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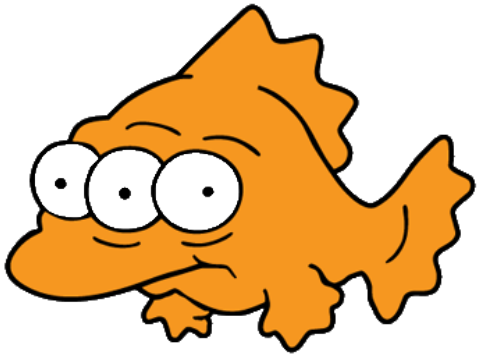
Pharmaceuticals and Personal Care Products (PPCPs) and Endocrine Disrupting Compounds (EDCs) in Surface Water
- A Case Study of the Assabet River, MA

10/29/2014

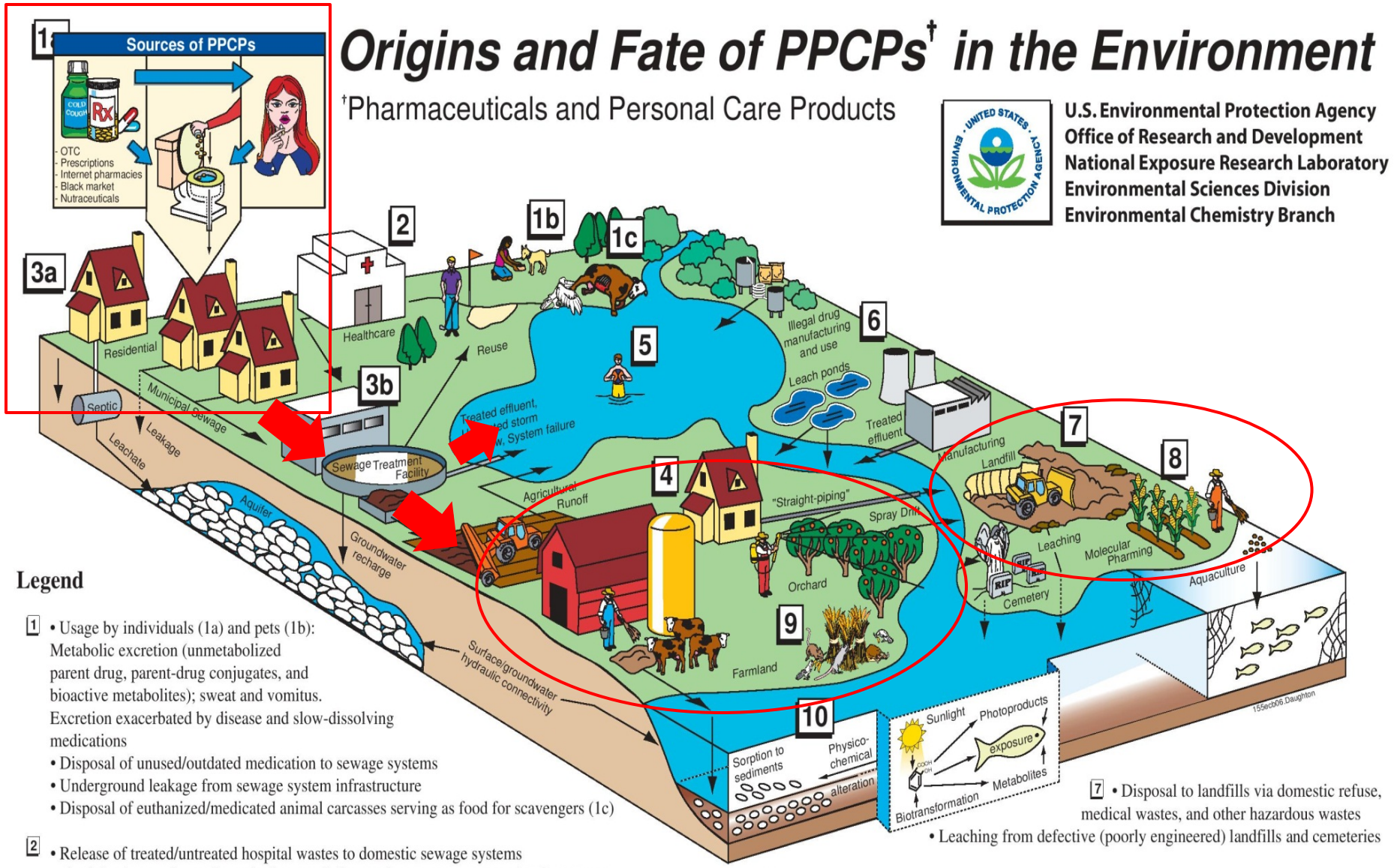
What are EDCs and PPCPs and Why Study Them?

- EDC- Endocrine Disrupting Compounds
  - EDCs are a class of compounds which alter the hormonal system of an organism.
  - Eg: DDT, 17-alpha Ethinylestradiol, Bisphenol A,etc.



- PPCP- Pharmaceuticals and Personal Care Products
  - Any products used for personal health or cosmetic reasons
  - Includes prescription and non-prescription drugs, veterinary drugs, fragrances and cosmetics

EDC/PPCP Sources



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Fate and Transport of EDCs and PPCPs

Analyte List

EDC / PPCP	
Acetaminophen	Gemfibrozil
Atenolol	Ibuprofen
Atorvastatin	Miconazole
Caffeine	Naproxen
Ciprofloxacin	Primidone
Cotinine	Propranolol
DEET	Ranitidine
Diclofenac	Salbutamol
Diphenhydramine	Sulfamethoxazole
Estradiol	TCEP
Estrone	Trimethoprim
Furosemide	Warfarin

Tracers
Gadolinium
Iodine
Sucralose

Analytical Methods

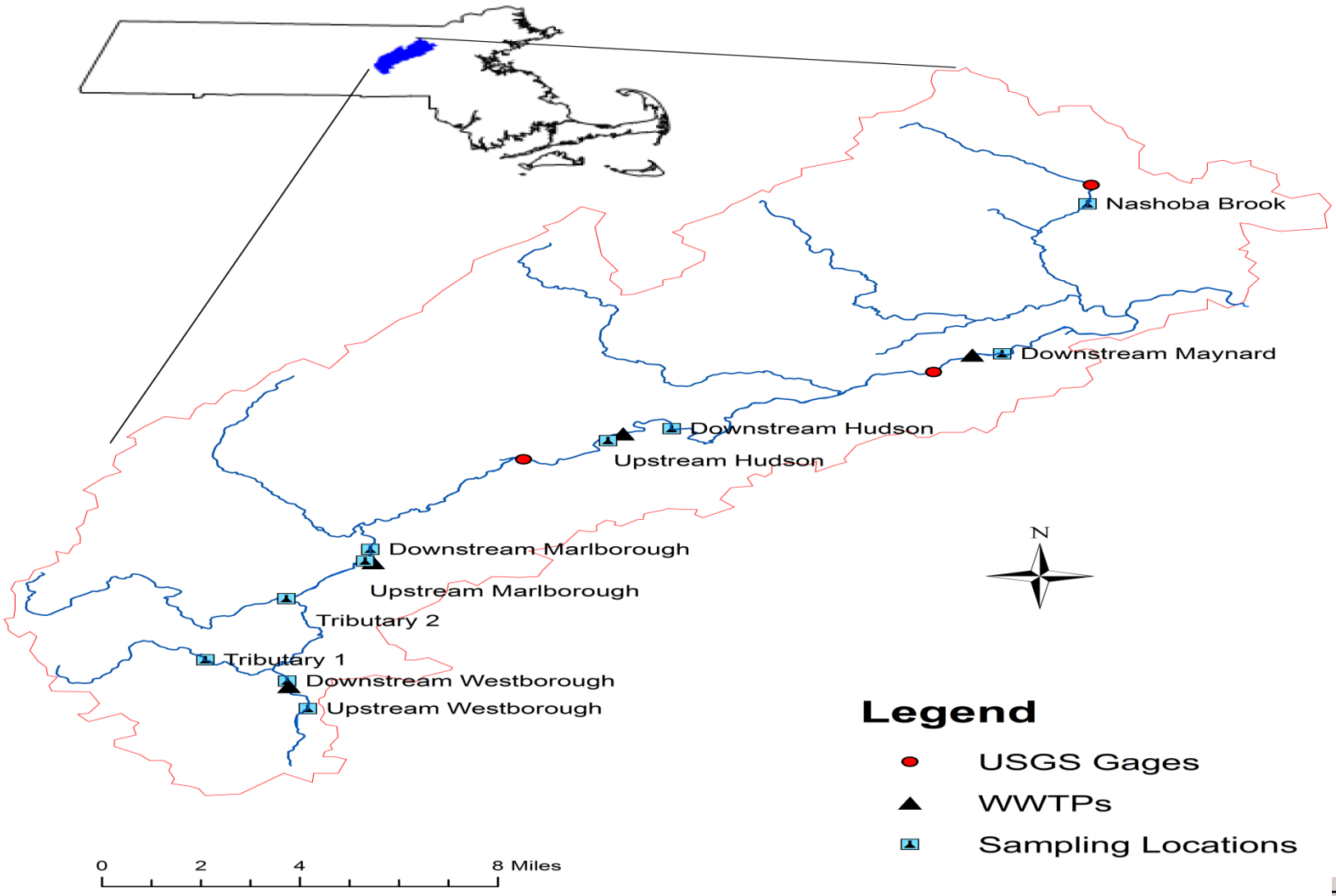
- EDCs/PPCPs
  - Solid Phase Extraction followed by UPLC-MS-MS
- Tracers
  - Gadolinium and Iodine: ICP-MS

MDL and MRLs

Compound	MDL (ng/L)	MRL (ng/L)
Acetaminophen	34.9	104.7
Atenolol	57.1	171.3
Atorvastatin	14.8	44.4
Caffeine	61.8	185.4
Ciprofloxacin	275.5	826.5
Cotinine	5.6	16.8
DEET	4.9	14.7
Diclofenac	3.3	9.9
Diphenhydramine	0.3	0.9
Estradiol	133.6	400.8
Estrone	8.1	24.3
Furosemide	11.5	34.5

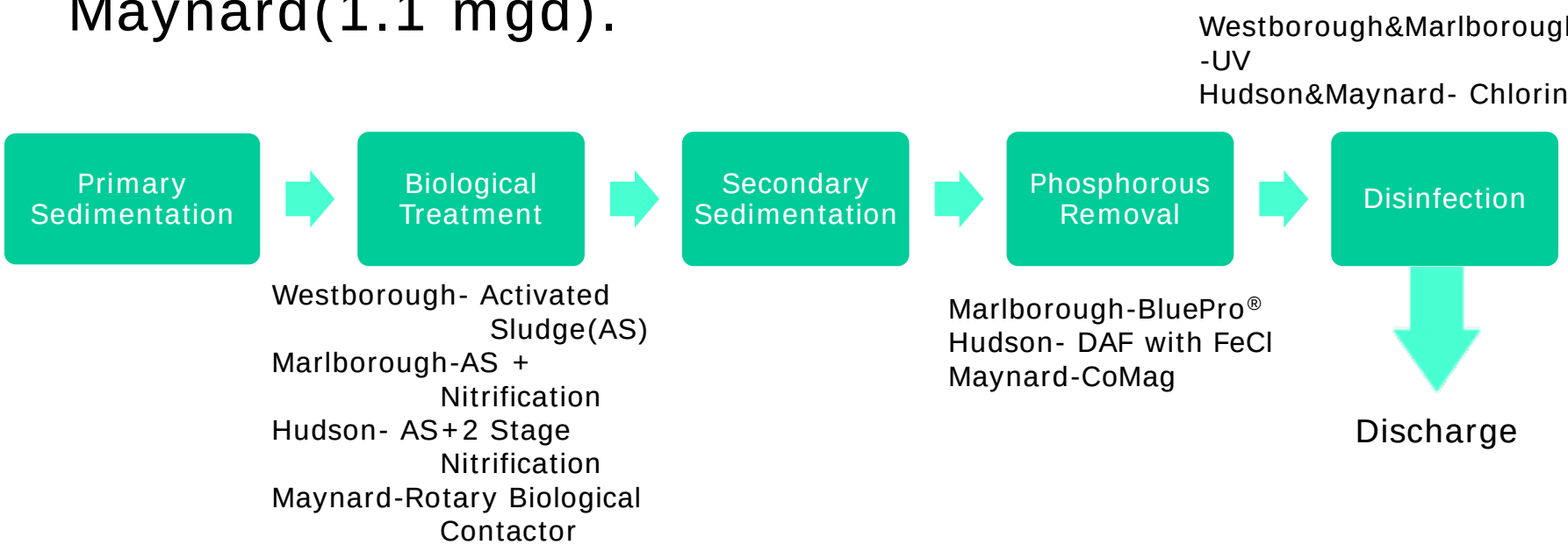
Compound	MDL (ng/L)	MRL (ng/L)
Gemfibrozil	0.7	2.1
Ibuprofen	11.6	34.8
Miconazole	0.9	2.7
Naproxen	11	33
Primidone	16.8	50.4
Propranolol	6.2	18.6
Ranitidine	61.7	185.1
Salbutamol	44.2	132.6
Sucralose	569.7	1709.1
Sulfamethoxazole	8.9	26.7
TCEP	14.4	43.2
Trimethoprim	15.2	45.6
Warfarin	26.1	78.3

Sampling Locations



Wastewater Treatment Plants(WWTPs)

- Four WWTPs- Westborough(20 mgd), Marlborough(2.95 mgd), Hudson(2.65 mgd) and Maynard(1.1 mgd).



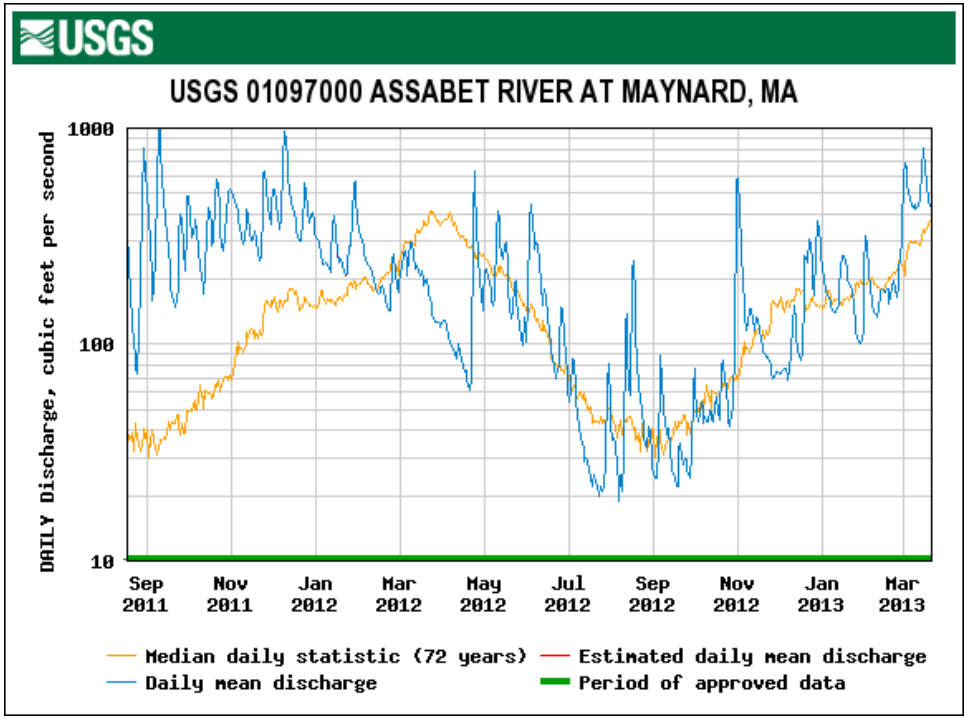
Sampling Procedures

- River samples- Grab Samples
- Amber Bottles
  - 1 Litre- EDC/PPCPs
  - 60 mL- Tracers
- Preservatives
  - EDC/PPCP- Sodium Azide & Ascorbic acid
  - Tracers- 2% Nitric Acid
- Conductivity, pH and Temperature measured during sampling
- Filtered and stored at 4 °C

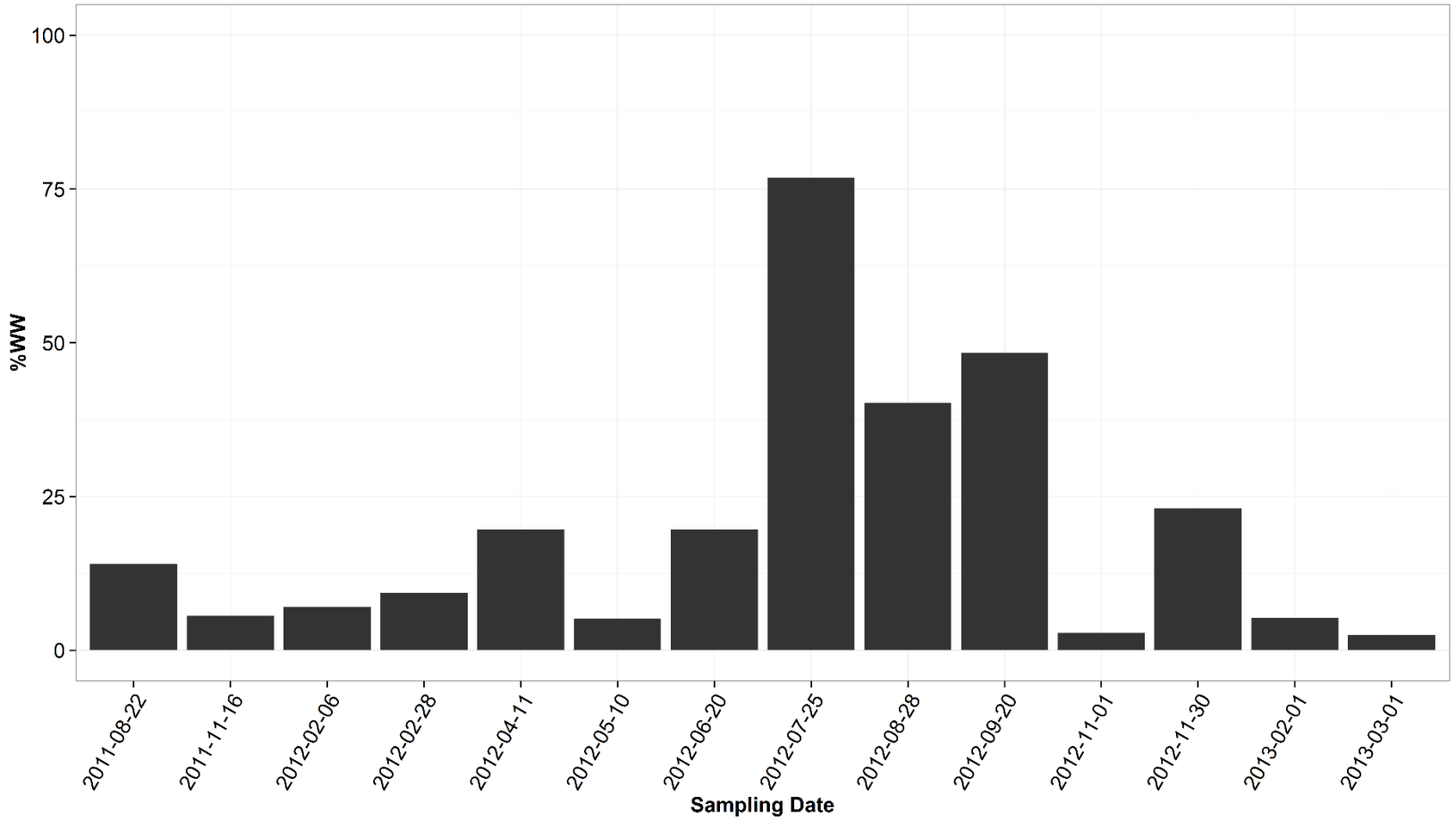
Sampling Dates

Sampling Date (MM/YYYY)	Flow at Maynard USGS Gage(cfs)
08/22/2011	121
11/16/2011	303
02/06/2012	241
02/28/2012	182
04/11/2012	86
05/10/2012	331
06/20/2012	86

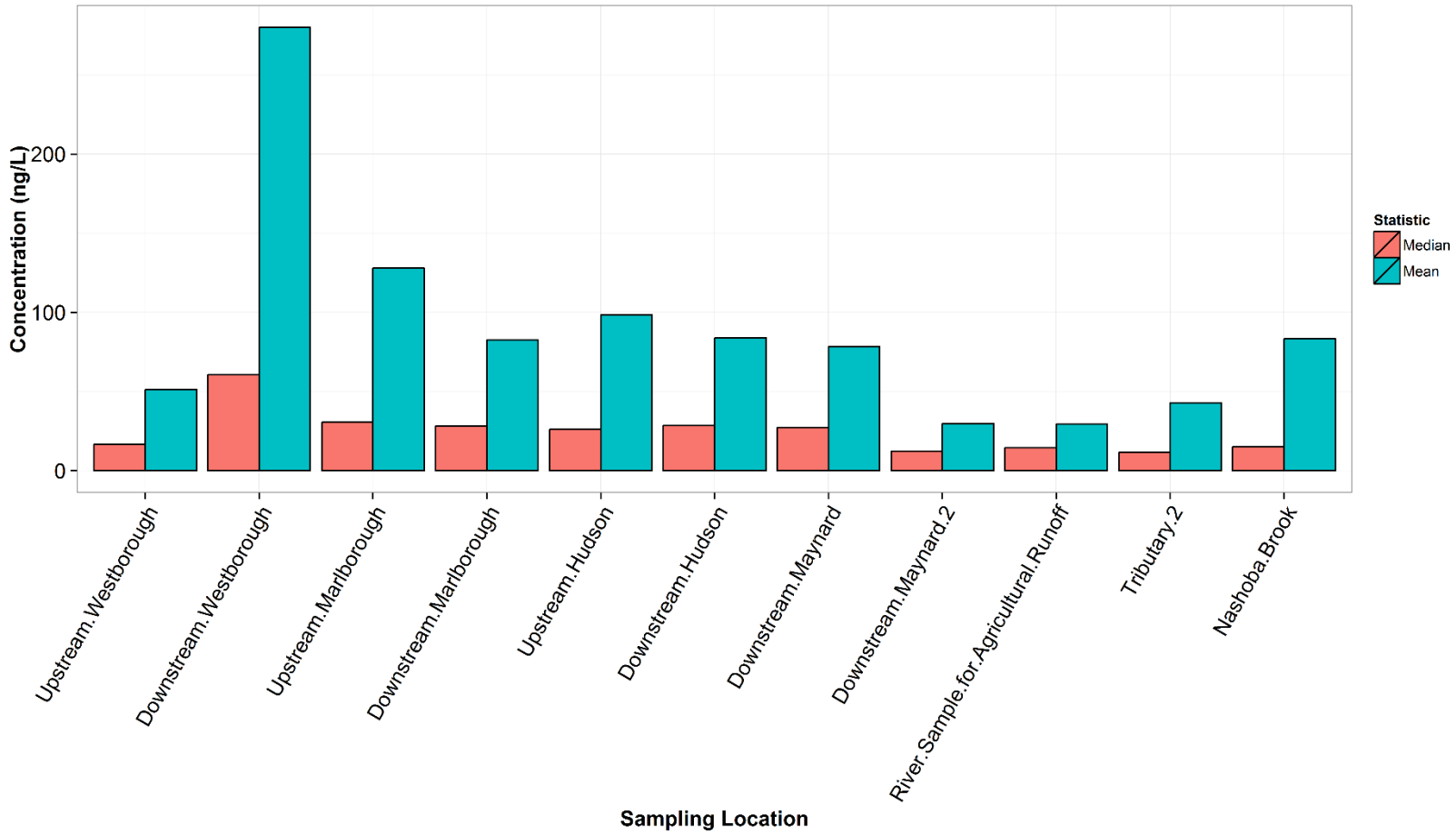
Sampling Date (MM/YYYY)	Flow at Maynard USGS Gage(cfs)
07/25/2012	22
08/28/2012	42
09/20/2012	35
11/01/2012	593
11/30/2012	73
02/01/2013	318
03/01/2013	687



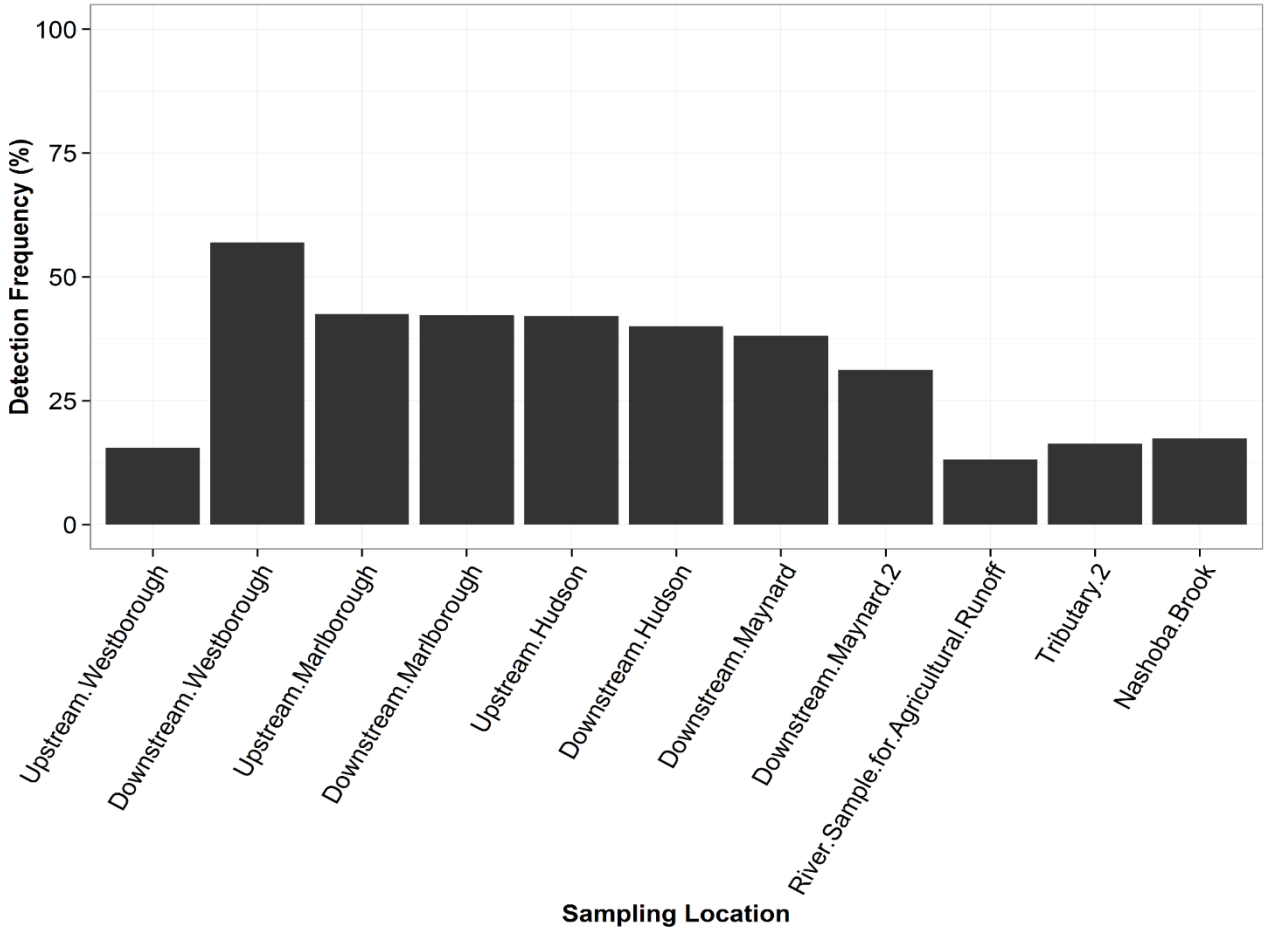
% Wastewater


100
75
50
25
0
%WW
2011-08-22
2011-11-16
2012-02-06
2012-02-28
2012-04-11
2012-05-10
2012-06-20
2012-07-25
2012-08-28
2012-09-20
2012-11-01
2012-11-30
2013-02-01
2013-03-01
Sampling Date

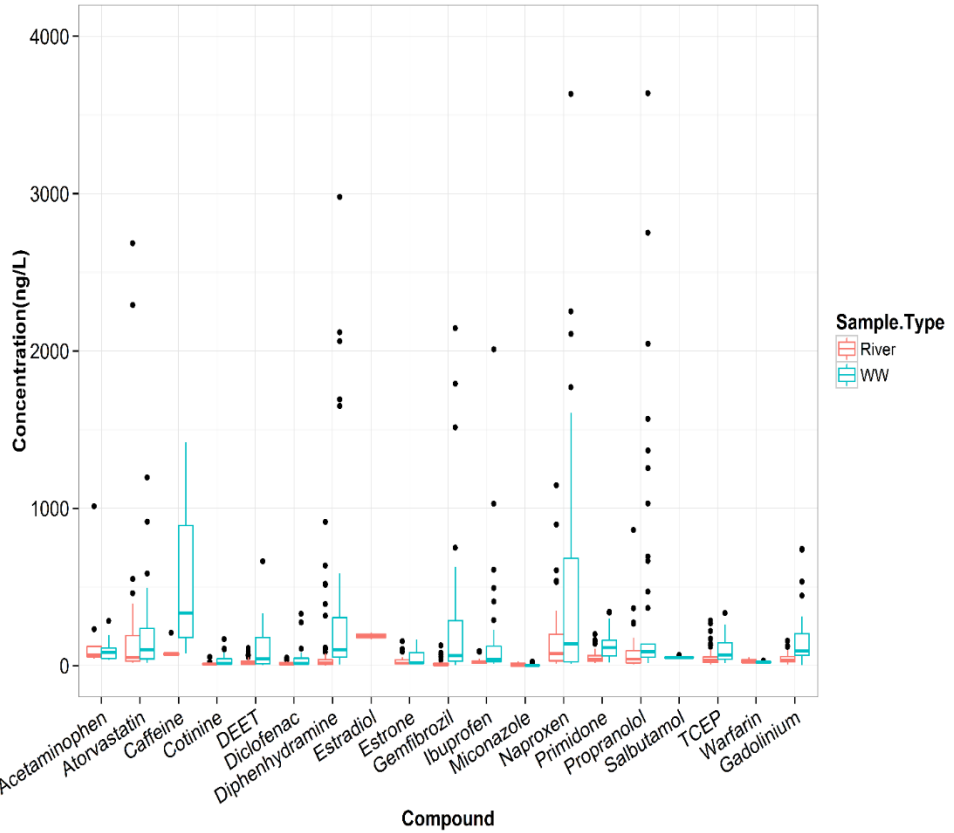
Sampling Locations

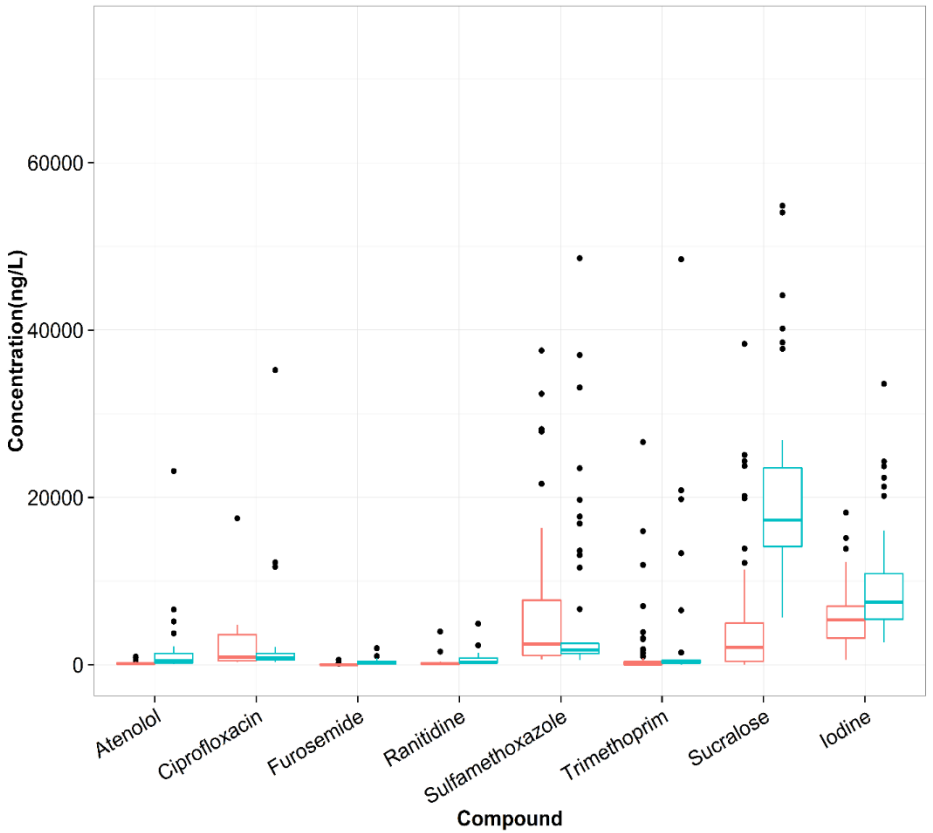


Sampling Locations

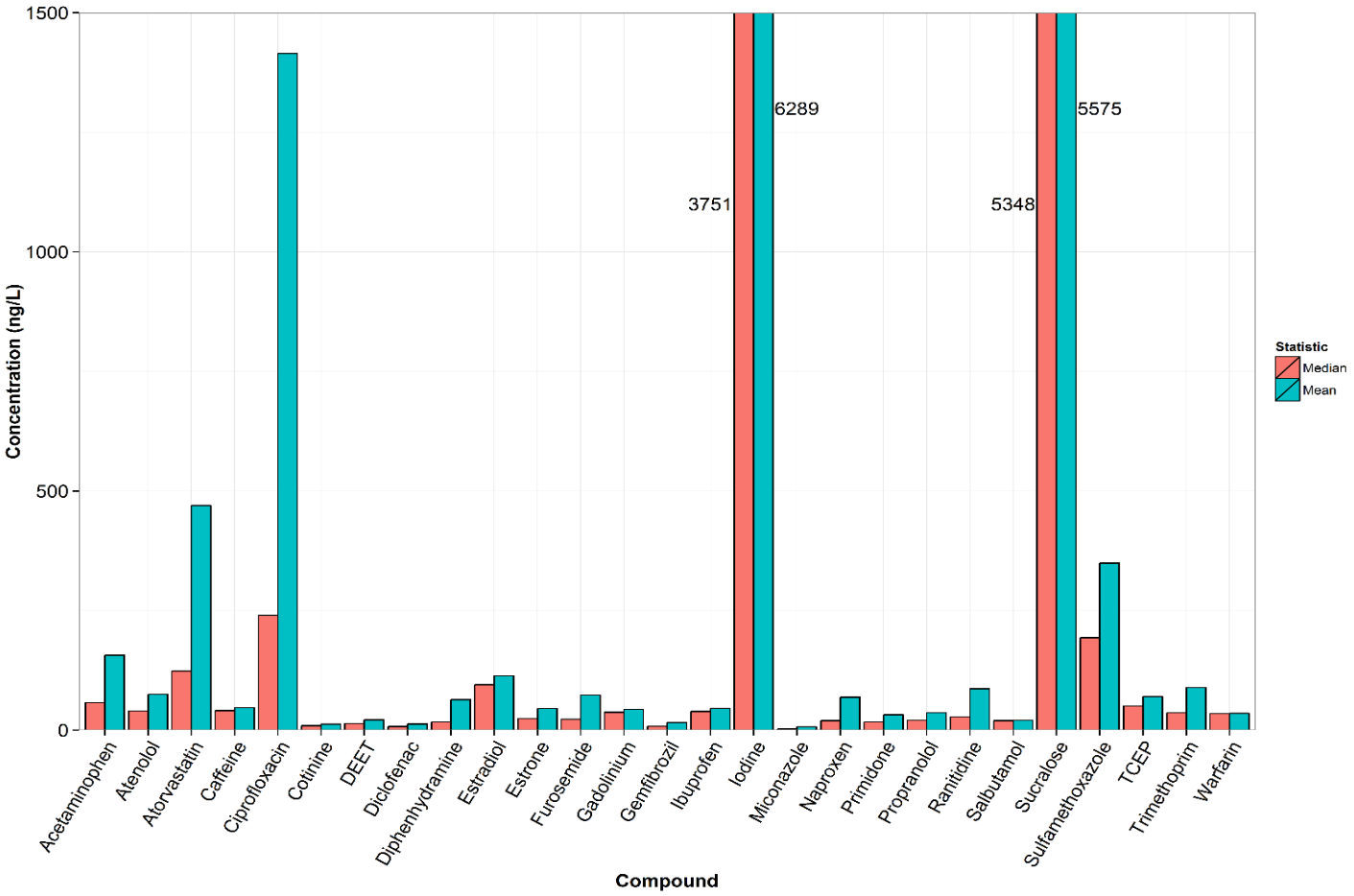


Results

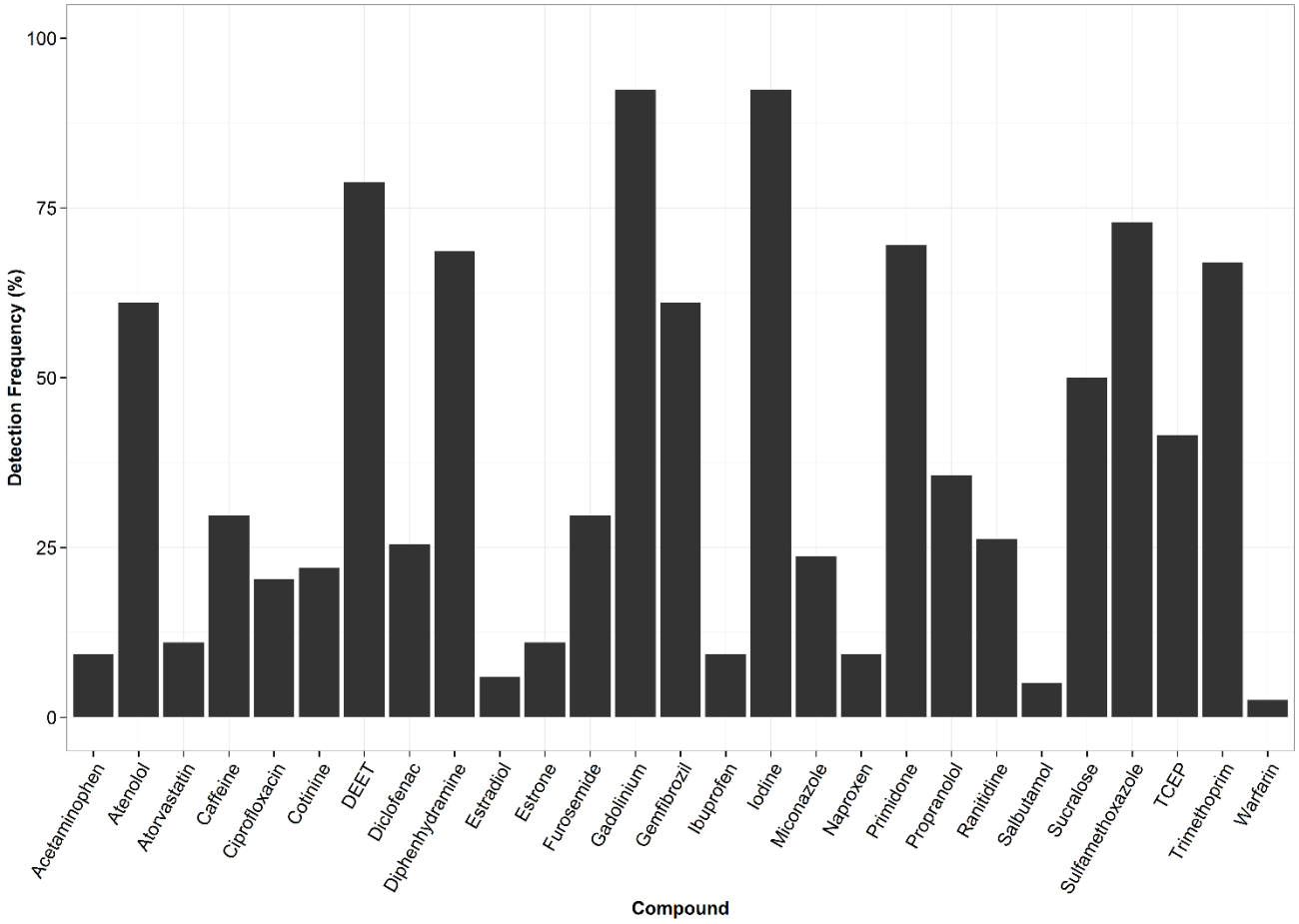

Concentration(ng/L)
4000
3000
2000
1000
0
Acetaminophen
Atorvastatin
Caffeine
Cotinine
DEET
Diclofenac
Diphenhydramine
Estradiol
Estrone
Gemfibrozil
Ibuprofen
Miconazole
Naproxen
Primidone
Propranolol
Salbutamol
TCEP
Warfarin
Gadolinium
Compound
Sample.Type
River
WW


Concentration(ng/L)
60000
40000
20000
0
Atenolol
Ciprofloxacin
Furosemide
Ranitidine
Sulfamethoxazole
Trimethoprim
Sucralose
Iodine
Compound

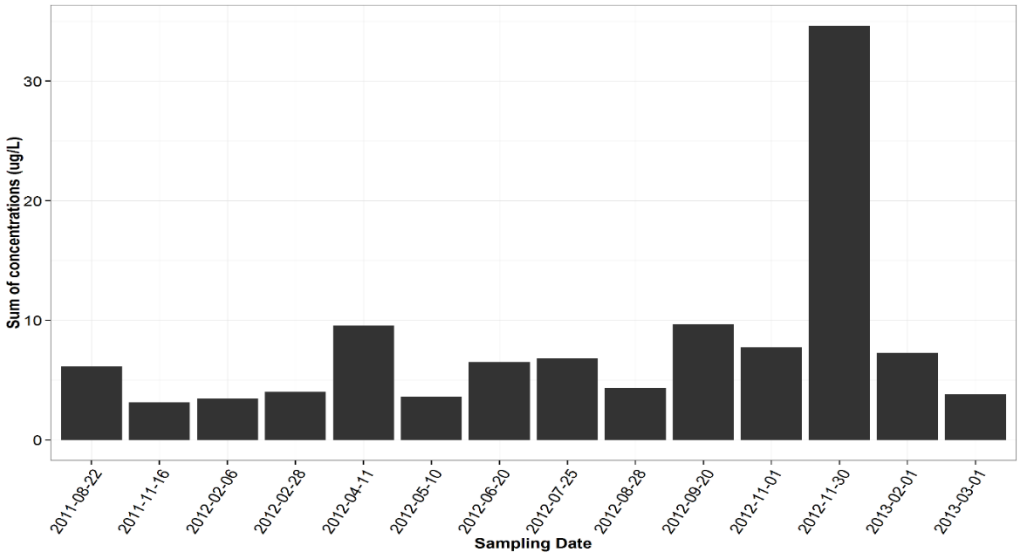
Compounds


1500
1000
500
0
Concentration (ng/L)
3751
6289
5348
5575
Statistic
Median
Mean
Acetaminophen
Atenolol
Atorvastatin
Caffeine
Ciprofloxacin
Cotinine
DEET
Diclofenac
Diphenhydramine
Estradiol
Estrone
Furosemide
Gadolinium
Gemfibrozil
Ibuprofen
Iodine
Miconazole
Naproxen
Primidone
Propranolol
Ranitidine
Salbutamol
Sucralose
Sulfamethoxazole
TCEP
Trimethoprim
Warfarin
Compound

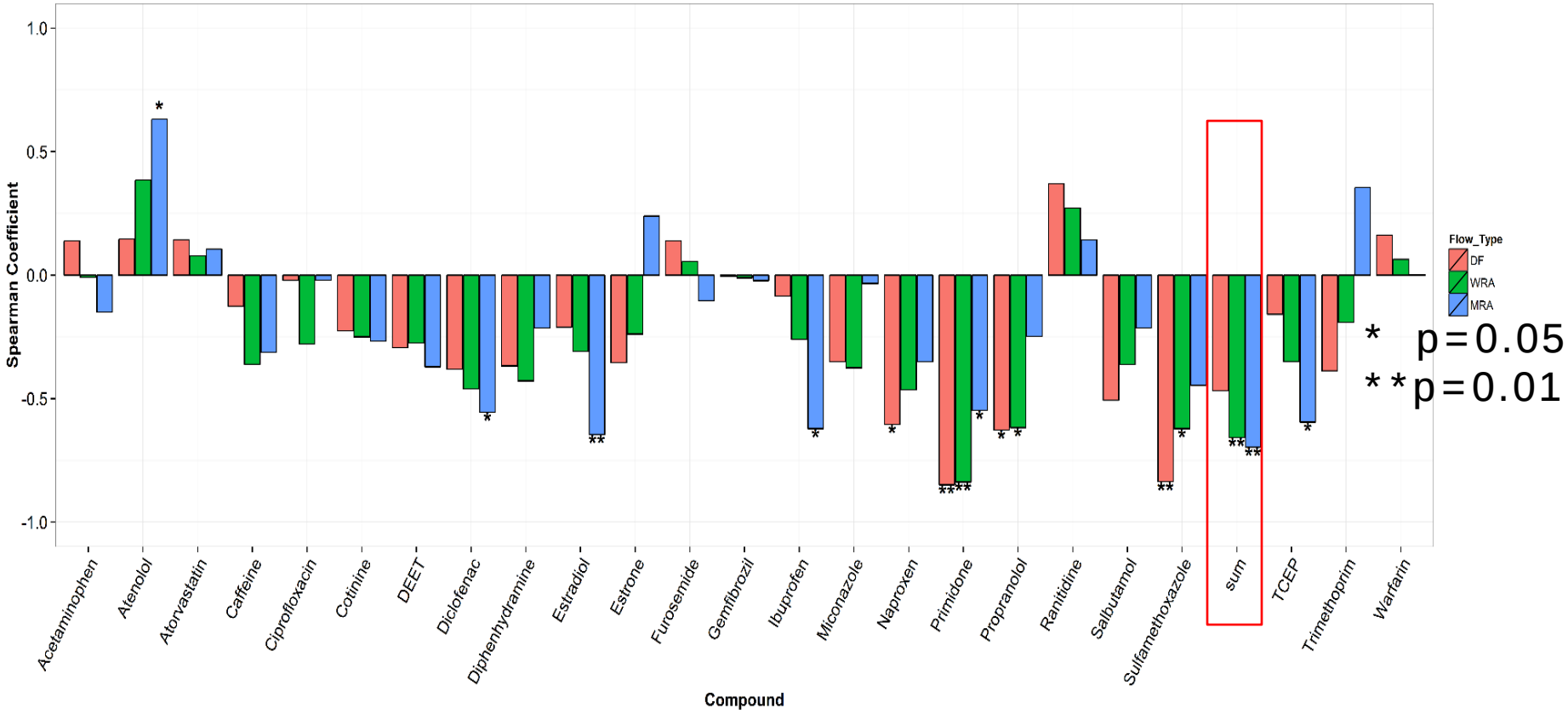
Compounds


100
75
50
25
0
Detection Frequency (%)
Acetaminophen
Atenolol
Atorvastatin
Caffeine
Ciprofloxacin
Cotinine
DEET
Diclofenac
Diphenhydramine
Estradiol
Estrone
Furosemide
Gadolinium
Gemfibrozil
Ibuprofen
Iodine
Miconazole
Naproxen
Primidone
Propranolol
Ranitidine
Salbutamol
Sucralose
Sulfamethoxazole
TCEP
Trimethoprim
Warfarin
Compound

Sum of Concentrations vs Sampling Date



Correlation with River Flow



Conclusions

- Wastewater has one of the major impacts on the occurrence of EDCs and PPCPs in surface water.
- There is a negative correlation between flows and the presence of EDCs and PPCPs.
- Sulfamethoxazole, sucralose,ciprofloxacin and atorvastatin are exhibit higher mean and median concentrations.
- Detection frequencies are higher downstream of a wastewater treatment plant and low in the tributaries.

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Developing a Watershed-Level Protocol for Choosing Indicators for EDCs/PPCPs Using Analytical Methods and Chemometrics

Department of Civil and Environmental Engineering

Why Develop such a Protocol?

- Sampling and measuring EDC/PPCPs is very expensive.
  - Cost of analysis for 30 analytes= $1020/sample
  - Cost of analysis for 10 analytes= $620/sample
- No. of compounds- very large.
- Will help identify sampling locations of most and least concern.

Current Regulations

- **State of California**
  - California Department of Public Health(CDPH) developed criteria for use of reclaimed municipal wastewater to recharge groundwater basins that are sources of drinking water supply.
  - Uses Total Organic Carbon(TOC) limits as means of ensuring lowest possible concentrations of unregulated WW-derived organic contaminants.
  - Additional monitoring of 38 organic contaminants.

Source: CDPH 2003;CDPH 2007; Drewes et al 2008

Objective

- To develop a protocol for monitoring EDCs/PPCPs using field-sampling, analytical methods and statistical tools.
- Such a protocol will help drinking water utilities to perform EDC/PPCP monitoring in a cost-effective manner.

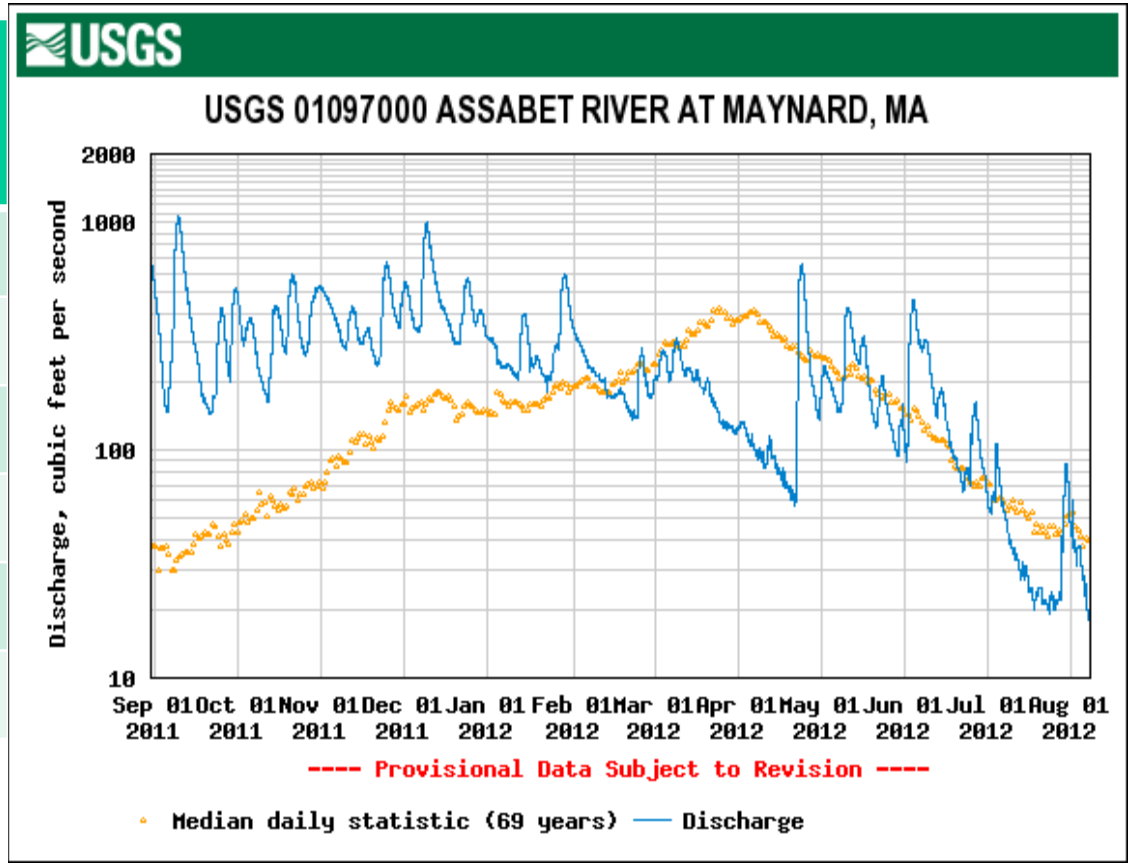
Previous Work

- Has focused on occurrence and fate of EDCs/PPCPs in various watersheds and drinking water.
- Indicators- selected using detection frequency, ability to indicate presence of wastewater or/and toxicological relevance(eg:Caffeine, Sulfamethoxazole, Nicotine, Artificial Sweeteners)
- The correlation of these compounds with EDCs/PPCPs has not been tested before

Sampling Dates

Sampling Date (MM/YYYY)	Flow at Maynard USGS Gage(cfs)
08/2011	121
11/2011	303
02/2012	241
03/2012*	182
04/2012*	86
05/2012*	331

* Datasets used for calibration



Statistical Analysis

Hierarchical Cluster Analysis

- Ward's Method
- Data Autoscaled ((Data-Mean)/SD)

Principal Component Analysis

- Correlation matrix used(Mean =0 & SD=1)

Correlation Analysis

- Pearson's r > 0.6
- Spread out scatter plots
- Indicator Compounds-Frequency of detection, good correlation and distribution of data.

Regression Models

- Both linear and quadratic models were tried.
- Linear models were fit better based on the p-values and R^2 values.

$$C = a * I + b$$

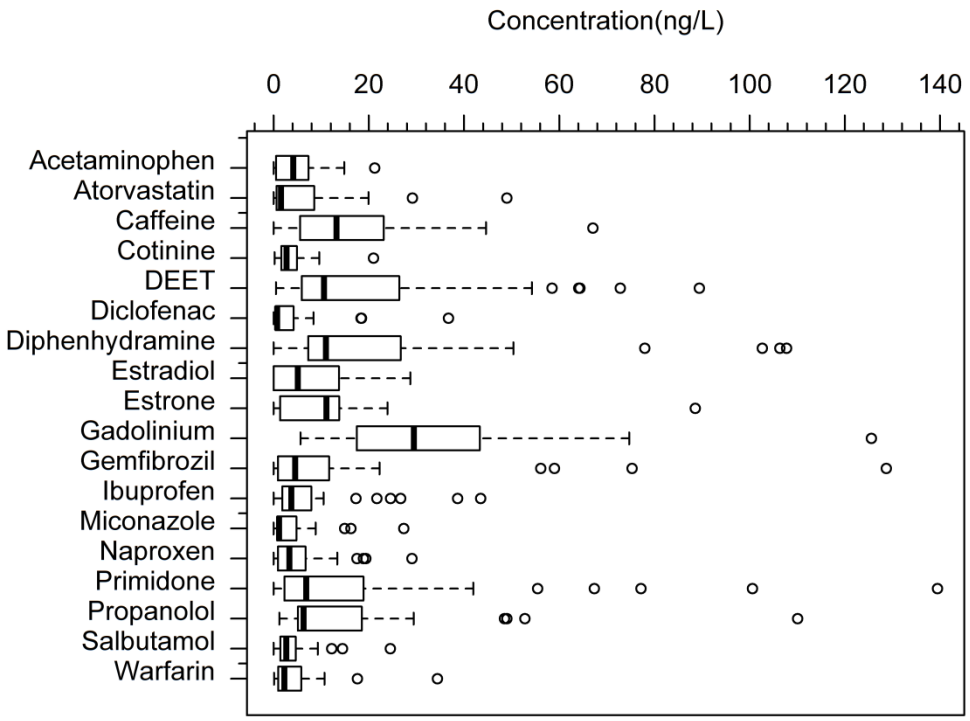
where

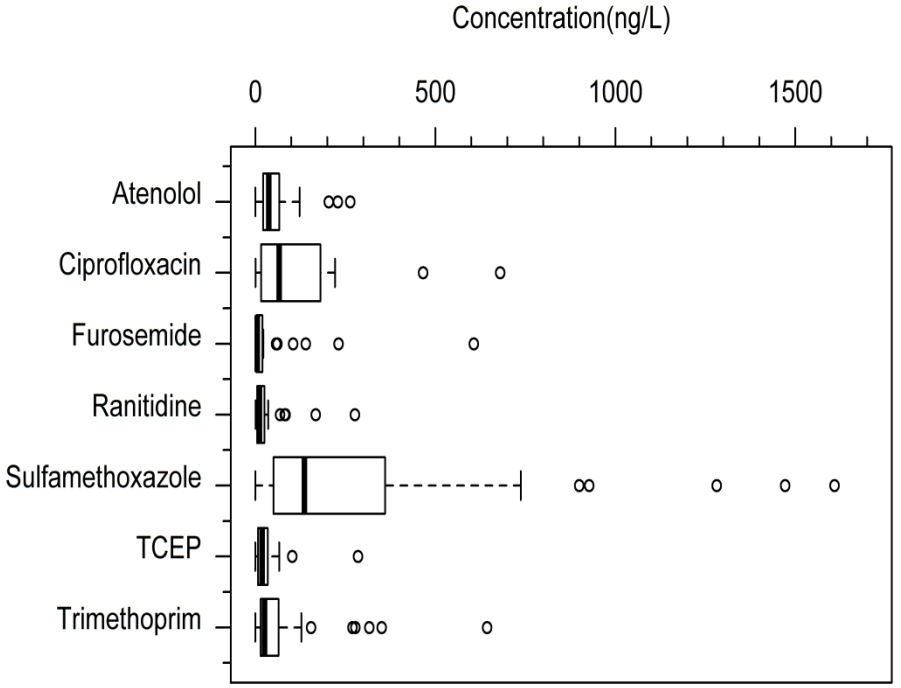
C- concentration of the contaminant

I- indicator concentration

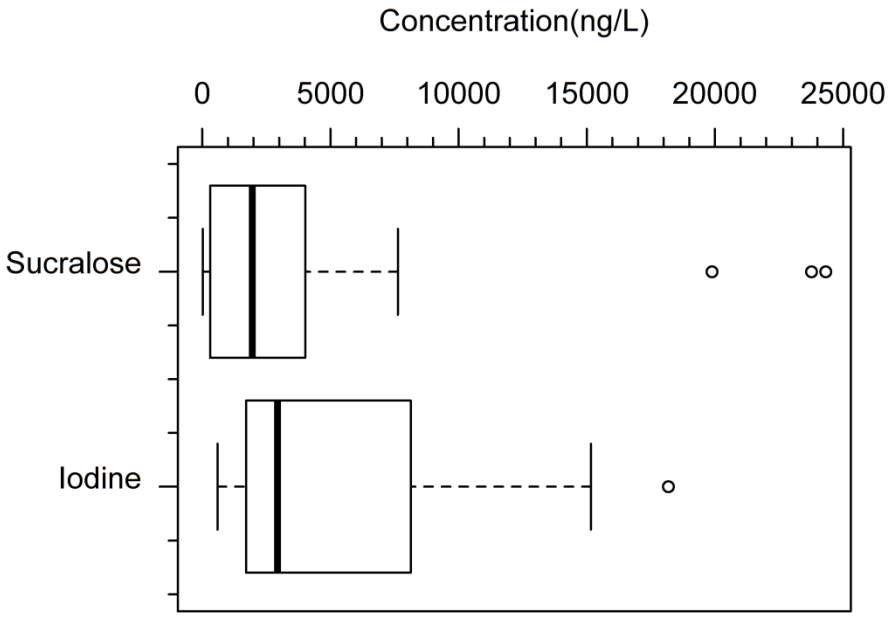
a,b- estimation parameters

Occurrence

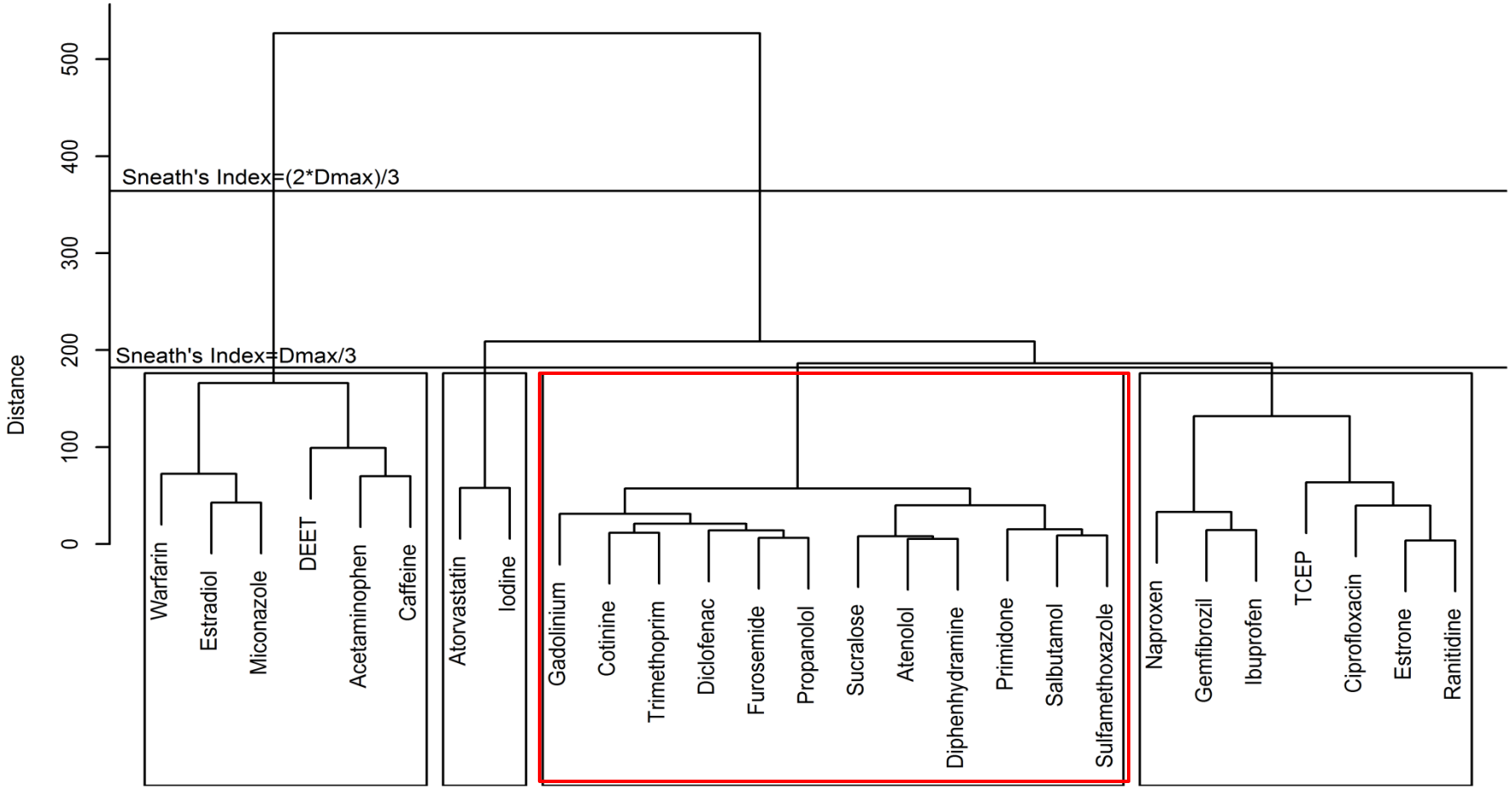

Concentration(ng/L)
0
20
40
60
80
100
120
140
Acetaminophen
Atorvastatin
Caffeine
Cotinine
DEET
Diclofenac
Diphenhydramine
Estradiol
Estrone
Gadolinium
Gemfibrozil
Ibuprofen
Miconazole
Naproxen
Primidone
Propanolol
Salbutamol
Warfarin


Concentration(ng/L)
0
500
1000
1500
Atenolol
Ciprofloxacin
Furosemide
Ranitidine
Sulfamethoxazole
TCEP
Trimethoprim

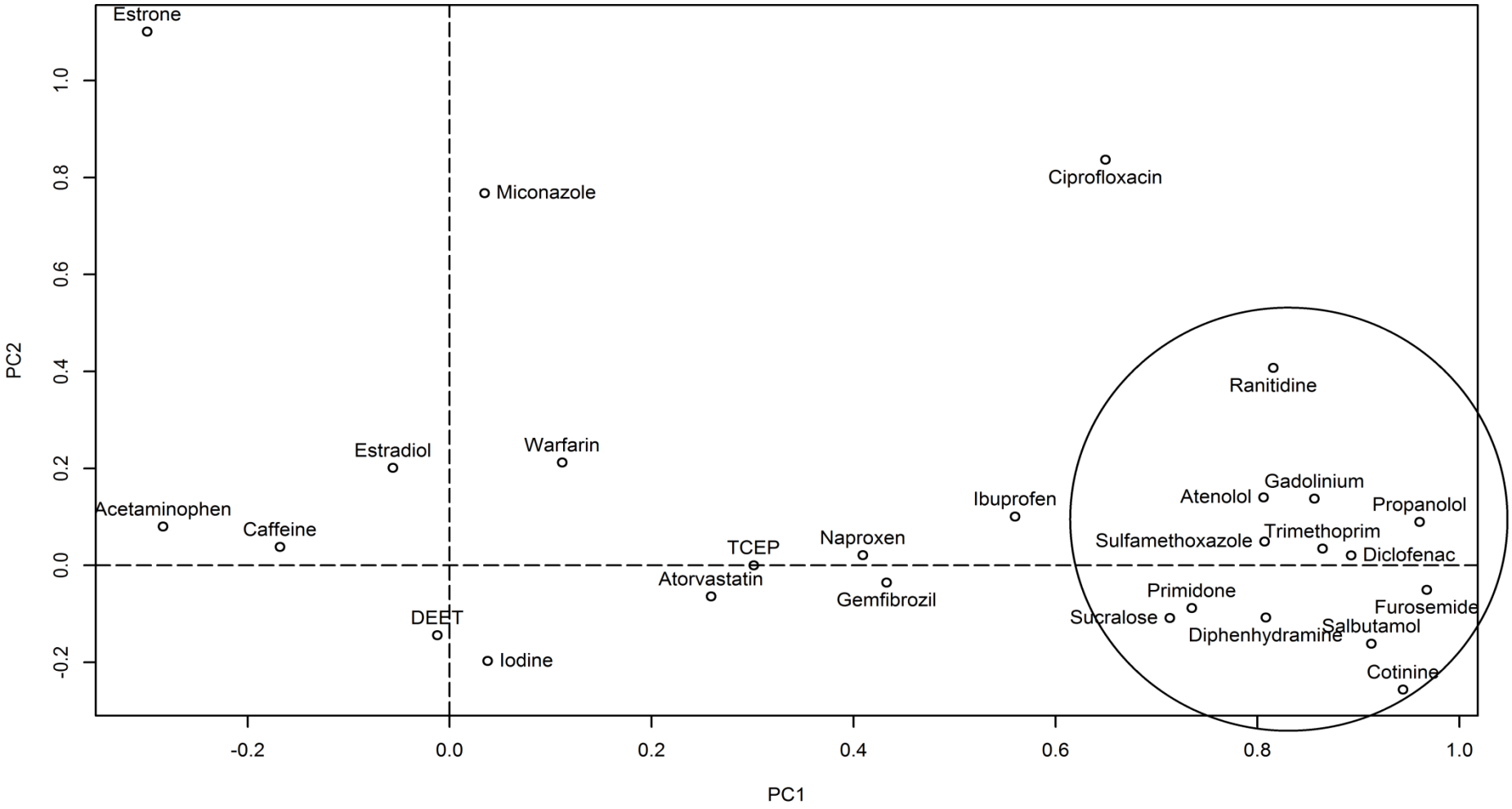
Occurrence


Concentration(ng/L)
0
5000
10000
15000
20000
25000
Sucralose
Iodine

Cluster Analysis



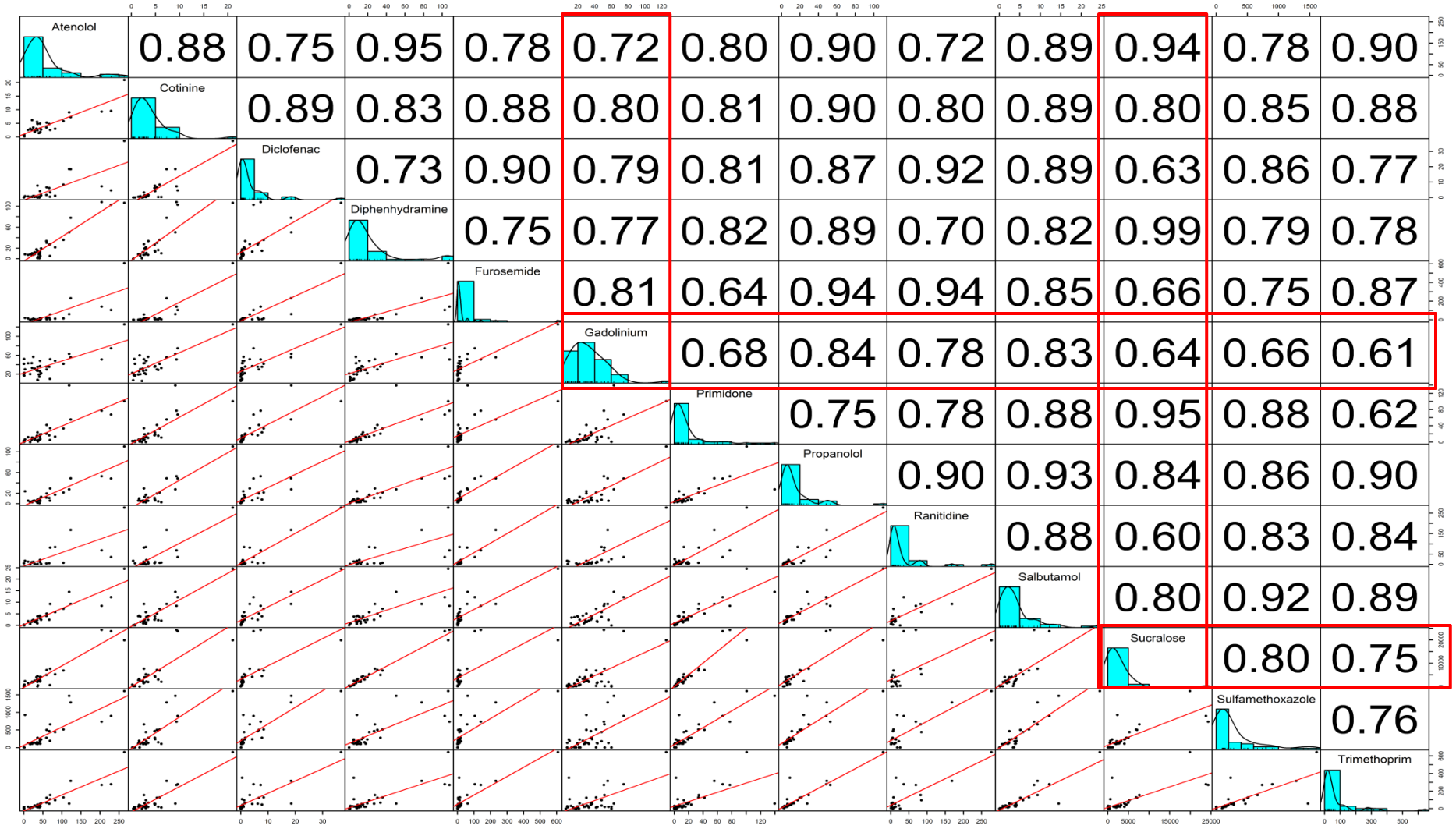
Principal Component Analysis



Analyte Grouping

Compound	Use	Compound	Use
Atenolol	Beta-blocker	**Primidone**	Anti-epileptic
Cotinine	Nicotine metabolite	**Propanolol**	Beta-blocker
Diclofenac	Anti-inflammatory	**Ranitidine**	Ulcers&heart burn
Diphenhydramine	Anti-histamine	**Salbutamol**	Asthma Treatment
Furosemide	Loop Diuretic	**Sucralose**	Artificial Sweetener
Gadolinium	Contrast Agent	**Sulfamethoxazole**	Antibiotic
Ibuprofen	Anti-inflammatory	**Trimethoprim**	Antibiotic

Correlation Analysis

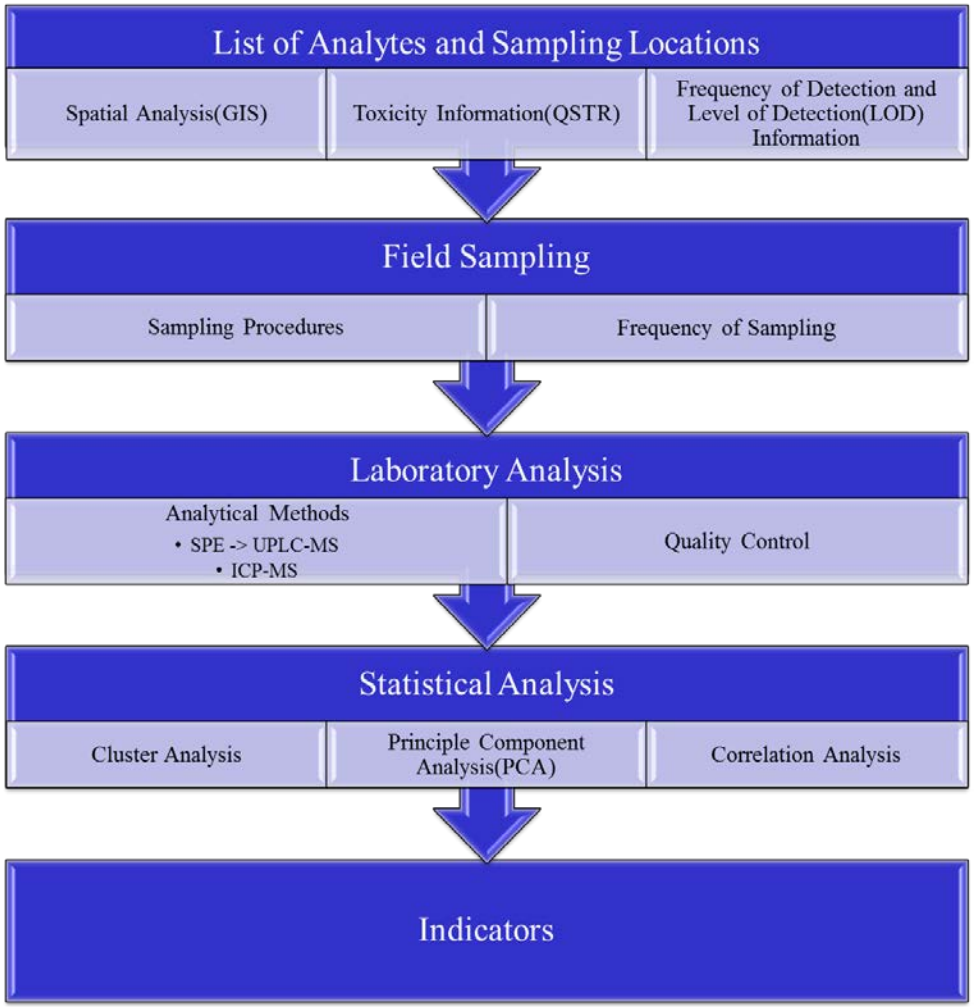


Compound	Predictor	R^2	Estimation Parameters	
			a (p-value)	b (p-value)
Atenolol	Gadolinium	0.56	2.21(<0.005)	-39.4 (0.04)
Cotinine	Gadolinium	0.61	0.15(<0.005)	-2.21(0.047)
Diclofenac	Gadolinium	0.77	0.31(<0.005)	-8.72(<0.005)
Diphenhydramine	Gadolinium	0.5	0.91(<0.005)	-12.6(0.206)
Furosemide	Gadolinium	0.84	5.45(<0.005)	-173(<0.005)
Primidone	Gadolinium	0.48	0.73(<0.005)	11.1(<0.005)
Propranolol	Gadolinium	0.76	0.96(<0.005)	-22.9(<0.005)
Ranitidine	Gadolinium	0.84	2.56(<0.005)	-81.3(<0.005)
Salbutamol	Gadolinium	0.73	0.19(<0.005)	-3.71(<0.005)
Sucralose	Gadolinium	0.33	0.49(<0.005)	7.34(0.256)
Sulfamethoxazole	Gadolinium	0.52	11.76(<0.005)	-242(0.025)
Trimethoprim	Gadolinium	0.001	0.01(0.884)	3.84(0.247)

Conclusions & Recommendations

- Its possible to cluster the compounds into distinct groups.
- It is also possible to choose indicators based on co-occurrence.
- Gadolinium serves as a good indicator for several pharmaceuticals.
- Clustering is dictated by usage patterns.

Suggested Protocol



List of Recommended Indicators

Indicator	Compounds	
Gadolinium	Atenolol	Propanolol
	Cotinine	Ranitidine
	Diclofenac	Salbutamol
	Diphenhydramine	Sucralose
	Furosemide	Sulfamethoxazole
	Ibuprofen	Trimethoprim
	Primidone	
Acetaminophen	Acetaminophen	
Atorvastatin	Atorvastatin	
Caffeine	Caffeine	
Ciprofloxacin	Ciprofloxacin	
DEET	DEET	
Estradiol	Estradiol	
Estrone	Estrone	
Gemfibrozil	Gemfibrozil	
Miconazole	Miconazole	
Naproxen	Naproxen	
TCEP	TCEP	
Warfarin	Warfarin	

To next lecture

Fish Pharm
These pills represent the relative amounts of four pharmaceutical drugs found in fish pulled from Chicago's North Shore Channel and tested by Baylor scientists.

* PERCENTAGES EXCEED 100 BECAUSE OF ROUNDING.
BLUE ANTIHISTAMINE PILLS (TOP) ARE NOT INCLUDED IN PERCENTAGES.

Questions ?

The traditional foe of water quality is waste from factories and farms, but now environmental regulators are eyeing a new pollution source: our medicine chests. Fish caught downstream from sewage treatment plants in five U.S. cities contained traces of pharmaceuticals and toiletries, Baylor University researchers found in a recent study. You'd have to eat tons of fish for such small concentrations to affect human health, but the products could pose a threat to marine life. To assess the risk, the EPA has expanded monitoring to 150 sites, with results due in 2011.

Ref: National Geographic

- To next lecture