Supporting Information

1. Precursor recovery (Section 2.3)

Recovery of NDMA precursors varied in the isolates from 63% to greater than 100% (Table 1 in main text). High recovery of precursors may be explained by low level contamination from the reagents, or column contamination. Although the Milli-Q control samples generally did not contain NDMA or NDMA FP, the isolates of Milli-Q water ranged from 0 to 5 ng/L of NDMA FP. Therefore, it is possible that the cartridge itself or reagents used during isolation may contribute NDMA or NDMA precursors.

In cases where the initial NDMA (T_0 NDMA, Table 1) was similar to NDMA FP, the high recovery of precursors may be partially explained by NDMA present in the initial samples that sorbed and eluted from the MCX cartridge. Based on the pKa of the NDMA nitroso group (3.5) and the pH during column loading (3), approximately 77% of the initial NDMA may have been retained (Chemicalize.org 2016), eluted into the isolate, and contributed to the reconstituted NDMA FP measurements. For example, the RO permeate from the older membranes in the first sampling event had precursor recovery in the isolate of 170% if we assume the initial NDMA is poorly extracted, but 77% when NDMA ionization and partial retention is considered (Table 1). However, applying the same assumptions of recovery of initial NDMA to other samples results in a calculated 0% recovery (all isolated NDMA FP is from NDMA present in the sample that is sorbed and eluted from the extraction columns).
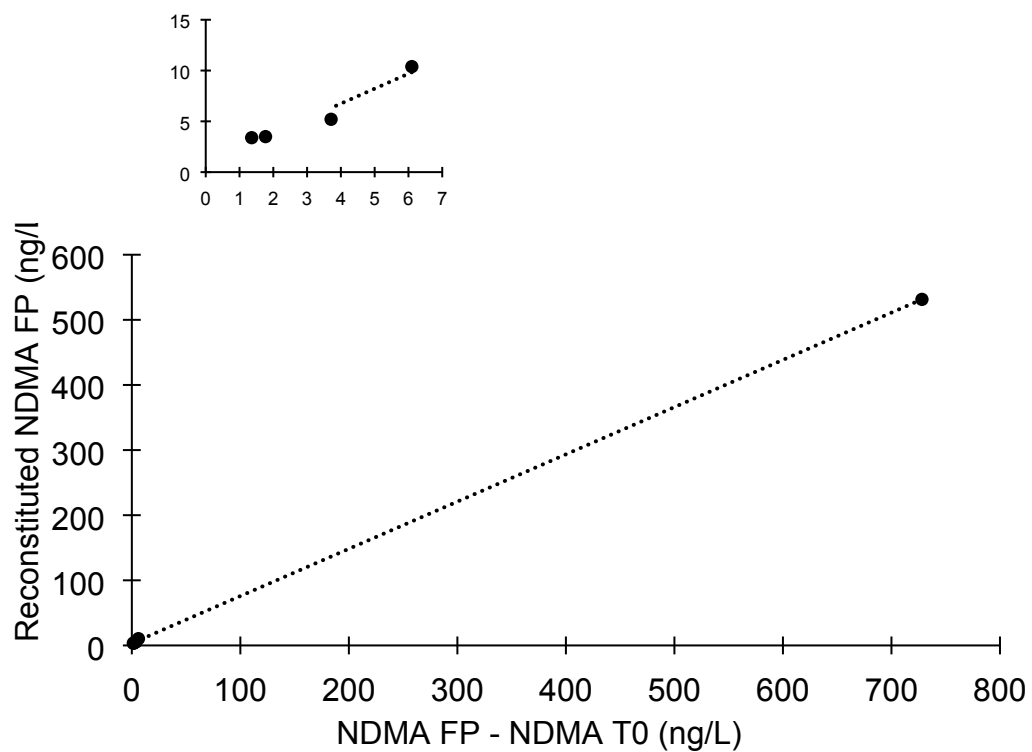
Figure SI-1. Comparison of NDMA FP of the as-collected samples versus the reconstituted isolate NDMA FP for the first sampling campaign. Inset shows linear correlation for samples with NDMA FP <15 ng/L.
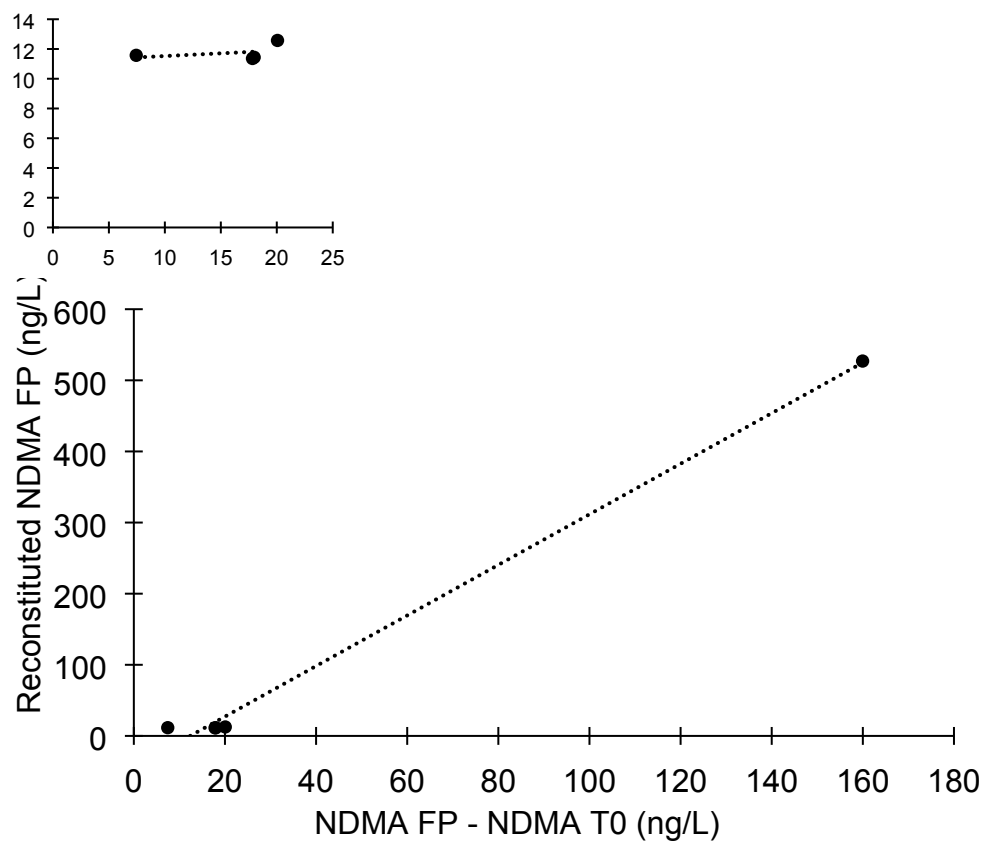
Figure SI-2. Comparison of NDMA FP of the as-collected samples versus the reconstituted isolate NDMA FP for the second sampling campaign. Inset shows linear correlation for samples with NDMA FP <15 ng/L.
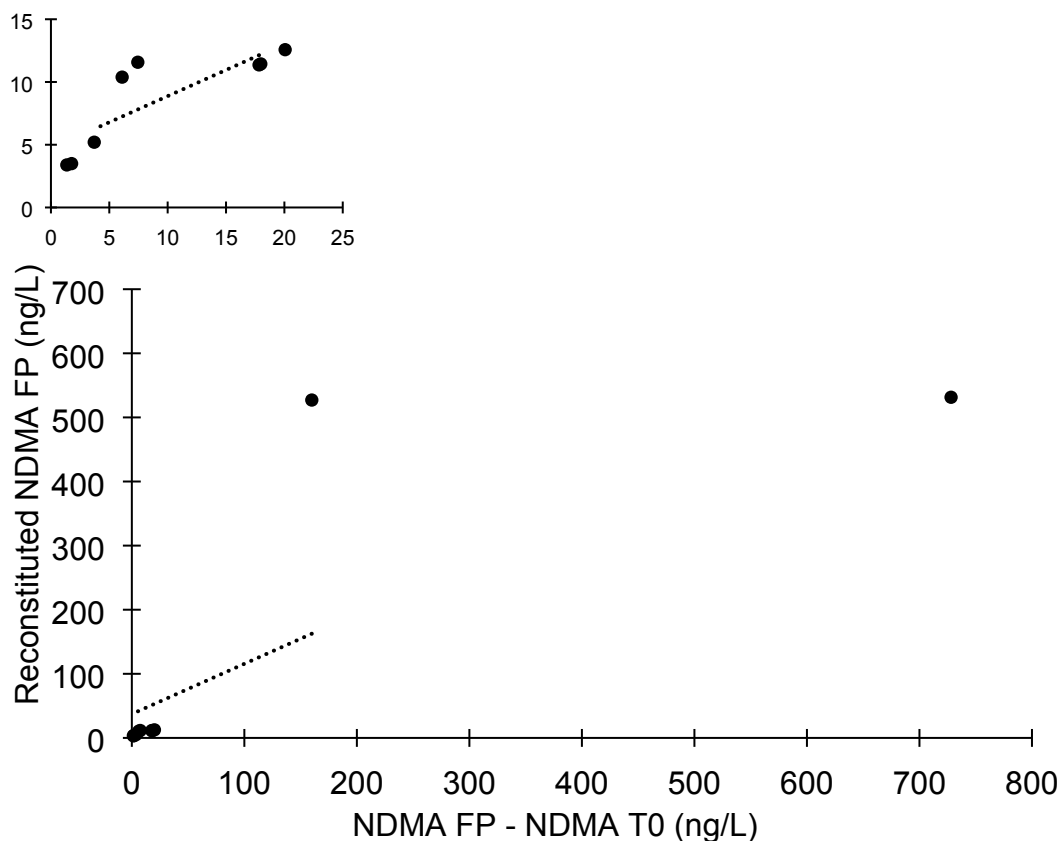
Figure SI-3. Combined data sets and regressions for comparison of NDMA FP of the as-collected samples versus the reconstituted isolate NDMA FP. Inset shows linear correlation for samples with NDMA FP <15 ng/L.

Table SI-1. RPD and percent recovery values for extraction procedure

	C_0 NDMA (ng/L)	C_3 (after chloramination) NDMA (ng/L)	RPD	NDMA FP ($C_3 - C_0$) (ng/L)	Reconstituted isolate NDMA FP (ng/L)	RPD	Percent recovery
First Sampling Event							
MFE	19	747	NA	728	531	9%	73%
ROP Older	7	14	NA	6	10	45%	>100%
ROP Newer	6	7	NA	1	3	1%	>100%
ROP Bulk	6	7	NA	2	3	10%	>100%
UVP	ND	4	NA	4	5	13%	>100%

Milli-Q	0	0	NA	NA	5	11%	>100%
Second Sampling Event							
MFE	44	204	17%	160	527	3%	>100%
ROP Older	21	39	1%	18	11	2%	64%
ROP Newer	16	34	4%	18	11	1%	64%
ROP Bulk	13	33	5%	20	13	8%	63%
UVP	3	10	2%	7	12	9%	>100%
Milli-Q	0	3	100%	3	5	100%	>100%

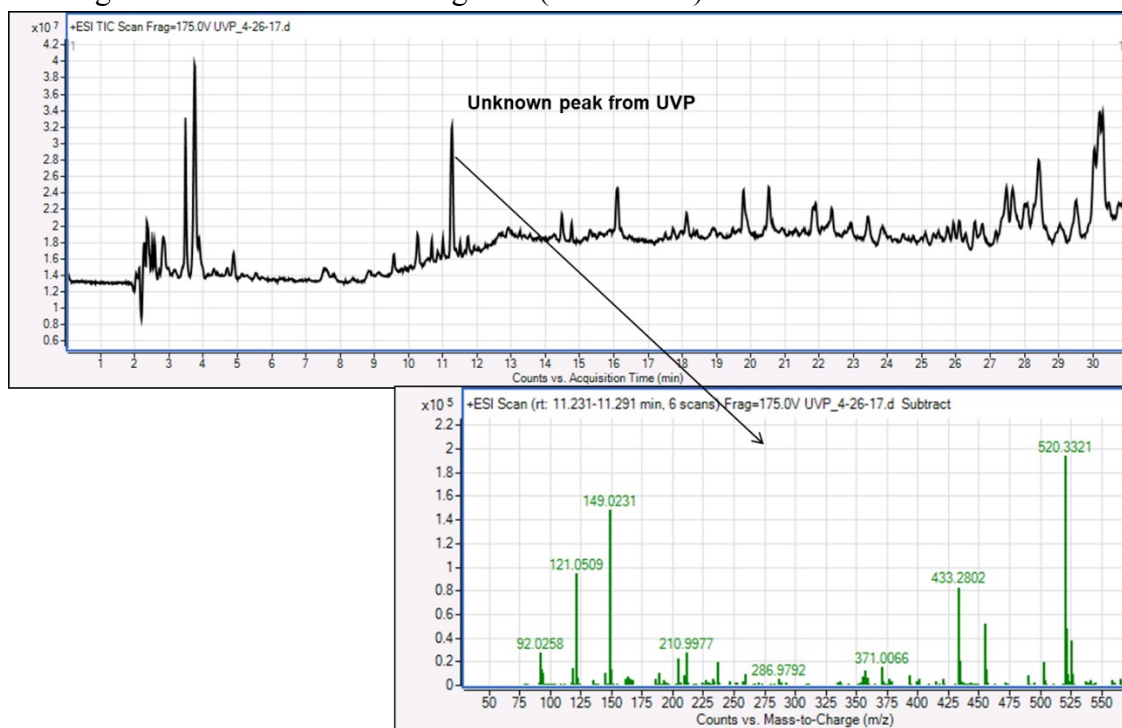2. Investigation of total ion chromatograms (Section 3.4)

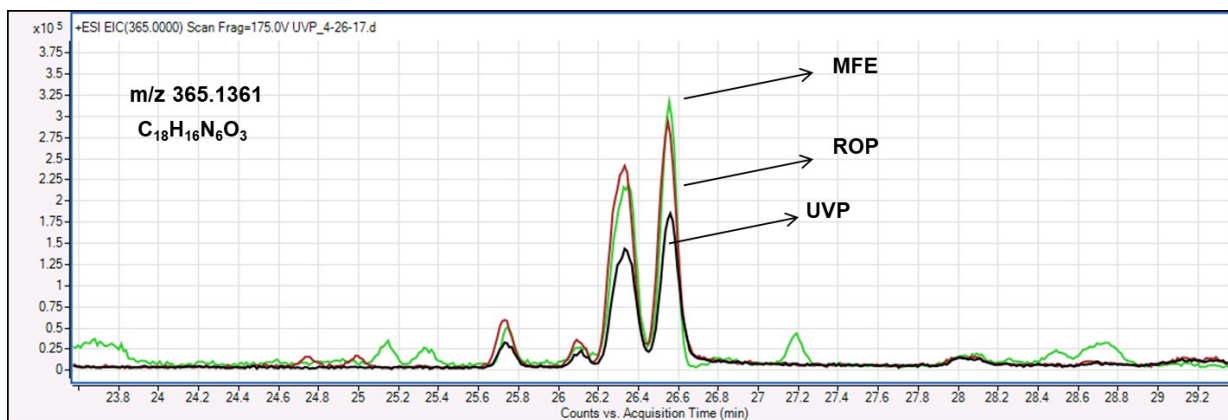Figure SI-4. Mass spectrum of unknown in UV effluent sample

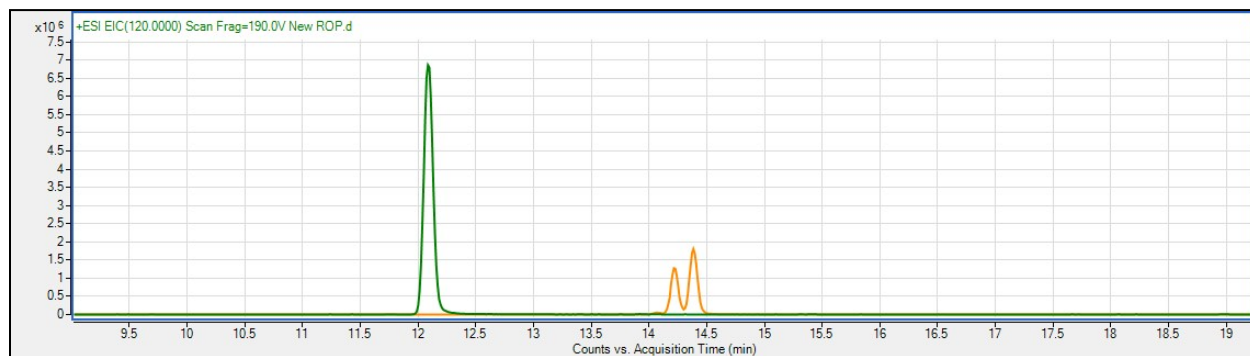Figure SI-5. Possible trimer in samples for Event 2.

Figure SI-6. Benzotriazole (green, m/z 120 EIC) and methylbenzotriazole isomers (yellow, m/z 134 EIC) in permeate from the newer membrane and UV permeate sample in event one, respectively.

Figure 6 shows the UV permeate and new membrane permeate TICs from the first event. These show a compound removed at approximately 12 minutes by UV/AOP treatment and the appearance of a set of isomers at 26-27 min with a single mass of m/z 365.1361. The peak at 12.0 minutes has a mass of m/z 120.0484. This compound was tentatively identified as benzotriazole, a common compound in wastewater that is used in dishwasher detergent as a corrosion inhibitor and is also contained in aircraft deicing fluids [12]. Its companion compound, methylbenzotriazole, at m/z 134 is also present in the ROP-New sample as two isomers (Figure 7). Both of these compounds are removed by UV/AOP treatment.
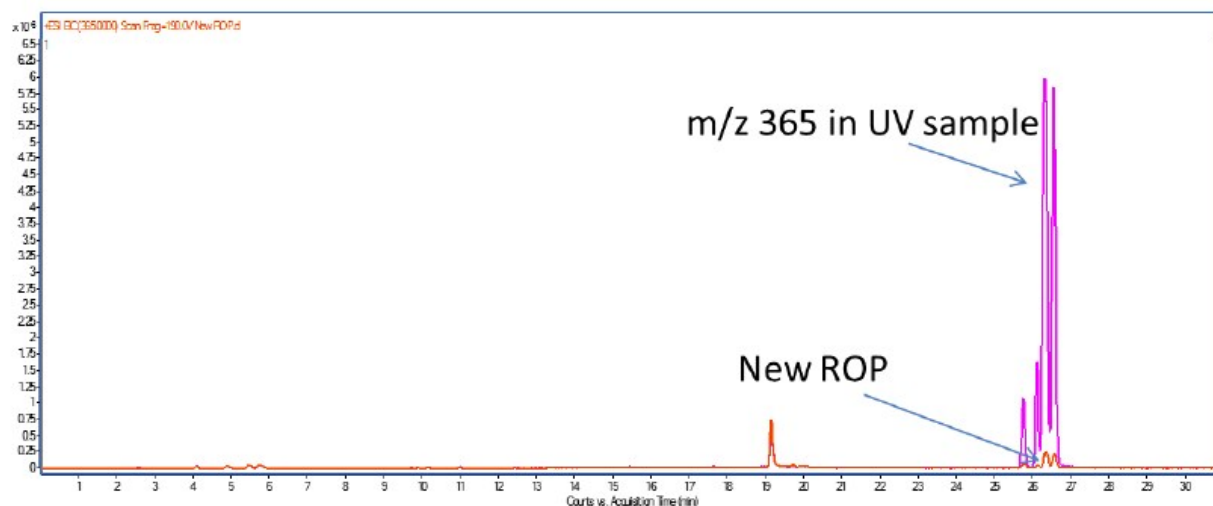

Figure SI-7. UV effluent sample (pink) has large m/z 365 peaks (benzotriazole isomers). Permeate from a newer membrane (orange) has trace levels.

However, in this event, it appears that their removal may actually be polymerization into a series of isomers at m/z 365 (7). The identity and structures of the m/z 365 ions are not known, but have the formula of $C_{18}H_{16}N_6O_3$, which is consistent with the replacement of one of the nitrogen atoms with oxygen and the formation of a trimer of the m/z 120 ion. Figure 8 shows that the m/z 365 ion is a major ion in the UV permeate sample and at a trace level in the new membrane permeate. Published literature does not show that benzotriazole forms a trimer during UV exposure alone, but the literature does not include any research related to UV/AOP, where oxidation is more likely.
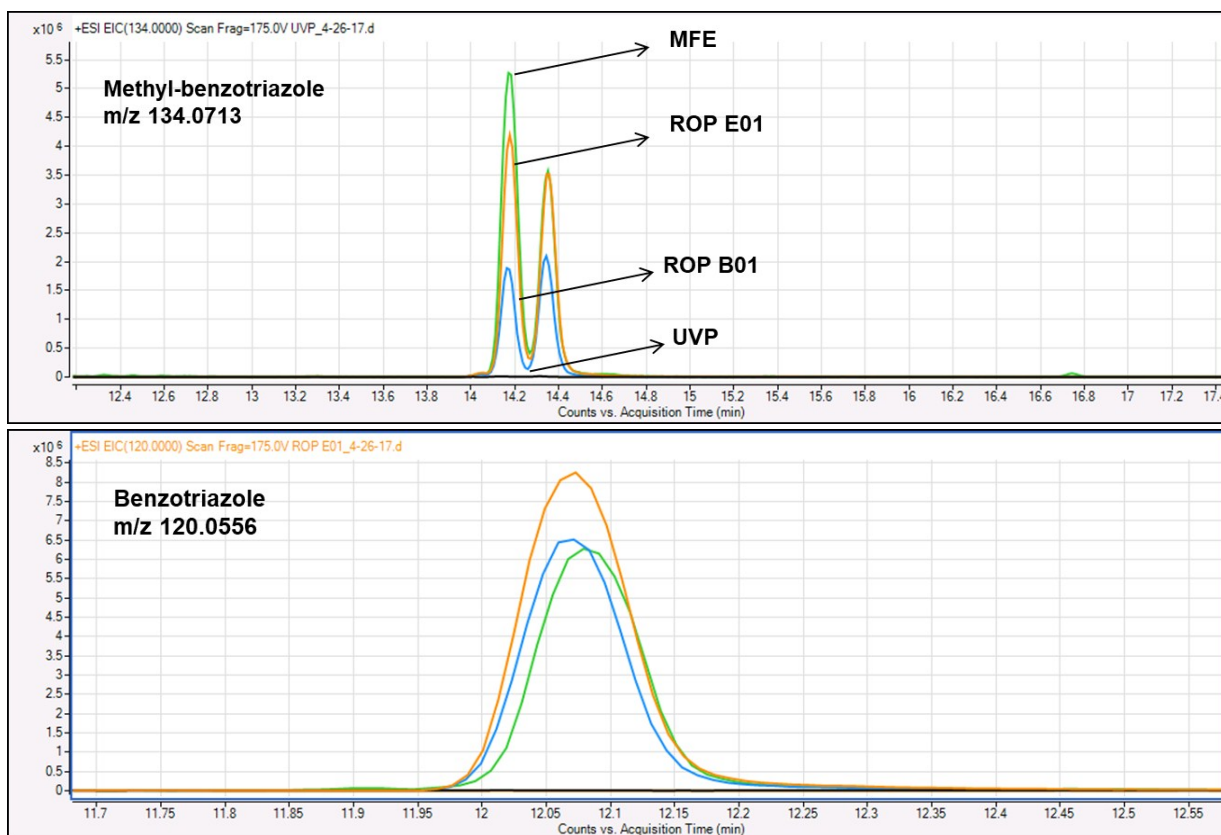
Figure SI-8. Methyl-benzotriazole and benzotriazoles in samples from event two
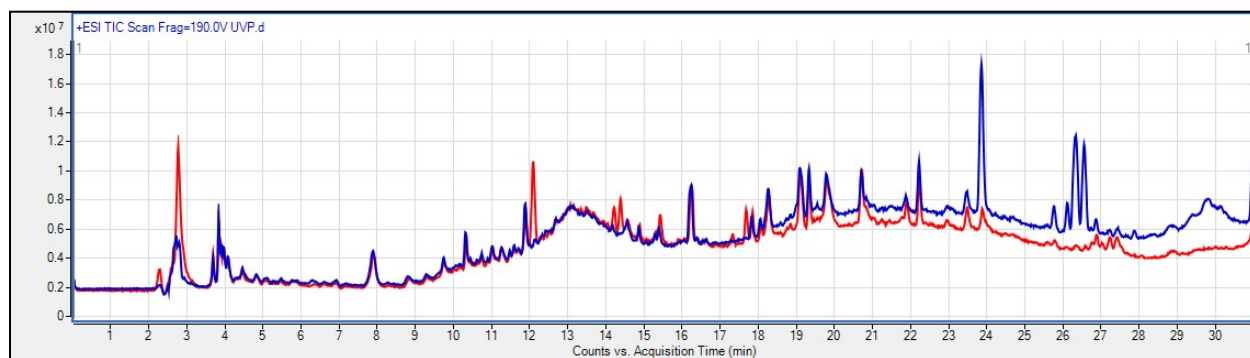

Figure SI-9. Permeate from a newer membrane (red) and UV effluent (Blue), total ion chromatogram.

3. Auto MS-MS analysis to detect known or potential NDMA precursors (Section 3.5)
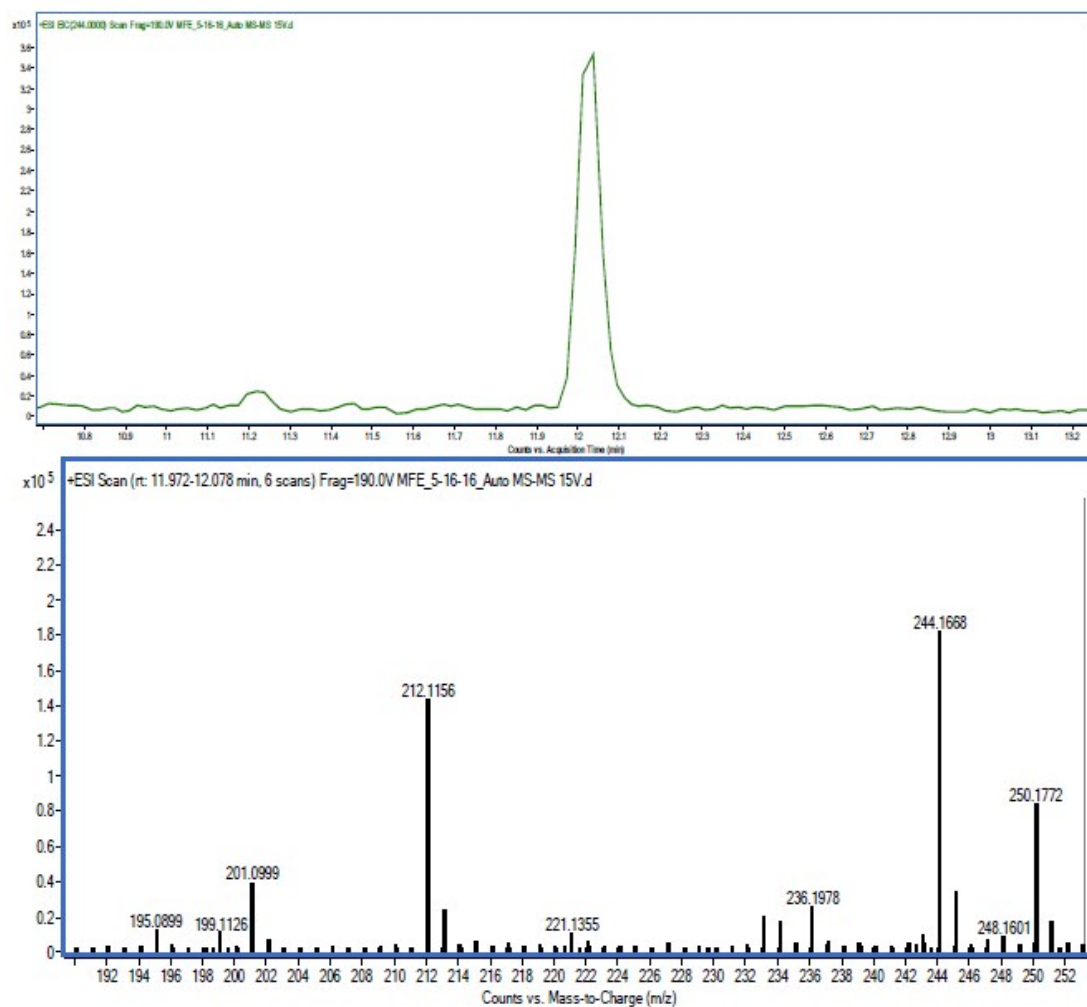

Figure SI-10. Top panel shows a chromatographic peak in the microfiltration effluent sample. The lower panel shows the mass spectrum with two peaks separated by a neutral loss of 45.06 u at 12 min during auto MS-MS (m/z 244 and m/z 199). This spectrum also shows the fragmentation pattern of the 244.1668 m/z ion, which is consistent with 3-hydroxymorphinan.
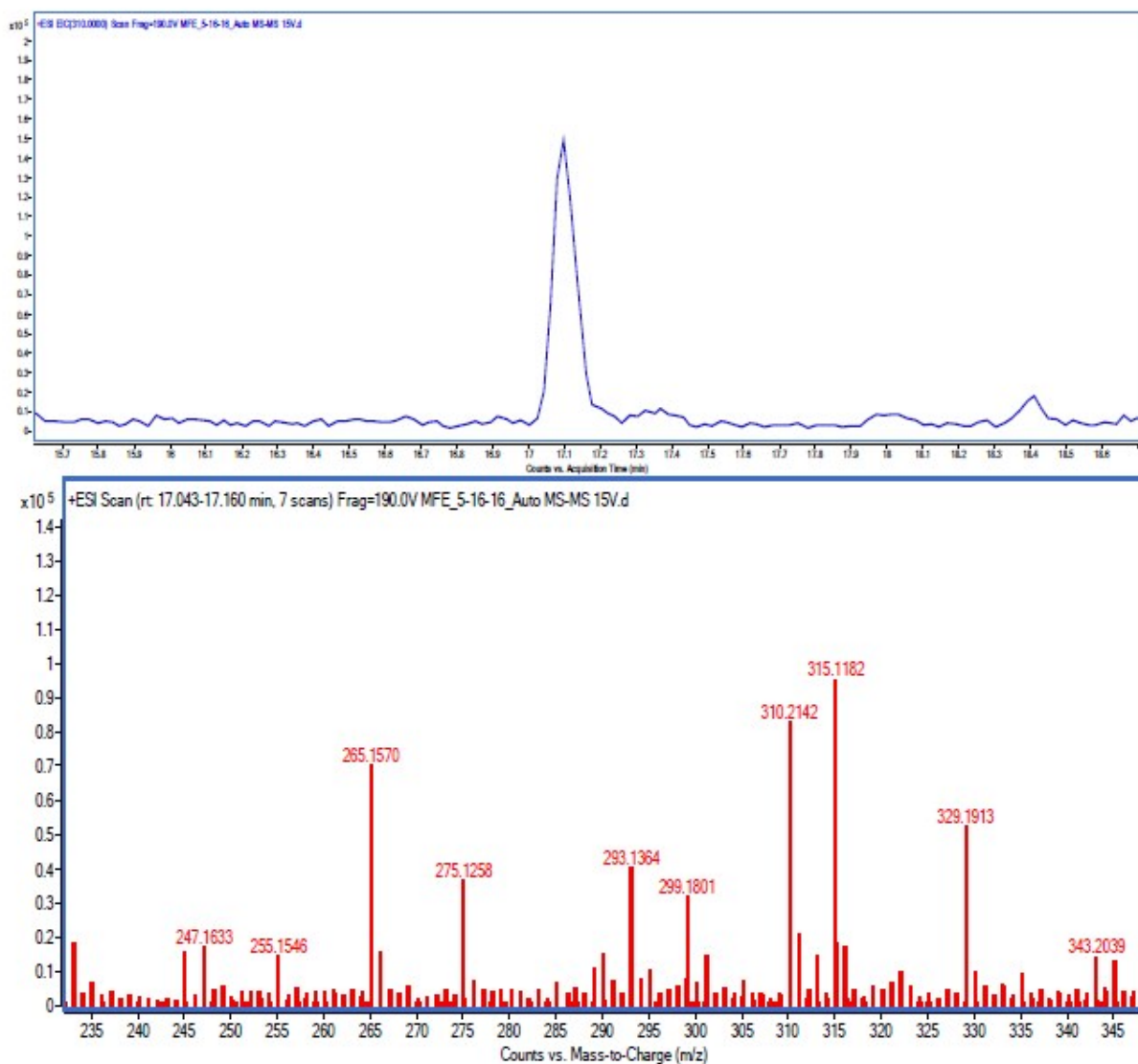
Figure SI-11. Top panel shows a chromatographic peak in the microfiltration effluent sample. The lower panel shows the mass spectrum with two peaks separated by a neutral loss of 45.06 u at 17.1 min during auto MS-MS (m/z 310 and m/z 265). This spectrum also shows the fragmentation pattern of the 310.2142 m/z ion, which is consistent with methadone.
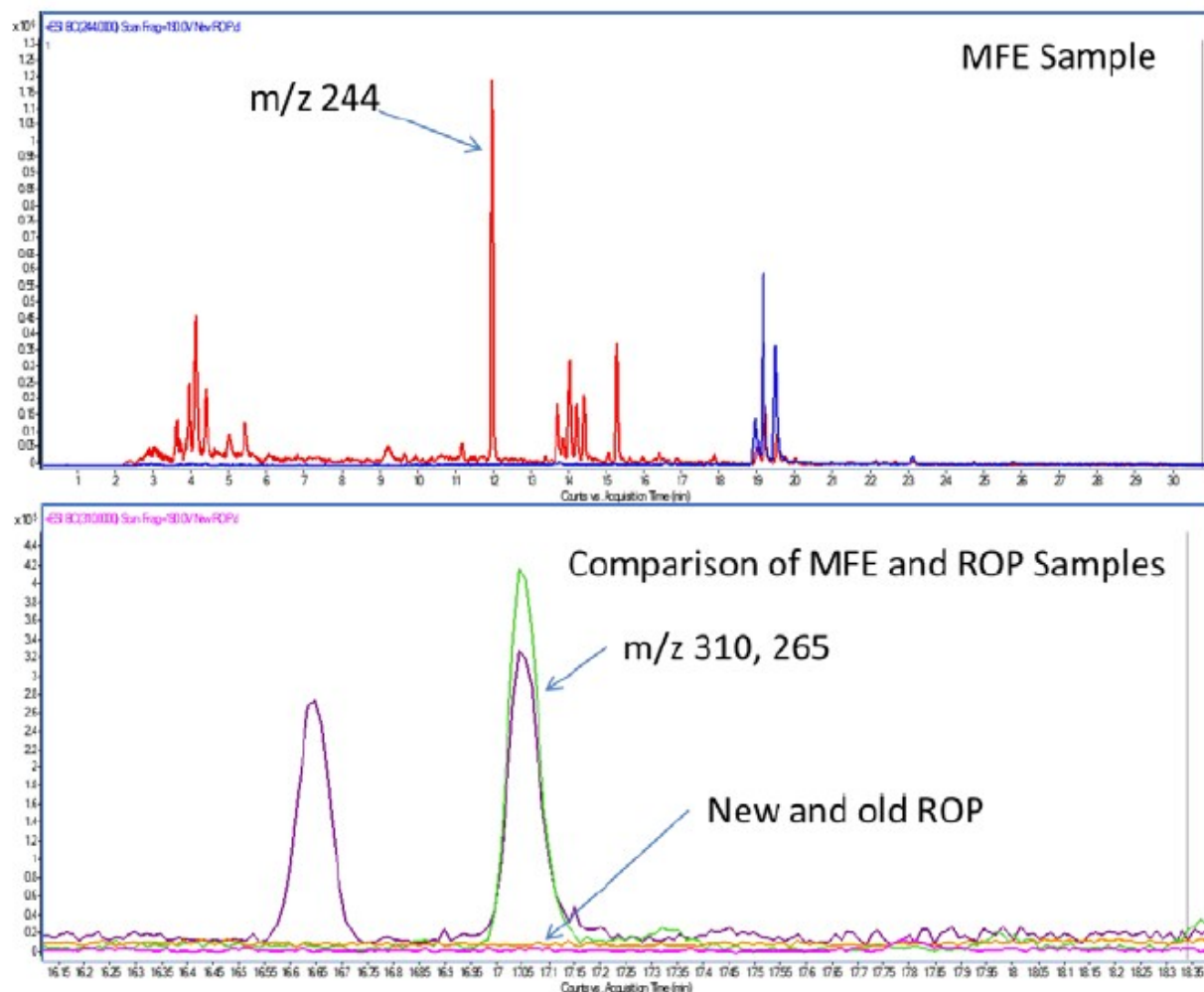
Figure SI-12. Top panel shows the extracted ion chromatograms for m/z 244 (3-hydoxymorphinan) for the microfiltration effluent (red) and permeate from a newer membrane (blue) isolates. The permeate from the older membrane sample was similar, showing that this compound is well rejected by both newer and older membranes. Bottom panel shows extracted ion chromatograms for m/z 310 (methadone, green) and its product ion, m/z 265 (purple), showing good rejection of this compound by both the older (orange) and new (pink) RO membranes
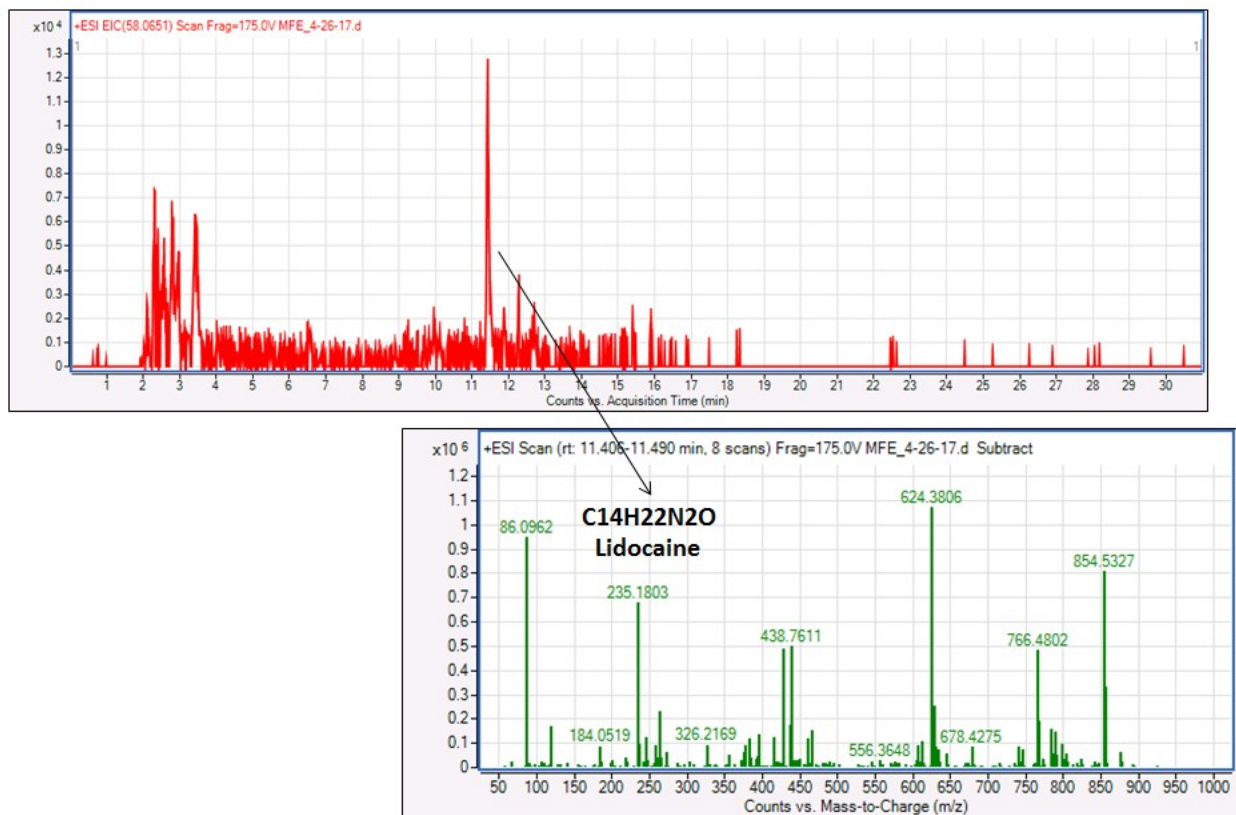
Figure SI-13. Extracted ion chromatogram of m/z 58.0651, tentatively identified as lidocaine
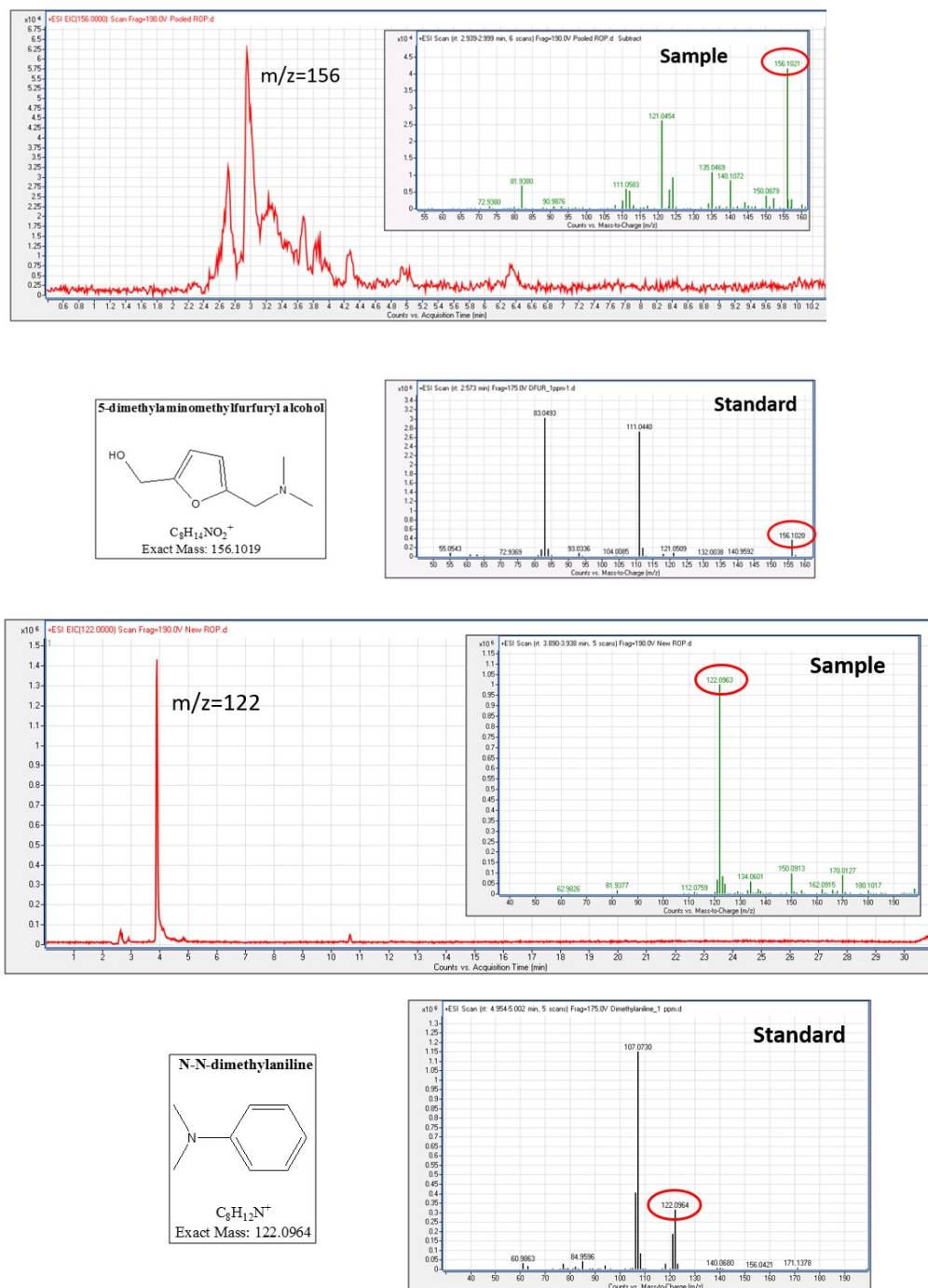
Figure SI-14. Extracted ion chromatograms and mass spectra for 5-dimethylaminomethylfurfuryl alcohol and *N-N*-dimethylaniline for both: samples and pure standards.

4. Non-target Analysis to Detect NDMA Precursors Using N-nitrosamine Precursor Database

(Section 3.6)

Table SI-2: Abundances (peak intensity) of NDMA precursor database matches in all samples.

Name	Event 1 Microfiltration Effluent	Event 2 Microfiltration Effluent	Event 1 New Membrane RO Permeate	Event 2 New Membrane RO Permeate	Event 1 Older Membrane RO Permeate	Event 2 Older Membrane RO Permeate	Event 1 RO Permeate (All units)	Event 2 RO Permeate (All units)	Event 1 UV Effluent	Event 2 UV Effluent
3-N,N-DAPSIS		281,594								
Amitriptyline		604,641								
Azithromycin	2,123,934	2,564,565								
Citalopram	426,963	687,116								
Clarithromycin	666,703	608,977								
DEET	1,899,831	1,560,950	18,668	19,830	25,933	22,729	30,852	16,996	16,248	12,740
Des-venlafaxine		1,443,480								
Diltiazem	173,739									
Dimethylaminoacetonitrile		295,393				66,560				
Dimethylaminoethanol		101,177								
Dimethylphenethylamine		30,851								
Dimethyltert-butylamine		401,626								
Diphenhydramine	71,026	142,941								
Dimethylaminomethylfurfuryl alcohol			44,931		37,162		47,835		11,181	
Diuron	11,865	26,448								
Lidocaine		1,406,411								
Methyl Orange		42,096								
Methylene blue		63,109								
N,N-Dimethylaniline		149,283	1,360,711		1,009,927		1,017,559		1,821,715	
N,N-Dimethylbuthylamine		401,626								
N,N-Dimethylisopropylamine		28,243								
Tramadol	1,277,428	957,344								
Venlafaxine	838,086	726,329								

5. Non-target Analysis to Detect Trace Organics Using a Proprietary Database of Anthropogenic Chemicals (Section 3.7)

Table SI-3: Abundances (peak intensity) of pharmaceutical and pesticide database matches in all samples.

Name	Event 1 Microfiltration Effluent	Event 2 Microfiltration Effluent	Event 1 RO Permeate B01 (Newer)	Event 2 RO Permeate B01 (Newer)	Event 1 RO Permeate E01 (older)	Event 2 RO Permeate E01 (older)	Event 1 RO Permeate (All units)	Event 2 RO Permeate (All units)	Event 1 UV Effluent	Event 2 UV Effluent
Acetaminophen	159,992	22,486								
Albuterol	136,287	105,613								
Atenolol	3,834,006	2,457,727			70,539	27,447	65,654			
Azithromycin	2,124,461	2,568,228								
Azoxystrobin	51,382	38,629								
Bupropion Metabolite	1,079,520	1,212,815								
Caffeine	272,752	118,482								
Carbamazepine	966,202	1,327,117								
10-Hydroxy-carbamazepine	1,008,311	258,166								
Carbendazim	383,495	363,764			36,134	27,102	25,226			
Clarithromycin	667,145	610,717								
DEET	1,899,831	1,560,950	18,668	19,830	25,933	22,729	30,852	16,996	16,248	12,740
Dehydronifedipine	95,532	91,908								
Desmethyl-venlafaxine	2,313,337	1,443,480								
Dextromethorphan	748,560	1,002,000								
Dextrorphan	5,252,477	4,508,742	10,784	14,934	28,146	22,610	26,058	14,089		
Diphenhydramine	71,026	142,941								
Diuron	11,865	25,809								
Erthyromycin	175,425	238,246								
Erthyromycin Anhydrate	333,239	243,324								
Fluoxetine		26,031								
Fluridone		17,747								
Gabapentin	801,399	262,721								
Imazalil	35,357	20,836								
Lamotrigine	3,218,367	2,072,689	40,527	38,639	218,378	149,425	204,918	49,455	32,058	6,848
Lamotrigine Glucuronide	54,905	28,733								
Methadone	407,130	302,423								
Metoprolol	4,466,477	3,028,674	24,194	16,586	153,802	73,134	147,962	23,444		
Oxycodone	88,710	77,141								
Parathion-methyl		15,688								
Prometon		540,122								
Propazine		124,400								
Propranolol	277,912	217,909								
Simazine		43,184								
Sucralose	38,038	43,335								
Sulfamethoxazole	58,014	98,022		10,162		6,094		7,575		11,708
Terbuthylazine	80,403	124,517								
Thiabendazole	359,778	294,223	16,663	13,104	74,822	42,946	50,144	10,114		
Tramadol	1,277,428	957,344								
Trimethoprim	1,926,449	1,216,299		8,683	41,976	38,459	49,950	10,712		
Venlafaxine	838,086	726,329								