Formation of nitrogenous disinfection by-products (N-DBPs) in drinking water: emerging concerns and current issue

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Abstract. Nitrogenous disinfection by-product (N-DBPs) has always been one of the most concerned disinfection by-products (DBPs) in recent years. The toxicity of regulated DBPs is generally less than that of N-DBPs, which have been widely detected in finished drinking water. Despite the fact that N-DBPs are highly toxic, there are currently no N-DBPS species officially regulated by governments around the world. This paper provides a review of the formation mechanism and precursors of nitrogen-containing disinfection by-products in drinking water treatment. Also, the species and inducing factors of N-DBPs were summarized. The data were mainly collected from 2000-2002 and 2006-2007 US Survey in effluents of US WTPs. Because nitrogen source is a prerequisite for the formation of nitrogen-DBP in drinking water, the occurrence of N-DBPs may increase due to the influence of sewage and algae blooms on water sources. Chloramine disinfection are used in most of developed countries for preferred secondary disinfection to reduce the formation of chlorine-related by-products, but this increases the formation potential of N-DBPs. Furthermore, the safety control of N-DBPs and suggestions for the further exploration of for efficient drinking water are discussed. Coagulation and filtration are not very effective in removing precursors (such as amino acids) of N-DBPs and the precursors need to be removed before disinfection.

1. Introduction
Chlorination is one of the most crucial water treatment processes because it is effective against most pathogens and provide public health in drinking water. And it is widely used in sewage treatment [1][2][3][4][5]. However, it is estimated that no less than 700 disinfection by-products (DBPs) have been discovered since the detection of chloroform in 1974 [6]. Continued efforts seek to control regulated DBPs, such as trihalomethanes (THMs) and haloacetic acids (HAAs), mostly via the use of alternative disinfectants. Because the formation of regulated DBPs can be inhibited by chloramine, many drinking water facilities use chloramine as a secondary disinfectant [4][7]. However, chloraminated water increases the formation of potentially highly toxic nitrogen-containing DBPs (N-DBPs). N-DBPs are commonly more cytotoxic, genotoxic, and developmentally toxic than regulated DBPs and have been found in finished drinking water [8][9]. Due to the high toxicity of N-DBPs, this has been cited as a research priority all around the world.

As early as the 1980s, the first group of N-DBPs was quantified in chlorinated raw water, which was dihaloacetonitriles (DHAN) [10][11]. In a sample survey conducted between 1988-1989 at 35 water treatment plants in the United States, scientists found THMs, HAAs, haloketones, chloral hydrate, and two N-DBPs: cyanogen chloride (CNCI) and chloropicrin (trichloronitromethane) [12]. Later 2000-2002 US survey reported Haloacetonitriles (HANs), halonitromethanes (HNMs), and haloacetamides (HAcAms) were detected in finished water, which is all far more cytotoxic and genotoxic than the non-nitrogenous THMs and HAAs. Until then, a very important N-DBPs was discovered, which was N-
nitrosodimethylamine (NDMA) as the predominant nitrosamine. NDMA has been used in the past to produce liquid rocket fuel, antioxidants, and other industrial applications. Initially, Canadians discovered a high concentration of NDMA in groundwater on-site (up to 400 μg L-1) and also in downgradient drinking water wells (up to 20 μg L-1) at rocket engine testing facilities in the 1980s [13]. Later, scientists found that NDMA was a DBP generated by the reaction between monochloramine (NH2Cl) and dimethylamine (DMA) [14]. As a result of the activated carbon cannot adsorb the NDMA due to the hardly degradation and involatile matter, NDMA in drinking water is difficult to remove. The US Environmental Protection Agency (US EPA) has set a maximum allowable concentration of NDMA in drinking water at seven nanograms per liter and has not set a maximum contaminant level (MCL) for drinking water regulation [15] and the United States Office of Environmental Health Hazard Assessment (OEHHA) have published a public health maximum concentration three ng L-1 for NDMA. Over-exposure to NDMA can reduce the liver's function and develop symptoms such as headache, fever, nausea, jaundice, vomiting, abdominal pain, scattered subcutaneous bleeding, drowsiness, nausea, and dizziness [16]. The risk of liver cancer may also be increased by long-term low-dose exposure. The oral lethal dose (LD50) of n-nitrosamine-dimethylamine mice was 37.0mg/kg. Although N-DBPs play an essential role in human carcinogenesis, no N-DBPs species are formally regulated by the government in drinking water agencies worldwide. Even though researchers worldwide have paid significant efforts to investigate the occurrence and toxicity of N-DBPs, their formation mechanisms, organic matter precursor, potential technology to suppress their formation, and health risks for humans remain unclear. This study reviewed the observed species and concentrations, possible precursors, and formation mechanisms of known and unknown N-DBPs.

2. Known N-DBP Species, concentrations, and toxicity

As shown in Figure 1, five groups of N-DBPs have been previously reported in drinking water: haloacetonitriles (HANs); haloacetamides (HAcAms); cyanogen halides (CNX); halonitromethanes (HNMs) and nitrosamines and the chemical structures for representative N-DBPs compound have been listed.

The median and maximum concentrations for five groups of N-DBPs were presented in Figure 2. According to the 2000-2002 US survey which summarized HANs, HAcAms, and HNMs occurrence in effluents of selected US WTPs, the concentration of HANs were highest with mainly range from 3 to 14 μg L-1 respectively, the median and maximum concentration of HNMs were 1, and 10 μg L-1, the mainly range of HAcAms were from 1.4 μg L-1 to 7.4 μg L-1 respectively. According to the 2006-2007 N-DBP survey, CNX formation occurred significantly in chloramination with median and maximum concentration were 2.6 μg L-1 and 7.8 μg L1. Compared with other N-DBPs groups, nitrosamines concentration was the lowest, with a maximum concentration is 1 μg L-1 in chloraminated raw water.

Based on data from prior literature [17], the median and maximum concentration of DBPs species for each group N-DBPs were presented in Figure 3. For HANs species, and DCAN and BCAN were the most prevalent species with the concentration range from 1 μg L-1 and 11 μg L-1, respectively. For HAcAms species, DCACAm and DBACAm were the most prevalent species with median concentration 1.3 μg L-1 and maximum concentration of 2.8 μg L-1 and 5.6 μg L-1, respectively. For HNMs species, bromopicrin, chloropicrin, dibromochloronitromethane, and bromodichloronitromethane were the most prevalent species with maximum concentration with a range from 2~5 μg L-1. For nitrosamines species, NDMA was the most critical species, with the mainly range from 45 to 1000 ng L-1, and other nitrosamines species, e.g., NPYR and NDEA, were found in low ng L-1 level in the water [17].
3. Formation of N-DBPs in drinking water treatment

3.1. Organic nitrogen sources
A nitrogen source is a precondition for the N-DBP formation. Naturally dissolved organic nitrogen (DON) is regarded as an essential source. DON is a complicated organic macromolecule containing large chemical groups. DON include proteins, amino acids, amides, nitriles, amino sugars, purines, pyrroles, and pyrimidines and the occurrence are from the product of metabolism of algae, plants, and animals [18]. Besides, amines and amides are thought to be the most critical nitrogenous functional groups in NOM [19]. N-DBPs concentration enhances wastewater, which contains lots of extensive DON than in raw natural water [20]. Furthermore, the disinfectant chloramines can extract the Nitrogen which is in N-DBPs; for example, dimethylamine (DMA) could be with monochloramine to form NDMA [14].

3.2. Precursors and formation mechanisms
Amino acids play a critical role as precursors of haloacetanilides (HANs) and cyanogen halides (CNX). Aspartic acid, tryptophan, and kynurenic acid have been demonstrated to produce DCAN [21][22]. CNCl can be observed directly in amino acids solutions after monochloramination [23]. Aldehyde and amides provide routes for HANs, CNX, HAcAms, and nitrosamines formation, respectively. DCAN can be formed by the reaction of monochloramine with acetaldehyde [17]. CNX can be formed by the post-chloramination of formaldehyde; a direct halogenation of amides results in the formation of HAcAms. Besides, HAcAms can be formed via the hydrolysis of HANs at alkaline pH [24][25] and or via the hydrolysis and subsequent chlorination of cyanooacetic acid [26]. An amine in monochloramination can produce a hydrazine intermediate and then subsequently oxidized to a nitrosamine [27].

Larger natural organic molecules (NOM) containing nitromethane moiety is thought to the precursors for HNMs such as chloropicrin in chlorination waters, and extensive hydrophilic NOM substances including amino acids, amino sugars, primary amines (monomethyl amine), and nucleic acids generate a little yield in chloropicrin waters [28]. DMA is the precursor for nitrosamines only, and it can generate unsymmetrical 1,1-dimethylhydrazine (UDMH) intermediate and then NDMA [14]. Also, wastewater in chlorination increased NDMA yields because it’s a critical source of precursors for NDMA. Five group N-DBPs species have different sensitivity to pH in water, but most of them are stable in acidic pH [25]. DCANs, the most prevalent species of HANs, can hydrolysis to generate DCAcAms and then subsequently hydrolyze to dihaloacetonic acids in alkaline pH [26][29]. It is reported that DCAN yield was highest at pH 5 after chlorination of aspartic acid for 3 hours [10] while the concentration of DCAcAms reached the highest point when pH ranged from 6.8 to 7.1 in the US 2000–2002 survey. The decomposition of CNX also increases with increasing pH in chlorinated water [30]. For HNMs, increase chloropicrin presence with the rise of pH values [31]. Regarding NDMA, its formation concentration comes to the summit via UDMH at pH 7–8 [27].

Disinfect types and procedures are critical in determining final N-DBPs levels. Nitrile formation via dichlorination of the terminal amine favors excess chlorine conditions. Besides, DCAN yield was about five times higher in chlorination than chlorination [32]. It has resulted from the decomposition of DCAN to DCAA in the presence of free chlorine [26]. Due to hypochlorite ion (OCl–) contributing to the decomposition of cyanogen chloride (CNCl), it rapidly decomposed in chlorinated water with half-life 60 min at free chlorine dose 0.5 mg L−1 while it keeps stable relatively and more frequent appearance in chloramination waters [33]. NDMA formation was higher in dichloramination than monochlorination [34].

4. Conclusion and Outlook
People's lives are affected by disinfection by-products. There is a range of evidence that a variety of DBPs will have a significant impact on human health. In the 1970s, halogenated by-products of chlorine disinfection were discovered. After that, many regulators had to control the number of DBPs to keep drinking water safe and eliminate potential cancer risks [35]. In many developed countries, chlorinated
amines are preferred for secondary disinfection to reduce chlorination-related by-product formation [35]. Although this can reduce the by-product of halogen disinfection, but will increase the formation of N-DBPs, such as nitrosamines [35]. Krasner et al. state that although the amount of N-DBPs is not as high as that of other DBPs, the toxicity of N-DBPs is much higher than that of other DBPs, so they are increasingly concerned by water management authorities in various countries around the world [35]. They also describe one way to address this problem is to minimize disinfectants and by-product precursors. Alternatively, technologies such as activated charcoal could be used instead of disinfectants to remove dissolved organic matter. However, no country currently regulates N-DBPs. Therefore, for the current understanding and challenges of N-DBPs, only one future research direction can be proposed: first identifying various N-DBPs in drinking water. Second, their precursors and formation patterns need to be studied. Finally, the systems engineering approach needs to be taken effectively to reduce the formation of N-DBPs in drinking water.

4.1. Figure captions/numbering

![Figure 1. Representative chemical structures of five groups of N-DBPs.](image-url)
Figure 2. The median and maximum concentration of N-DBPs group in finished water [17].

Figure 3. The median and maximum concentration of HANs, HAcAms, nitrosamines, and HNMs species in finished water [17].
5. References

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