

Sex and Drugs: I Swear I Didn't Want to Use this Title but the Organizers Made Me To See if You Were All Paying Attention



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Kaitlyn Colella, Dana Kolpin,
Ed Furlong, William Foreman

<http://toxics.usgs.gov/regional/emc/index.html>



USGS Toxics Program – NY WSC



I am much more comfortable with:

How and When to Sample for Microconstituents



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USGS Toxics Program
United States Geological Survey – NY WSC

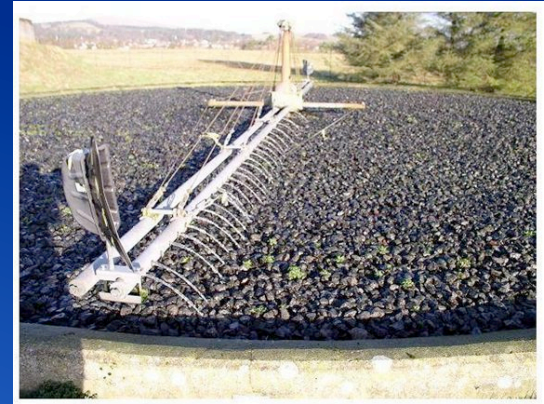


What are You Going to Learn From This Talk?

- If You Don't Sample Carefully, you will have a hard time defending your conclusions
- Hormone and Pharmaceuticals vary daily, and some can vary weekly, seasonally, and on a decadal time series
- Data that can address long-term and seasonal variability at WWTP are lacking

What Factors Affect Pharmaceutical Concentrations?

- Changes in PMF Formulation
- Changes in Plant Technology
- Diurnal Variability
- Extreme Events CSO Discharges
- Seasonal Occupancy/Depopulation of Areas (College Students)



Causes of Variability in Concentrations of Emerging Contaminants in Wastewater

- Sampling at Select WWTP between 2003-2013 allows for long-term trend assessment of pharmaceuticals
- Additional Sampling allows for assessment of concentration variability on differing time scales
- Use these data to assess factors affecting pharmaceutical (and other EC) variability

Analytical Methods

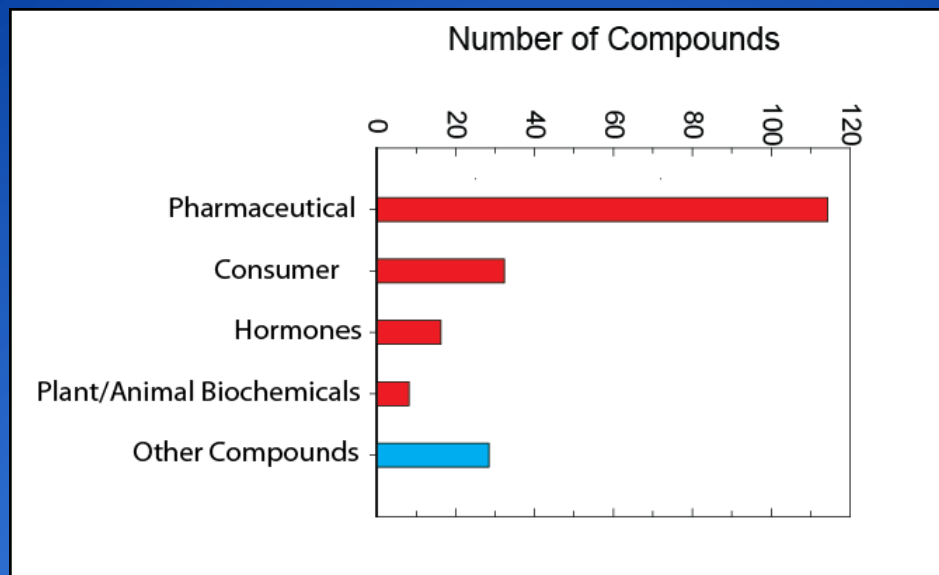
- For Trends work, used USGS NWQL Wastewater Method
- Wastewater Method Supplemented by added Pharmaceuticals (Phillips and others, 2010; Zaugg and others, 2014).
- QA – Some low-level blank detects, replicate differences around
- In last few years, began use of NWQL Hormone and new Pharmaceutical Methods

Use of New Methods

- New Hormone Method Used in Phillips and others, 2012 (CSO Study)
- New Pharmaceutical Method (SH2440) and Wastewater Addon (LC8144) used in variety of Studies:
 - PMF Study (described today)
 - Septic System Studies in New England/New York
 - Different Small Studies of Effluent/Influent that are designed to characterize various time scales over which Pharmaceutical concentrations vary

Study Design – Analytical Methods

- LC9017 (New Pharmaceutical Method)
- Sh1433/LC8144 (Wastewater Indicators/Custom Pharmaceutical Method)
- LC 2433 (Filtered Hormones)



Approach: All Pharmaceuticals Included Will be Discussed, Using Small Print and No Graphics, and you will hate me for it

Table 1
Concentrations across all 50 effluent samples.

Analyte	CasNumber	Method ^a	RL ^b (ng/L)	Number of measurements	Number of detections	PEC ^c (ng/L)	Mean ^d (ng/L)	Max ^d (ng/L)
10-Hydroxy-amitriptyline	64520-05-4	1	5	50	6	5029	<RL	<RL
Acetaminophen	103-90-2	1	5	50	7	306,955	79 (300)	1500 (4500)
Albuterol	18559-94-9	1	9.7	50	27	473	1.4	35
Alprazolam	28981-97-7	1	9.1	50	15	103	10	31
Amitriptyline	549-18-8	1	5	50	20	5029	11	110
Amlodipine	111470-99-6	1	5	50	11	94	6.9	18
Amphetamine	51-63-8	1	1.6	50	5	387	3.5	40
Atenolol	29122-68-7	1	6	50	48	4137	940	3000
Atorvastatin	134523-00-5	1	38	48	4	2906	<RL	<RL
Benzotropine	86-13-5	1	10	50	0	33	ND	ND
Carbamazepine	298-46-4	1	4.4	50	48	5607	97 (140)	240 (460)
Ciprofloxacin	85721-33-1	1	10	49	30	2561	67 (72)	280 (320)
Clonidine	4205-91-8	1	35	50	0	43	ND	ND
Desmethylsertraline	79902-63-9	1	9.4	50	9	615	9.9 (10)	24
Diltiazem	33286-22-5	1	2.8	49	41	3343	85	340
Diltiazem-desmethyl	130606-00-9	1	1.6	50	34	3343	24	100
Enalapril	76095-16-4	1	1	50	9	369	4.5	38
Enalapril	76095-16-4	2	11	49	13	369	13	32
Enalaprilat	76420-72-9	2	9	49	5	369	14 (18)	150
Flufenicol	73231-34-2	2	60	49	0	NA	ND	ND
Fluocinonide	356-12-7	1	10	50	0	12	ND	ND
Fluoxetine	59333-67-4	1	28	48	18	NA	8.7	31
Fluticasone	57-83-0	1	19	50	0	42	ND	ND
Furosemide	54-31-9	1	38	50	45	7283	280 (350)	810 (2100)
Gemfibrozil	25812-30-0	1	10	50	38	NA	420 (480)	2300
Hydrochlorothiazide	58-93-5	1	10	50	50	13,947	1100 (1200)	2800
Hydrocodone	143-71-5	1	38	50	22	2561	22 (24)	92 (100)
Hydrocortisone	50-23-7	1	25	50	0	2368	ND	ND
Ibuprofen	15687-27-1	1	12	50	23	20,257	460 (690)	4200 (4600)
Lincomycin	859-18-7	2	8	49	0	NA	ND	ND
Lisinopril	83915-83-7	2	45	49	23	814	180 (1700)	3300 (13,000)
Melengestrol acetate	2919-66-6	2	9	49	0	NA	ND	ND
Methylprednisolone	83-43-2	1	25	50	0	250	ND	ND
Metoprolol	56392-17-7	1	14	50	49	1451	410 (450)	660 (1200)
Norethindrone	68-22-4	1	6.9	50	0	111	ND	ND
Norflouxacin	83891-03-6	1	7.2	46	8	NA	7.7	15
Norverapamil	67814-42-4	1	4.4	48	25	5328	5.8	20
Ofloxacin	82419-36-1	2	10	49	44	NA	160	660
Oxycodone	124-90-3	1	2.5	50	30	NA	53	310
Paracetamol	110429-35-1	1	5	50	0	NA	ND	ND
Prednisolone	50-24-8	1	11	50	0	1421	ND	ND
Prednisone	53-03-2	1	30	50	0	2194	ND	ND
Progesterone	80474-14-2	1	188	50	2	NA	<RL	<RL
Progesterone	80474-14-2	2	9	49	0	NA	ND	ND
Promethazine	58-33-3	1	5	50	0	1668	ND	ND
Propoxyphene	1639-90-7	1	16	48	12	8300	17	34 (46)
Propranolol	318-98-9	1	4.4	50	44	991	33	260
Ranitidine	66357-59-3	1	11	50	19	NA	120	1400
Sertraline	79559-97-0	1	5	50	32	615	21	71
Simvastatin	79902-63-9	1	41	50	12	548	<RL	<RL
Sulfamethoxazole	122-11-2	2	1	49	9	NA	ND	ND
Sulfamethazine	57-68-1	2	10	49	1	NA	12	87
Sulfamethoxazole	723-46-6	1	1.6	50	40	NA	910	2900
Sulfamethoxazole	723-46-6	2	1	49	44	NA	330	1000
Testosterone	58-55-9	1	3.5	50	0	NA	ND	ND
Testosterone	58-55-9	2	1	49	0	NA	ND	ND
Theophylline	58-55-9	1	88	50	4	5696	<RL (88)	<RL (100)
Triamterene	396-01-0	1	1.3	50	35	4504	37	170
Trimethoprim	738-70-5	1	2.5	43	37	NA	170	370
Trimethoprim	738-70-5	2	1	49	40	NA	90	210
Valsartan	396-01-0	1	11	41	40	2528	1600 (1700)	5300 (8200)
Verapamil	137862-53-4	1	2.5	49	39	5328	26	97
Warfarin	81-81-2	1	11	50	0	28	ND	ND

^a Method employed.

^b Reporting limit, defined as 3X the EPA MDL (method detection limit) or the lowest calibration point, whichever is greater.

^c Predicted national average concentration from Kustich and Lazarus (2009).

2010 PMF Study – Highest Pharmaceuticals at P03 (NY2), P04 (NY3)

Pharmaceutical Formulation Facilities as Sources of Opioids and Other Pharmaceuticals to Wastewater Treatment Plant Effluents

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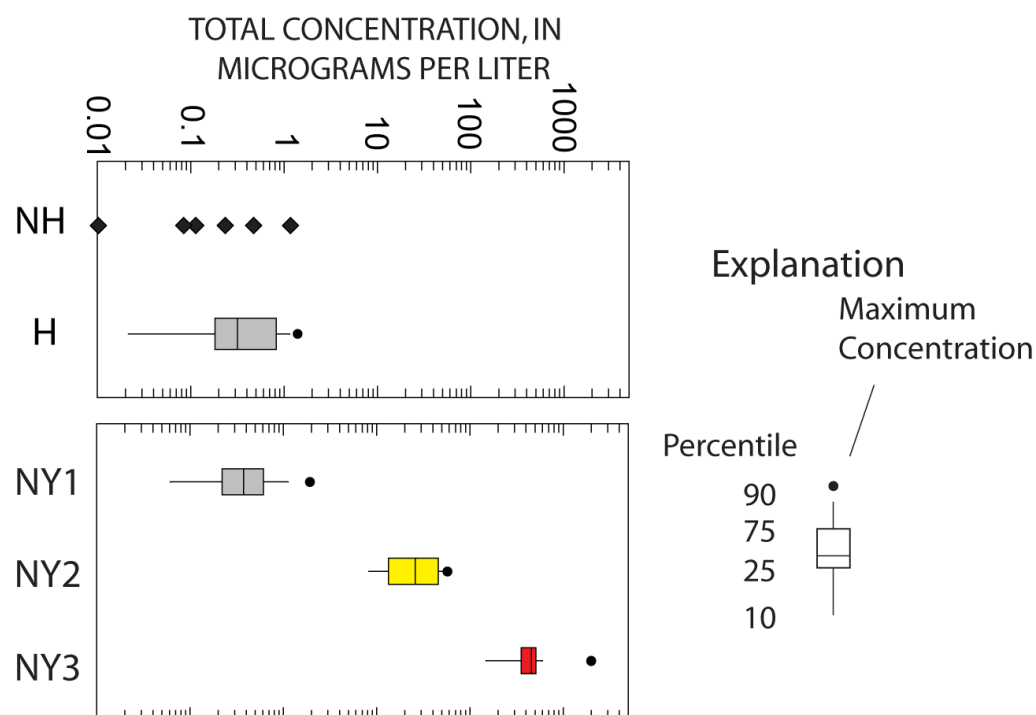
Introduction

Over the past decade, the occurrence of pharmaceuticals in the environment has become a major concern. Improvements in wastewater treatment technology have expanded the range of pharmaceuticals that can be removed from effluents. However, the effects of these pharmaceuticals on the environment are still poorly understood. This study was designed to investigate the occurrence of pharmaceuticals in wastewater treatment plant effluents and to identify the sources of these pharmaceuticals.

The pharmaceuticals currently in use in the United States (PPE) are listed in Table 1.

A. Individual Samples from 23 WWTPS across the US

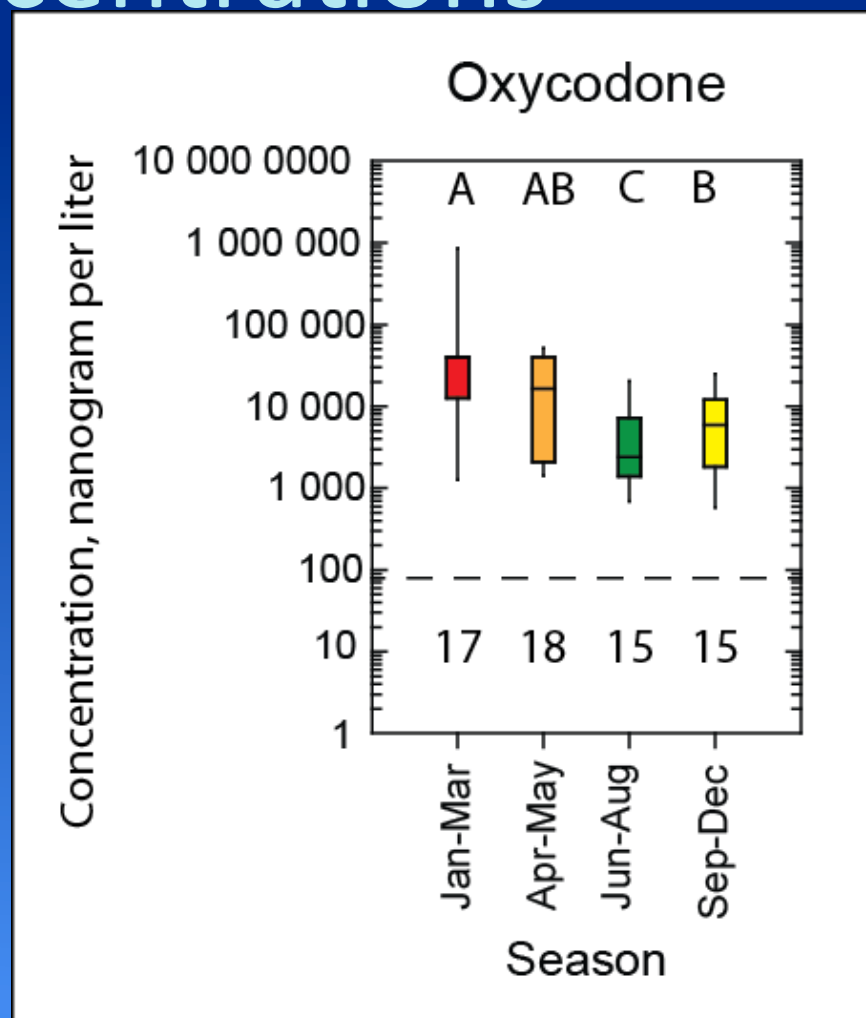
B. Multiple Samples from WWTPs NY1, NY2, and NY3



- Key Difference – National Study is One-Time Sampling

Few Examples of Seasonal Differences in Concentrations

- P03 Samples had highest concentrations for some Pharmaceuticals in Jan-Mar; Due to Formulation?
- Other sites showed highest DEET concentrations in Summer



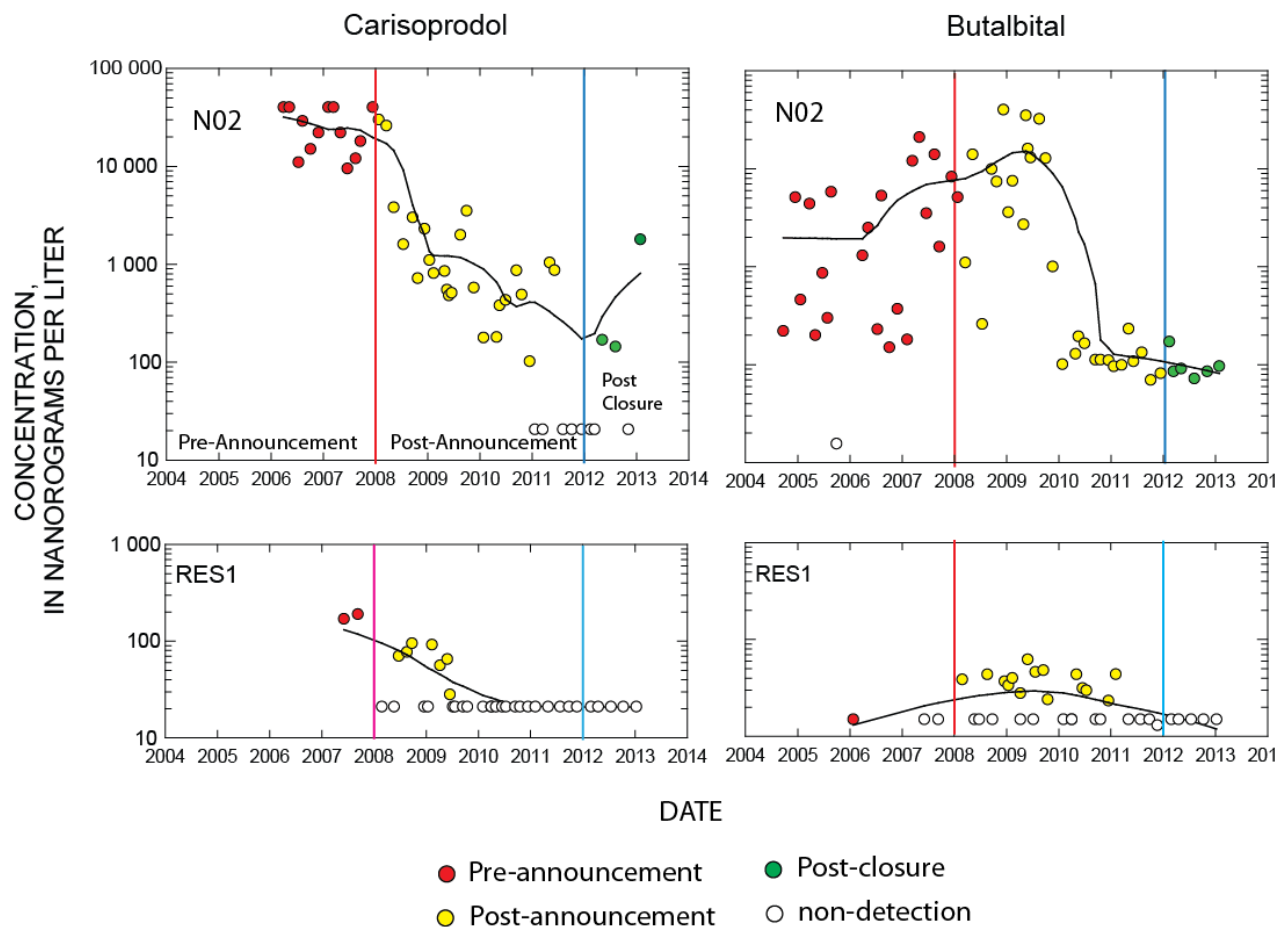
Phase out of PMF at NY2

- PMF phase-out announced January 2008
- Production ceased January 2012
- Did pharmaceuticals in effluent change?



N02/P14: Decreases Corresponding to PMF Shutdown

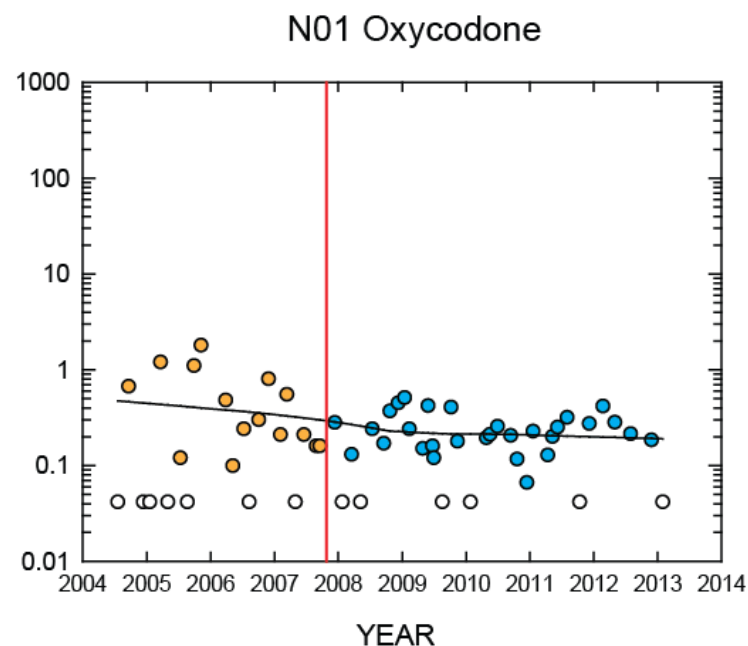
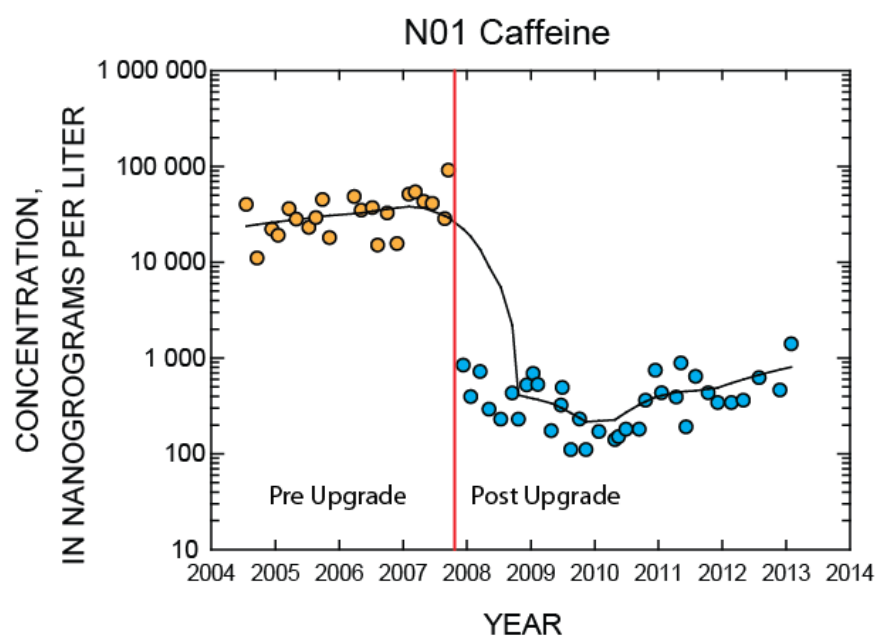
Similar
Decreases for
Oxycodone,
Diazepam



N01 Treatment Upgrade

- Occurred in August-September 2007
 - Trickling filter media was changed
 - Rotating Biological Contactors added
 - Microfiltration added
 - Storm flow equalization tank added

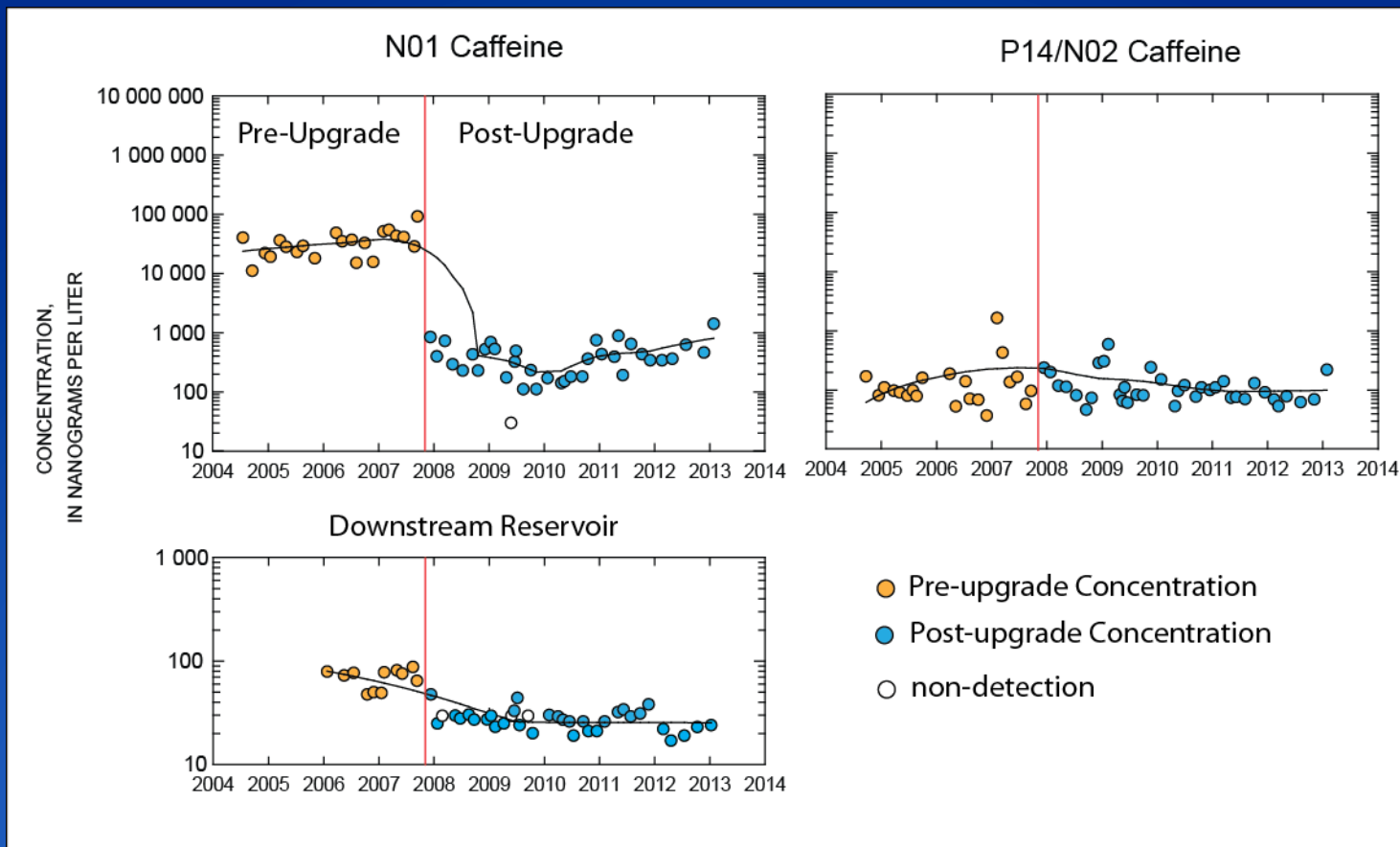
N01 – Decrease in Caffeine, no Change in Pharmaceutical Concentrations in Response to Upgrade



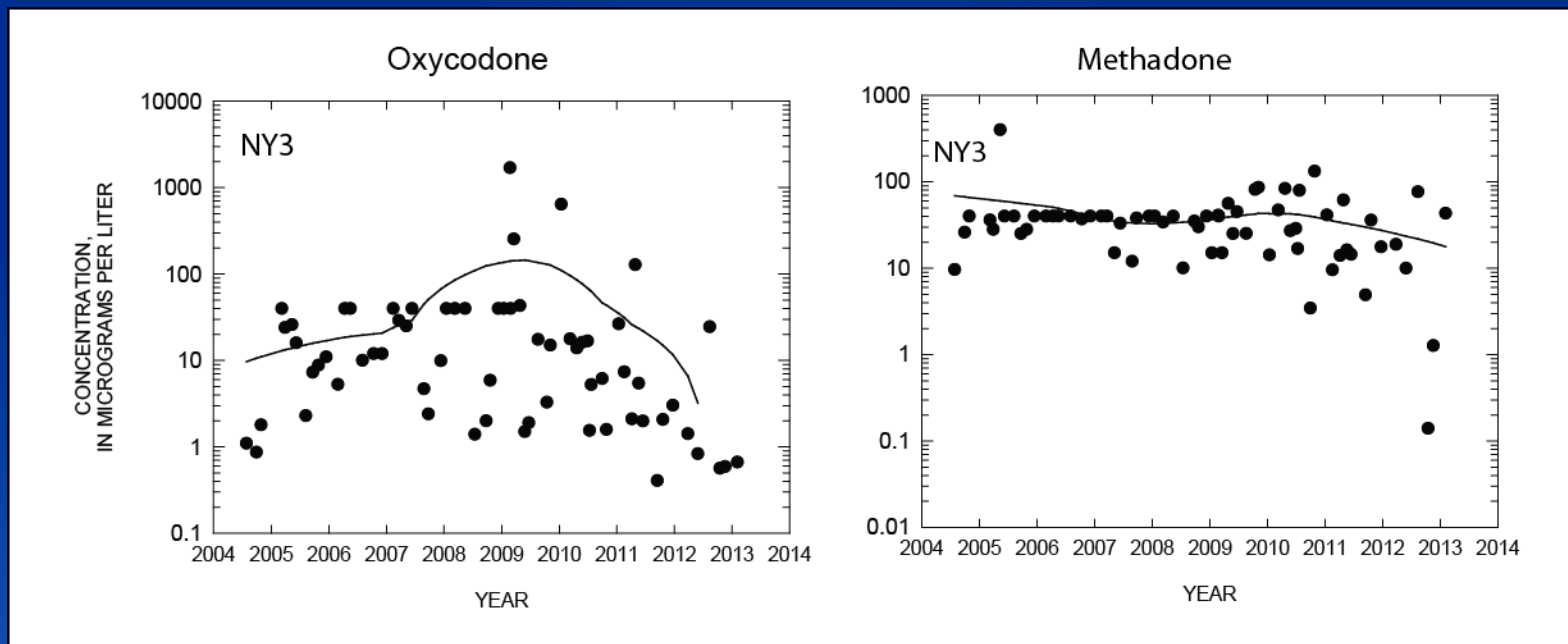
● Pre-Upgrade Concentration
● Post-Upgrade Concentration

— Lowess Trend Line
○ Non-detection

Effects of Upgrade at N01 are Noticeable in Downstream Reservoir



P03– Decrease in Oxycodone since 2010, no Change in Methadone

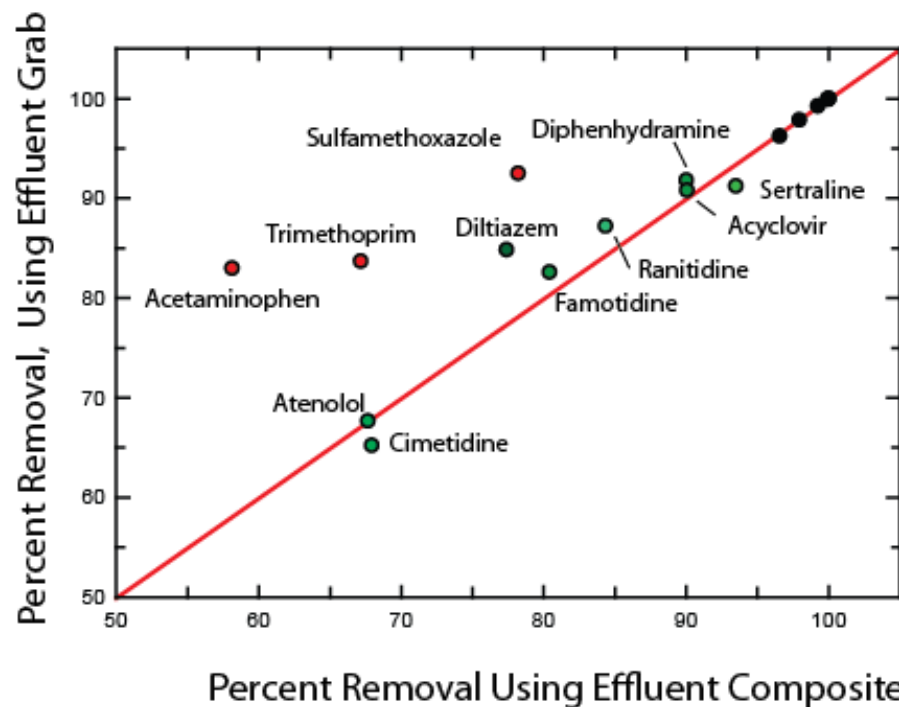


December 2012 Diurnal Experiment

- Diurnal Variability Assessed at NO3, December 2012
- Grab, 24 hour composite, and 6x4 Hour Composites Both Influent and Effluent
- New Pharmaceutical Method, Hormone Method used
- Useful for Assessing New Methods (Removal, Diurnal Variability)



High Diurnal Variability for Some Pharmaceuticals

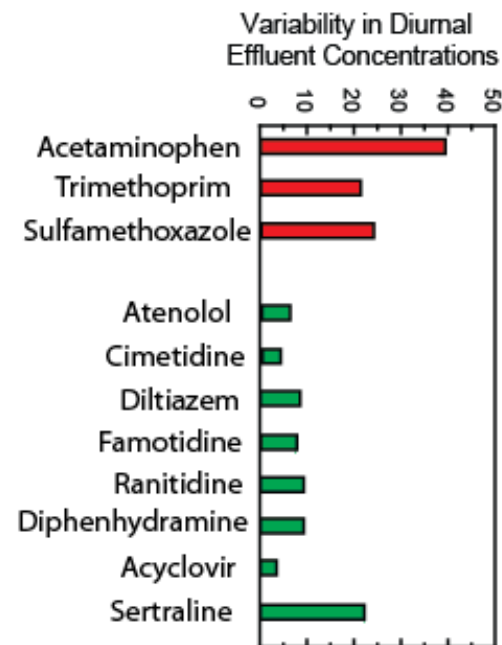


● Compounds with removal overestimated by using Effluent Grab

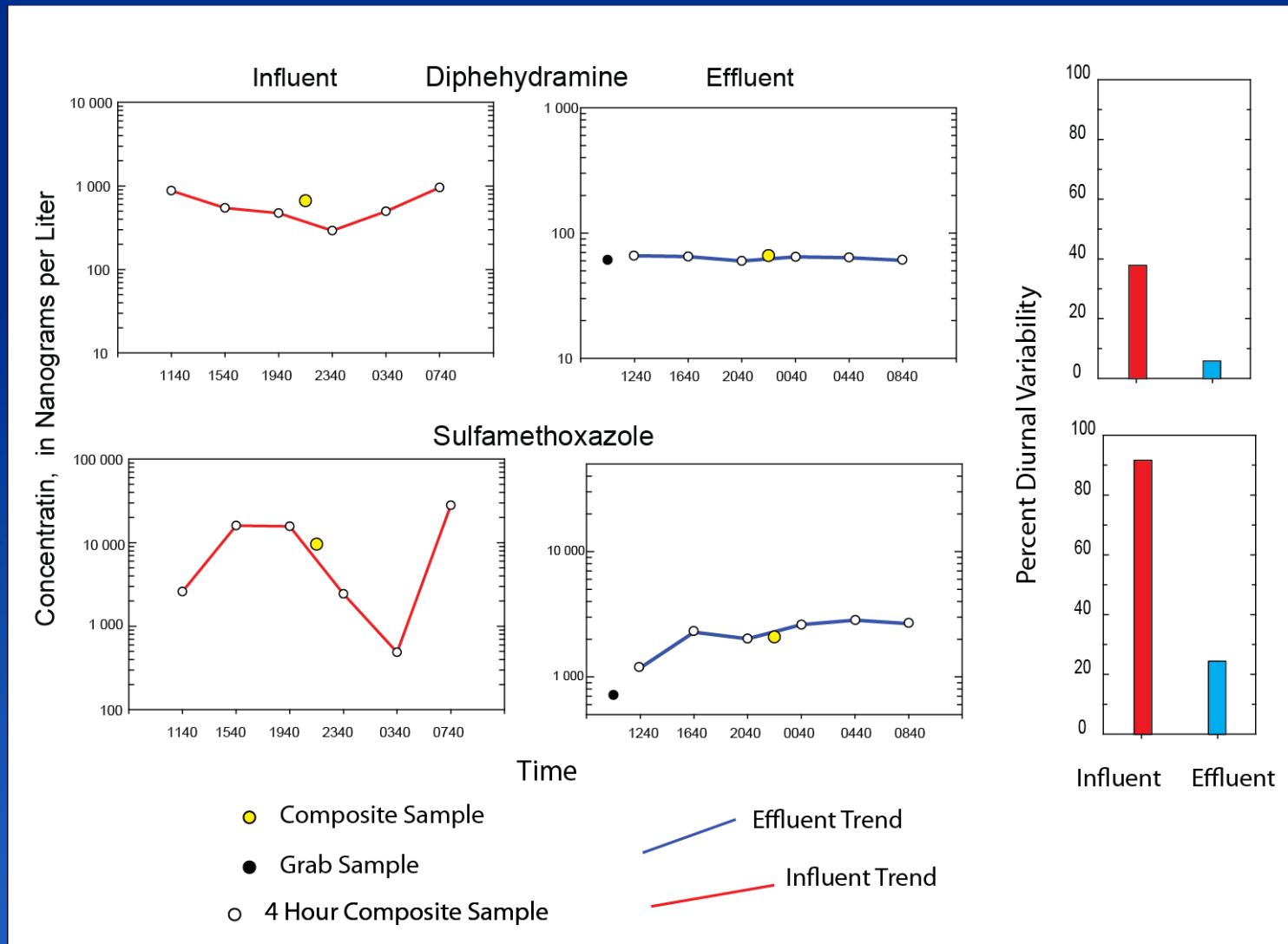
● Compounds with removal value not affected by using Effluent Grab

● Compounds with removal greater than 95%

1:1 Line for removals

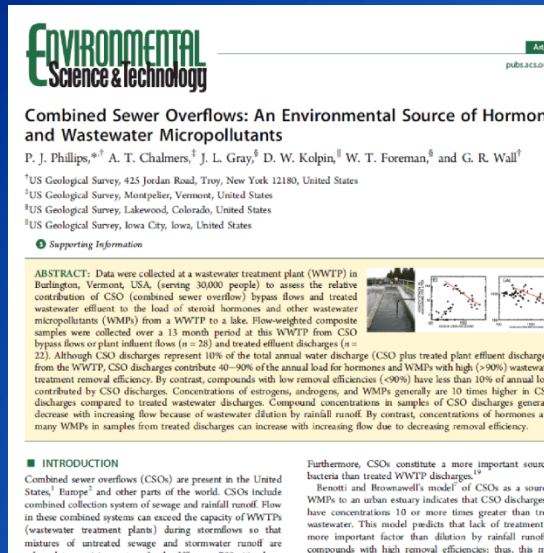
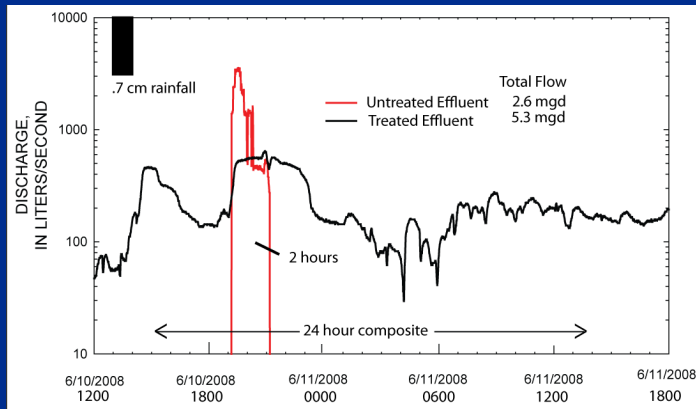


Effluent Diurnal Concentrations Compound Dependent

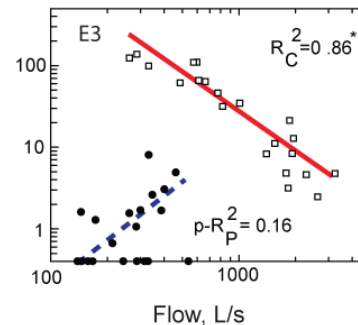
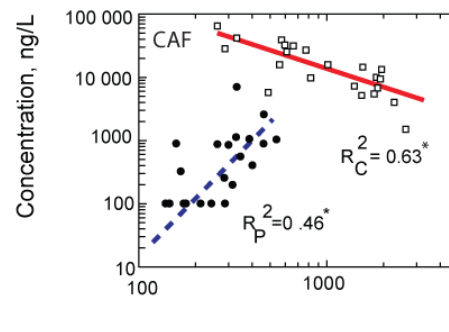


Effects of Extreme Events -

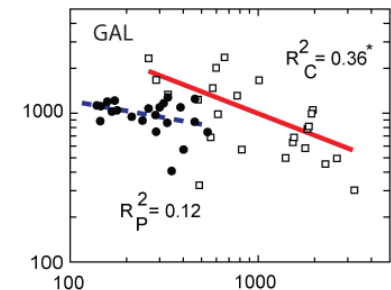
Elevated Flows over a days/
year account for >90% of
Hormone Loads



Compound Well
Removed by treatment



Compound Poorly
Removed by treatment



EXPLANATION

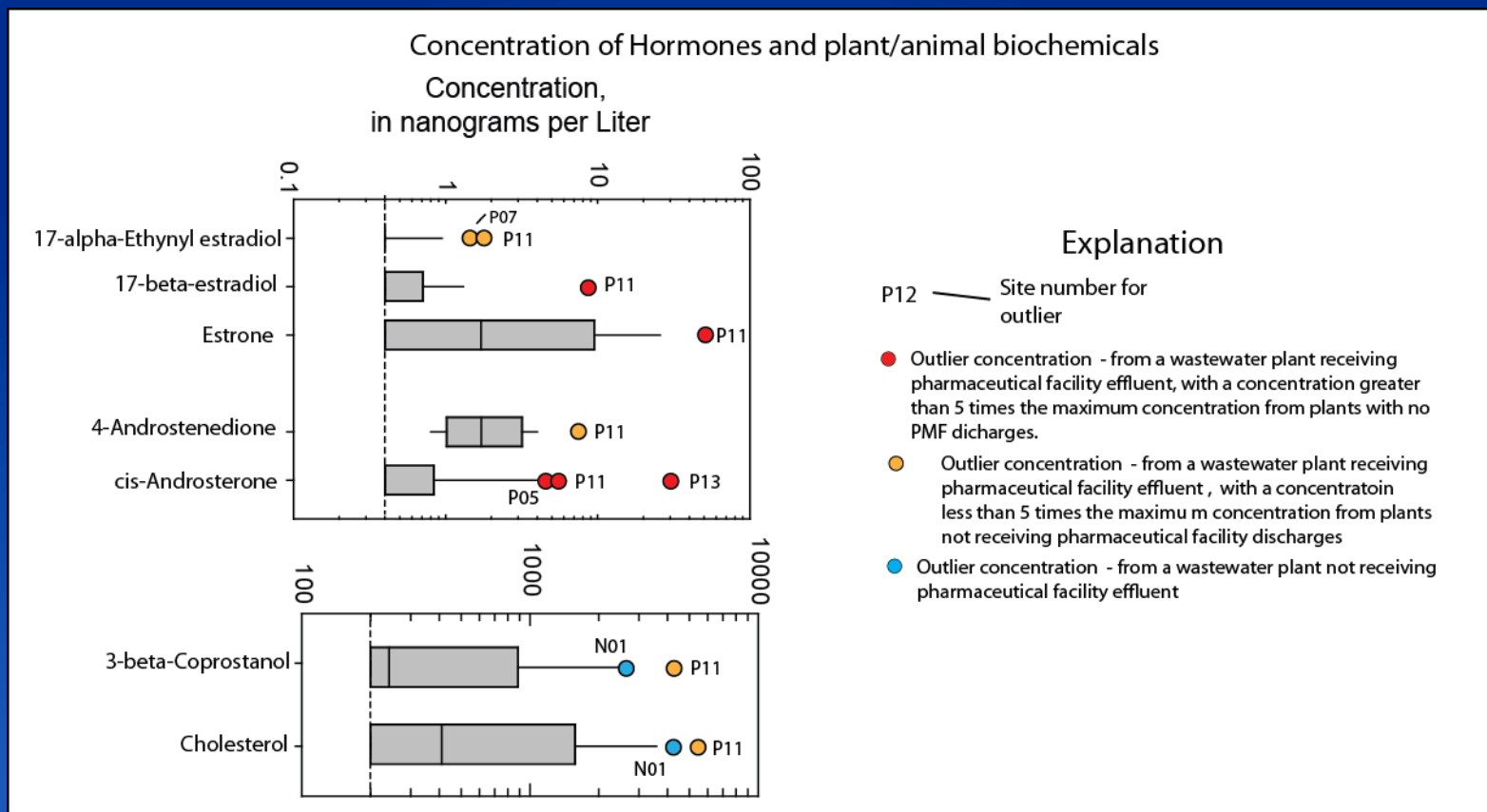
CSO Trend Line

Treated Sample
Trend Line

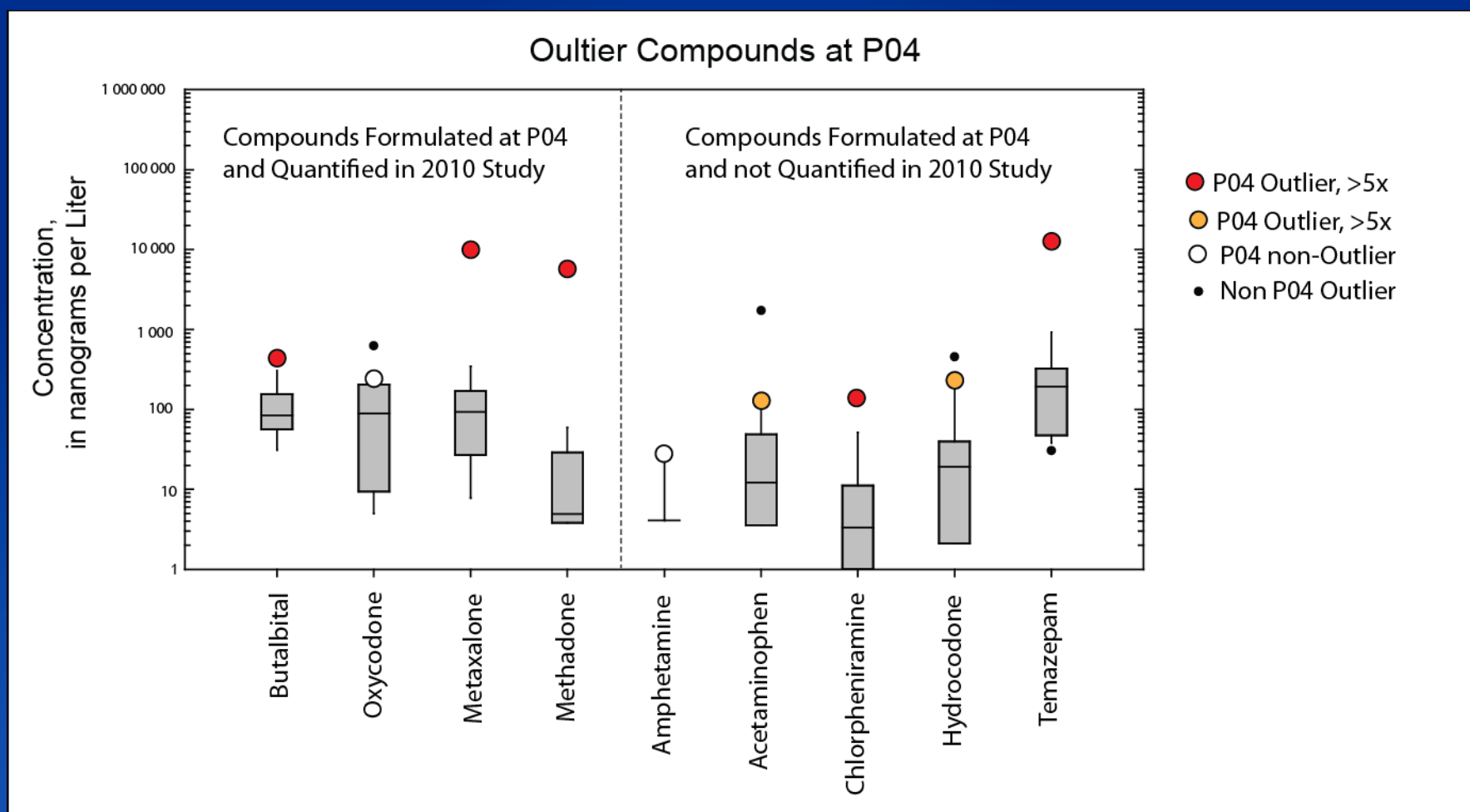
Observations about Sex and Drugs Picked up over the Last Few Years



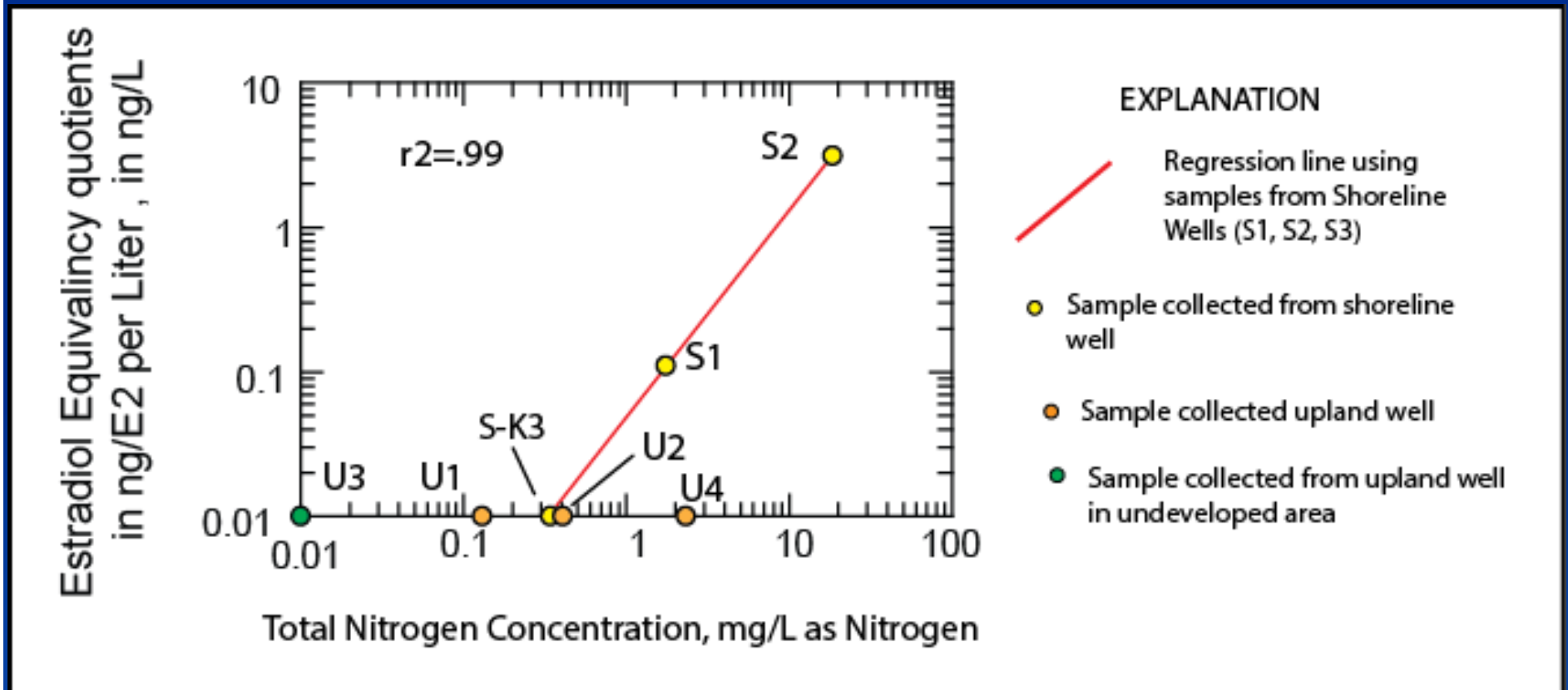
EE2 is not Commonly present in Effluent



New Method Shows Additional Pharmaceuticals at Site Analyzed in 2010 PMF Study



Septic Systems Are A source of Hormones to Groundwater on Long Island (and New England besides the Cape)



Summary

- Variability occurs on time spans over 24 hours to multi-year
- Phaseout of PMF formulation, WWTP Technology changes cause variability over decade period
- Shorter term (24 hour) variability ranges in influent and effluent and extreme events (CSOs) can cause high variability
- Will get data back soon on effects of population changes
- Need greater focus on both longer term (decadal) changes and short term (extreme events)

Assessment of trends

- It's difficult & uncommon.
- Requires
 - A consistent laboratory and analytical methods
 - Methods that are sensitive enough
 - A long and well maintained data set
 - fixed frequency sampling over all seasons
 - Sophisticated data analysis techniques, including a censoring strategy.

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