Occurrence and Formation of Nitrogenous Disinfection By-Products
[Project #3014]

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OBJECTIVES:
The objectives of this project were to (1) perform an occurrence survey of organic and inorganic nitrogen precursors in source waters and nitrogenous disinfection by-products (N-DBPs) in chlorinated and chloraminated finished waters; and (2) determine organic and inorganic nitrogen precursor characteristics and water quality parameters that contribute to N-DBP formation, and mechanisms of N-DBP formation.

BACKGROUND:
Although DBP research has traditionally focused on the formation of carbonaceous chlorination DBPs (C-DBPs), two trends in the drinking water industry make the study of N-DBPs increasingly important. N-DBPs are a specialized subset of the C-DBPs, wherein the characteristic functional group is nitrogen-based. First, due to population growth, an increasing number of drinking water supplies exhibit elevated dissolved organic nitrogen (DON) concentrations resulting directly from wastewater discharges or from algal activity fostered by increased inorganic nitrogen loadings (e.g., agricultural runoff, stormwater runoff, wastewater discharges, septic tank releases, etc.). Secondly, drinking water utilities are considering altering disinfection schemes from chlorination to other disinfectant combinations to meet more stringent standards on trihalomethanes and haloacetic acids promulgated under the USEPA’s DBP Rules.

HIGHLIGHTS:
1. NDMA formation during chloramination can be reduced by adding pre-formed monochloramine to minimize the concentration of dichloramine.
2. The colloidal, hydrophilic base and hydrophilic acid/neutral fractions of dissolved organic matter (DOM) isolated from algal- or wastewater-impacted source waters were important sources of precursors for certain N-DBPs. Unfortunately, hydrophilic DOM is poorly removed during traditional treatment processes.
3. NDMA formation was associated with chloramination of source waters impacted by wastewater with utilities employing polyDADMAC (a coagulation polymer) or with the use of certain resins. Pre-oxidation of waters with free chlorine or ozone destroyed or transformed NDMA precursors.
4. The mechanisms of formation and the impact of treatment/disinfection processes on N-DBPs often differed from that of C-DBPs. Nonetheless, there are ways of optimizing the overall treatment/disinfection process to control the formation of emerging N-DBPs and regulated C-DBPs.

APPROACH:
First, pathways responsible for the degradation of simply amino precursors and their transformation into nitriles, aldehydes, HNMs, and nitrosamines were examined. Second, algal- and wastewater-impacted waters were fractionated and subjected to formation potential (FP) tests to examine which DOM fractions yielded the highest concentrations of N-DBPs. Third, N-DBP FP tests were used to evaluate precursor levels in a range of algal-
and wastewater-impacted source waters. Precursor removal was examined within drinking water treatment process units. Finally, N-DBP concentrations were quantified in the effluents of treatment plants employing a range of disinfection schemes.

RESULTS/FINDINGS:
Formation pathway studies indicated that nitrosamine formation during chloramination can be substantially accounted for by reactions involving dichloramine. Nitrosamine formation was also promoted under certain breakpoint chlorination conditions, or from the use of certain anion exchange resins. The cyano groups in cyanogen chloride or haloacetonitriles can form by elimination of hydrochloric acid from intermediate organic chloramines, or by reaction of inorganic chloramines with aldehydes. As a result of the latter case, chloramination may promote the formation of cyano-based N-DBPs. Halonitromethane formation during chlorination/chloramination was less important, but higher during chloramination in model studies.

Studies involving DOM isolates indicated that nitrogen-rich colloidal, hydrophilic base and hydrophilic acid/neutral fractions were significant sources of certain N-DBP precursors. Although certain isolates were nitrogen-rich, NDMA precursors were particularly associated with fractions obtained from wastewater treatment plants. Chloramination formed cyanogen chloride, and the nitrogen in this DBP was split between the DON and the inorganic chloramines, where more came from the DON in nitrogen-rich DOM isolates.

The survey showed that DON tended to be higher in wastewater and/or algal-impacted waters. The survey confirmed that NDMA precursors were associated with wastewater-impacted supplies, but also indicated that polyDADMAC was a significant source of NDMA precursors. Ozonation was found to increase HNM FP or that of cyanogen chloride, whereas it sometimes destroyed NDMA FP. Biofiltration was often found to decrease the FP for HNMs or cyanogen chloride.

IMPACT:
Due to population growth, wastewater and algal impacts to water supplies are likely to continue to increase, resulting in more DON and precursors for N-DBPs in source waters, which may result in increased formation of certain N-DBPs. The field survey indicated the range of concentrations of N-DBPs likely to form in utilities treating wastewater- and/or algal-impacted source waters. Moreover, the results of the survey showed ways to optimize the treatment/disinfection process to control the formation of N-DBPs. In addition, the formation pathway studies and the characterization of N-DBP precursors will provide utilities with information on how to better understand and design treatment/disinfection processes that minimize N-DBP formation.

RESEARCH PARTNER:
U.S. Environmental Protection Agency

PARTICIPANTS:
The participating water utilities assisted with obtaining samples and answering questions regarding water treatment and quality information.