Characterization of N-nitrosamines in wastewater combining Orbitrap high resolution mass spectrometry and chemiluminescence detection

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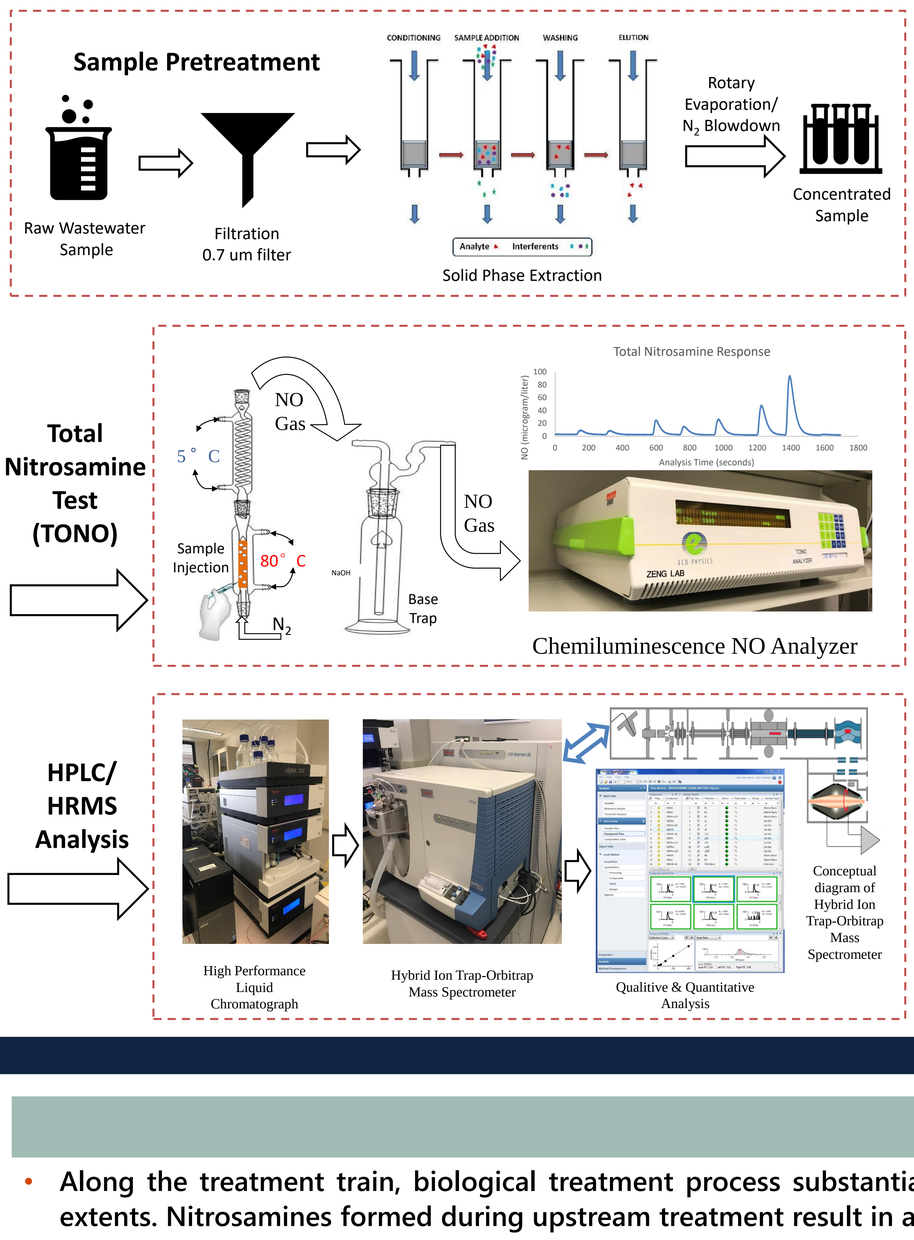
INTRODUCTION

N-nitrosamines are probable human carcinogens. Arising from upstream processes such as wastewater treatment, N-nitrosamines and their precursors have been detected in drinking water supplies and have drawn increasing concern. The US EPA developed a method for seven volatile N-nitrosamine species and developed detection methods. However, due to the complex matrix of municipal wastewater and the transformation in aquatic environment, these targeted N-nitrosamines only represents a small fraction (<10%) of the total N-nitrosamine (TONO) pool, and limited information exists concerning the toxicity, sources and environmental fate of so far unknown N-nitrosamines and their precursors during wastewater treatment.

In this work, we seek to combine chemiluminescence detection and high-resolution mass spectrometry (HRMS) to characterize the fate and composition of wastewater-derived TONO and their precursors. Samples are collected as 24 hour-composite across the treatment trains at six municipal WWTPs in Central New York. TONO concentrations are measured by a previously developed chemiluminescence method, and qualitative and quantitative analysis for specific nitrosamines are performed on LC-HRMS. Our results demonstrate the potential of combining Orbitrap mass spectrometry and chemiluminescence detection as a new tool to more comprehensively characterize the sources and fate of N-nitrosamines in WWTPs and wastewater-impacted aquatic environments.

METHODS



SCREENING AND QUANTIFICATION OF SPECIFIC N-NITROSAMINES

Table 1. Identified/Confirmed N-nitrosamines Species in Wastewater Samples Screening (Partial Results)

Compound Name	Found State	Formula	RT (min)	m/z	Δ m/z (ppm)
N-Methyl-N-nitrosourethane	Confirmed	C4H8N2O3	2.23	133.0608	0.50
N-nitroso-5-methyloxazolidine-4-carboxylic acid	Confirmed	C5H8N2O2	2.29	129.0660	1.12
N-Nitrosobamethan	Confirmed	C12H18N2O3	17.43	239.1403	5.18
N-Nitrosodi-n-butylamine	Confirmed	C8H18N2O	11.62	159.1498	3.90
N-Nitrosoephedrine	Identified	C10H14N2O2	12.85	195.1131	1.37
N-nitrosoethambutol	Identified	C10H23N3O3	16.94	234.1794	-7.98
N-Nitrosoheptamethyleneimine	Confirmed	C7H14N2O	2.26	143.1182	2.13
N-Nitrosomethamphetamine	Identified	C10H14N2O	13.44	179.1181	1.19
N-Nitrosomethylethylamine	Confirmed	C3H8N2O	2.29	89.0710	1.01

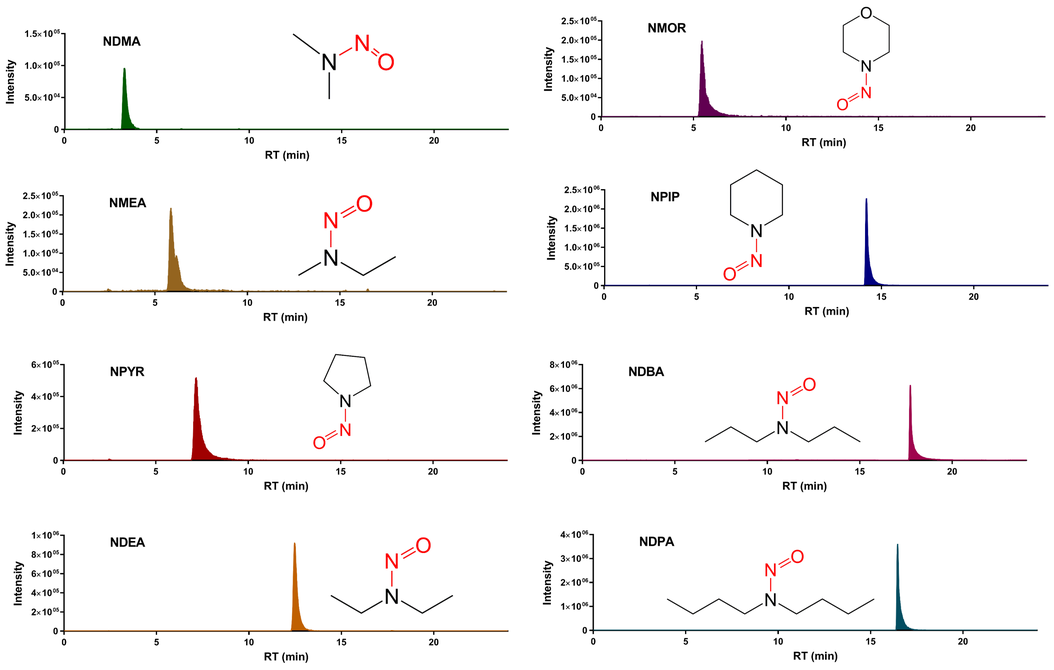


Figure 1. Chromatogram of eight specific N-nitrosamines including N-Nitrosodimethylamine (NDMA), N-Nitrosomethylethylamine (NMEA), N-Nitrosodiethylamine (NDEA), N-Nitrosodi-n-propylamine (NDPA). N-Nitrosodi-n-butylamine (NDBA), N-Nitrosopyrollidine (NPYR), N-Nitrosopiperidine (NPIP) and N-Nitrosomorpholine (NMOR). A Phenyl-Hexyl reversed phase column is used. Standard concentration is 100 ng ml^{-1}.

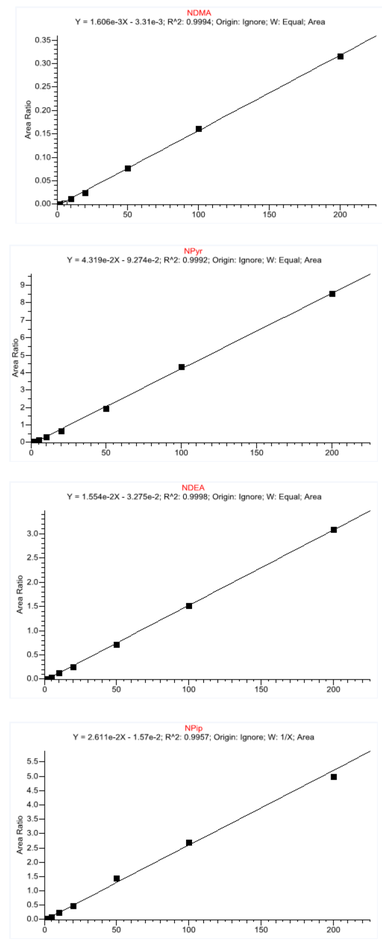


Figure 2. Calibration curves of four N-nitrosamines (NDMA, NPYR, NDEA and NPIP). Calibration standards were prepared in H_2O/MeOH 95:5 (v/v) at analyte concentrations of 1, 2, 5, 10, 20, 50, 100 and 200 ng mL^{-1}. Data is from a full MS scan that set resolution = 15,000.

TOTAL N-NITROSAMINES AND PRECURSORS IN WASTEWATER TREATMENT PLANTS

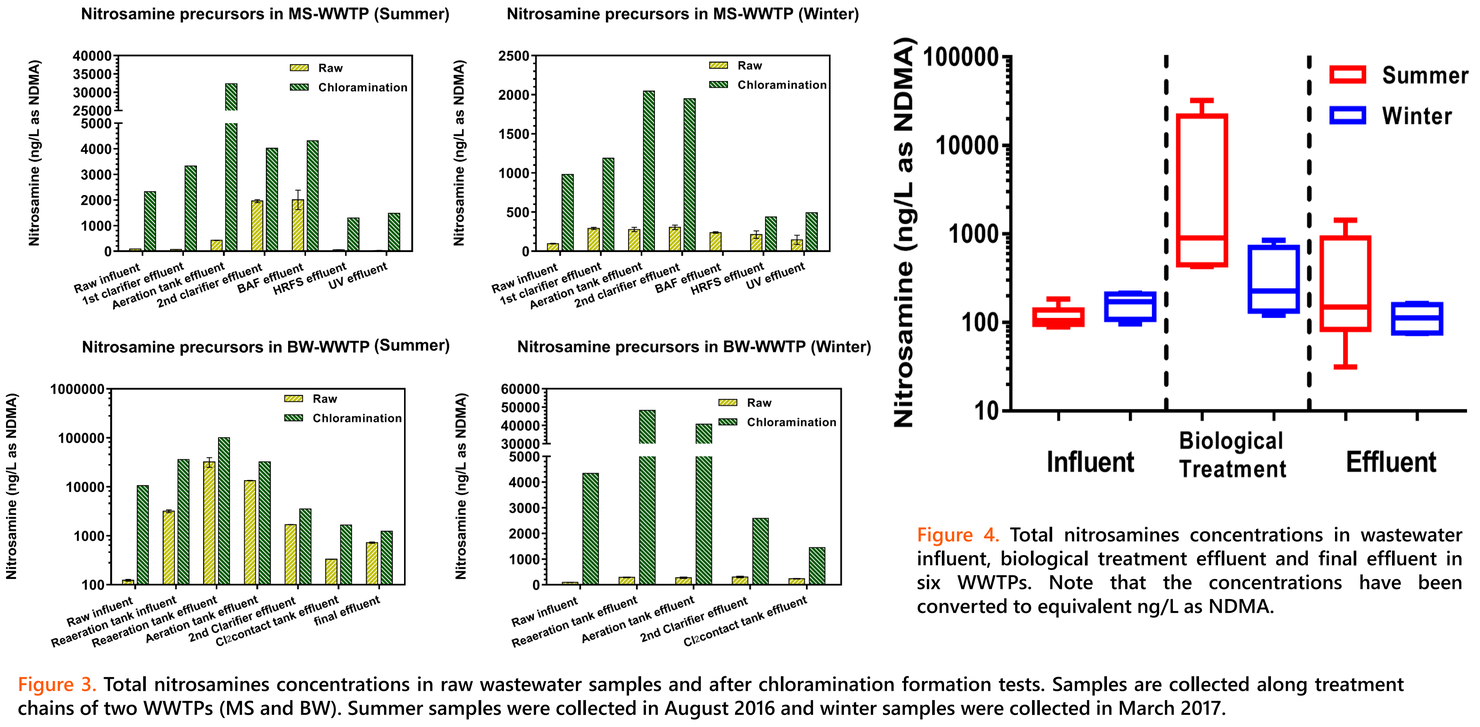


Figure 3. Total nitrosamines concentrations in raw wastewater samples and after chloramination formation tests. Samples are collected along treatment chains of two WWTPs (MS and BW). Summer samples were collected in August 2016 and winter samples were collected in March 2017.

Figure 4. Total nitrosamines concentrations in wastewater influent, biological treatment effluent and final effluent in six WWTPs. Note that the concentrations have been converted to equivalent ng/L as NDMA.

MAIN FINDINGS

- Along the treatment train, biological treatment process substantially increases TONO concentration. Both UV and chlorine disinfection can effectively remove nitrosamines to different extents. Nitrosamines formed during upstream treatment result in an overall increase in nitrosamine levels in 5 out of 6 WWTPs.
- Significantly higher concentrations (up to 35000 ng/L) of TONO occurred in samples collected in summer than those collected in winter. Chloramination promoted the formation of (up to 50 times) total nitrosamines in wastewater, indicating that a considerable amount of nitrosamine precursors are formed within WWTPs.
- By testing performance of five columns on HPLC, a Phenyl-Hexyl column showed the best separation and retention for most nitrosamines. Peaks of all nitrosamines are detected under Full Scan mode at resolution = 15,000, resulting mass accuracy within 10 ppm.
- Regulated and unregulated nitrosamines have been detected by target screening of MS data. A compound database containing 80 nitrosamines and 130 nitrosamine precursors has been established. Quantification of selected N-nitrosamines is in progress to determine their relative importance in TONO pool.

REFERENCES

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[2] Herrmann, Susan Strange, Lene Duedahl-Olesen, and Kit Granby. "Simultaneous determination of volatile and non-volatile nitrosamines in processed meat products by liquid chromatography tandem mass spectrometry using atmospheric pressure chemical ionisation and electrospray ionisation." Journal of Chromatography a 1330 (2014): 20-29.

ACKNOWLEDGEMENTS

We acknowledge support from the Syracuse Center of Excellence (SyracuseCoE) and EMPOWER program. This research is funded by the National Science Foundation under Grant No. DGE-1449617. We also greatly appreciate support from participating water utilities.