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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

Department of Civil and Environmental Engineering

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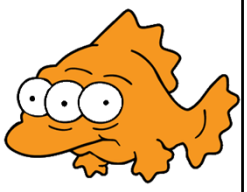
What are EDCs and PPCPs and Why Study Them?

- 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

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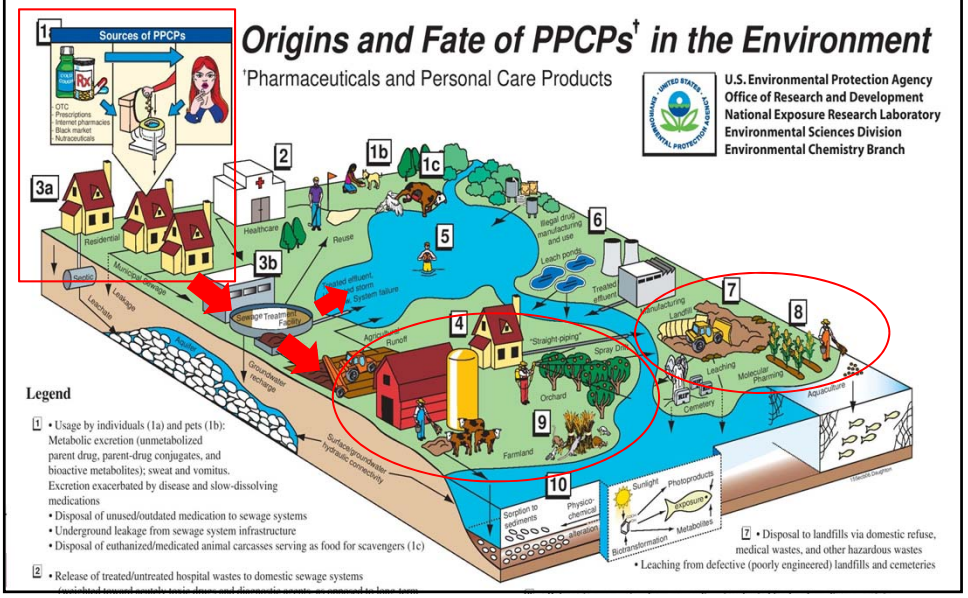
EDC/PPCP Sources



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Fate and Transport of EDCs and PPCPs

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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

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Analytical Methods

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

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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

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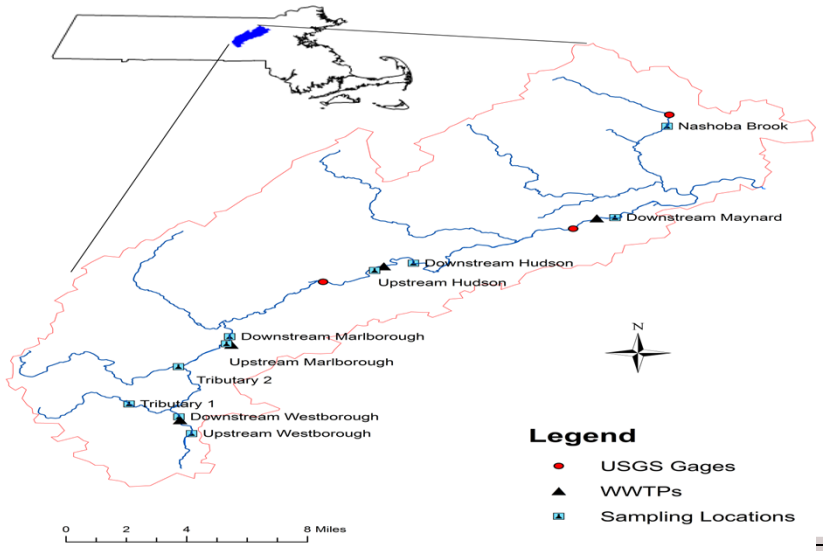
Sampling Locations



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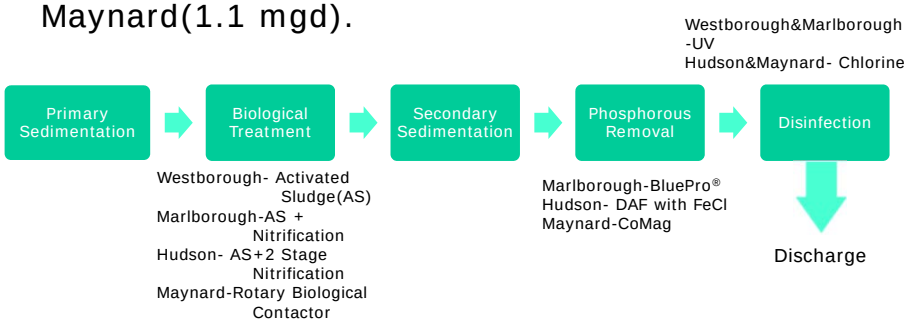
Wastewater Treatment Plants(WWTPs)

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



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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

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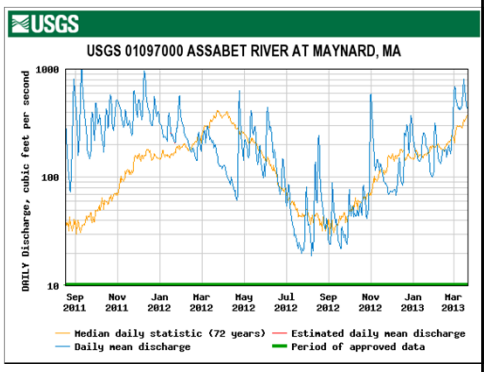
Sampling Dates

Sampling Date (MM/YYYY)	Flow at Maynard USGS Gage(cfs)	Sampling Date (MM/YYYY)	Flow at Maynard USGS Gage(cfs)
08/22/2011	121	07/25/2012	22
11/16/2011	303	08/28/2012	42
02/06/2012	241	09/20/2012	35
02/28/2012	182	11/01/2012	593
04/11/2012	86	11/30/2012	73
05/10/2012	331	02/01/2013	318
06/20/2012	86	03/01/2013	687



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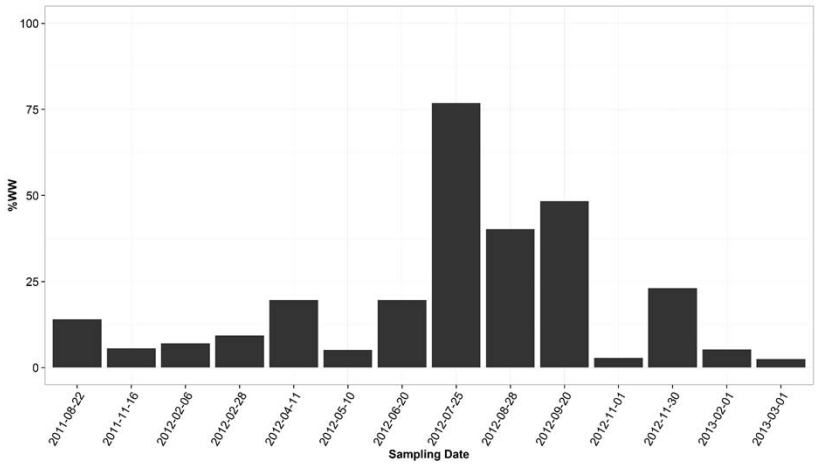
% Wastewater



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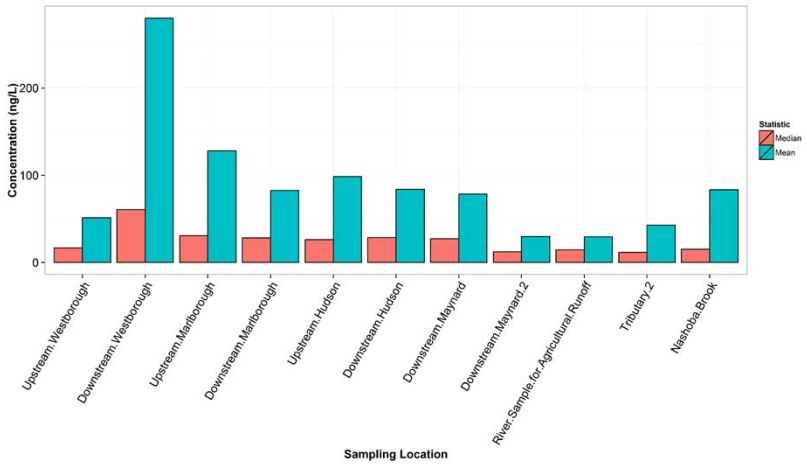
Sampling Locations



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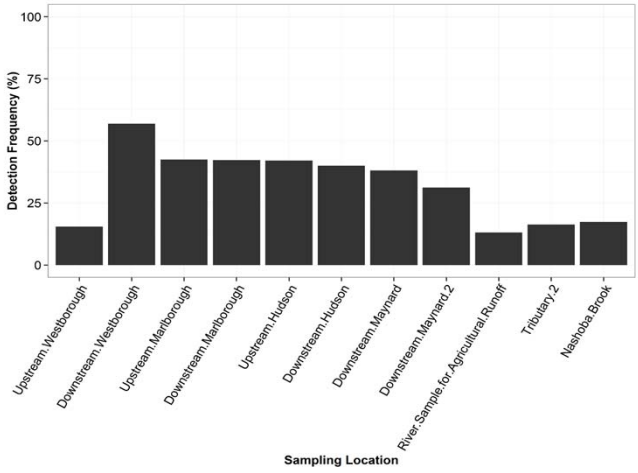
Sampling Locations



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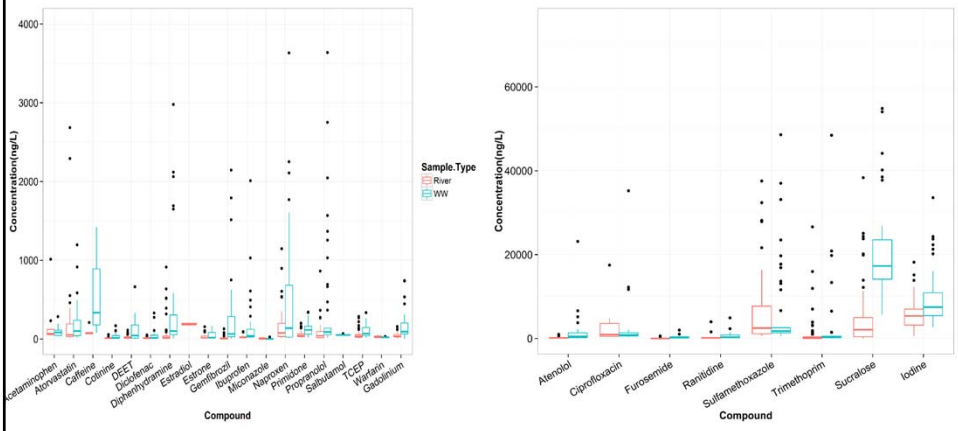
Results



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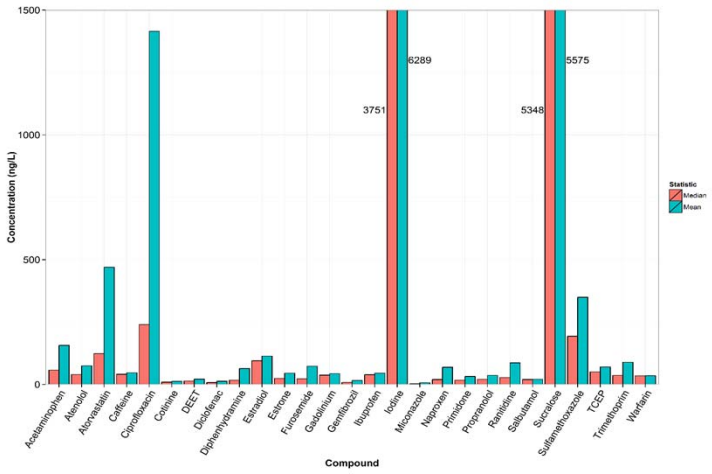
Compounds



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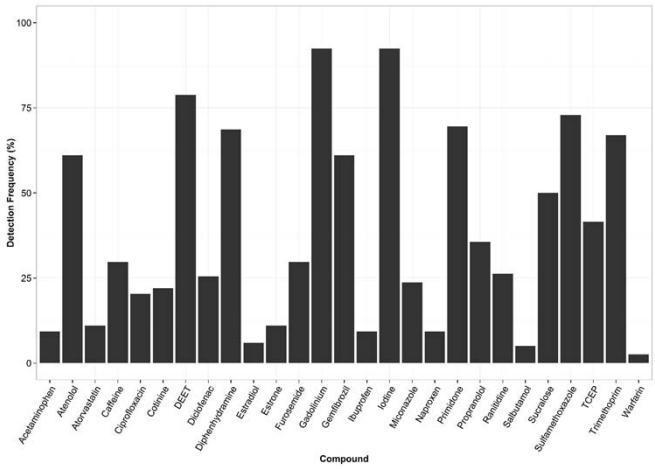
Compounds



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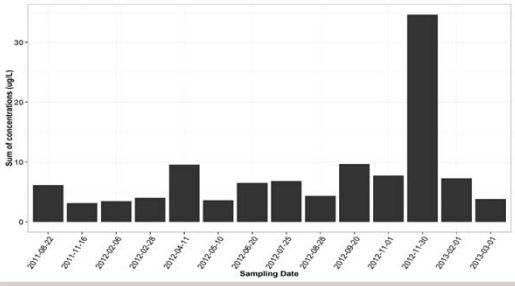
Sum of Concentrations vs Sampling Date



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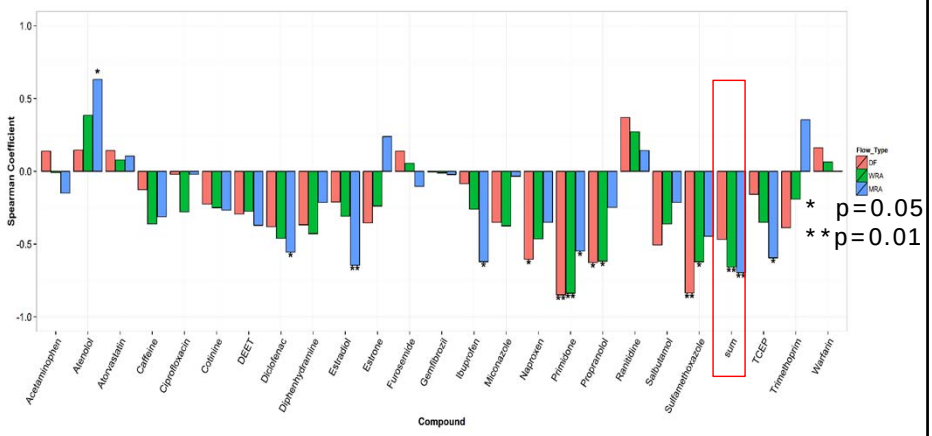
Correlation with River Flow



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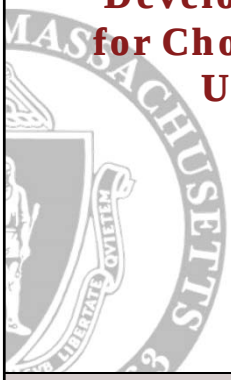
Developing a Watershed-Level Protocol for Choosing Indicators for EDCs/PPCPs Using Analytical Methods and Chemometrics



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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.

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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

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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.

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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

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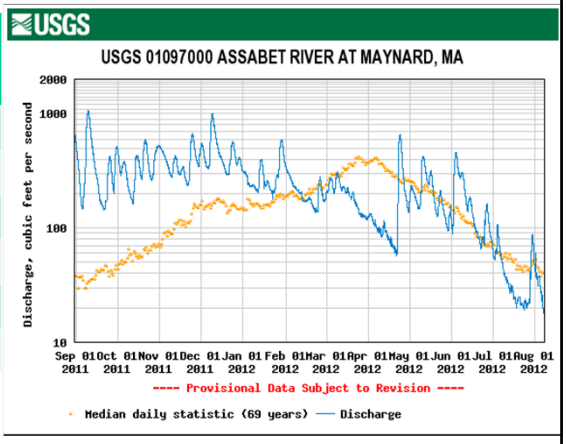
Sampling Dates

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



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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.

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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

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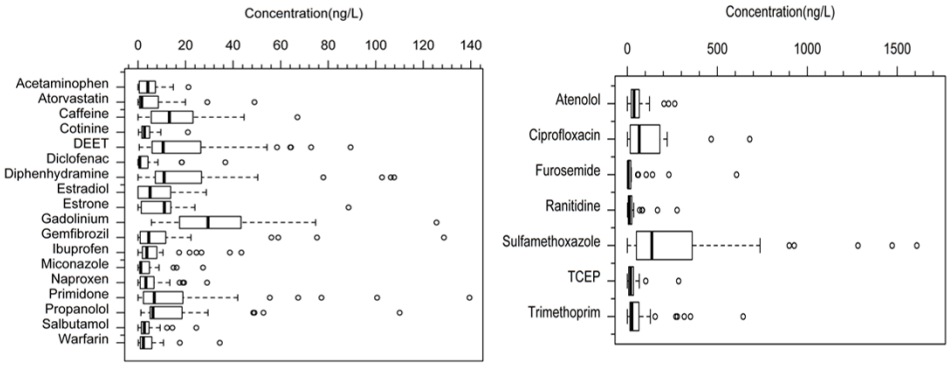
Occurrence



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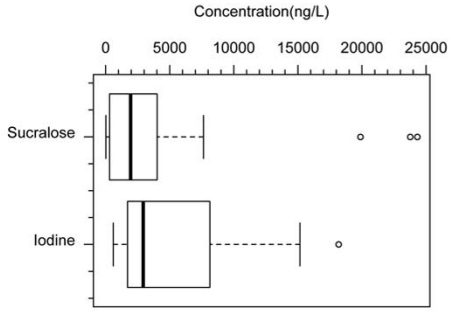
Occurrence



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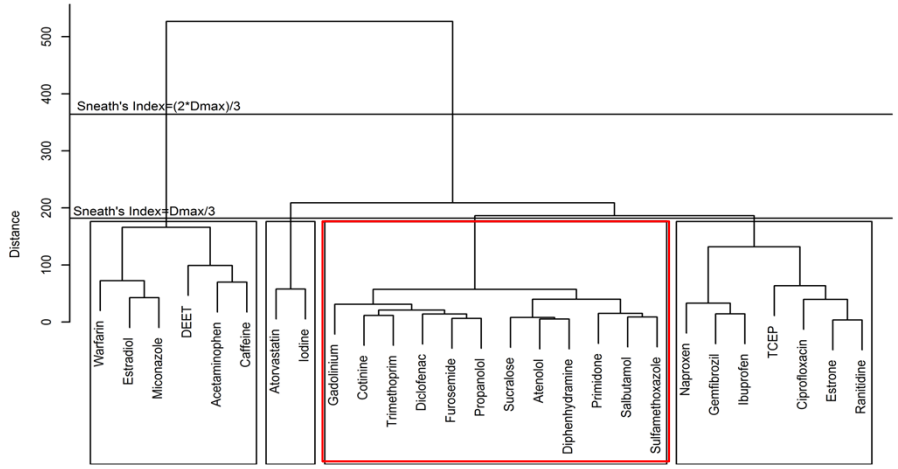
Cluster Analysis



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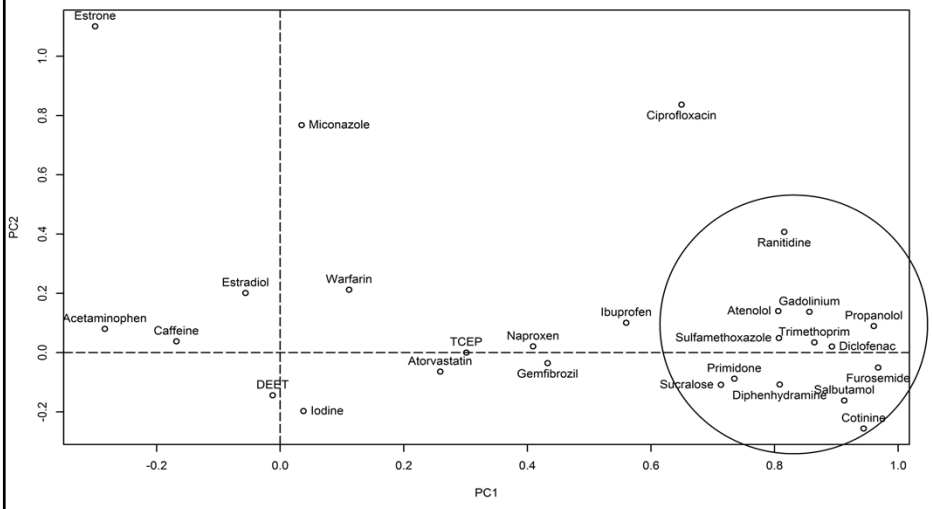
Principal Component Analysis



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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

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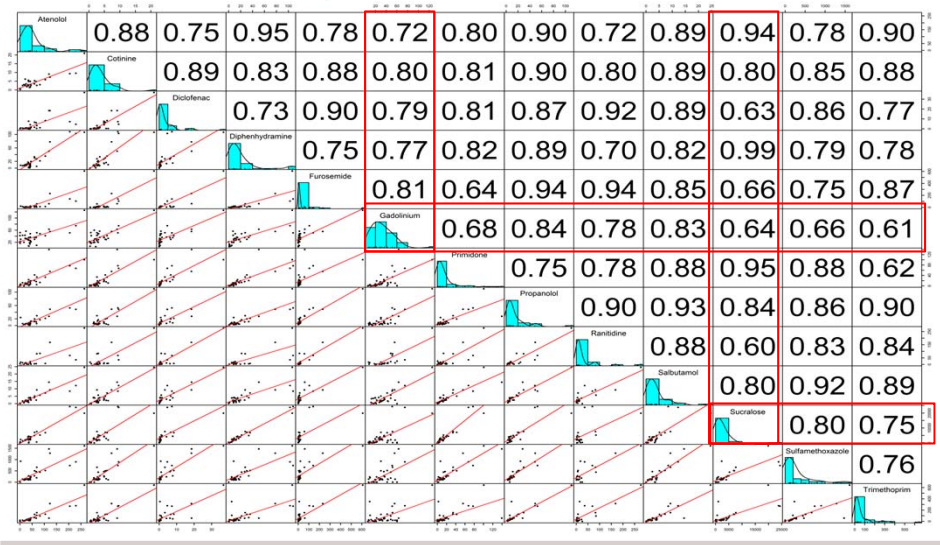
Correlation Analysis



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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)

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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.

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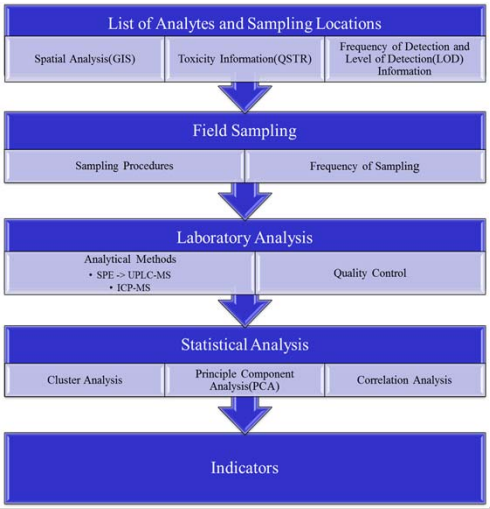
Suggested Protocol



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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	

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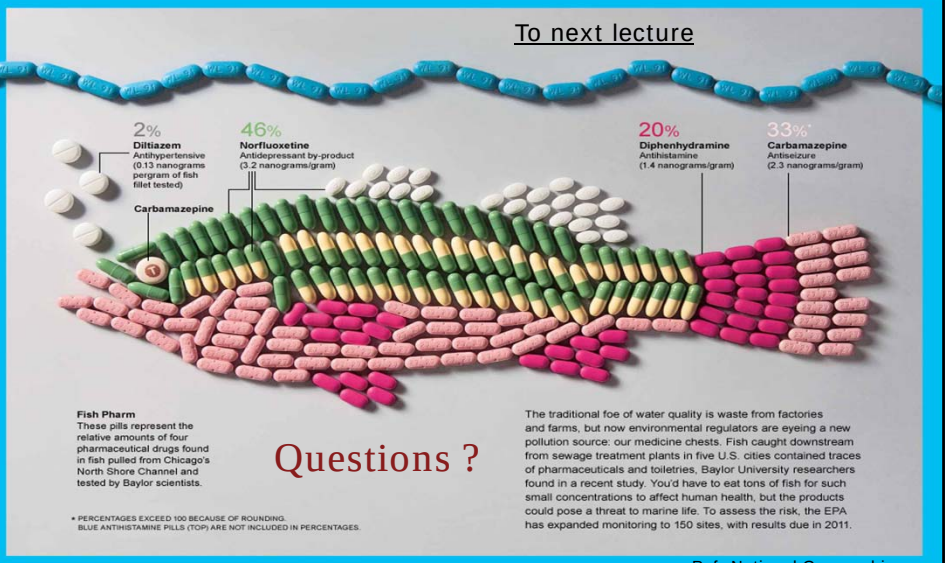

Questions ?

Ref: National Geographic