Occurrence and fate of high volume pharmaceuticals in wastewater impacted environments

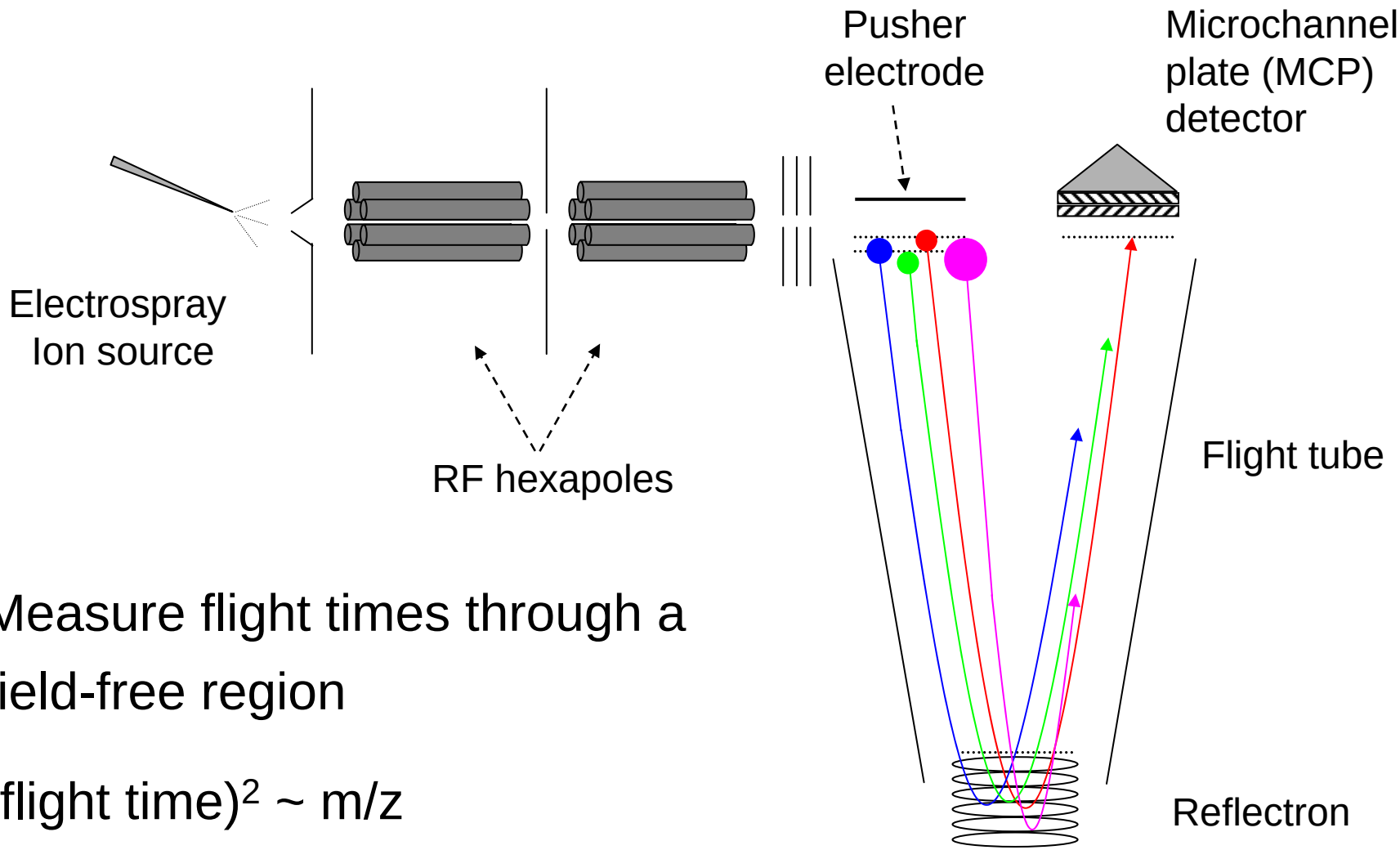
Mark J. Benotti and Bruce J. Brownawell

Marine Sciences Research Center, Stony Brook University, Stony Brook, NY 11794-5000

Objectives

- Develop LC-ToF-MS methodology for the analysis of pharmaceuticals in wastewater-impacted environments
- Determine occurrence of selected pharmaceutically active compounds (PhACs) in Long Island groundwater
- Elucidate processes governing compound mobility (e.g. sorption or degradation)
- Compare PhAC occurrence and fate between surface and groundwater
- *Which compounds make the best tracers?*

The oaToF mass analyzer: Micromass LCT™



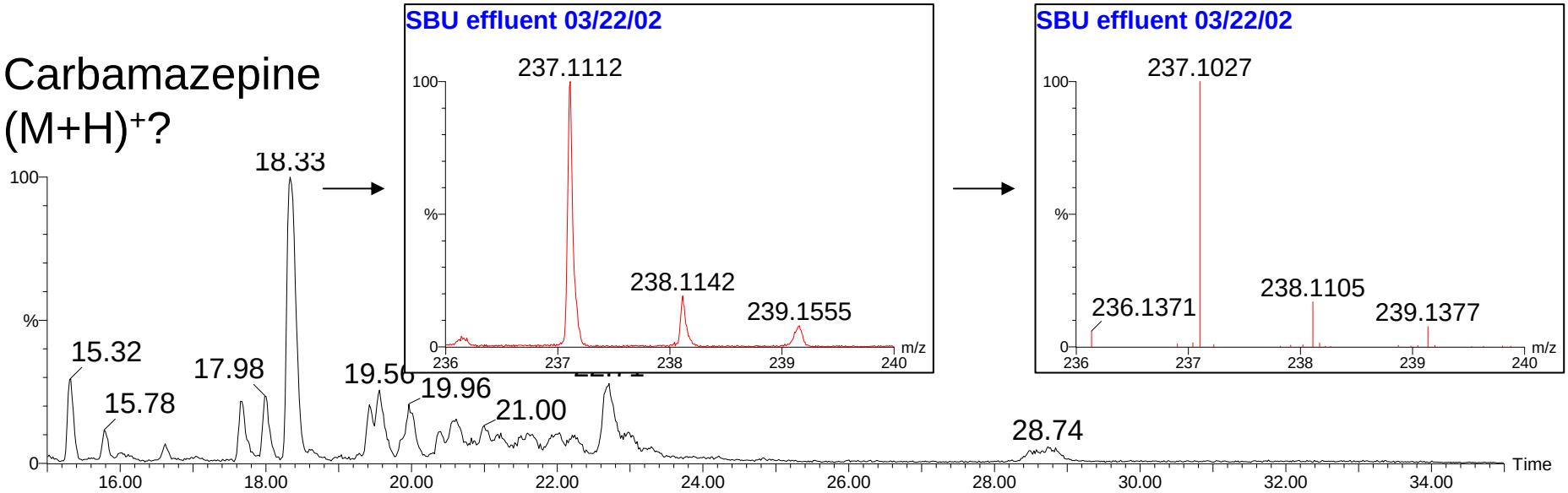
- Measure flight times through a field-free region
- (flight time)^2 ~ m/z

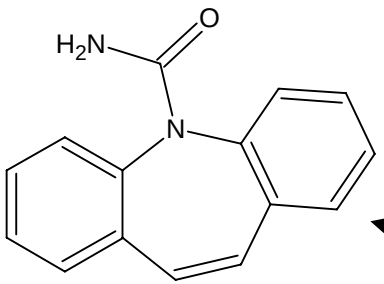
Benefits of ToF-MS

- Higher resolution than commonly used mass spectrometers
  - ➢ Increased sensitivity and selectivity
  - ➢ Accurate mass estimation and elemental composition calculation
- Full spectral sensitivity (instrument “sees” all ions in defined mass range)
  - ➢ Investigation of unknowns or non-target compounds

Accurate mass estimation and elemental comp.

Carbamazepine
$(M+H)^+$?





$C_{15}H_{12}N_2O$
(M+H)+=237.1028

Elemental Composition

File Edit View Process Help

Single Mass Analysis

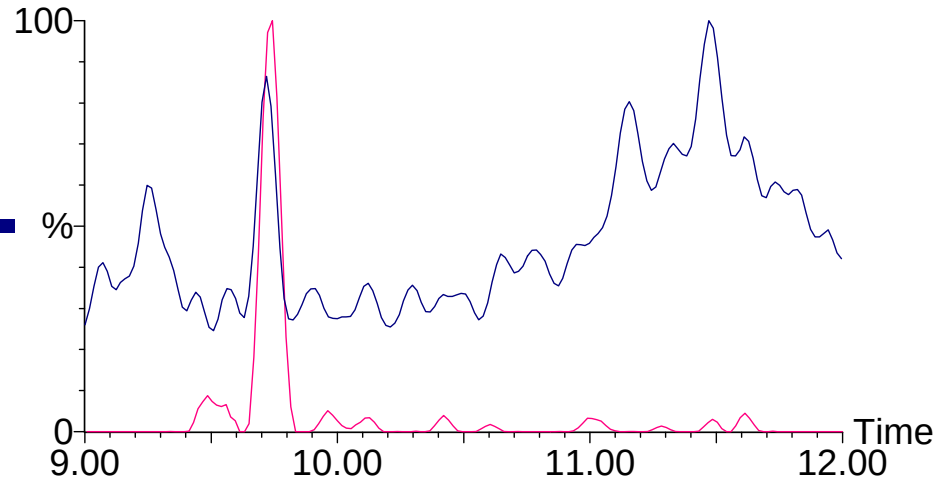
Tolerance = 10.0 PPM / DBE: min = -0.5, max = 50.0

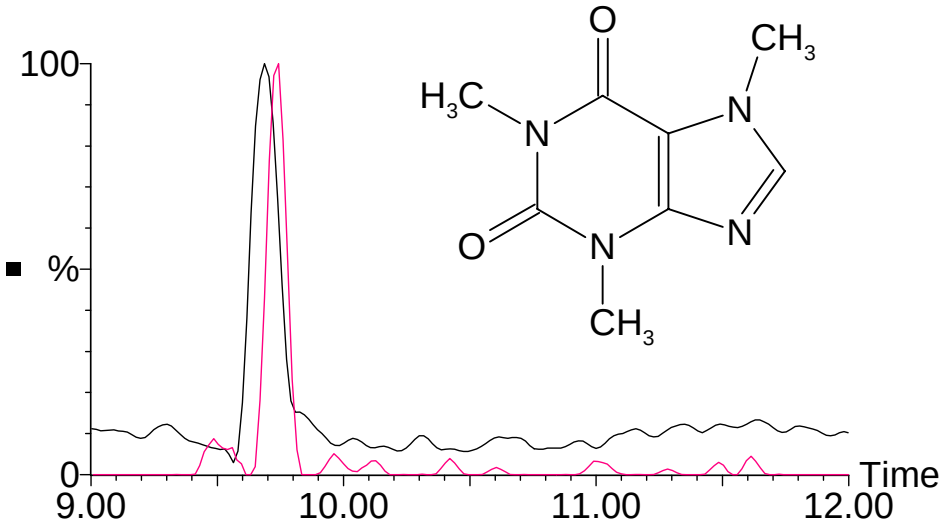
Mass	Calc. Mass	mDa	PPM	DBE	Formula	C	H	N	O	S
237.1027	237.1028	-0.1	-0.3	10.5	C15 H13 N2 O	15	13	2	1	
	237.1021	0.6	2.4	1.5	C7 H17 N4 O3 S	7	17	4	3	1
	237.1035	-0.8	-3.3	1.0	C9 H19 N O4 S	9	19	1	4	1
	237.1014	1.3	5.3	11.0	C13 H11 N5	13	11	5		
	237.1008	1.9	8.1	2.0	C5 H15 N7 O2 S	5	15	7	2	1
	237.1048	-2.1	-8.9	6.0	C10 H15 N5 S	10	15	5		1

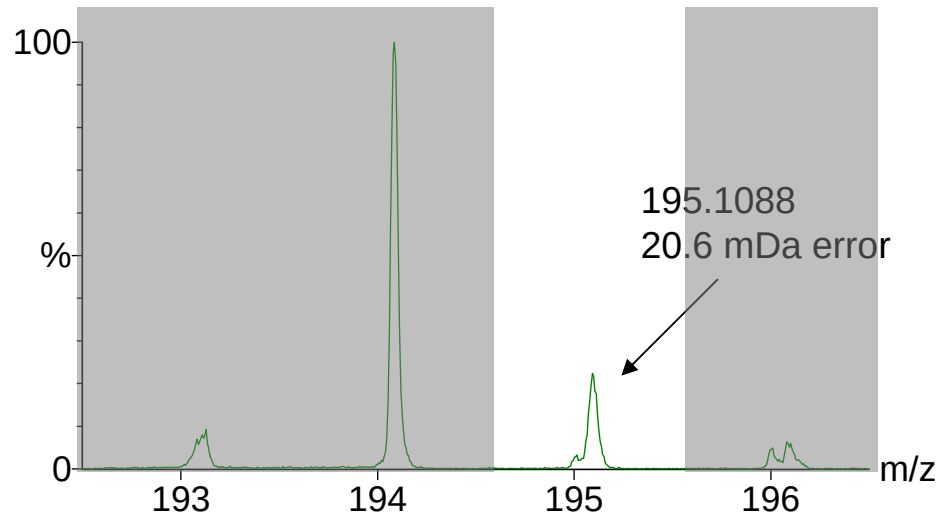
For Help, press F1

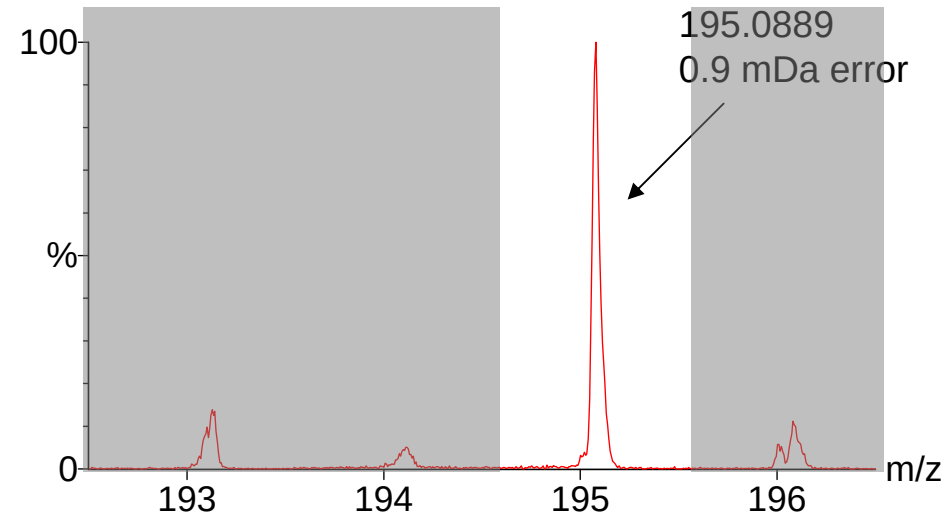
Identification of interferences/false positives

Caffeine in extracts from separate WWTPs

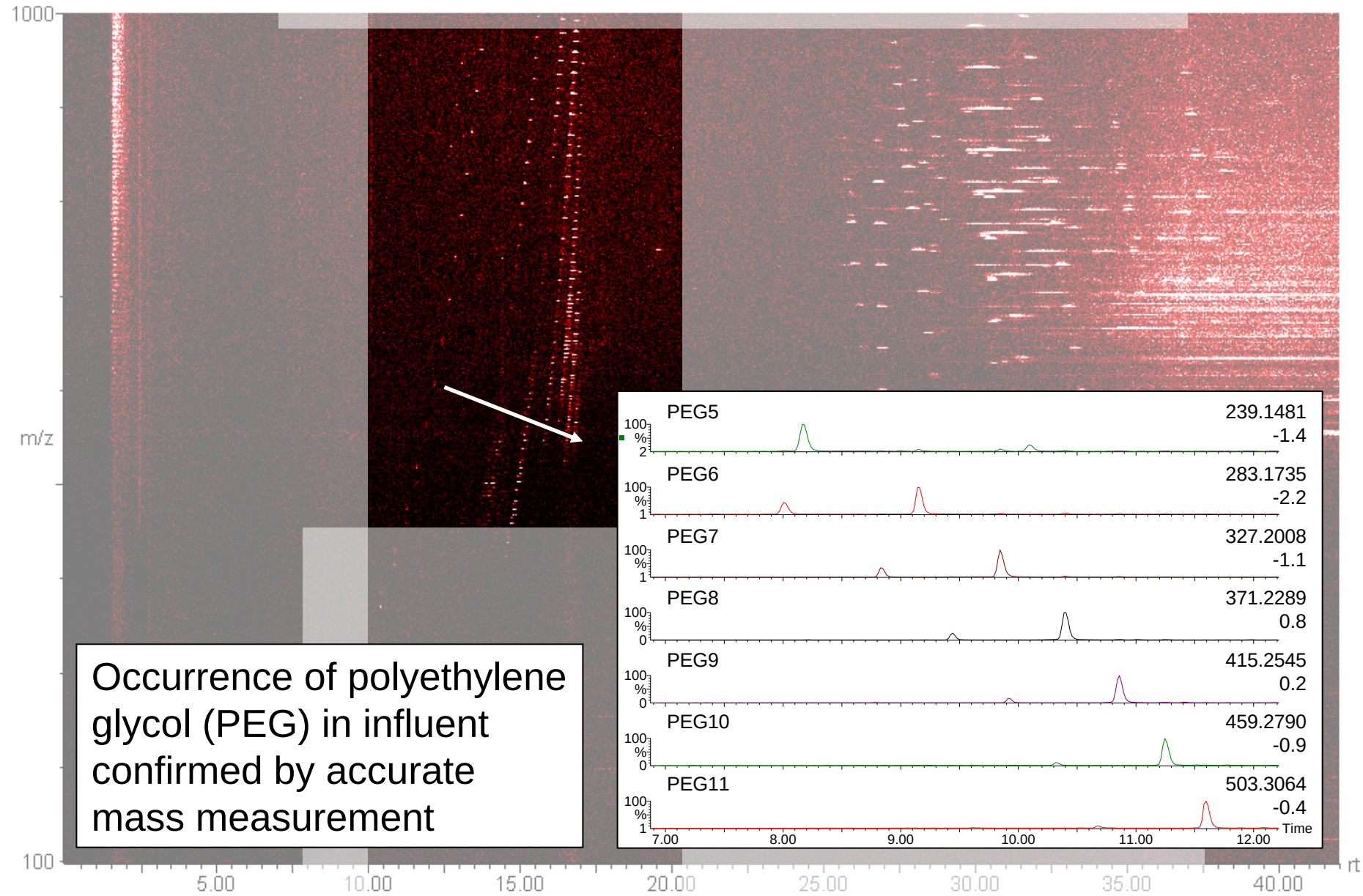








TOF-MS: Identification of unknowns



Occurrence of polyethylene glycol (PEG) in influent confirmed by accurate mass measurement

ToF-MS conclusions

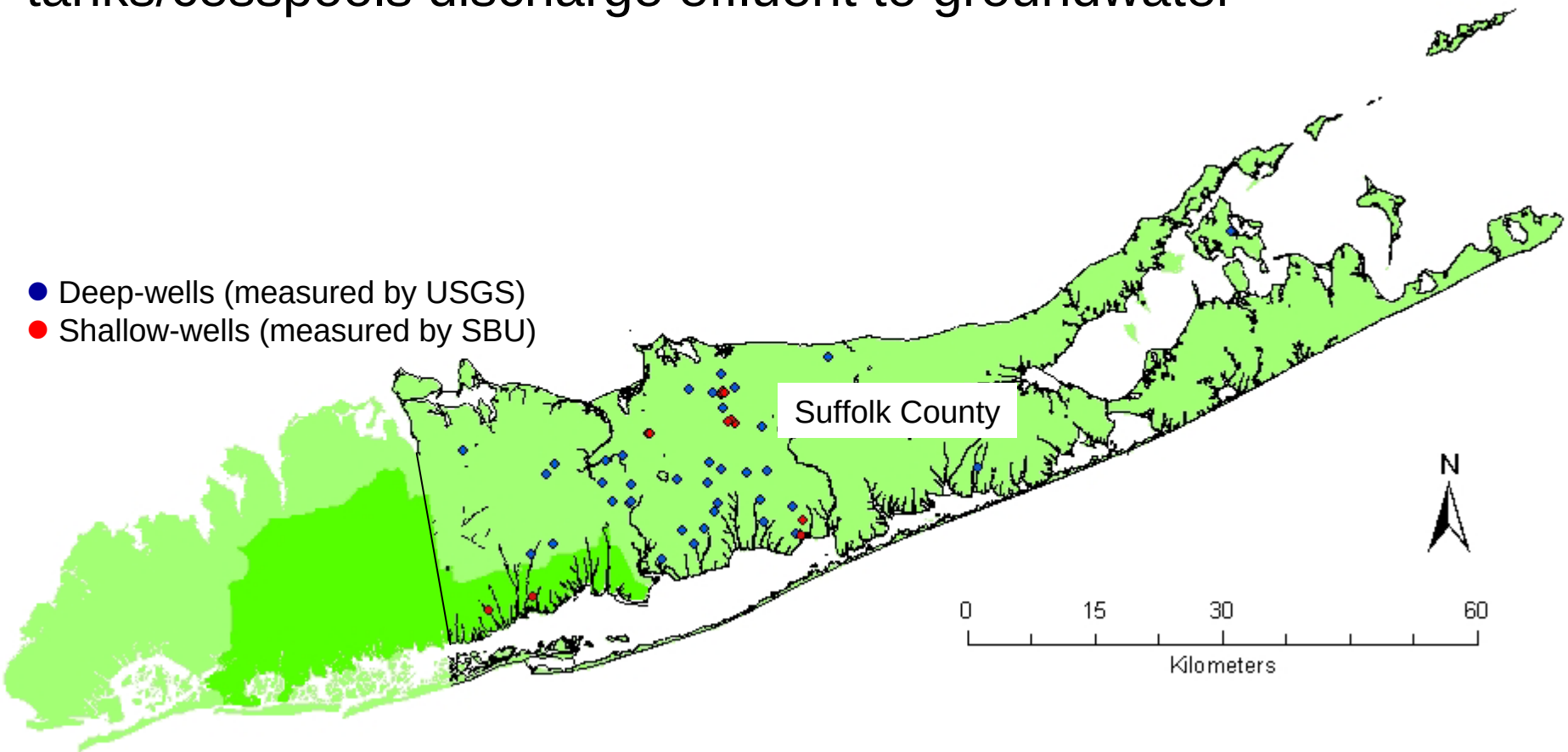
- We can detect a wide range of target and non-target compounds in aqueous samples using accurate mass and elemental composition for confirmation and/or structure identification
- Methods have been applied to investigate…
  - ➢PhACs in groundwater, estuarine surface water, and effluent
  - ➢Estrogens and APEOs in water and sediments
  - ➢Removal of emerging contaminants during RO wastewater treatment
  - ➢Polyethoxylated homologous series of surfactants and surfactant metabolites

PhACs in groundwater

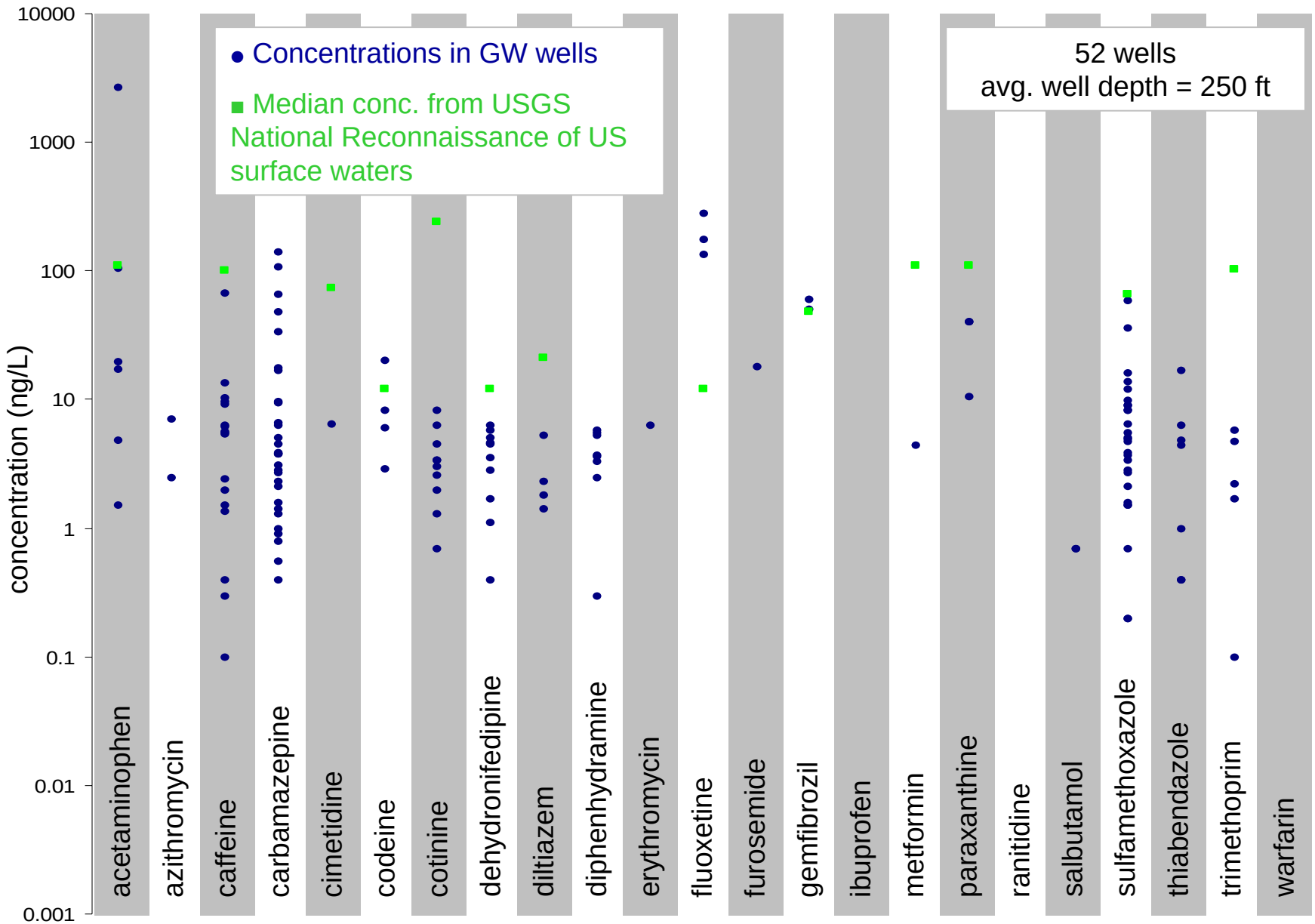
- Investigations of environmental occurrence have focused primarily on surface waters
- 23% of US households utilize on-site sewage-treatment (i.e. cesspools or septic tanks)
- Recent increases in “beneficial” re-use of wastewater (e.g. irrigation and artificial recharge) potentially impact groundwater quality
- Many US water supplies are drawn in part or exclusively from groundwater

Long Island

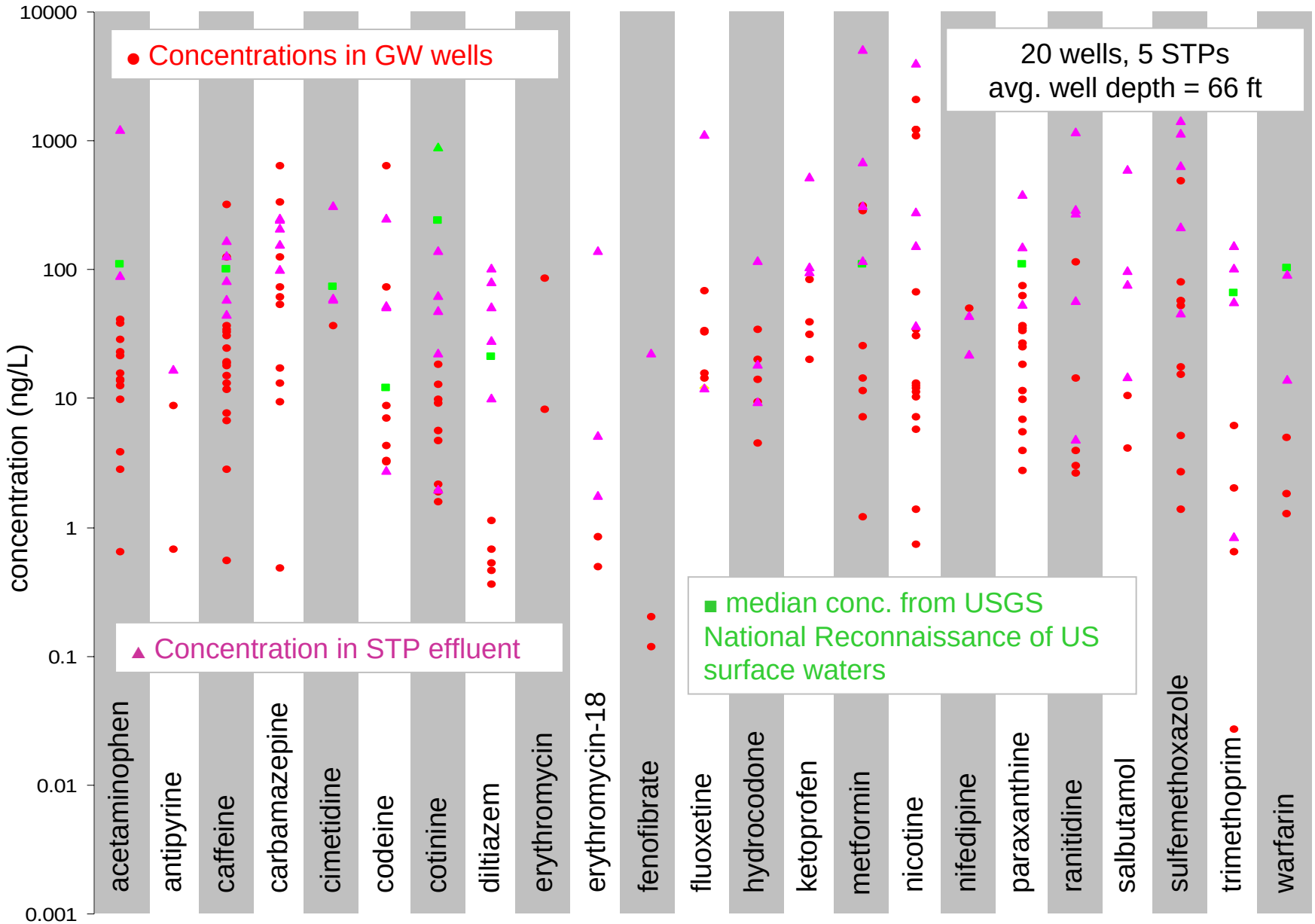
- Largest population with a sole-source aquifer in the US
- Many municipal and private STPs, as well as all domestic septic tanks/cesspools discharge effluent to groundwater



Deep-well data (USGS analysis)



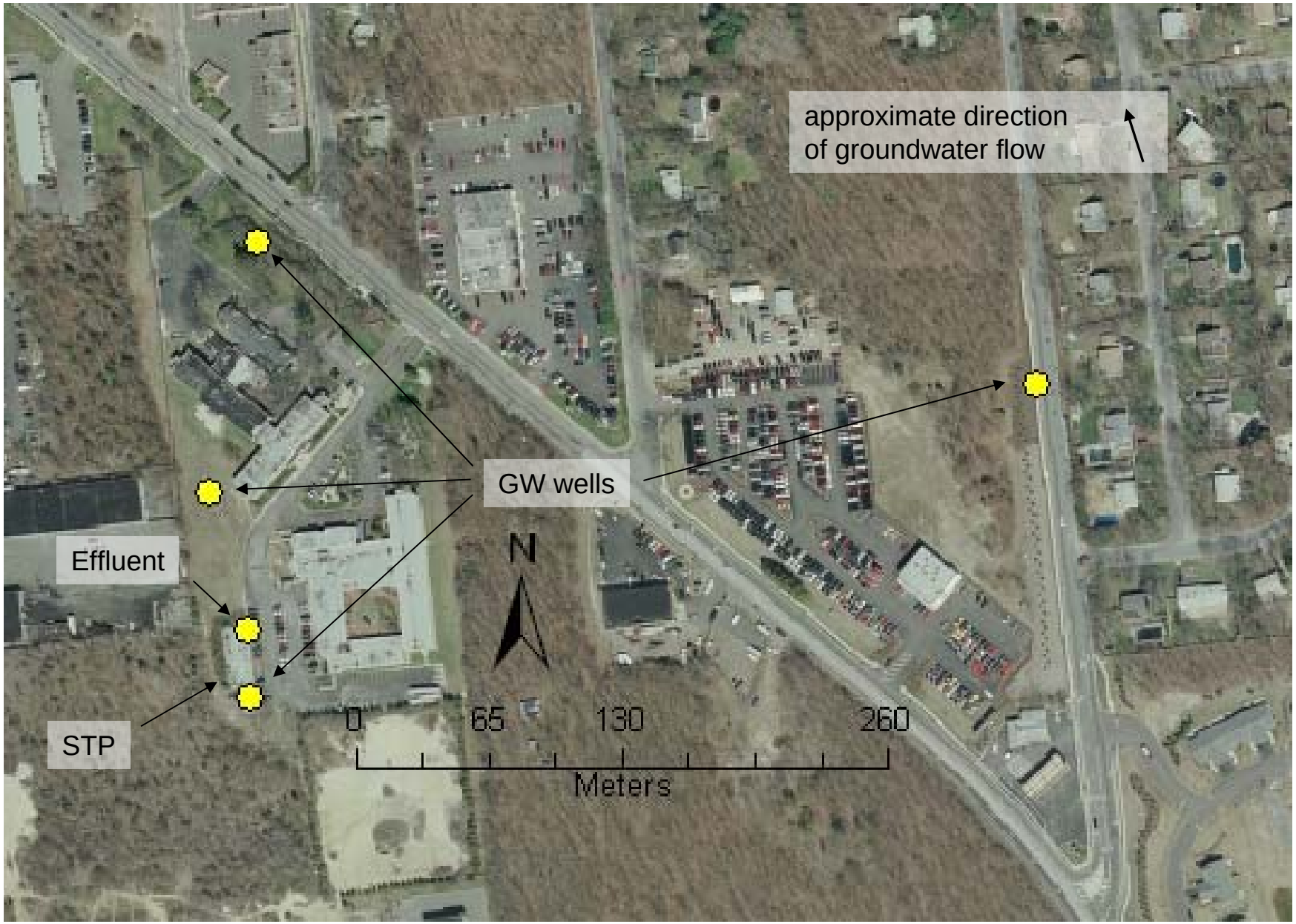
Shallow-well data (SBU analysis)



Cumulative GW data

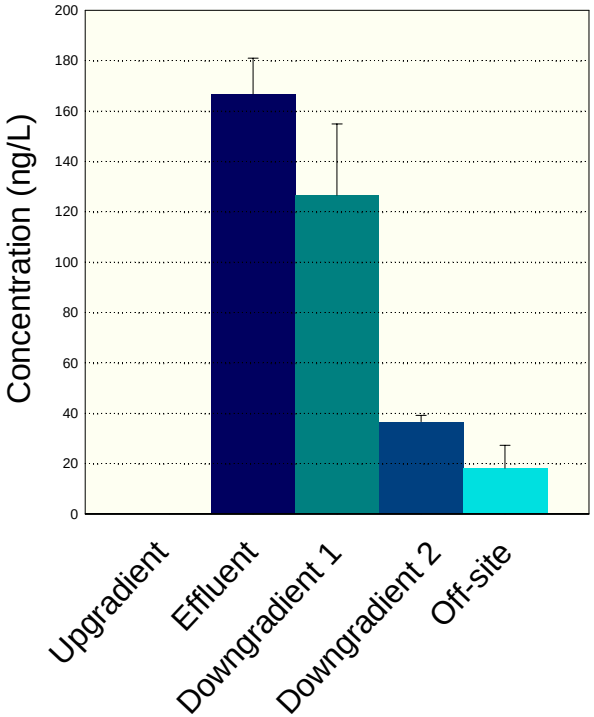
Compound	*USGS Nat'l Recon. median concentration for SW (ng/L)*	Shallow-well median concentration (ng/L)	Frequency of detect (n=20)	Deep-well median concentration (ng/L)	Frequency of detect (n=52)
Acetaminophen	*110*	14.2	65	18.5	11.5
Caffeine	*100*	18.8	85	5.5	32.7
Carbamazepine		57.9	50	3.8	55.8
Cimetidine	*74*	36.7	5	6.5	1.9
Codeine	*12*	7.0	35	9.4	7.7
Cotinine	*240*	5.2	50	3.5	19.2
Diltiazem	*21*	0.5	25	2.0	7.7
Erythromycin		47.4	10	6.3	1.9
Fluoxetine	*12*	33.1	25	174	5.8
Metformin	*110*	14.5	50	4.5	1.9
Paraxanthine	*110*	21.8	70	40.1	5.8
Ranitidine		3.9	25	nd	0
Salbutamol		7.3	10	0.7	3.8
Sulfamethoxazole	*66*	35.0	50	4.9	51.9
Trimethoprim	*103*	1.3	20	2.9	9.6

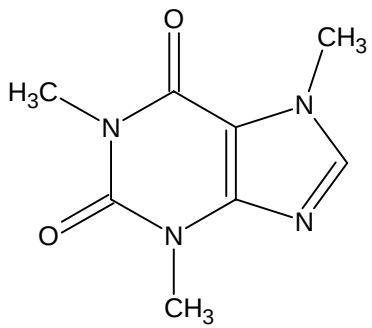
Nursing home with on-site STP



Transport through well field and sorption

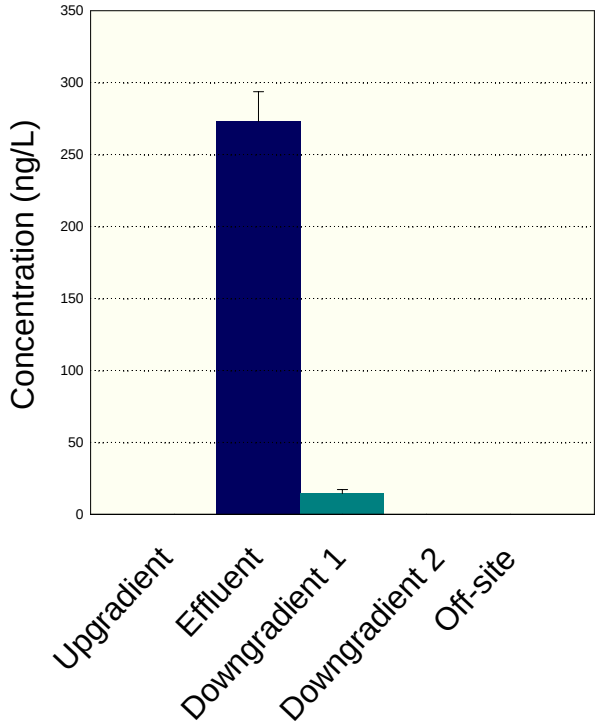
Caffeine

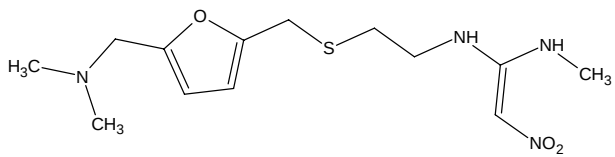




K_D = 5.0

Ranitidine





K_D= 350

Summary of nursing home and sorption data

	Transport	K_D
Caffeine	Best	5.0
Carbamazapine	Best	3.7
Ketoprofen	Best	9.4
Paraxanthine	Best	8.2
Sulfamethoxazole	Best	3.4
Acetaminophen	Limited	12.9
Codeine	Limited	17.3
Fluoxetine	Limited	58.6
Nicotine	Limited	10.0
Trimethoprim	Limited	15.8
Cotinine	Negligible	20.9
Diltiazem	Negligible	585
Hydrocodone	Negligible	22.8
Metformin	Negligible	13.5
Nifedipine	Negligible	12.6
Raniditine	Negligible	350
Salbutamol	Negligible	3.0
Warfarin	Negligible	1.5

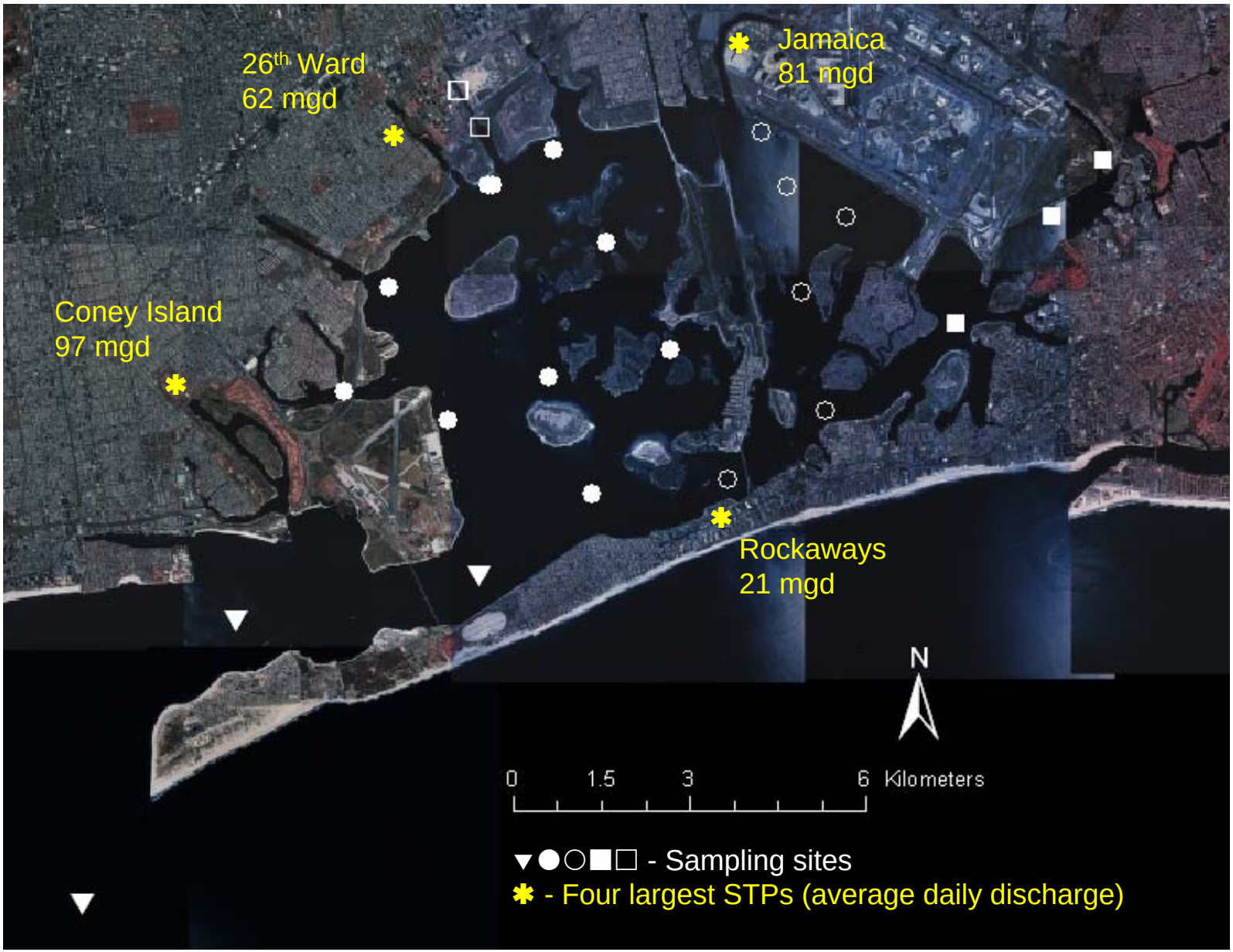
Those compounds that moved well with groundwater are not degraded nor strongly adsorbed

"Best" transported compounds have low K_Ds

Those PPCPs that do not move well with groundwater are either strongly adsorbed or degraded

Some "negligibly" transported compounds have high K_Ds suggesting adsorption and some have low K_Ds suggesting microbial degradation

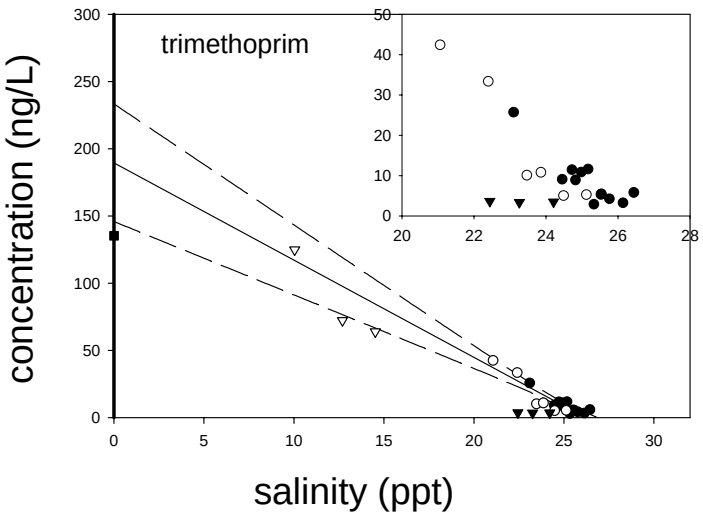
Jamaica Bay – a sewage estuary



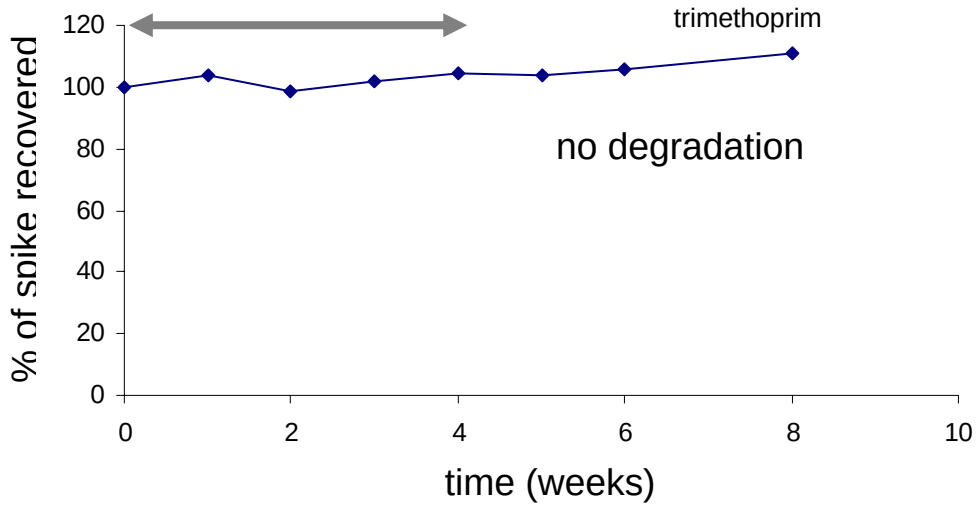
Do compounds behave conservatively in JB?

During dry periods, wastewater is only source of freshwater to the bay, thus concentrations should behave conservatively with salinity if no removal, and y intercept (salinity=0) should predict effluent concentration

Occurrence

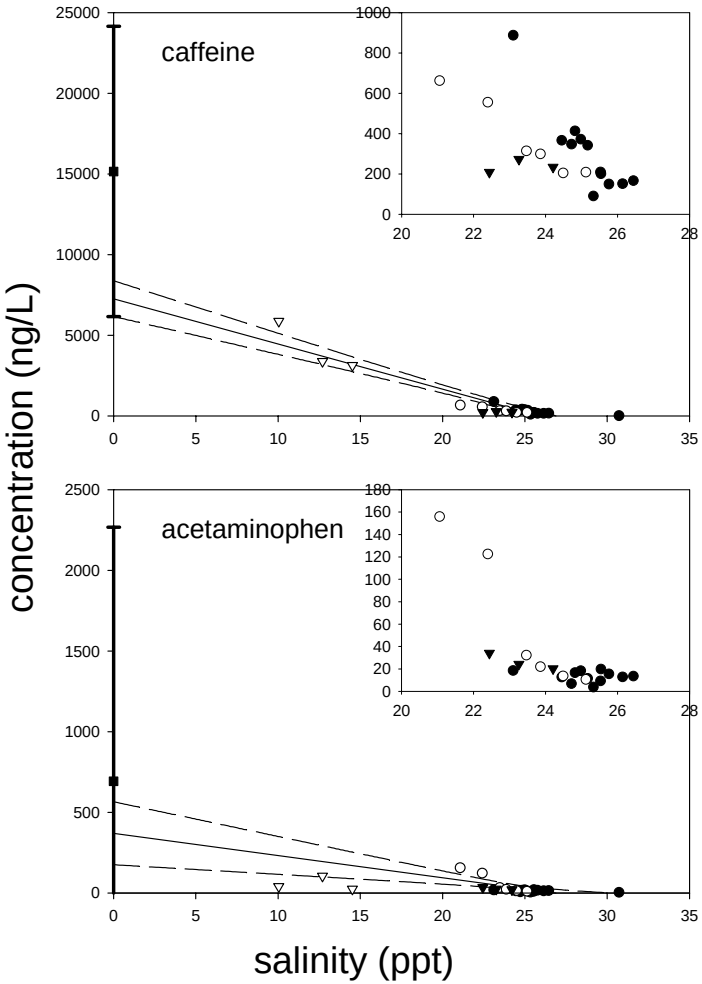


Degradation

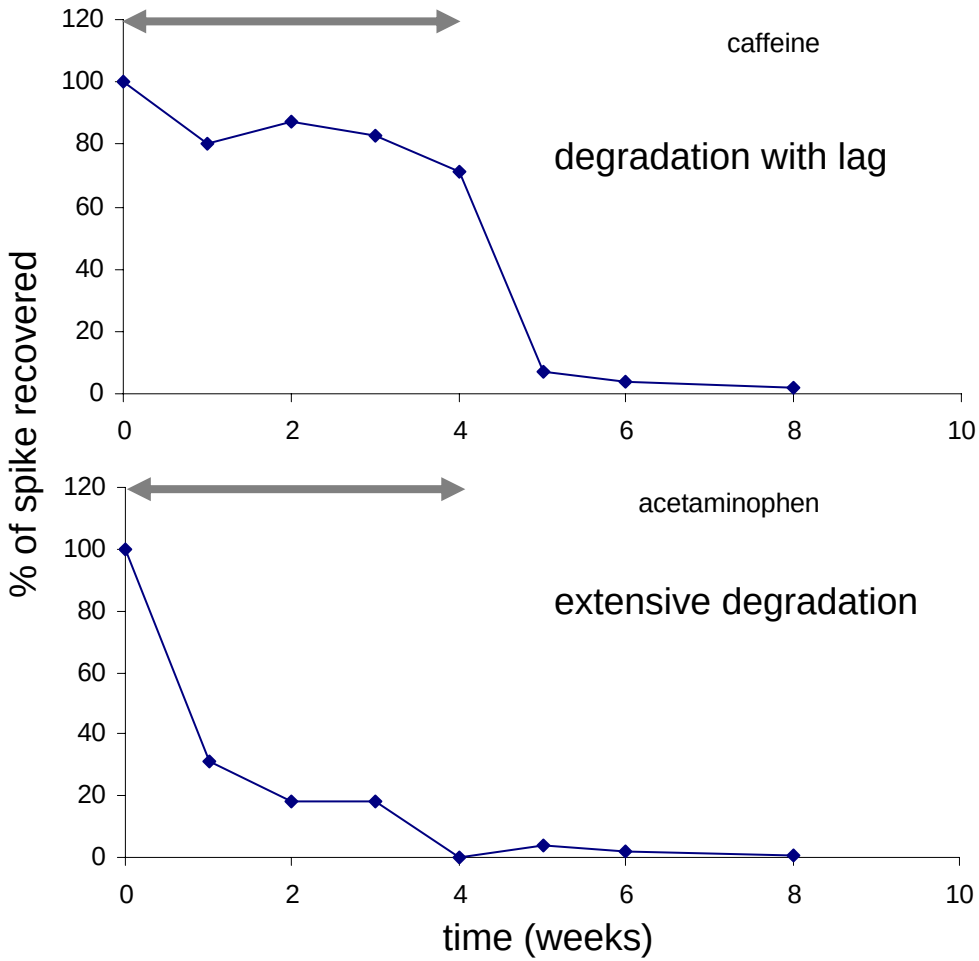


Do compounds behave conservatively in JB?

Occurrence



Degradation



Jamaica Bay and degradation conclusions

Compound	Measured effluent concentration (ng/L, ± std. dev.)	Dynamic range	Microbial degradation (amount of spike removed at 4 weeks)
Carbamazepine	65.3 (± 15.6)	66.6	None (<5%)
Cotinine	4010 (± 2390)	1260	None (<5%)
Hydrocodone	8.6 (± 3.5)	36.6	None (13%)
Trimethoprim	121 (± 71)	76.3	None (<5%)
Caffeine	15200 (± 4600)	1330	Some (29%)
Cimetidine	11.8 (± 6.9)	112	Some (51%)
Paraxanthine	24900 (± 5690)	5060	Some (31%)
Sulfamethoxazole	139 (± 94)	97.9	Some (24%)
Acetaminophen	859 (± 289)	579	Extensive (>99%)
Codeine	168 (± 40)	407	Extensive(~80%)
Diltiazem	52.5 (± 25.2)	499	Extensive(~79%)
Nicotine	2140 (± 1690)	2060	Extensive(>99%)

Which compounds make the best tracers?

✱ Those compound that showed the highest frequency of detection in GW studies

⭘ Compounds exhibiting “best” or “limited” transport through the nursing home well field

◆ Compounds with median GW concentrations > 20ng/L

Groundwater	Compound	Surface water
✱ ⭘	Acetaminophen	✖
	Antipyrine	
✱ ⭘	Caffeine	✖ ⦿ ◈
✱ ⭘ ◆	Carbamazepine	✖ ⦿
◆	Cimetidine	✖ ⦿
✱ ⭘	Codeine	✖
✱	Cotinine	✖ ⦿ ◈
	Diltiazem	✖
⭘ ◆	Fluoxetine	
	Hydrocodone	✖ ⦿
⭘	Ketoprefen	
	Metformin	
⭘	Nicotine	✖ ◈
⭘ ◆	Paraxanthine	✖ ⦿ ◈
	Ranitidine	
	Salbutamol	
✱ ⭘ ◆	Sulfamethoxazole	✖ ⦿
	Trimethoprim	✖ ⦿
	Warfarin	

✖ Compounds detected throughout Jamaica Bay

⦿ Compounds showing “no” or “some” degradation

◈ Compounds with the largest “dynamic range”

Conclusions

- LC-ToF-MS is a powerful tool for the analysis of PhACs in wastewater-impacted systems
- Pharmaceuticals are present in susceptible Long Island groundwaters at concentrations typically lower than those previously reported for impacted US streams and rivers
  - ➢Groundwater concentrations are highest in shallow wells and/or adjacent to point source discharge
- Mobility in groundwater is limited by adsorption and degradation
  - ➢Compounds that migrate best through groundwater have low K_Ds (measured) and biodegradation rates

Conclusions (continued)

- Carbamazepine and sulfamethoxazole appear to be the best tracers of wastewater in subsurface environments
  - ➢Caffeine and paraxanthine are less persistent, but at certain sites may serve as tracers due to their local high loading
- In Jamaica Bay most PhACs are relatively persistent over the hydraulic residence time-scale of the Bay
  - ➢Most compounds do not degrade extensively within four weeks
  - ➢Caffeine, paraxanthine and cotinine are possible estuarine wastewater tracers measured in greatest abundance

Acknowledgements

Suffolk County Dept. of Health – Geralynn Rosser, Sy Robbins

USGS, Coram, NY – Stephen Terracciano, Jack Monti, Shawn Fisher, Irene Abbene

USGS, Denver, CO – Dr. Edward T. Furlong, Jeffrey D. Cahill, Stephen L. Werner