> 60% of the total chloroform yield) and TCAA (70%) precursors. Hydrophilic matter, however, was the main DCAA (51.1%) precursor.

Molecular Weight (MW)

The effect of MW of NOM on the production of N-nitrosamines during processes such as chlorination and chloramination was examined by Kristiana *et al.* (2013). Regardless of the MW, the chloramination of NOM fractions produced more N-nitrosamines, namely NDMA, than chlorination. However, NOM fractions with apparent MW (MW range) of less than 2.5 kDa were showed to form higher concentrations of NDMA and total N-nitrosamines. The optimal concentrations of NDMA ranged from 0.027 to 0.08 nM upon chlorination and from 0.03 to 0.18 nM upon chloramination. It was claimed that inorganic nitrogen is the source for the N-nitrosamines formation rather than the organic one.

Disinfectants

Chlorination/Chloramination

General Findings

Cyanobacterial toxins are abundant in surface waters. Their concentrations may exceed $10.0 \mu\text{g L}^{-1}$ (Hoeger *et al.* (2005)), values higher than $1.0 \mu\text{g L}^{-1}$, a value allowed by the World Health Organization (WHO). Treatment of cyanobacterial cells (CBs) in waters with disinfecting chlorine was found to behave differently (Zamyadi *et al.* (2012)). The exposure of CBs from different in-laboratory-cultured bacteria (*Anabaena circinalis*, *M. aeruginosa*, *Cylindrospermopsis raciborskii*, and *Aphanizomenon issatschenkai*) to chlorine at

a rate of less than 4 mg min L⁻¹ led to a damage greater than 60% of the cells. The detected by-products were THMs and HAAs and were estimated to be as low as $\leq 40 \mu\text{g L}^{-1}$ even at a greater exposure rate 220 $\mu\text{g min L}^{-1}$. The other DBP was NDMA, in a measured quantity of less than 10 ng L⁻¹. Huang and his co-workers (2013) undertook a comparative investigation on the DBPs formation upon chlorination between the secondary effluents of a domestic wastewater treatment plant and the suspensions of bacteria (*Escherichia coli*, *Enterococcus faecalis*), as secondary effluents consist of bacterial cells. Formation of HANs (namely DCAN), and haloacetamides (namely dichloro- and trichloroacetamides) in the secondary effluents accounted for 26-46% of the total DBPs. Besides, *E. faecalis* formed more DCAN, but less DCACAm and trichloroacetamide than *E. coli* did under identical chlorination conditions. For both suspensions, all DBPs concentrations were found to increase with prolonging contact time up to 72 h. However, variable profiles were seen for the chlorine dosage and pH dependence. Yet, neutral pH conditions upon chlorine adding of the bacterial suspensions encouraged the formation of these DBPs.

Zong and his collaborators (2013) embarked on work to elucidate the DBPs from chlorination of microcystin-LR-containing waters; microcystin-LR (MC-LR) is a cyclic heptapeptide (Fig. 6A) that is responsible for cyanobacterial toxicity. MC-LR was allowed to react with hypochlorous acid, and the formed MC-LR DBPs were identified, using liquid chromatography-mass spectrometry technique, as C₃₄H₅₄N₁₀O₁₂ (1.4%), C₄₉H₇₆N₁₀O₁₄ (16.1%),

C₄₉H₇₅N₁₀O₁₃Cl (5.8%), C₄₉H₇₇N₁₀O₁₅Cl (3.3%), C₄₉H₇₆N₁₀O₁₄Cl₂ (0.7%). All these MC-LR DBPs and their multiple isomers had some biological toxicity. Acero *et al.* (Acero *et al.* (2005), Rodríguez *et al.* (2007a), Rodríguez *et al.* (2007b), Rodríguez *et al.* (2007c)) shed light on the kinetics of the oxidative disinfection of MC-LR, cylindrospermopsin (Fig. 6B) and anatoxin-a (Fig. 6C), cyanobacterial toxins, with chlorine, monochloramine, and permanganate. In each case, second-order kinetics was observed. While the oxidation of cylindrospermopsin with the latter two disinfectants was somewhat slow (apparent rate constant, $k_{\text{app}} < 1 \text{ M}^{-1} \text{ s}^{-1}$ at pH = 7.1 and at 20°C), that with the former one was faster ($k_{\text{app}} = 1265 \text{ M}^{-1} \text{ s}^{-1}$ at pH = 7.1 and at 20°C). The reaction of anatoxin-a with chlorine and chloramine was also very low ($k_{\text{app}} < 1 \text{ M}^{-1} \text{ s}^{-1}$ at pH = 7.1 and at 20°C). The apparent rate constant for the chlorination of MC-LR at 20°C was showed to be pH-dependent: 475 M⁻¹ s⁻¹ at pH of 4.8 and 9.8 M⁻¹ s⁻¹ at pH of 8.8. The chlorination of cylindrospermopsin produced 5-chloro-cylindrospermopsin. In contrast to chlorine and chloramines, a temperature-dependence of the rate constant for cylindrospermopsin/permanganate reaction was noticed; the rate constant at pH = 7 increased from 0.17 M⁻¹ s⁻¹ at 10°C to 0.45 M⁻¹ s⁻¹ at 30°C, with an activation energy of about 34.4 kJ mol⁻¹. Results of the oxidation of natural water containing cylindrospermopsin and anatoxin-a revealed that chlorination is a convenient solution for the oxidation of cylindrospermopsin upon water treatment; however, the oxidation of anatoxin-a is too slow and needs a high chlorine dose that would conduct to total THM production.

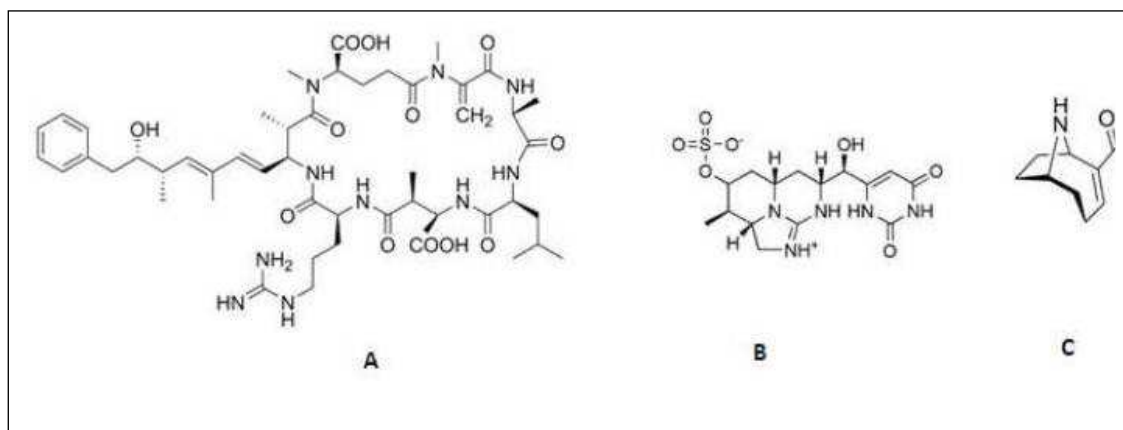


Fig. 6. A, microcystin-LR; B, cylindrospermopsin; C, anatoxin-a.

Ye *et al.* (2013) examined the effects of the concentration of the disinfecting ClO_2 , the concentrations of iodide ion and DOC present in water, and its pH on the production of I-DBPs upon disinfecting artificial waters; the I-DBPs included iodoform (CHI_3), IAA and triiodoacetic acid (TIAA). Overall, CHI_3 and TIAA were produced in higher yields than those of IAA. The production of CHI_3 and TIAA rose with augmenting pH and dropped beyond a pH of 8, and that of IAA did not vary appreciably with pH. The lower yields of CHI_3 and TIAA upon acidic conditions were attributed to the transformation of molecular iodine I_2 to iodate ion IO_3^- and the reduction of reaction rate of I_2 with humic substance (HS). I-DBPs augmented with augmenting ClO_2 content up to a certain level and fell off afterwards; higher concentration induced the production of ClO_2^- and the oxidation of iodide ions to iodine radicals and iodate ions. The formation of CHI_3 and TIAA peaked at a level of $37.0 \mu\text{g L}^{-1}$, and that for IAA was seen at $74.1 \mu\text{g L}^{-1}$. However, the extents of CHI_3 and TIAA increased with increasing concentration of iodide ion, but the formation of IAA remained nearly unaffected which was explained as being due to the competition of iodide ion with ClO_2 for NOM. The formation of I-DBPs was found to increase with DOC concentration and declined beyond a critical concentration; the maximum yields for CHI_3 and TIAA were quantified at DOC content of 4.7 mg C L^{-1} , and that for IAA was 7.03 mg C L^{-1} . The decrease observed was explained by

a higher consumption of ClO_2 by NOM, hence reducing the dose of ClO_2 required for the oxidation of iodide ion to reactive iodine species.

Because iodinated THMs (I-THMs) are usually formed in low concentrations (ng L^{-1} range) upon disinfection, compared to Cl- and Br-THMs (above $\mu\text{g L}^{-1}$), Allard and his collaborators (2012) employed some techniques to detect I-THMs at their ng L^{-1} levels.

Yang and his team (2013) proved that ClO_2 treatment oxidized NOM to more hydrophilic and smaller MW fractions. Fluorescence and IR analyses suggested that the ClO_2 broke the aromatic and conjugated form of NOM and converted large aromatic and long aliphatic chain organic constructions to small and hydrophilic organics. It was also demonstrated that the formation of only chlorite ions (ClO_2^-) upon treatment with ClO_2 alone, and no appreciable amounts of THMs and HAAs were detected. The treatment with ClO_2 followed by chlorination decreased THMs, HAAs, HANs and chloral hydrate; and ClO_2 /chloramination treatment, however, did not change THMs concentrations. Also, increasing ClO_2 doses was seen to improve the decrease of most DBPs except halonitromethanes and HKs. Yet, the presence of bromide elevated the formation of DBPs and also changed DBPs to more brominated ones. ClO_2 was found not to interact with HAs to develop THMs, but

promoted the formation of chlorite (ClO_2^-) and chlorate ions (ClO_3^-), which were thought to conduct to hemolytic anemia and to increase methemoglobin (Korn et al. (2002)). The prediction of levels of these ions upon ClO_2 treatment of raw water could be computed via $\text{NPOC} \times \text{UV}_{254}$ (non-purgeable organic carbon \times UV absorbance measured at 254 nm), a factor set by Korn and his collaborators (Korn et al. (2002)).

Hua and Reckhow (2012) investigated the chlorination and chloramination of Cambridge water. The pH variation affected more substantially the formation of brominated THMs than that of chloroform, indicating that the bromine reactivity with NOM was less influenced by the pH modification than Cl_2 for THM production; within 72-hour treatment and by raising the pH from 5 to 10, the chloroform formation increased to 216% and that of bromodichloromethane increased to only 90%.

However, the effect of the chlorination type on the range of the DBPs and their distribution was undertaken on high-bromide containing water by Qu and his group (Tian et al. (2013)). In this work, three chlorination processes were examined: Cl_2 process (NaClO), NH_2Cl process (NH_2Cl solution), and $\text{Cl}_2\text{-NH}_2\text{Cl}$ process ($\text{NaClO} + \text{NH}_4\text{Cl}$). With the first process, the bromine incorporation factor (BIF) values of THMs and HAAs decreased from 0.64 to 0.39 and from 0.52 to 0.29, respectively, with residence period elevating from 30 min to 72 h. For the second process, the corresponding BIFs increased from 0.36 to 0.74 and from 0.09 to 0.32, respectively. Also, the formation of these DBPs was diminished by 88% and 85% and by 68% and 65% in NH_2Cl and $\text{Cl}_2\text{-NH}_2\text{Cl}$ processes, respectively, when compared with Cl_2 one. The same behaviors were reported for the formation of halonitriles (HANs) upon these disinfection scenarios. That is, a decrease in HANs concentration from 6.5 of 2.5 nM at this span time, in the case of the first process, and an increase during chloramination; besides, after 72-h residence period, the content of HANs in $\text{Cl}_2\text{-NH}_2\text{Cl}$ process was

3.9 and 2.5 times of that in chlorination and chloramination, respectively.

Pollutants as Precursors and Degradation Kinetics

The environment has been assaulted by the wastes of the modern living. These are of diverse chemistries, including food, drugs, pesticides, plastics and additives, dyes, oils, soaps, detergents, paints, varnishes, solvents, etc. Their fate is that they are obviously driven into the different water reservoirs. The various chemistries of the contaminants, upon chemical disinfection, would certainly engender products of different kinds. To understand the degradation course of such pollutants, researchers embarked on the study of the disinfection of these wastes in ultrapure water, and establish kinetics behind. Results were then compared with the disinfection of waters spiked with these harmful substances. Acero and his group (2013) determined the apparent rate constants (k_{appS}) for the chlorination and bromination of five emerging water contaminants in ultrapure water, which are benzotriazole, *N,N*-diethyl-*m*-toluamide, 3-methylindole, chlorophene and nortriptyline HCl; hypochlorous and HBrO s being the reactive chlorine/bromine species. The reactions were second-order and the respective k_{appS} for the bromination at neutral pH were 8.50, 0.09, 109, 193, and $7.42 \text{ M}^{-1} \text{ s}^{-1}$. Those for chlorination were 0.20, 1.30×10^{-3} , 5.75×10^3 , 28.4, and $0.40 \text{ M}^{-1} \text{ s}^{-1}$. k_{app} was found to decrease with increasing pH for the first three contaminants and to increase for the last two ones. From these apparent rate constants, it appears that chlorination is suitable for the decomposition of methylindole, and to a lesser significance for that chlorophene and nortriptyline, and inappropriate for that of benzotriazole, *N,N*-diethyl-*m*-toluamide. Also, adding chlorine when bromide is present showed that low bromide contents increased slightly their decomposition. These kinetic parameters were within the range of those reported for chlorination, bromination, and chloramination of different DOCs (Tian et al. (2013)).

Sutthivaiyakit and his research team (Chusaksri et al. (2012)) were interested in the kinetics of chlorination (NaClO) of four phenylurea-based herbicides, which are: *N*-phenylurea, 3,4-dichlorophenylurea, 3,4-dichloro-3'-*N*-methylphenylurea, metoxuron (3-(3-chloro-4-methoxyphenyl)-1,1-dimethylurea), and monuron (3-(*p*-chlorophenyl)-1,1-dimethylurea). At pH 5, the reactions followed third-order kinetics, except for 3,4-dichloro-3'-*N*-methylphenylurea; second order with respect to chlorine and first order with respect to phenylurea. For 3,4-dichloro-3'-*N*-methylphenylurea, the reaction exhibited two-order kinetics; one order with respect to chlorine and the phenylurea. The k_{app} s at this pH and at 25°C were, respectively: 26 700 M⁻² s⁻¹, 17 000 M⁻² s⁻¹, 19.70 M⁻¹ s⁻¹, 2.07 M⁻² s⁻¹, 0.33 M⁻² s⁻¹. A dramatic decrease of k_{app} for *N*-phenylurea, 3,4-dichlorophenylurea occurred at basic and neutral pHs. Even, the nature and number of chlorination products depended on working pH. Under acidic conditions, seven main products were identified: 3'-*N*-chlorophenylurea, 2-chlorophenylurea, 1'-*N*-chlorophenylurea, 2,3'-*N*-dichlorophenylurea, 4-chlorophenylurea, 4,3'-*N*-dichlorophenylurea, and 2,4-dichlorophenylurea. At basic and neutral pHs, other unidentified compounds appeared. Xu and collaborators (2012, 2011) investigated the chlorination (NaClO) and chloramination (NaOCl + NH₄Cl) of chlortoluron (3-(3-chloro-4-methylphenyl)-1,1-dimethylurea) (Fig. 7B) within a range of pHs. The reactions fitted second-order kinetics pattern; first-order in chlorine (Cl₂)/monochloramine (NH₂Cl) and first-order in chlortoluron. For chloramination (Xu et al. (2012)), the apparent rate constants k_{app} s were in the spectrum of 2.5-66.3 M⁻¹ h⁻¹, with a minimum at pH 4, a maximum at pH 6 and a medium at alkaline conditions. And, the chief DBPs of this chloramination were NDMA, chloroform, DCAN, 1,1-dichloropropanone, 1,1,1-trichloropropanone and TCNM, and fourteen intermediates were detected. NDMA and chloroform were the DBPs formed in higher concentrations. For chlorination (Xu et al. (2011)), k_{app} was lower than 3 100 M⁻¹ h⁻¹, with a minimum at

pH 6, a maximum at pH 3 and a medium at alkaline conditions. The rate constant of each predominant elementary reaction (i.e., the acid-catalyzed reaction of chlortoluron with HOCl, the reaction of chlortoluron with HOCl and the reaction of chlortoluron with OCl⁻) was calculated as 3.12 × 10⁷ M⁻² h⁻¹, 3.11 × 10² M⁻¹ h⁻¹ and 3.06 × 10³ M⁻¹ h⁻¹, respectively. The main DBPs from chlorination process were the same as with chloramination with the exception of NDMA. Rate constants of chlorination of heterocyclic substances such as ametryn (2-ethylamino-4-(isopropylamino)-6-(methylthio)-s-triazine) (Fig. 7A), trimethoprim (5-(3,4,5-trimethoxybenzyl)pyrimidine-2,4-diamine) (Fig. 7C), phenol, and bisphenol A (BPA) were found to be 7.22 × 10², 1.6 × 10², 0.36, and 1.84 M⁻¹ s⁻¹ (Xu et al. (2009)). At 25°C and pH of 7, the chlorination of ametryn followed second-order kinetics, first-order with respect to the concentration of chlorine and ametryn. The activation energy for this degradation reaction was 14.42 kJ mol⁻¹, hinting at the slight effect of temperature. The reaction rate was relatively high under acidic and neutral conditions with the apparent second-order rate constant larger than 5 × 10² M⁻¹ s⁻¹, and decreased with increasing pH. And, the presence of bromide ions accelerated the degradation, as confirmed by the higher rate constant of reaction of ametryn with HOBr, that is, 9.07 × 10³ M⁻¹ s⁻¹. Earlier Mascolo et al. (1994) and Lopez et al. (1997) investigation on the degradation of triazine-based herbicides such as prometryn, terbutryn, ametryn, desmetryn, and isoproturon, with disinfectants such as ClO₂ and NaClO revealed that the degradation took place at the sulfur atom of the molecule; for ametryn, by-products as sulfoxide (R-SO-CH₃), sulfone (R-SO₂-CH₃), and sulfonate ester (R-SO₂-CH₃) and its hydrolysis products (R-OH) were produced. As to the chlorination of trimethoprim, second-order kinetics was established with an apparent rate constant of 56 M⁻¹ s⁻¹ (Dodd and Huang (2007)). Besides, a trace of degradation products was observed upon chlorination of trimethoprim, but polyhalogenated and hydroxylated products were detected in relatively higher amounts.

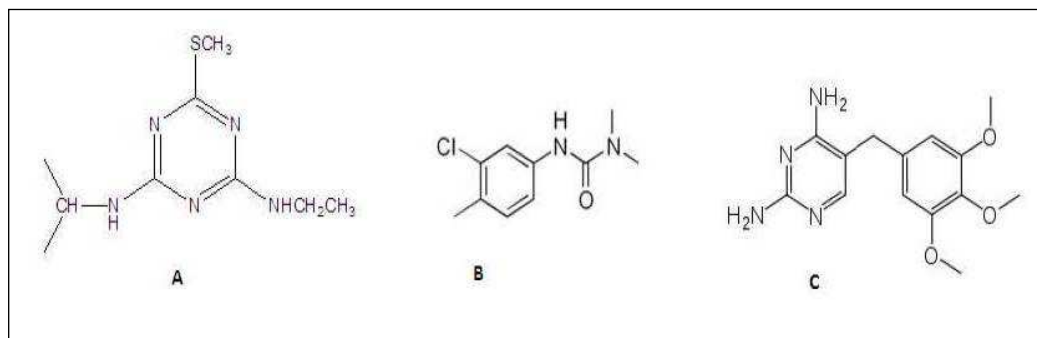


Fig. 7. Some amino-based herbicides: A, ametryn (2-ethylamino-4-isopropylamino-6-methylthio-1,3,5-triazine) ; B, chlortoluron (3-(3-chloro-4-methylphenyl)-1,1-dimethylurea); C, trimethoprim (5-(3,4,5-trimethoxybenzyl)pyrimidine-2,4-diamine).

Acero's research team (Acero et al. (2008)) provided results on the chlorination of organophosphorus pesticides (chlorpyrifos, chlorfenvinfos and diazinon) in ultrapure water at different pHs and temperatures (Fig. 8). The oxidation reactions obeyed second-order kinetics pattern with k_{app} s of 110.9, 0.004 and 191.6 $M^{-1} s^{-1}$ for chlorpyrifos, chlorfenvinfos and diazinon, respectively, at 20°C and pH 7. These magnitudes would give an insight into the higher reactivity of the phosphorothioate group in chlorpyrifos and diazinon, compared to the lower one for phosphate moiety in chlorfenvinfos; the reactivity of these pesticides towards chlorine was in

this order: diazinon > chlorpyrifos > chlorfenvinfos. On the other hand, elevating pH led to a reduction of the rate constant, that is, the degradation speed. And, increasing the temperature for the reaction of chlorpyrifos from 11 to 30°C led to an increase of rate constant from 80.4 to 177.1 $M^{-1} s^{-1}$. Its activation energy was estimated at 29.6 $kJ mol^{-1}$. The chlorination of natural water containing these pesticides proved that chlorine doses of 2.5 $mg L^{-1}$ oxidized diazinon and chlorpyrifos almost completely, chlorfenvinfos remained almost unaffected. With this chlorine dose, THMs were formed at acceptable levels.

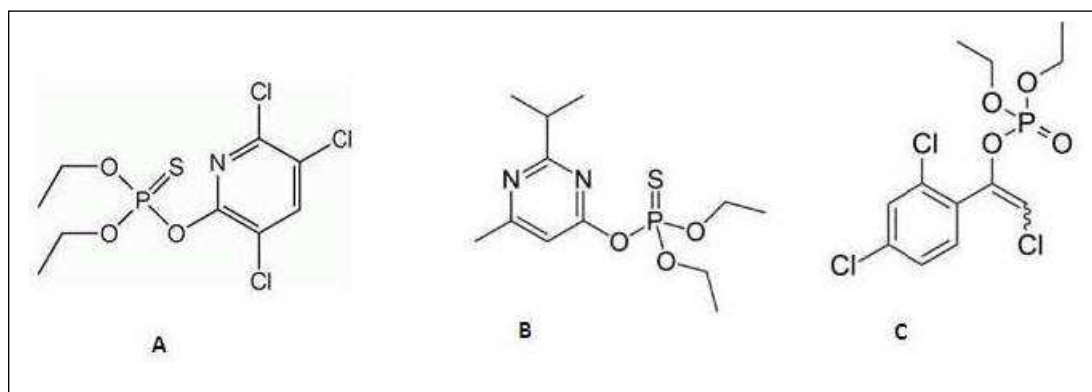


Fig. 8. Organophosphorus pesticides: A, chlorpyrifos (*O,O*-diethyl *O*-3,5,6-trichloropyridin-2-yl phosphorothioate); B, diazinon (*O,O*-Diethyl *O*-[4-methyl-6-(propan-2-yl)pyrimidin-2-yl] phosphorothioate); C, chlorfenvinfos ((*EZ*)-2-Chloro-1-(2,4-dichlorophenyl)ethenyl] diethyl phosphate).

A detailed study on the chlorination of bisphenol A (BPA) at acidic and alkaline pHs

at room temperature (20-25°C) was reported (Yamamoto and Yasuhara (2002),

Hu et al. (2002), Gallard et al. (2002)). At the initial stage of BPA chlorination at pH of 8-9 in ultrapure water (Yamamoto and Yasuhara (2002)), five products were identified: 2-chlorobisphenol A, 2,6-dichlorobisphenol A, 2,2'-dichlorobisphenol A, 2,2',6-trichlorobisphenol A, and 2,2',6,6'-tetrachlorobisphenol A. These intermediate products were finally cleaved to several chlorinated phenolic compounds, including 2,4,6-trichlorophenol, DCBQ, 2,6-dichloro-1,4-hydroquinone, 3,5-dichloro-4-hydroxyphenyl)-propan-2-ol, 2-(3,5-dichloro-4-hydroxyphenyl)-prop-1-ene), 2-(3,5-dichloro-4-hydroxyphenyl)-2-methoxypropane. In addition to these products, others were identified by Hu *et al.* (2002). However, Gallard and his collaborators (2002) disclosed that the BPA chlorination followed second-order kinetics and the apparent rate constant depended on the form of the BPA, that is un-ionized BPA (at acidic pH), ionized BPA (BPA⁻, BPA²⁻ at alkaline pH) and was found to be $k_{app} = 3.10 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ for BPA⁻ species and $6.62 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ for BPA²⁻ form. Early works (Rebenne et al. (1996), Gallard and von Gunten (2002)) dealt with the chlorination of phenolics and dihydroxybenzenes such as resorcinol, and results served as supports for those found for BPA.

Zhang *et al.* (2012) investigated the production of DBPs from the chlorination of representative algal odorants and studied the kinetics of the degradation of these precursors during treatment. β -Cyclocitral, β -ionone, heptanal, dimethyl sulfide and dimethyl trisulfide were chosen as representative odor-causing compounds released by *M. aeruginosa*. While β -ionone and heptanal degradation exhibited a pseudo second-order kinetics trend, chlorination (NaOCl) of β -cyclocitral followed a pseudo first-order kinetics pattern. At pH 7, the rate constants were 0.093 min^{-1} , $5.99 \times 10^{-4} \text{ L } \mu\text{g}^{-1} \text{ min}^{-1}$, and $3.08 \times 10^{-5} \text{ L } \mu\text{g}^{-1} \text{ h}^{-1}$ for degradation of β -cyclocitral, β -ionone and heptanal, respectively. The reactivities of the odorants towards chlorination followed the sequence: β -ionone > β -cyclocitral >> heptanal; β -ionone and β -cyclocitral reacted more rapidly via the existing unsaturations,

and heptanal showed some solidity because of its saturated aliphatic structure. The most likely intermediate oxidation products formed upon $\text{Cl}_{2(g)}$ adding of these odorants were: cyclohexanone, 1-cyclohexene-1-methanol for β -cyclocitral; 3-buten-2-ol, 3-oxo- β -ionone, and 4-penten-2-one for β -ionone; 2-chloro-hexanal for heptanal. No HAAs were appreciably formed from all five targeted models, and THMs were well quantified from only β -ionone, β -cyclocitral, and heptanal. After six days of chlorination, the yields of chloroform produced were 4487, 835, and $60 \mu\text{g L}^{-1}$ for the latter three odorants, respectively. The yield order reflects on the mentioned reactivity of the odorants towards chlorination. Chloroform yield was found to increase with increasing pH (from 2 to 12). Besides being relatively stable at acidic and alkaline conditions, chloroform is the ultimate hydrolysis product of many DBPs.

Pretreatment

Intensive research has put forward the benefits of oxidizing pretreatment of waters that are subjected to final disinfecting process; such pretreatment is considered a disinfection by itself. The pretreatment considers several issues: preoxidation, separation via resin and exchange resin, coagulation/sedimentation/filtration cycle, etc. (Gheraout and Gheraout (2012), Gheraout et al. (2010)). The commonly employed oxidizing agents or oxidizing systems for preoxidation include: ozone, hydrogen peroxide, potassium permanganate, and ClO_2 .

The impact of ozone as a powerful disinfecting agent of waters, in the formation of DBPs precursors, has been investigated (Coral et al. (2013)). Disinfection by ozone, via its potential oxidation of OM and its germicidal power, results in bacterial cell wall disintegration, commonly known as lysis. Water-borne cyanobacteria or blue-green bacteria (or blue-green algae) are omnipresent. Ozonation of water would damage cyanobacterial (CB) cells and generate by-products thereof. To understand the formation of DBPs caused by such

ozonation, Coral *et al.* (2013) subjected two CBs in their suspension forms, *Microcystis aeruginosa* (toxic strain) and *Anabaena flos-aquae* (non-toxic strain) to ozonation (dissolved ozone) at 20°C and at pHs of 6 and 8. The ozonation of these cells led to the formation of DOC which increased with ozone dosages at higher pH; at alkaline pHs, the hydroxyl ions promoted the decomposition of ozone molecules and the formation of hydroxyl radicals which are prone to degrade the cell. Upon ozonation, a total loss of viability for both CBs species after exposure to ozone (0.5 mg L⁻¹) of less than 0.2 mg min L⁻¹ was noticed. Also, treatment of suspensions of *A. flos-aquae* at pH = 8 brought about the production of THMs and HAAs in 174 and 65%, respectively. For *aeruginosa* cell, the prevalent chlorinated DBPs produced were chloroform and DCAA, and for the latter, they were chloroform, DCAA, and TCAA.

Yang *et al.* (2012) demonstrated the effect of the pretreatment of water (China's Pearl River) with ozone and ozone/hydrogen peroxide on the yields of DBPs after subsequent chlorination/chloramination. For the latter, four oxidizing systems were evaluated as disinfecting treatment: O₃/Cl₂, O₃/H₂O₂/Cl₂, O₃/NH₂Cl, and O₃/H₂O₂/NH₂Cl. Such pretreatment improved the formation of chloral hydrate (CH), TCNM and HKs but diminished the yields of HANs upon chlorination processes. Chlorination after pretreatment using ozone/hydrogen peroxide produced more CH, TCNM and HKs than after pretreatment with ozone alone. Whereas, chloramination after pretreatment with ozone and ozone/hydrogen peroxide reduced THM, HAA, and HAN production significantly without augmenting CH, TCNM, or HKs. Also, it was shown that such pretreatment would be of value for chloramination process in disinfecting waters with low bromine content.

Serbian workers Molnar *et al.* (2012) examined the catalytic effect of titanium dioxide (TiO₂, 80/20 anatase/rutile ratio) on the ozonation outcome of waters (groundwater from the Central Banat Province of Vojvodina, a water rich in mostly of hydrophobic character NOM) and

on the formation of the THMs and HANs after subsequent chlorination operation. TiO₂-catalyzed process reduced significantly the content of total NOM (up to 18% DOC) compared to ozonation alone (up to 6% DOC), and improved THM precursor content removal (FP reaching 80%). Such treatment induced a change in the NOM composition: the HA fraction of NOM was totally oxidized and the structure of residual NOM consisted of hydrophilic compounds (up to 70%). The latter hydrophilic species were the most reactive in producing THMs and HANs.

Jones *et al.* (2013) compared the effects of the preoxidation of natural water by three oxidizing agents, potassium permanganate (KMnO₄), chlorine dioxide (ClO₂), and hydrogen peroxide (H₂O₂) before chloramination on the production of iodinated THMs (I-THMs). Pretreatment with KMnO₄ enhanced I-THM formation after chloramination treatment, mainly as iodoform and brominated I-THMs (CHBrClI, CHBrI₂, CHBr₂I). However, ClO₂ preoxidation decreased the formation of I-THMs (CHI₃, CHCl₂I) and that of H₂O₂ had a very slight effect.

Recently, the use of pretreatment of waters with magnetic ion exchange resin resulted in the reduction of C-DBP precursors (39-86%) in surface waters and effluent waters (Gan *et al.* (2013)). However, a slight removal of N-DBP precursors (10-33%), particularly as halonitromethanes, was noted. Surprisingly, such pretreatment did not eliminate nor contribute to NDMA production to an important quantity in drinking waters. Subsequent chlorination yielded NDMA in a low extent.

Chu and his co-workers (2011a) examined the benefits of the pretreatment of natural waters with powdered activated carbon (PAC) adsorption, KMnO₄ oxidation and biological contact oxidation (BCO). After chlorination, such pretreatments were advantageous for the removal of algae, OM, and for the reduction of nitrogenous and carbonaceous DBPs. PAC adsorption was found to eliminate successfully the precursors of chloroform (42.7%), DCAN (28.6%), (DCAcAm) (27.2%) and TCNM

(35.7%), a better result than with KMnO_4 and BCO pretreatments. However, the removal efficiency of DOC was 76.5% by BCO process, 69.9% by PAC adsorption, and 61.4% by KMnO_4 oxidation.

Li *et al.* (2011) evaluated photocatalysis (UV irradiation using a 10 W-pressure mercury lamp of $\lambda = 254$ nm), electrochemical oxidation (TiO_2/Ti film electrode as anode and RuO_2/Ti as cathode) and photoelectrocatalysis process, as profitable pretreatment of waters and in the degradation of HAs. The latter method was shown to be a better process than the former two as far as the elimination of HA and the reduction possibility of DBPs were concerned. With photoelectrocatalysis process, DOC concentration was reduced by 75.0% and a UV_{254} nm by 92.0%. Also, about 90% of HAAs (monochloro-, monobromo-, dichloro-, bromochloro-, dibromo-, bromodichloro-, bromodichloro-, dibromochloro-, trichloro- and tribromoacetic acid) FP and 90% of THMs (CHCl_3 , CHBrCl_2 , CHBr_2Cl , CHBr_3) FP could be reduced within 180 min. It was observed that photoelectrocatalysis oxidation preferentially decomposed the large MW (>100 kDa) fractions and the hydrophobic nonpolar fractions of HA; the hydrophobic nonpolar fractions were composed of large aromatic units. The phenolic hydroxyl and conjugated double bonds present in these fractions were prone to the attack by hydroxyl radicals (HO^\bullet) upon photoelectrocatalysis process; these groups were productive with $\text{Cl}_{2(\text{g})}$ to form the cited DBPs. The hydrophilic and transphilic fractions were less decomposed because the existing amino, carboxyl and alcoholic hydroxyl groups are relatively difficult to be decomposed upon photoelectrocatalysis technique. Photocatalytic oxidation by means of UV/ TiO_2 ($\lambda = 254$ nm; suspended TiO_2 and nano-structured thin film support coated with 300 nm of TiO_2) was also employed by Kent *et al.* (2011) to enhance the water treatment efficiency (French River water, Canada). The results were that treatment with UV/suspended TiO_2 did not improve substantially the removal of THMs (only 20% decrease), but was rather efficient in the elimination of total HAAs

even at low TiO_2 concentration (88% decrease). Most of the removed HAAs were di- and TCAAs. Moreover, it was deemed that about 75% of both THMs (mostly chloroform) and HAAs (mostly di- and TCAAs) precursors were found to be associated with the hydrophobic fraction as observed with photoelectrocatalysis process. In general, suspended TiO_2 was less effective than the coated one in the removal of DBPs.

A reverse pretreatment process was undertaken by Gao and his team (Chu *et al.* (2011b), that is, chloramination followed by classical water treatment processes involving coagulation, sedimentation, and sand filtration. In this processing, higher levels of dihalogenated N-DBPs (DCAcAm, DCAN, bromochloroacetonitrile, dibromoacetonitrile and dichloroacetone) were measured in summer and in the beginning of autumn season. However, tri-X-DBPs (chloroform, TCNM and trichloroacetone) seemed not to be importantly influenced by seasons. And, in contrast to the formation of tri-X-DBPs and Br-DBPs, the N-DBPs were associated with the DON/DOC ratio.

Conclusions

The outcome of the widespread research on the disinfection of water to be potable has showed the concomitant risk and danger to which man is being exposed. As outlined in this non-exhausted review on the DBPs, the challenge is by far realized. It is therefore crucial to draw some remarks for alleviating the *statu quo* of what modern man has been facing:

1. Reducing the DBPs limits in drinking water below a certain level seems no to be a compromised solution since the advancement in analytical methods and techniques and the related human health research revealed that the appropriate limit of the DBPs' must be within ng L^{-1} instead of $\mu\text{g L}^{-1}$ scale for safer drinking water. Removal of such hazardous DBPs, or at best the inhibition of their formation, remains a challenging reality and, henceforth, the ultimate focus of research.

2. For a better performance of disinfecting operation, pretreatment such as coagulation/flocculation before the final treatment, i.e. chlorination is highly recommended. The addition of disinfectant is preferentially made at a reduced rate, to avoid the instantaneous formation of organic DBP precursors.

Acknowledgements

The present research work was undertaken by the Binladin Research Chair on Quality and Productivity Improvement in the Construction Industry funded by the Saudi Binladin Constructions Group; this is gratefully acknowledged. The opinions and conclusions presented in this paper are those of the authors and do not necessarily reflect the views of the sponsoring organisation.

List of abbreviations

2,5-DBBQ	2,5-dibromo-1,4-benzoquinone
2,6-DBBQ	2,6-dibromo-1,4-benzoquinone
Br-DBPs	Brominated DBPs
BrO-	Hypobromite ion
CB	Cyanobacterial cell
DCAcAm	Dichloroacetamide
DCAN	Dichloroacetonitrile
DCBQ	2,6-dichloro-1,4-benzoquinone
DBPs	Disinfection by-products
C-DBPs	Carbonaceous DBPs
C-DBP-FP	Carbonaceous DBPs FPs
DCAA	Dichloroacetic acid
DEA	Diethylamine
DIIA	Diiodoacetic acid

DMA	Dimethylamine
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
DON	Dissolved organic nitrogen
FA	Fulvic acid
FP	Formation potential
HAAs	Haloacetic acids
HANs	Haloacetonitriles
HAcAms	Haloacetamides
HBQs	Halo-benzoquinones
HBrO	Hypobromous acid
HKs	Haloketones
HA	Humic acid
HS	Humic substance
IAA	Iodoacetic acid
MW	Molecular weight
NDMA	<i>N</i> -nitrosodimethylamine
N-DBPs	Amine-based DBPs
N-DBP-FP	Nitrogenous DBPs FPs
NMEA	Nitrosomethylethylamine
NMOR	<i>N</i> -nitrosomorpholine
NOM	Natural organic matter
NPIP	<i>N</i> -nitrosopiperidine
NPYR	<i>N</i> -nitrosopyrrolidine
OM	Organic matter
SUVA ₂₅₄	Specific UV absorbance at 254 nm
TCAA	Trichloroacetic acid

TCNM	Trichloronitromethane	7.Badawy, M.I., Gad-Allah, T.A., Ali, M.E.M. & Yoon, Y. (2012). "Minimization of the Formation of Disinfection by-Products," <i>Chemosphere</i> (89) 235-240.
THMs	Trihalomethanes	
UV ₂₅₄	UV light absorbance at $\lambda = 254$ nm	8.Bellar, T.A., Lichtenberg, J.J. & Kroner, R.C. (1974). "The Occurrence of Organohalides in Chlorinated Drinking Water," <i>Journal (American Water Works Association)</i> . (66) 703-706.
X-DBPs	Halogenated DBPs	

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