OBJECTIONS

The objective of this project was to determine the occurrence of nitrosamines at plants in the United States and Canada that were representative of the range of precursor loadings in drinking water, and that used different treatment/disinfection processes that may impact nitrosamine formation. The goal was to fill critical data gaps in nitrosamine occurrence by developing “informed” evidence, i.e., occurrence data with sufficient ancillary data for key water quality parameters, and information on treatment and operations on the day of sampling to support conclusions or possible pathways to better understand NDMA formation and control.

BACKGROUND

N-Nitrosodimethylamine (NDMA) is a disinfection by-product (DBP) preferentially formed by chloramines. Sources of NDMA precursors include treated wastewater and certain polymers used in drinking water treatment (e.g., polydiallyldimethylammonium chloride [polyDADMAC], polyamine). Previous surveys (e.g., the Unregulated Monitoring Rule 2 [UCMR2]) did not always, or completely, identify which plants distributed water with chloramines, especially when chlorine was added to ammonia-containing waters where breakpoint was not achieved. Moreover, previous surveys did not document wastewater impacts or polymer usage.

Previous research showed that NDMA precursors can be destroyed or transformed during pre-oxidation with chlorine or ozone. In addition, activated carbon (AC) and riverbank filtration (RBF) have been shown to remove wastewater-derived precursors. In that research, powdered and granular activated carbon (PAC, GAC) were shown to be ineffective at removing polyDADMAC-derived precursors. In contrast, limited studies showed that PAC could remove polyamine-derived precursors. Previous surveys (e.g., UCMR2) did not document the treatment/oxidation practices or track the fate of NDMA precursors through the treatment process. In addition, more research was needed on the efficacy of GAC to remove different types of polymer-derived precursors.
Previous surveys included seasonal monitoring, but did not include event-driven sampling where nitrosamine formation and control might be significantly impacted. In addition, more information was needed on year-to-year variability in nitrosamine occurrence.

**APPROACH**

The research team determined the occurrence of nitrosamines at 37 plants, as well as 6 consecutive systems, in the United States and Canada. These locations were representative of the range of precursor loadings in drinking water (range of wastewater impacts and polymer usage), and used different treatment/disinfection processes that may control nitrosamine formation (e.g., pre-oxidation with chlorine and/or ozone, PAC or GAC adsorption).

The research team sampled the plant influent (to see if there were nitrosamines from upstream wastewater discharges), the plant effluent, and the distribution system at average and maximum detention times to determine nitrosamine occurrence. The research team measured the presence of the artificial sweeteners sucralose and acesulfame-K, which are conservative wastewater tracers. Moreover, the research team conducted nitrosamine formation potential (FP) tests on selected samples to determine precursor loadings in raw water (watershed-derived) and in settled water after polymer usage, and after ozone, RBF, PAC, GAC, and biofiltration to determine the destruction or removal of precursors.

Furthermore, the research team conducted nitrosamine-simulated distribution system (SDS) tests on selected waters to understand the impact of chloramination practices (e.g., free chlorine contact time, pH, temperature) on nitrosamine formation and control. Finally, the research team obtained information from participating plants on the day of sampling on river flow and critical operational parameters (e.g., polymer type and dose, ozonation and chlorination CTs, free chlorine contact time, activated carbon [AC] usage, such as time since GAC last regenerated or replaced). Furthermore, the team evaluated NDMA yields (in bench-scale tests) from selected polymers used at some of the participating plants.

The research team sampled quarterly to provide seasonal information. Moreover, at selected plants, the team conducted event-driven samplings: e.g., storms or low-flow conditions, raw-water ammonia events when breakpoint chlorination was not achieved, periodic switch back to free chlorine in the distribution system, and different polymer dosages. The research team also examined year-to-year variability.

In addition to measuring the Method 521 nitrosamines, the team measured N-nitrosomorpholine (NMOR) (a commonly detected nitrosamine in treated wastewater), N-nitrosodiphenylamine (NDPhA) (which is not amenable to gas chromatographic [GC] methods), and tobacco-specific nitrosamines (TSNAs) (a class of nitrosamines that had been hypothesized to be present in water).

**RESULTS/CONCLUSIONS**

Sources of NDMA precursors in watersheds were found to be wastewater-derived or from other (unidentified) sources in the watershed; and in the plant from the use of certain polymers (e.g., polyDADMAC, polyamine), an anion exchange resin or biofilters.

Pre-oxidation with chlorine or ozone was typically effective at destroying NDMA precursors. RBF, PAC, and GAC removed wastewater-derived precursors. GAC had varying efficacies removing different types of polymer-derived precursors.
Chloramine plants often produced NDMA, whereas chlorine plants typically did not. Other nitrosamines were typically not detected, except for NMOR, which tended to be a wastewater or groundwater contaminant and not a DBP per se. Precursors for TSNAs were detected in wastewater-impacted drinking waters, but TSNAs were only detected at one drinking water plant, which did not have breakpoint chlorination.

Ozone by itself produced very low levels of NDMA, if at all (median = 1.7 ng/L). Alternatively, NDMA formation tended to increase in chloraminated distribution systems (the median, 75th percentile, and 90th percentile increase between the plant effluent and distribution system/maximum detention time was 1.7, 6.3, and 18 ng/L, respectively). In some consecutive systems, there was a higher occurrence of NDMA than in the distribution system of the wholesaler.

Certain events impacted NDMA formation: periodic switch to chlorine (typically reduced NDMA formation), spring runoff and the presence of raw-water ammonia (typically increased NDMA formation if breakpoint chlorination was not achieved), and an increase in polyDADMAC dose (typically increased NDMA formation).

**APPLICATIONS/RECOMMENDATIONS**

Utilities that have significant levels of NDMA in their finished water need to conduct testing to determine the source(s) of precursors and how best to control NDMA formation.

Measuring artificial sweeteners and conducting FP tests will help utilities elucidate the source(s) of precursors. Data on river flow will help utilities understand seasonal variations in watershed impacts or runoff events. Utilities should develop site-specific relationships between river flow, artificial sweeteners, and NDMA FP.

Utilities that use certain polymers, anion exchange resins, and biofilters should determine the NDMA FP before and after these treatment processes to determine if these are important sources of precursors. Moreover, utilities that use ozone, RBF, PAC or GAC should measure NDMA FP before and after these unit processes to see if they are effective at destroying or removing precursors. Furthermore, utilities should conduct SDS testing to determine if changes in free chlorine contact time or pH can improve NDMA control.

Utilities should examine nitrosamine occurrence, precursor loadings, and treatment efficacy on a seasonal and year-to-year basis. Moreover, they should consider event-driven sampling where appropriate.

Moreover, utilities will need to consider how changes in treatment practices may impact the formation of other DBPs, as well as other regulatory and operational issues.