Supplementary Information

For

Validation of a Novel Direct-Injection Chemiluminescence-Based Method for N-Nitrosamine Analysis in Advanced-Treated Recycled Water, Drinking Water, and Wastewater

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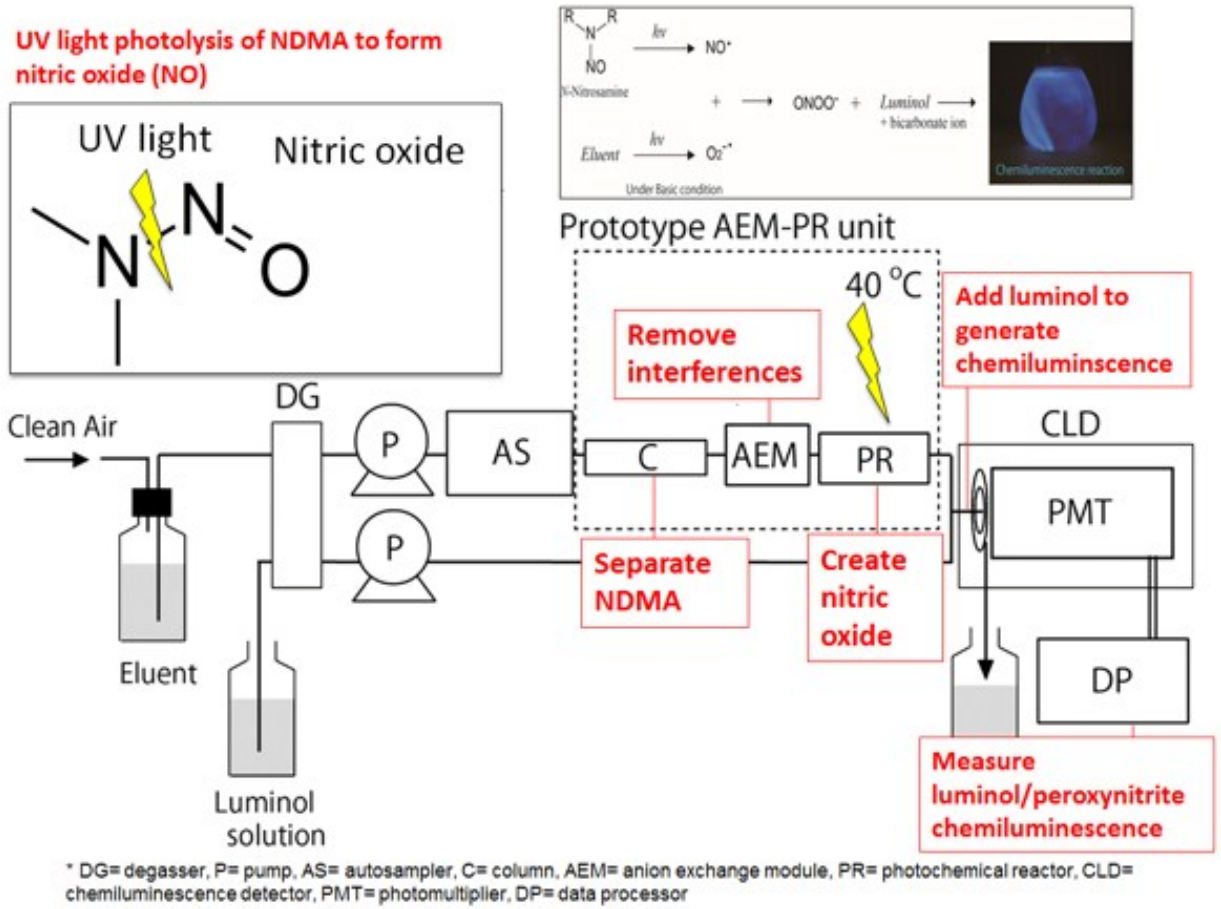
Figure S1: HPLC-AEM-PR-CL

* DG= degasser, P= pump, AS= autosampler, C= column, AEM= anion exchange module, PR= photochemical reactor, CLD= chemiluminescence detector, PMT= photomultiplier, DP= data processor

Table S1. Typical Water Quality During Sampling Period at OCWD's AWPF

Average Secondary Wastewater Effluent Water Quality Data						
Parameter	Units	Count	Minimum	Maximum	Average	Std Dev
Biological oxygen demand	mg/L	4	6.4	11	8.5	2.4
Ca	mg/L	12	57.8	89.6	74.4	11.6
Cl-	mg/L	12	244	298	272	18.4
EC	um/cm	83	1140	1720	1609.8	83.7
Fe	ug/L	12	230	603	339.1	100.9
MBAS*	mg/L	12	0.1	0.26	0.2	0.0
Mg	mg/L	12	24.1	27.8	25.8	1.1
Mn	ug/L	12	33.8	108	53.1	19.4
NH3-N	mg/L	52	0.1	4.2	1.7	0.9
NO2-N	mg/L	72	0.3	0.9	0.5	0.2
NO3-N	mg/L	72	7.7	15.7	11.4	1.7

Organic-N	mg/L	52	0.0	2.5	1.0	0.6
pH	UNITS	72	6.9	7.4	7.2	0.1
PO4-P	mg/L	51	0.2	0.9	0.4	0.2
SiO2	mg/L	12	13.2	28.8	20.8	4.7
SO4	mg/L	12	162	223	189.3	18.6
Suspended Solids	mg/L	140	1.5	24	4.9	2.2
Total Dissolved Solids	mg/L	51	822	1070	956.7	54
Total Kjeldahl Nitrogen	mg/L	52	0.3	4.4	2.7	1
Total Organic Carbon	mg/L	415	7.4	10.7	9	0.6
Total Potassium	mg/L	12	130	188	166.1	17.3
Turbidity	NTU	72	1.3	3.2	1.9	0.5
Average RO Feed Water Quality Data						
Ca	mg/L	12	59.2	85.9	73.2	10
Cl-	mg/L	12	230	294	272.5	17.6
EC	um/cm	71	1160	1730	1615.9	96.3
Fe	ug/L	12	105	165	130.8	20.3
MBAS*	mg/L	12	0.13	0.3	0.2	0.0
Mg	mg/L	12	23.8	26.9	25.3	1.1
Mn	ug/L	12	40.3	60.3	53.2	5.8
NH3-N	mg/L	20	0.7	3.9	2	0.9
NO2-N	mg/L	20	0.1	1.8	0.5	0.4
NO3-N	mg/L	20	9.4	13.3	10.9	1.0
Organic-N	mg/L	20	0.0	1.7	0.6	0.6
pH	UNITS	72	6.9	7.6	7.1	0.1
SiO2	mg/L	12	14.2	27.7	20.6	3.8
SO4	mg/L	12	172	235	197.3	17.7
Total Dissolved Solids	mg/L	52	852	1100	984.7	51.7
Total Kjeldahl Nitrogen	mg/L	20	0.7	3.8	2.5	0.9
Total Organic Carbon	mg/L	366	6.0	10.8	8	0.5
Total Potassium	mg/L	12	129	166	150.8	11.8
Total Cl2	mg/L	72	1.3	3.1	2.1	0.4
Average Finished Product Water Quality Data						
Ca	mg/L	53	10.6	14.8	13.2	0.9
Cl-	mg/L	13	4	6.5	5.1	0.8
EC	um/cm	362	66	116	96	6.7
Fe	ug/L	5	0.1	0.5	0.3	0.2
MBAS*	mg/L	5	0.0	0.0	0.0	0
Mg	mg/L	13	0.1	0.1	0.05	0
Mn	ug/L	5	0.1	0.1	0.1	0
NH3-N	mg/L	116	0.0	0.6	0.2	0.1

NO2-N	mg/L	116	0	0.1	0.0	0.0
NO3-N	mg/L	116	0.6	1.5	1	0.1
Organic-N	mg/L	116	0.0	0.2	0.0	0.0
pH	UNITS	73	6.9	8.7	7.8	0.3
PO4-P	mg/L	5	0.0	0.0	0.0	0
SiO2	mg/L	5	0.1	1.2	0.3	0.5
SO4	mg/L	13	0.1	0.7	0.5	0.2
Total Dissolved Solids	mg/L	53	40	66.5	49.9	5.5
Total Kjeldahl Nitrogen	mg/L	116	0.0	0.5	0.1	0.1
Total Organic Carbon	mg/L	364	0.0	0.3	0.1	0.0
Total Potassium	mg/L	53	29.5	42	35.6	2.7
Total Cl2	mg/L	5	0.7	1.1	0.9	0.1

*MBAS assay, is a colorimetric analysis test method that uses methylene blue to detect the presence of anionic surfactants (such as a detergent or foaming agent)

Table S2. N-nitrosamine concentrations in 20 ng/L N-nitrosamine spiked samples used to calculate accuracy and precision

Milli-Q									
Sample #	true value	conc. NDMA	Recovery	conc. NMOR	Recovery	conc. NMEA	Recovery	conc. NPYR	Recovery
1	20	20.0	100%	21.2	106%	24.9	125%	21.3	107%
2	20	20.5	102%	20.7	103%	25.8	129%	25.3	126%
3	20	20.2	101%	20.8	104%	23.2	116%	25.1	126%
4	20	20.2	101%	20.3	102%	25.6	128%	27.1	136%
5	20	20.6	103%	21.4	107%	24.6	123%	25.9	129%
ave		**20.3**	**102%**	**20.9**	**104%**	**24.8**	**124%**	**24.9**	**125%**
SD		0.2		0.4		1.0		2.2	
RSD		1%		2%		4%		9%	
Q1									
1	20	15.7	78%	23.5	118%	13.9	69%	17.7	89%
2	20	22.2	111%	20.1	101%	16.0	80%	15.4	77%
3	20	17.0	85%	21.3	107%	13.7	68%	13.2	66%
4	20	16.3	81%	18.2	91%	14.7	73%	13.8	69%
5	20	17.8	89%	22.3	112%	18.2	91%	12.8	64%
ave		**17.8**	**89%**	**21.1**	**105%**	**15.3**	**76%**	**14.6**	**73%**
SD		2.6		2.0		1.9		2.0	
RSD		14%		10%		12%		14%	
ROF									
1	20	18.6	93%	22.2	111%	19.7	98%	11.9	59%
2	20	21.1	105%	21.3	106%	21.3	106%	NA	NA
3	20	25.0	125%	21.3	107%	21.5	108%	17.7	88%
4	20	20.8	104%	21.1	105%	22.2	111%	13.7	68%
5	20	20.1	101%	22.4	112%	24.3	121%	15.0	75%
ave		**21.1**	**106%**	**21.7**	**108%**	**21.8**	**109%**	**14.6**	**73%**
SD		2.4		0.6		1.7		2.5	
RSD		11%		3%		8%		17%	
FPW									
1	20	19.1	95%	21.6	108%	25.8	129%	27.8	139%
2	20	19.0	95%	19.2	96%	23.0	115%	23.3	117%
3	20	19.8	99%	20.6	103%	26.4	132%	26.1	131%
4	20	20.4	102%	19.8	99%	26.0	130%	25.8	129%
5	20	20.0	100%	21.6	108%	24.6	123%	23.5	118%
ave		**19.7**	**98%**	**20.6**	**103%**	**25.2**	**126%**	**25.3**	**127%**
SD		0.6		1.1		1.4		1.9	
RSD		3%		5%		6%		7%	

*Q1= Secondary Wastewater Effluent

Table S3. Detection limit determinations for 4 N-nitrosamines

		NDMA								
				MRL					**MDL**	
spike	measured conc.	mean	sd	Hrpir	PIR	Upper PIR limit	Lower PIR limit	MRL criteria met?	t	DL
1.2	1.0							Upper PIR limit <150%		
1.2	1.1							Lower PIR limit >50%		
1.2	0.9	1.0	0.103	0.410	1.4	119%	50%		3.707	0.38
1.2	1.1									
1.2	0.9							yes		
1.2	1.0									
1.2	1.2									
1.5	1.6									
1.5	1.6									
1.5	1.3									
1.5	1.6	1.5	0.112	0.442	2.0	131%	72%	yes	3.707	0.41
1.5	1.4									
1.5	1.6									
1.5	1.6									
		NMOR								
1.8	1.9									
1.8	1.4									
1.8	1.7	1.7	0.200	0.792	2.5	140%	52%	yes	3.707	0.74
1.8	1.9									
1.8	1.6									

1.8	1.8									
1.8	1.8									

NPYR

3	3.4									
3	2.6									
3	2.6									
3	3.1	3.1	0.363	1.439	4.5	150%	54%	no	3.707	1.35
3	3.5									
3	3.2									
3	3.1									
5	4.3									
5	5.0									
5	4.5									
5	4.8	4.7	0.267	1.058	5.7	115%	73%	yes	3.707	0.99
5	4.9									
5	4.4									
5	4.9									

NMEA

3	5.8									
3	5.8									
3	6.3									
3	6.5	5.9	0.671	2.660	8.6	287%	110%	no	3.707	2.49
3	4.6									
3	6.1									
3	6.5									
5	6.6	6.1	0.306	1.212	7.4	147%	99%	yes	3.707	1.13
5	6.3									

5	5.8
5	5.8
5	6.0
5	6.2
5	6.4

Text S1: Additional samples for four participating utilities.

The water samples consisted of:

- Utility 1 – 13 drinking water samples collected on one occasion
- Utility 2 – 23 tertiary recycled water samples collected on 12 different occasions
- Utility 3 – 4 advanced treated potable reuse water samples collected on one occasion
- Utility 4 – 24 secondary treated wastewater (Orange County Sanitation District) samples collected on six different occasions

The samples from Utility 3 and Utility 4 were also analyzed by the Orange County Water District (OCWD) Philip L. Anthony Water Quality Laboratory resulting in a three-way split.

Text S2: *N*-nitrosamine analytical method for OCWD Analytical Laboratory

The method employs an isotopic dilution technique for the calculation of results - using NDMA-d_6 and NMOR-d_8 as the surrogate. One liter of sample is extracted with methylene chloride in a separatory funnel. The methylene chloride extract is concentrated to a volume of 1 mL. Analysis is performed by a GC/MS system equipped with an ion trap detector using methanol chemical ionization.

Table S4. *N*-nitrosamine analytical methods used in split sampling campaigns.

Laboratory	Method	Extraction	Instrument	MDL
OCWD Laboratory	Internal method	liquid-liquid with MC[a]	GC/MS ion trap	2 ng/L
Utility 1	Modified EPA 521	coconut charcoal SPE	GC/MS/MS	2 ng/L
Utility 2	Modified EPA 1625B	coconut charcoal SPE	GC/MS	50 μg/L
Utility 3	EPA 521	coconut charcoal SPE	GC/MS/MS	2 ng/L
Utility 4 (OCSD)	Internal method	liquid-liquid with MC	GC/MS	5 ng/L

[a]MC- methylene chloride

Table S5. Wastewater split samples

Date	Lab	Sample location NDMA (ng/L)			
		Plant 1 effluent	P1 Filtrate	P2 Filtrate	Plant 2 effluent
5/24-25/17	OCSD	17.4	37.7	199	54.8
	AWQAL	15.1	19.2	333	39.9
	R&D	15.7	42.3	226.5	38.5
5/30-31/17	OCSD	34.6	40.4	260	26.1
	AWQAL	28.2	33.6	229	12.6
	R&D	26.3	68.9	445.2	23.1
6/6-7/17	OCSD	40.6	104	257	37.3
	AWQAL	30.1	40	138	23.5
	R&D	35.2	67.3	4825.8	24.7
6/12-13/17	OCSD	37	3180	3380	25.5
	AWQAL	18.8	25.8	138	16.4
	R&D	18.8	45.8	1385.7	20
6/22-23/17	OCSD	39.6	83.24	247.82	43.96
	AWQAL	20.3	27.7	499.3	16.9
	R&D	23.3	57.7	1277.4	20.9

6/29-30/17	OCSD	30.36	64.23	168.09	17.76
	AWQAL	16.5	19.8	31.3	10.1
	R&D	21.4	18.6	296.2	28.3