Supporting Information for

Comparing Industrial and Domestic Discharges as Sources of *N*-Nitrosamines and Their Chloramine or Ozone-Reactive Precursors

Yi-Hsueh Chuang[1], Farzaneh Shabani[2], Joline Munoz[2], Roshanak Aflaki[2], Slavica D. Hammond[3], William A. Mitch[1,*]

[1] Department of Civil and Environmental Engineering, Stanford University, 473 Via Ortega, Stanford, California 94305, United States

[2] City of Los Angeles, USA

[3] Parsons Corporation, USA

*Corresponding author: email: wamitch@stanford.edu, Phone: 650-725-9298, Fax: 650-723-7058

Contents

Table S1. Cancer risk and regulatory levels for *N*-nitrosamines in drinking water

N-Nitrosamine	10^{-6} Risk Level (ng/L)	Notification Level[1] (ng/L)	Response Level[2] (ng/L)
N-Nitrosodiethylamine (NDEA)[3,4]	1	10	100
N-Nitrosodimethylamine (NDMA)[3,5]	3	10	300
N-Nitrosodi-n-propylamine (NDPA)[3,4]	5	10	500
N-Nitrosodi-n-butylamine (NDBA)[3,4]	3	NA	NA
N-Nitrosomethylethylamine (NMEA)[3,4]	1.5	NA	NA
N-Nitrosopiperidine (NPIP)[4]	3.5	NA	NA
N-Nitrosopyrrolidine (NPYR)[3,4]	15	NA	NA

NA = not applicable

[1] Notification Levels for NDEA, NDMA, and NDPA are established in California at 10 ng/L, somewhat above the *de minimis* level, to take into account the very low detection limits and their potential presence in association with drinking water treatment.

[2] Response Levels are drinking water concentrations at which California recommends removing the source from service. They correspond to a 10^{-4} risk, 100 times the *de minimis* (10^{-6}) value.

[3] Chemical is on US EPA's Unregulated Contaminant Monitoring Rule List 2.

[4] Risk levels for *N*-nitrosamines in drinking water can be derived from the 10^{-5} lifetime cancer risk levels in California's 27 CCR §25705, which sets forth "no significant risk" levels of carcinogens for the purposes of Proposition 65, in terms of daily exposures. From these, *de minimis* cancer risks (i.e., lifetime cancer risks of 10^{-6}), commonly used by California for Notification Levels for other carcinogens can be calculated, using an assumed drinking water consumption of two liters per day.

[5] California's Office of Environmental Health Hazard Assessment (OEHHA)'s public health goal (PHG) for NDMA is established at the 10^{-6} risk level.

Text S1. Analytical methods

Basic water quality analyses: Water samples were filtered upon receipt using 0.7-μm glass-fiber filters pre-baked at 450 °C for 3 h and stored at 4 °C. Table S2 provides basic water quality results. UV_{254} was measured using an Agilent Cary 60 UV-Vis spectrophotometer and dissolved organic carbon (DOC) was measured using a Shimadzu TOC-L CPH total organic carbon analyzer. Specific ultraviolet absorbance at 254 nm ($SUVA_{254}$) was calculated by normalizing UV_{254} by DOC.

N-nitrosamine analysis: A modified US EPA Method 521 was used to measure 8 *N*-nitrosamines, including NDMA, NMOR, NMEA, NDEA, NDPA, NDBA, NPYR and NPIP. Briefly, 500-mL samples were spiked with 20 ng/L deuterated NDMA (NDMA-d6) and NMOR (NMOR-d8) for isotope dilution analysis and then extracted using Enviro-Clean Method 521 solid phase extraction cartridges (United Chemical Technologies, Inc, Horsham, PA). The cartridges were eluted with methylene chloride. The methylene chloride extracts were dried with sodium sulfate and concentrated to ~1 mL under a gentle stream of nitrogen gas. The extracts were analyzed using an Agilent 7890N gas chromatography system coupled with a 240 Ion Trap mass spectrometry system using large volume (5 μL) injections and methanol chemical ionization in the tandem mass spectrometry (i.e., MS/MS) mode. Method reporting limits were 7 ng/L due to the dilution of the samples described above.

UFC details: The DOC concentrations in the primary effluent samples ranged from 35-84 mg/L, while those in the industrial discharges varied from 5 mg/L in one of the electronics/metal finishing facility discharges to 904 mg/L in one of the cosmetics/personal care product manufacturing discharges (Table S2). Because the maximum ozone stock concentration was ~50

mg/L, some samples were diluted by the addition of the ozone stock solution to achieve the 0.8 mg O_3/mg DOC target. Samples for background *N*-nitrosamine analysis and the chloramination UFC test were diluted with deionized water to the same extent to maintain a consistent dilution of matrix components.

Table S2

Basic Water Quality Results

Sample	pH	DOC	UV_{254}	$SUVA_{254}$
		mg/L	cm^{-1}	$L\ mg^{-1}\ m^{-1}$
Primary effluent				
1	6.9	84	0.65	0.77
2	7.5	35	0.50	1.40
3	NA	39	NA	NA
4	7.2	52	0.49	0.93
5	7.2	41	0.50	1.23
6	7.7	41	0.51	1.24
7	7.7	51	0.48	0.95
8	7.5	48	0.46	0.95
Domestic sewage composite				
1	7.8	74	0.38	0.51
2	8.2	205	0.62	0.30
3	7.9	185	0.57	0.31
Domestic/commercial sewage composite				
1	7.5	84	0.39	0.46
2	7.9	190	0.63	0.33
3	8.1	185	0.63	0.34
Metal finishing/electronics				
1	7.2	5	0.07	1.33
2	8.7	10	0.14	1.43
3	9.9	81	0.32	0.39
4	7.2	22	0.35	1.61
5	7.1	29	0.27	0.92
Cosmetic/personal care product manufacturing				
1	6.6	517	1.09	0.21
2	7.3	62	0.22	0.36
3	7.9	904	0.93	0.10
Elastic waist band manufacturing				
1	10.3	88	0.67	0.76
Beer brewing				
1	8.2	19	0.28	1.46

NA = not analyzed

Table S3

Flowrates for industrial discharges

Discharge	Flowrate gallons/day	Percentage of Primary
Metals finishing/electronics	138000	0.25%
1	400	0.00073%
2	2500	0.0045%
3	1600	0.0029%
4	65	0.00012%
5	2800	0.0051%
Cosmetics	91000	0.17%
1	25000	0.045%
2	18000	0.033%
3	35000	0.064%
Elastic waistband manufacturer	22000	0.040%
Brewery	1034000	1.9%
Total industrial	**1285000**	**2.3%**