

Survey of the New York City Watershed for the Presence of Pharmaceuticals

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Project Goals

- ◆ Determine if detectable levels of selected pharmaceutical analytes are present in the NYC Watershed

Why?

To address concerns in recent scientific and popular literature regarding the potential for contamination of surface waters by hormones and human-use pharmaceuticals

Media Headlines

- ◆ Rx-Drug H₂WOE *New York Post, 8/23/04*
- ◆ Stay calm everyone, there's Prozac in the drinking water
London Observer, 8/8/04
- ◆ Household supplies appear in water: Drugs, disinfectants worry state panel *The Arizona Republic, 7/23/04*
- ◆ Eat, drink and be wary: Chemicals often linger in water after treatment *Poughkeepsie Journal (NY), 1/18/04*
- ◆ Fish off Arctic city get drug cocktail from sewers
Reuters, 11/24/03
- ◆ Frogs, fish, and pharmaceuticals a troubling brew...
CNN, 11/14/03
- ◆ Drugs in your drinking water? Take a valium
The Globe and Mail (Canada), 2/12/03

Project Goals (continued)

- ◆ characterize input to watershed from effluent of four WWTPs (day-of-week, seasonality, variability within and between plants)
- ◆ monitor major inputs and output of key reservoirs
- ◆ monitor terminal reservoir to determine if any analytes are detectable prior to distribution

Project Goals (continued)

What did we look for (and why)?

Basic compounds

amoxicillin (antibiotic)

atenolol (beta-blocker)

caffeine (stimulant)

cephalexin* (antibiotic)

sulfamethoxazole (antibiotic)

trimethoprim (antibiotic)

*to our knowledge, these compounds have not been previously investigated

Acid/neutral compounds

17 α -ethinylestradiol (steroid)

17 β -estradiol (steroid)

estrone (steroid)

ibuprofen (analgesic)

valproic acid* (antiepileptic)

carbamazepine (pilot)

Total Retail Units Prescribed, 2002

Product	Total **	Elimination From Body	Approx DDD
amoxicillin	34,046,000	60% unchanged (urine)	750 mg
atenolol	39,368,000	40-50% unchanged (urine) 50% unchanged (feces)	50-100 mg
cephalexin	24,154,000	90% unchanged (urine)	1000 mg
ibuprofen	22,660,000	1% unchanged (urine), 14% conjugated (urine), 45-79% met (urine)	800-1600 mg
trimethoprim/ sulfamethoxazole	13,313,000	66.8% free trimethoprim; 54.5% sulfamamide met, 30% free sulfamethoxazole	320 mg trimeth./ 1600 mg sulfameth.
valproic acid (from Depakote)	6,279,000	3% unchanged (urine) 30-50% conjugated (urine)	250-750+ mg

** Total retail units prescribed, 2002

DDD: Defined Daily Dose

met: metabolite(s)

Source: www.drugtopics.com

Methodology

- ◆ Four-liter grab samples (pharmaceuticals)
 - silanized amber glass bottles
- ◆ Field measurements for conductivity, dissolved O₂, pH, redox potential, salinity, and temperature

Methodology

- ◆ Samples are extracted within 48 hours of collection on Empore SDB-XC extraction disks
- ◆ Analysis via Agilent 1100 HPLC and ThermoQuest LCQ Ion Trap LC/MS with ESI (electrospray ionization)
 - SIM for all analytes, except amoxicillin and cephalexin (MS/MS)

*Methodology developed by Dr. Patrick O'Keefe, NYSDOH WCLR;
Method Detection Limit (MDL) study approved by US EPA*

Methodology

- ◆ Detection limits (from MDL study)

<u>Basic cmpds</u>	<u>ng/L</u>	<u>Env. Conc.</u>	<u>Acid/neutral cmpds</u>	<u>ng/L</u>	<u>Env. Conc.</u>
amoxicillin	367	n/a	17 α -ethinylestradiol	39	42
atenolol	9	3-241	17 β -estradiol	40	64
caffeine	80	9-14000	estrone	30	2-70
cephalexin*	502	n/a	ibuprofen	20	8-81
sulfamethoxazole	111	400	valproic acid*	199	n/a
trimethoprim	4	2-240			

*to our knowledge, these compounds have not been previously investigated

-Environmental concentrations are those found in surface waters or WWTP effluents in the literature

Project Description

- ◆ Pilot Study (June 2003)
3 consecutive days
- ◆ Full Study-4 seasonal sampling events (8/03-05/04)
7 consecutive days
- ◆ EOH (2 WWTPs + 6 surface water locations)
WOH (2 WWTPs + 4 surface water locations)

Characteristics of the WWTPs

	Carmel SD #2	Yorktown Heights	Margaretville	Walton
◆ Year Built	1965	1961	1998	1978
◆ Year Updated	1999	1973	-	2002
◆ Design Flow (MGD)	0.35	1.5	0.4	1.17
◆ Population (approx.)	3,000	10,000	800	3,500
◆ Population Type	suburban	suburban	rural	rural
◆ Waste Sources	pharm. lab	none known	hospital	nursing home, dairy

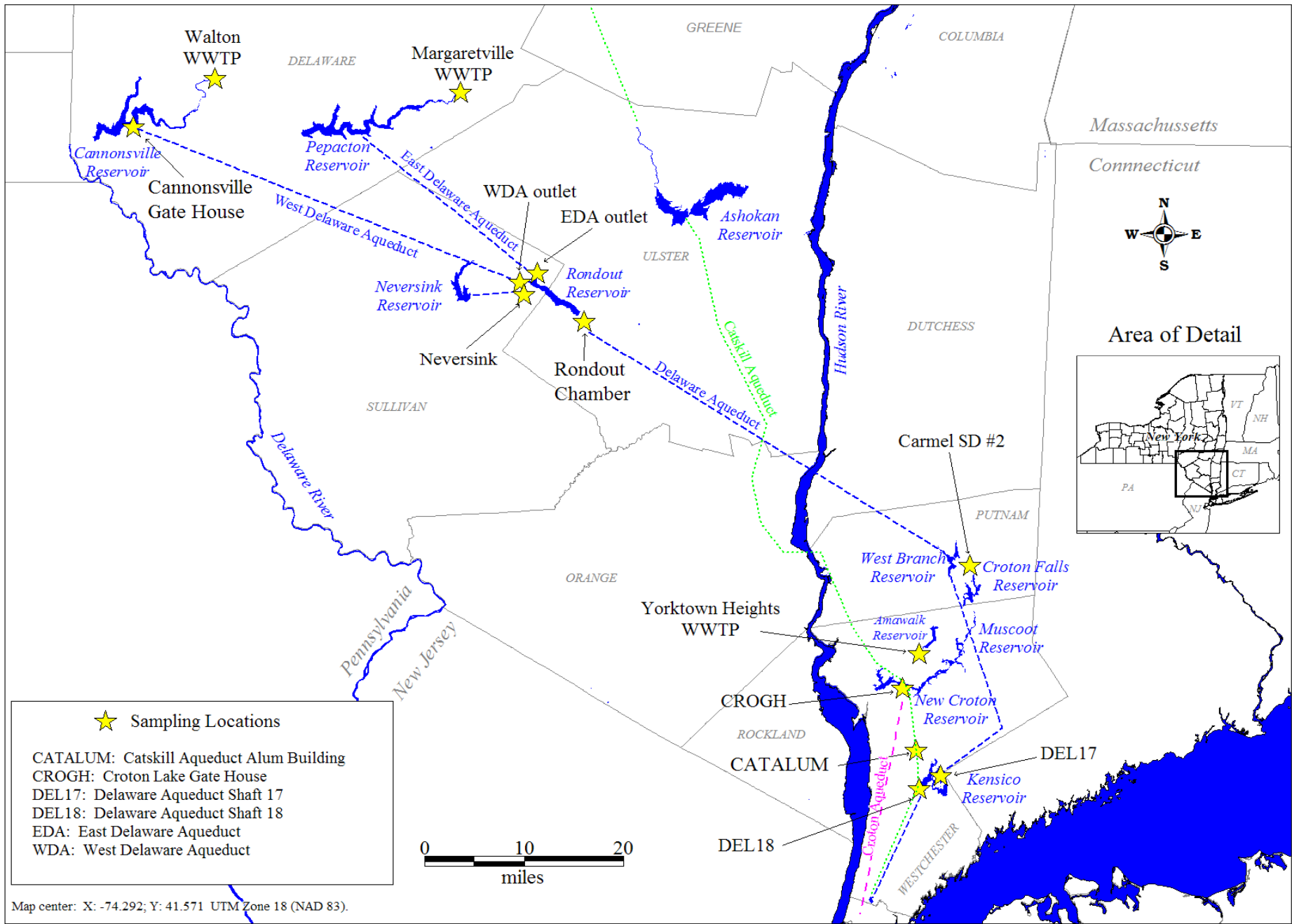


Figure 1. Map of WWTP and Reservoir Sampling Locations, August 2003 - May 2004.

WWTP Pilot Study Results

Location	Date	Amoxicillin (367 ng/L)	Caffeine (80 ng/L)	Cephalexin (502 ng/L)	Atenolol (9 ng/L)	Sulfamethoxazole (111 ng/L)	Trimethoprim (4 ng/L)	Valproic acid (199 ng/L)	Ibuprofen (20 ng/L)	Estrone (30 ng/L)	17 β -Estradiol (40 ng/L)	17 α - Ethinylestradiol (39 ng/L)
Yorktown	6/10/03	ND	21000	ND	883	ND	91	ND	338	ND	ND	ND
		ND	20200	ND	1250	ND	93	ND	161	ND	ND	ND
	6/11/03	ND	17800	ND	2140	ND	127	ND	26	ND	ND	ND
		ND	22200	ND	1600	ND	104	ND	127	ND	ND	ND
	6/12/03	ND	15800	ND	709	ND	111	ND	ND	ND	ND	ND
	ND	15700	ND	ND	757	ND	116	ND	169	ND	ND	ND
Carmel	6/10/03	ND	220	ND	264	ND	495	ND	ND	ND	ND	ND
		ND	563	ND	367	ND	400	ND	ND	ND	ND	ND
	6/11/03	ND	666	ND	349	ND	383	ND	ND	ND	ND	ND
		ND	518	ND	267	ND	402	ND	ND	ND	ND	ND
	6/12/03	ND	443	ND	253	ND	455	ND	ND	31	ND	ND
	ND	391	ND	ND	214	ND	379	ND	49	ND	48	ND
Walton	6/24/03	ND	ND	ND	107	ND	ND	ND	26	ND	ND	ND
		ND	ND	ND	72	ND	ND	ND	ND	ND	ND	ND
	6/25/03	ND	ND	ND	146	ND	ND	ND	ND	ND	ND	ND
		ND	ND	ND	176	ND	ND	ND	ND	ND	ND	ND
	6/26/03	ND	ND	ND	177	ND	ND	ND	ND	ND	ND	ND
	ND	ND	ND	ND	154	ND	ND	ND	166	ND	ND	ND
Margaretville	6/24/03	ND	ND	ND	908	ND	70	ND	23	ND	ND	ND
		ND	ND	ND	824	ND	81	ND	126	ND	ND	ND
	6/25/03	ND	ND	ND	716	ND	63	ND	ND	ND	ND	ND
		ND	158	ND	847	ND	69	ND	26	ND	ND	ND
	6/26/03	ND	ND	ND	524	ND	39	ND	249	ND	ND	ND
	ND	ND	ND	ND	854	ND	39	ND	79	ND	ND	ND

Notes

ng/L: nanograms per liter

ND: not detected

WOH Surface Water Pilot Study Results

Location	Date	Amoxicillin (367 ng/L)	Caffeine (80 ng/L)	Cephalexin (502 ng/L)	Atenolol (9 ng/L)	Sulfamethoxazole (111 ng/L)	Trimethoprim (4 ng/L)	Valproic acid (199 ng/L)	Ibuprofen (20 ng/L)	Estrone (30 ng/L)	17β-Estradiol (40 ng/L)	17α- Ethinylestradiol (39 ng/L)
Neversink	6/24/03	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	6/25/03	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
		6/26/03	ND	ND	ND	ND	ND	50 SR	ND	ND	ND	ND
EDA	6/24/03	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	6/25/03	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
		6/26/03	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
WDA CANN*	6/24/03	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	6/25/03	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
		6/26/03	ND	ND	ND	ND	ND	ND	ND	32 SR	ND	ND
Rondout	6/24/03	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	6/25/03	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
		6/26/03	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Notes

EDA: East Delaware Aqueduct

WDA: West Delaware Aqueduct

CANN: Cannonsville Reservoir

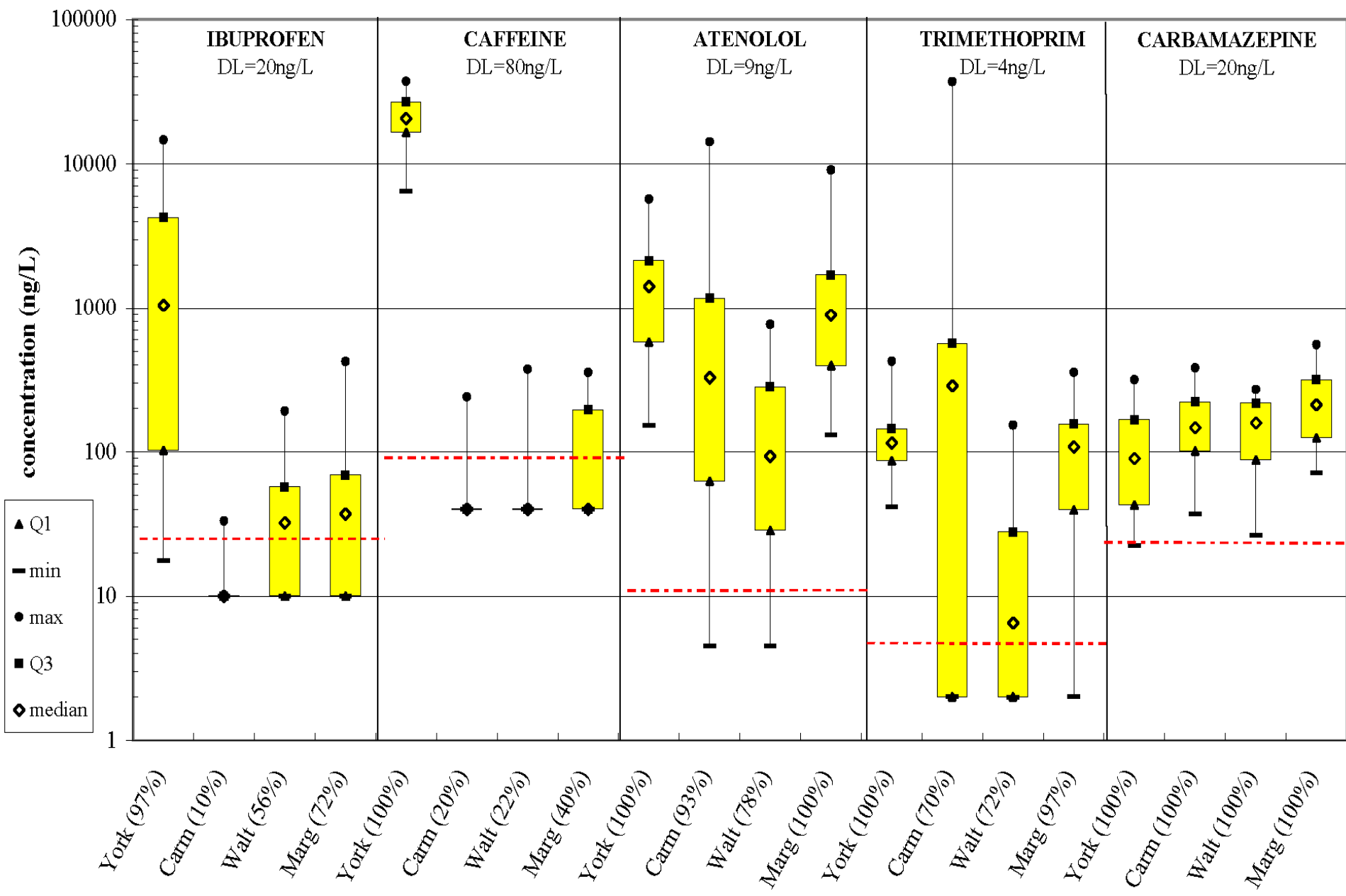
ng/L: nanograms per liter

ND: not detected

SR: suspect result

*For the first two days of the pilot study, samples were collected at the WDA Intake Chamber at the Cannonsville Reservoir. The third day's samples were collected at the WDA outlet at the Rondout Reservoir.

Concentration for Select Analytes by WWTP



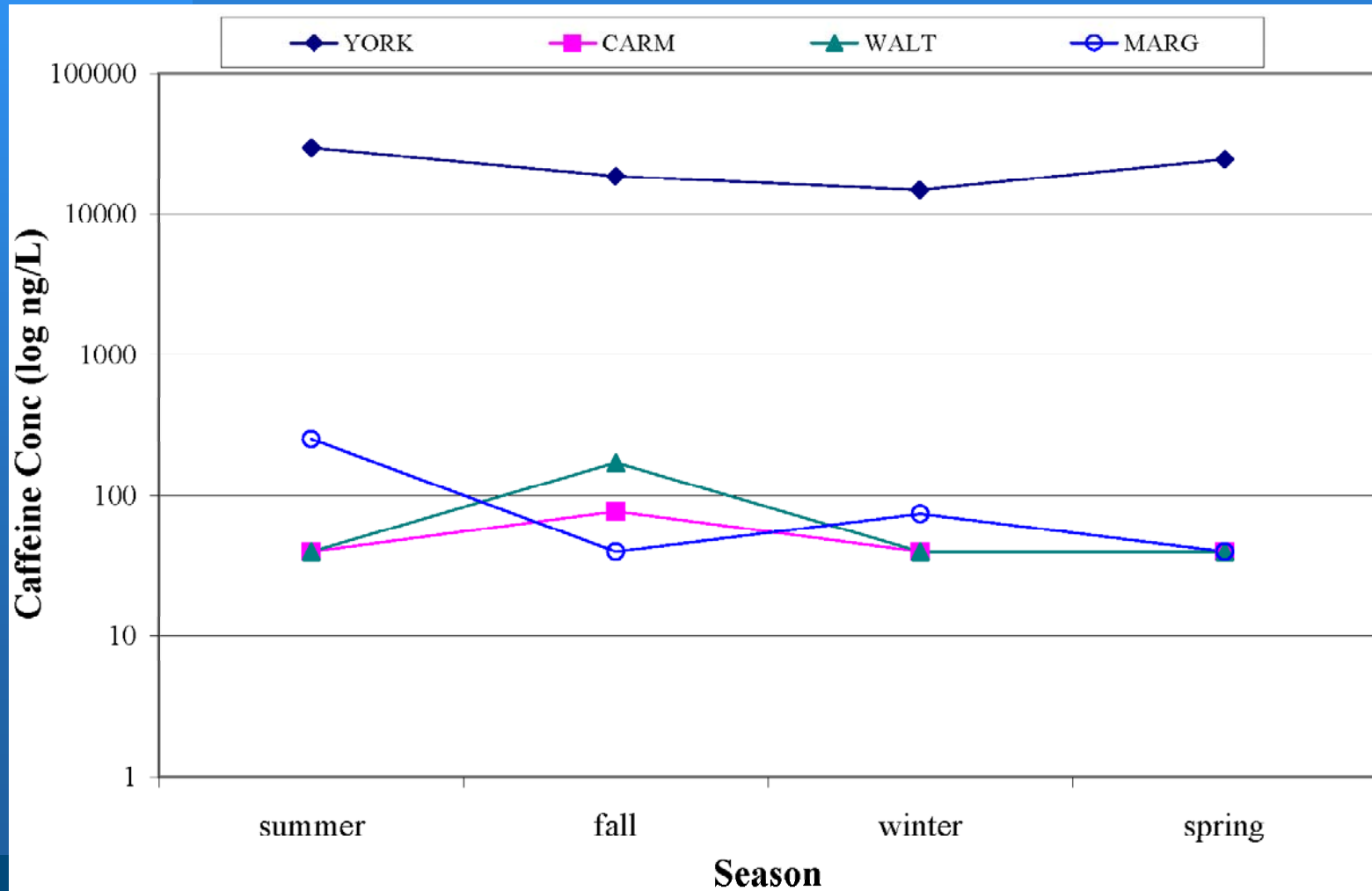
Mean Concentration (ng/L) for Selected Analytes

	<u>Caffeine</u>	<u>Atenolol</u>	<u>Trimethoprim</u>	<u>Carbamazepine</u>
Yorktown	21899 (34/34)	1681 (34/34)	126 (34/34)	110 (32/32)
Carmel	132 (7/30)	2337 (28/30)	3502 (21/30)	167 (28/30)
Walton	165 (9/32)	228 (25/32)	231 (23/32)	152 (32/32)
Margaretville	225 (13/32)	1894 (32/32)	121 (31/32)	239 (32/32)

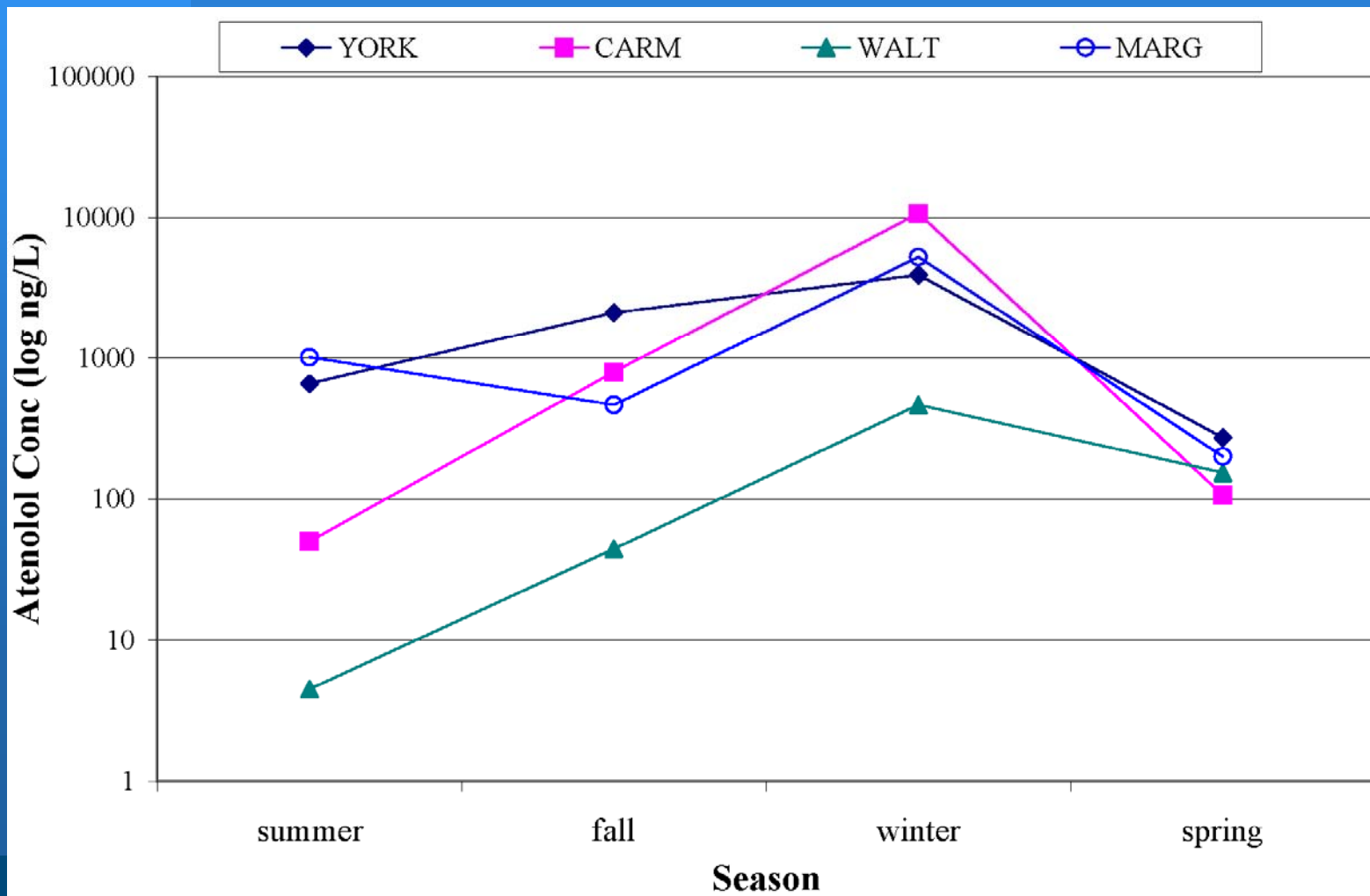
Trimethoprim concentrations (ng/L)

Location	Measure	Overall	Summer	Fall	Winter	Spring
● Yorktown	Samples/detects	34/34	11/11	8/8	8/8	7/7
	Minimum	42	77	85	106	42
	Median	115	115	146	127	48
	Mean	126	112	174	146	72
	Maximum	424	147	424	246	154
● Carmel	Samples/detects	30/21	7/7	8/0	8/7	7/7
	Minimum	9	260	-	131	9
	Median	332	300	-	6490	566
	Mean	3502	302	-	4267	5937
	Maximum	37000	361	-	8090	37000

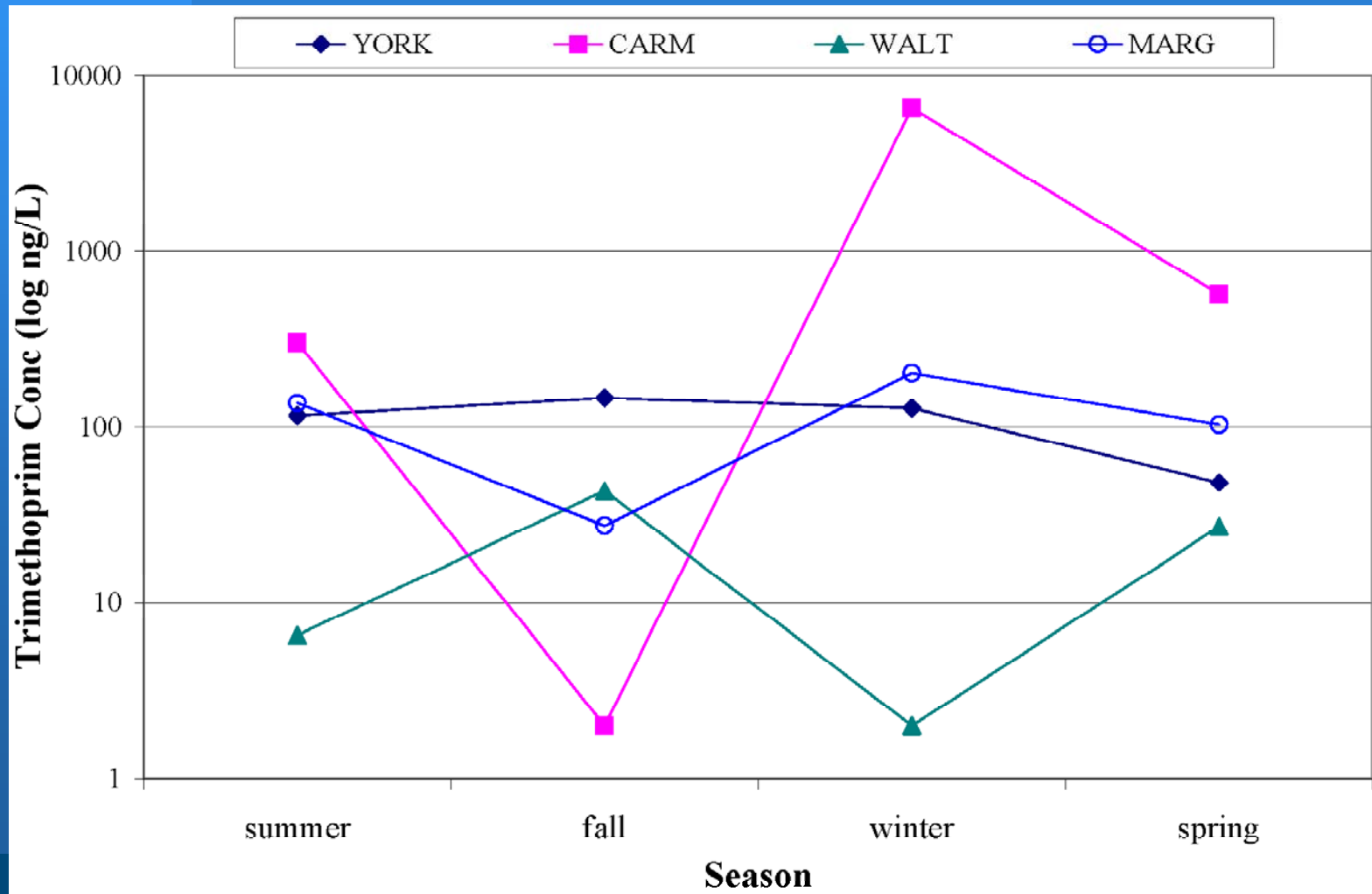
Caffeine by Season



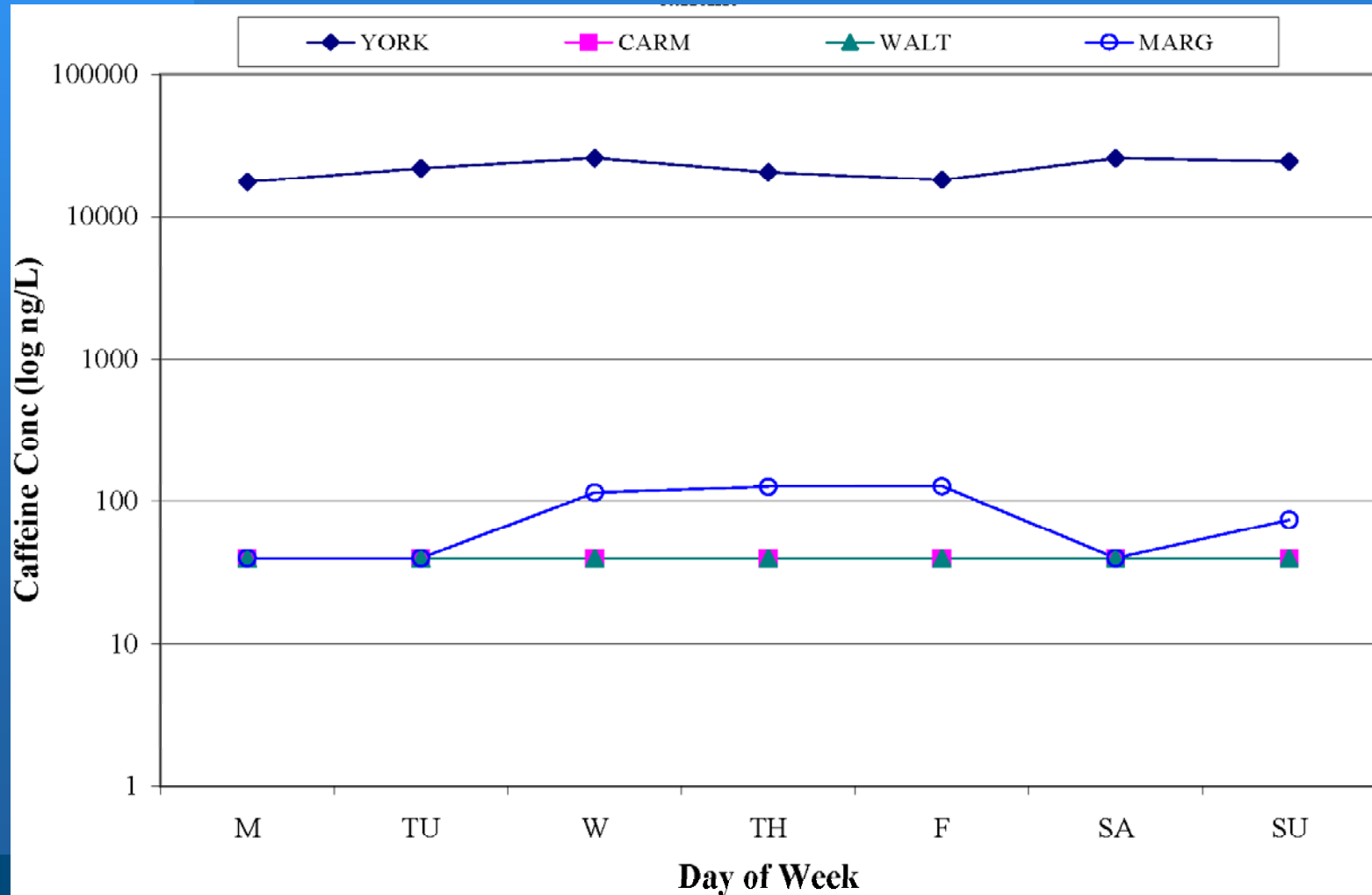
Atenelol by Season



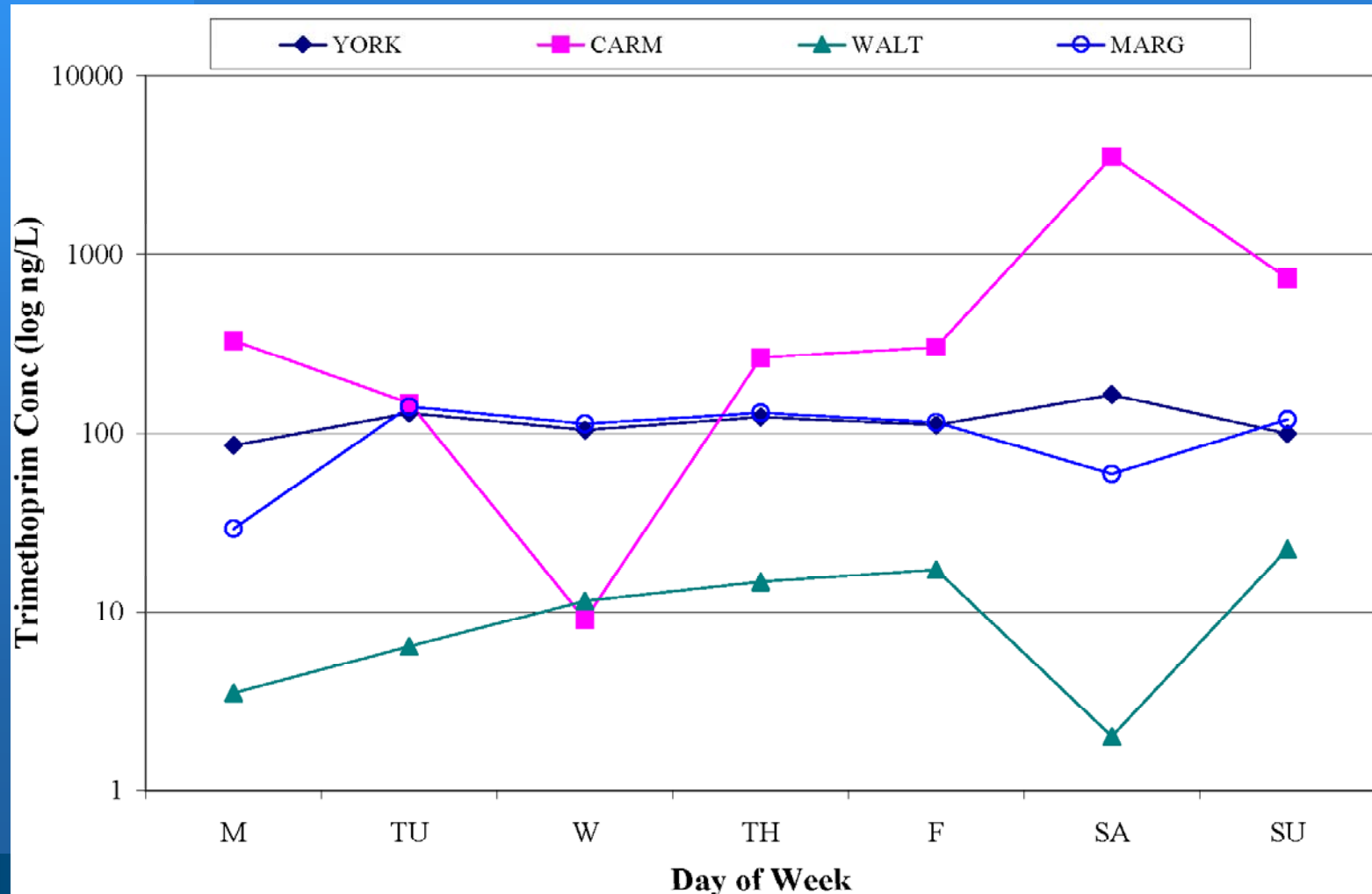
Trimethoprim by Season



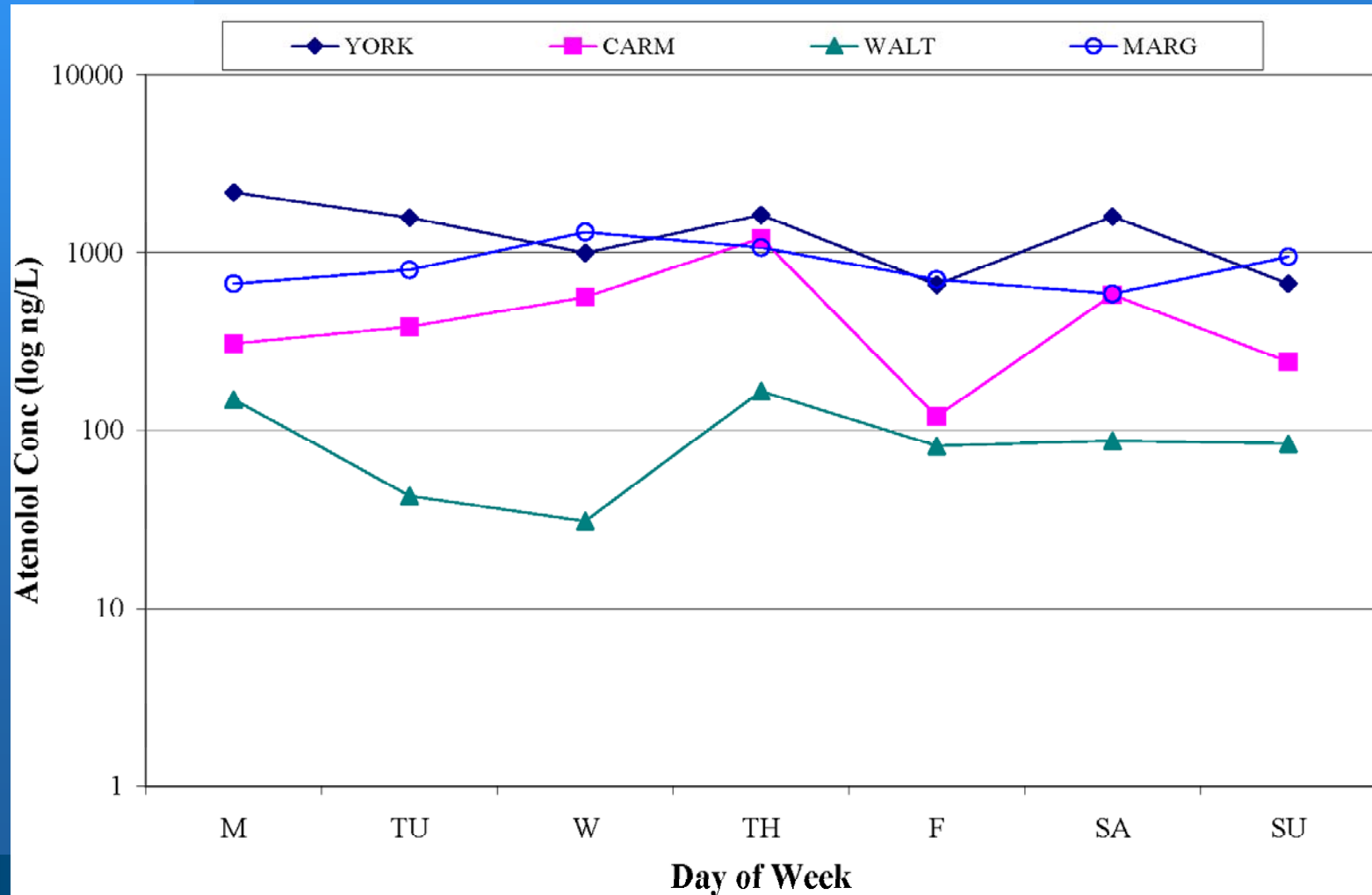
Caffeine by Day of the Week



Trimethoprim by Day of the Week



Atenolol by Day of the Week



Conclusions

- ◆ WWTPs are discharging PPCPs into Surface Waters
- ◆ Inter-WWTP and Intra-WWTP variability can be significant for specific contaminants (caffeine, trimethoprim)
- ◆ Inter-WWTP and Intra-WWTP variability is remarkably small for some PPCPs (carbamazepine)

Conclusions

- ◆ Very few detections in reservoir samples (and many not in duplicates), did see more frequent detections in EOH (less dilution?)
- ◆ Consistent with literature especially when considering detection limits. However this may be due to method detection limits
- ◆ WWTP effluent concentrations (ng/L) are orders of magnitude lower than therapeutic doses (mg/day)

Next Steps

- ◆ Sampling with tighter spatial resolution
- ◆ Sediment sampling
- ◆ Laboratory work to evaluate degradation

Acknowledgements

We would like to thank the following people for their assistance in the design and implementation of this project:

Ken Markussen, NYS Department of Environmental Conservation

Patrick Phillips, US Geological Survey

Charles Cutietta-Olson, NYC Department of Environmental Protection

Dennis McChesney, US Environmental Protection Agency

This work was funded by the US EPA under a New York City Watershed Protection Grant from the Safe Drinking Water Act. This grant was administered by the NYS DEC.