

# **Monitoring Pharmaceuticals and Personal Care Products in the Aquatic Environment**

Patrick O'Keefe

Wadsworth Center, New York State Department  
of Health and Department of Environmental  
Health Sciences, University at Albany, State  
University of New York

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

Lloyd Wilson<sup>1</sup>, Patrick O'Keefe<sup>2</sup>, Patrick Palmer<sup>1</sup>,  
Robert Sheridan<sup>2</sup>, Robert Briggs<sup>2</sup>, and Thomas King<sup>2</sup>

<sup>1</sup>Center for Environmental Health, NYS Department of Health, Troy, NY

<sup>2</sup>Wadsworth Center for Laboratories and Research, NYS Department of Health, Albany, NY

# 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

# 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)?

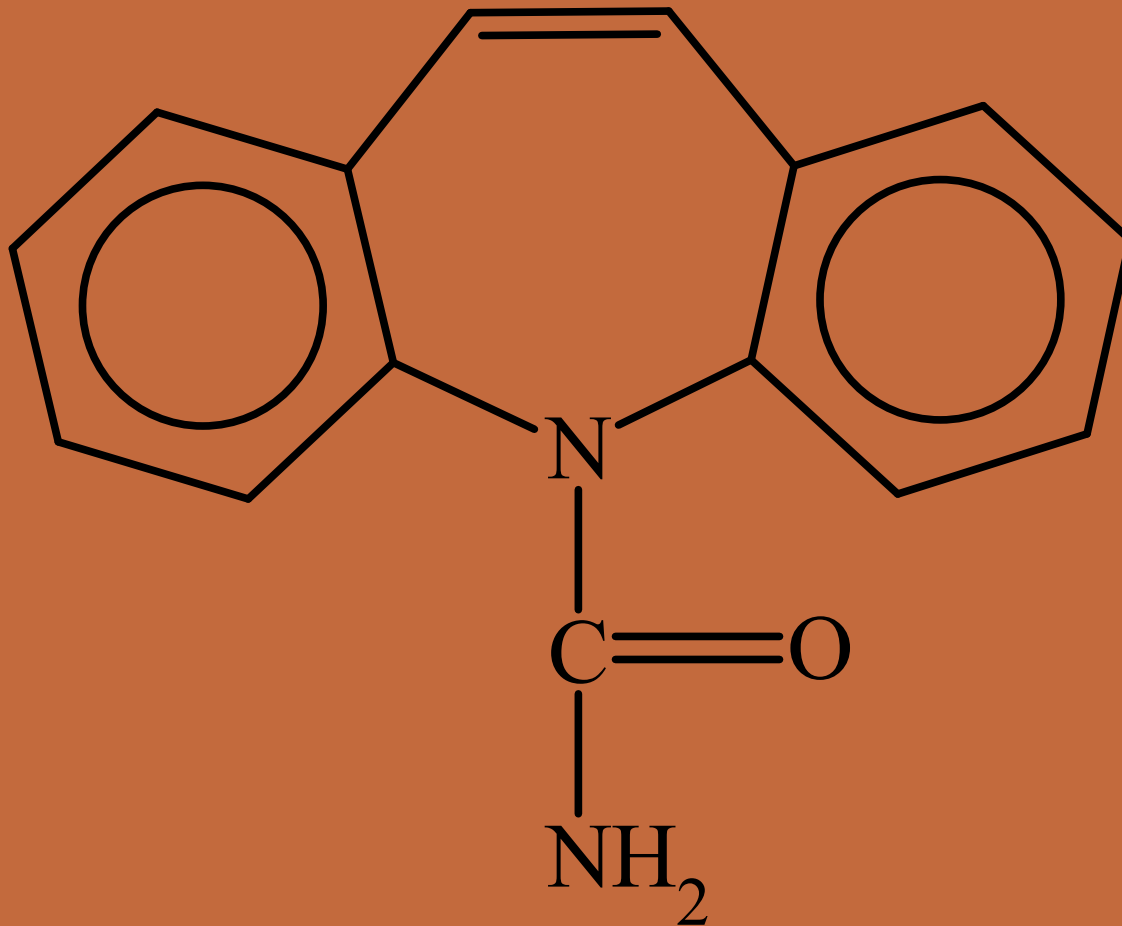
### Basic compounds

amoxicillin (antibiotic)  
atenolol (beta-blocker)  
caffeine (stimulant)  
cephalexin\* (antibiotic)  
sulfamethoxazole (antibiotic)  
trimethoprim (antibiotic)

### Acid/neutral compounds

17 $\alpha$ -ethinylestradiol (steroid)  
17 $\beta$ -estradiol (steroid)  
estrone (steroid)  
ibuprofen (analgesic)  
valproic acid\* (antiepileptic)  
carbamazepine (seasonal study)

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



**Carbamazepine (anticonvulsant)**

# Methodology

- ◆ Four-liter grab samples (pharmaceuticals)
  - silanized amber glass bottles
- ◆ Field measurements for conductivity, dissolved O<sub>2</sub>, pH, redox potential, salinity, and temperature

# Analytical Methodology

## (1) Extraction (within 48 hr)

### Acid/Neutral Compounds

- Adjust 2-L sample to pH 2.5 and pass through an Empore SDB-XC disk.
- Elute analytes with pH 8.5 methanol followed by acetone.
- Cleanup extract with silica gel and concentrate to 100  $\mu\text{L}$ .

### Basic/Amphoteric Compounds

- Pass 1-L sample through a 500 mg Carboprep 200 cartridge using silanized glassware.
- Elute analytes with pH 2.9 methanol, methylene chloride (80:20) and acetone. Final volume 500  $\mu\text{L}$ .

# Analytical Methodology

## (2) Analysis

- Prior to extraction all samples were spiked with internal standards using labeled (D or  $^{13}\text{C}$ ) compounds for valproic acid, ibuprofen, estrogens and caffeine and unlabeled analogs for other compounds.
- Analysis by ThermoQuest LCQ ion trap MS in ESI mode.
- Mobile phase for acid/neutrals was acetonitrile/10mM N-methyl morpholine (pH 9.4) and  $(\text{M}-\text{H})^-$  ions were monitored.
- Mobile phase for basics was acetonitrile/formic acid and  $(\text{M} + \text{H})^+$  ions were monitored (MS/MS for penicillins).

# 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 $\alpha$ -ethinylestradiol	39	42
atenolol	9	3-241	17 $\beta$ -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)

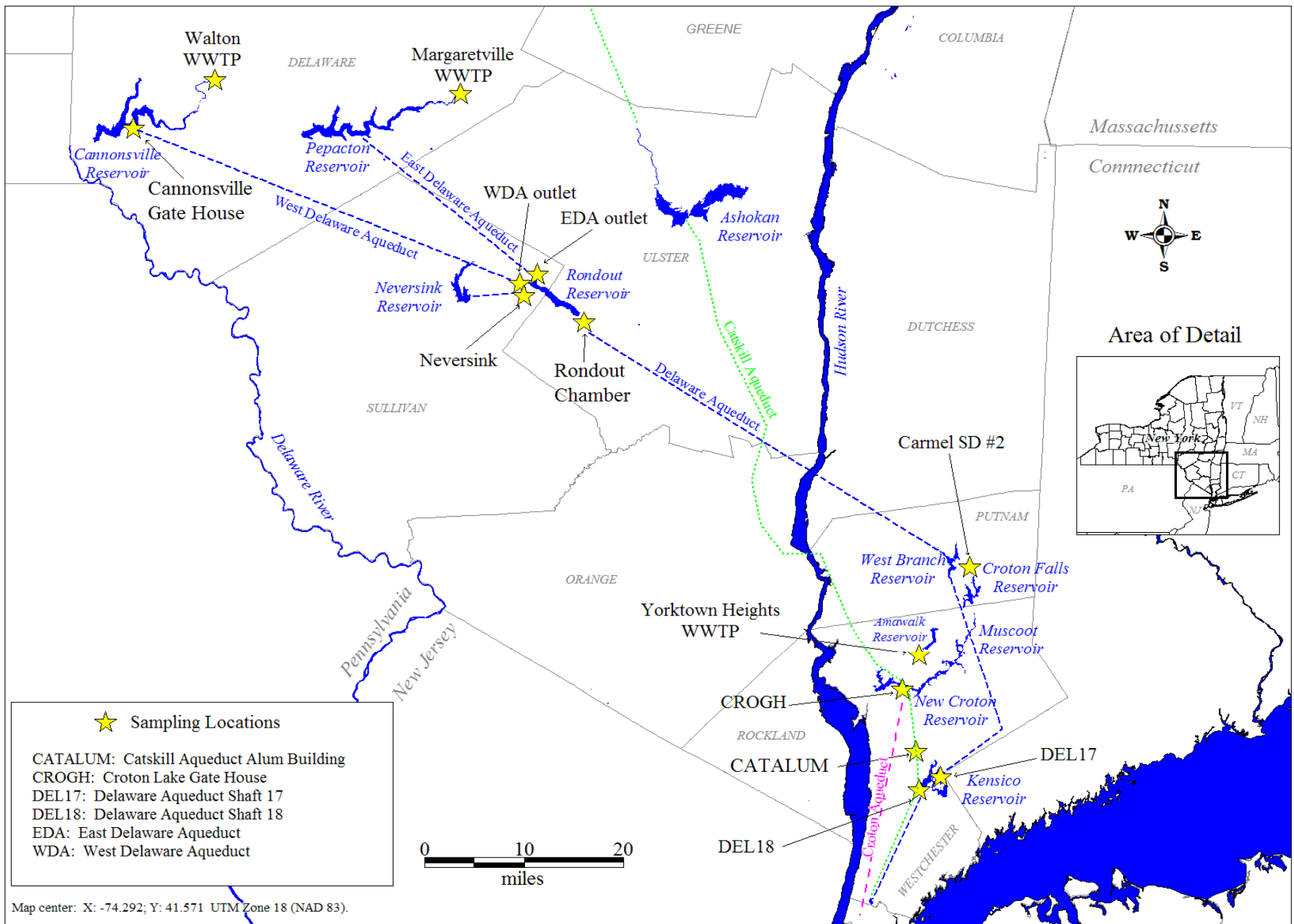


Figure 1. Map of WWTP and Reservoir Sampling Locations, August 2003 - May 2004.

# 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

# Operating Features of WWTPs

- CARMEL: 757,000 gpd; activated sludge; membrane microfiltration (proposed upgrade)
- YORKTOWN: 1,993,000 gpd; trickling filter; sand filtration
- WALTON: 1,112,000 gpd; activated sludge; continuous backwash upflow dual sand filtration (CBUDSF)
- MARGARETVILLE: 213,000 gpd; rotating biological contactors (RBCs); membrane filtration; UV and hypochlorite disinfection

# MEDIAN CONCENTRATIONS OF PHARMACEUTICALS DETECTED AT WWTPs

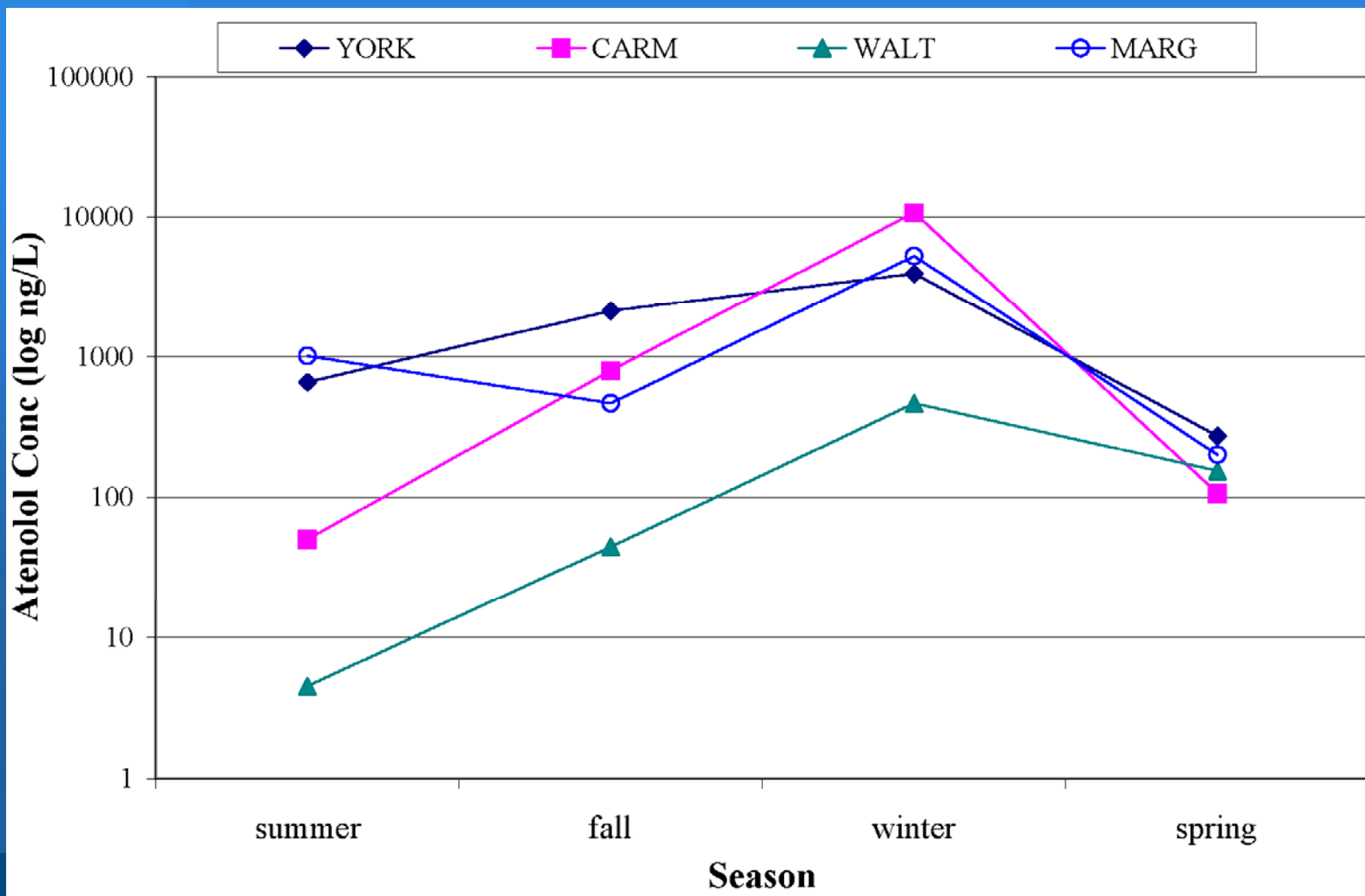
Table 2. Median Seasonal Concentrations<sup>a</sup> (in ng/L)

Location	Season	Analyte and Detection Limit				
		atenolol 9 ng/L	caffeine 80 ng/L	carbamazepine 20 ng/L	ibuprofen 20 ng/L	trimethoprim 4 ng/L
Yorktown	summer	656	29600	62	41	115
	fall	2115	18500	30	729	146
	winter	3925	14750	181	2845	127
	spring	272	24500	166	5340	48
Carmel	summer	50	40	118	10	300
	fall	794	77	82	10	2
	winter	10700	40	268	10	6490
	spring	106	40	199	10	566
Walton	summer	5	40	70	10	7
	fall	44	171	127	10	43
	winter	464	40	220	41	2
	spring	154	40	211	112	27
Margaretville	summer	1008	250	120	178	136
	fall	465	40	137	10	27
	winter	5240	74	455	25	201
	spring	200	40	243	50	103

<sup>a</sup>For nondetects, a value of half the detection limit was used to calculate the median

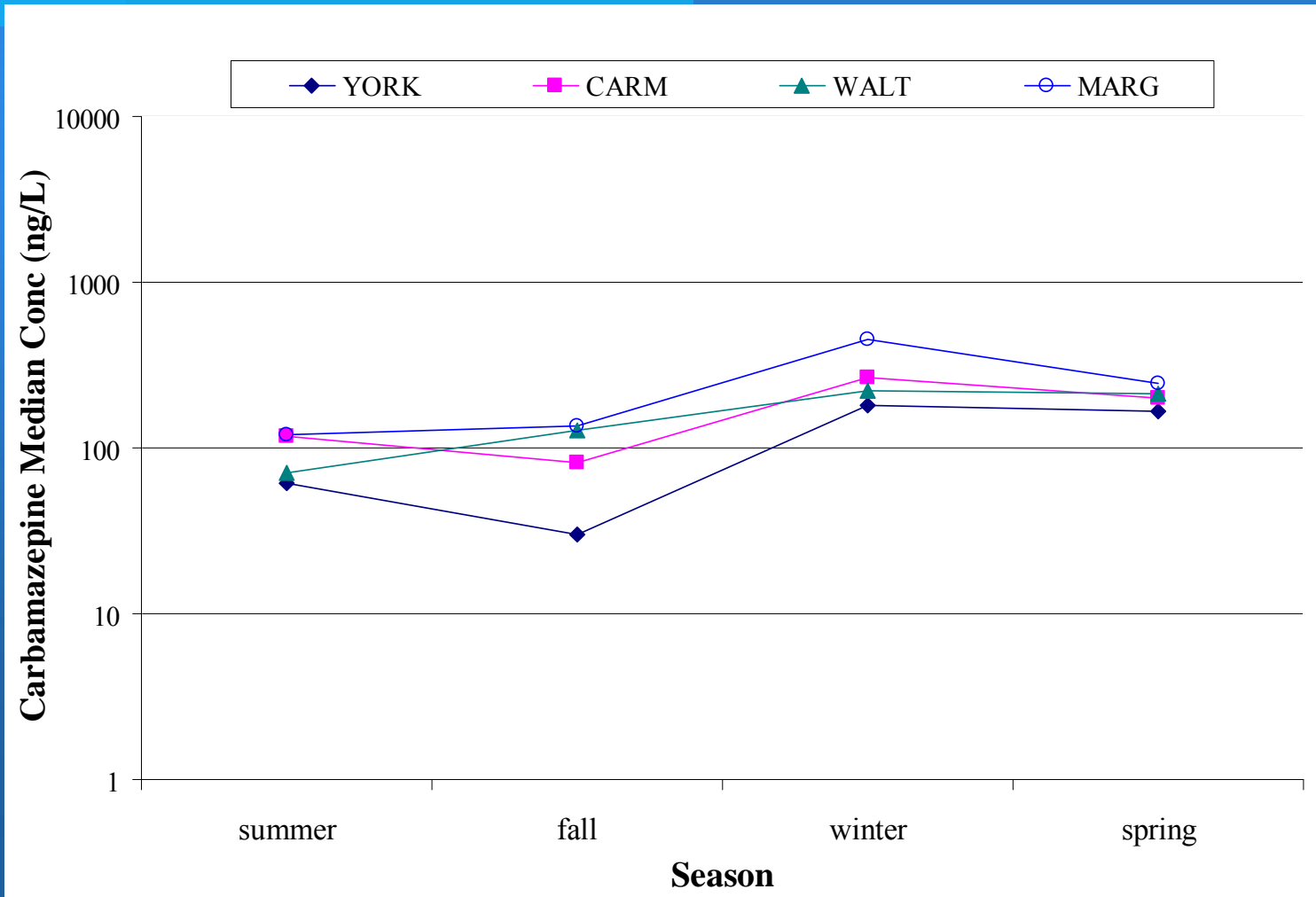
# Atenelol by Season

(Median Concentrations)



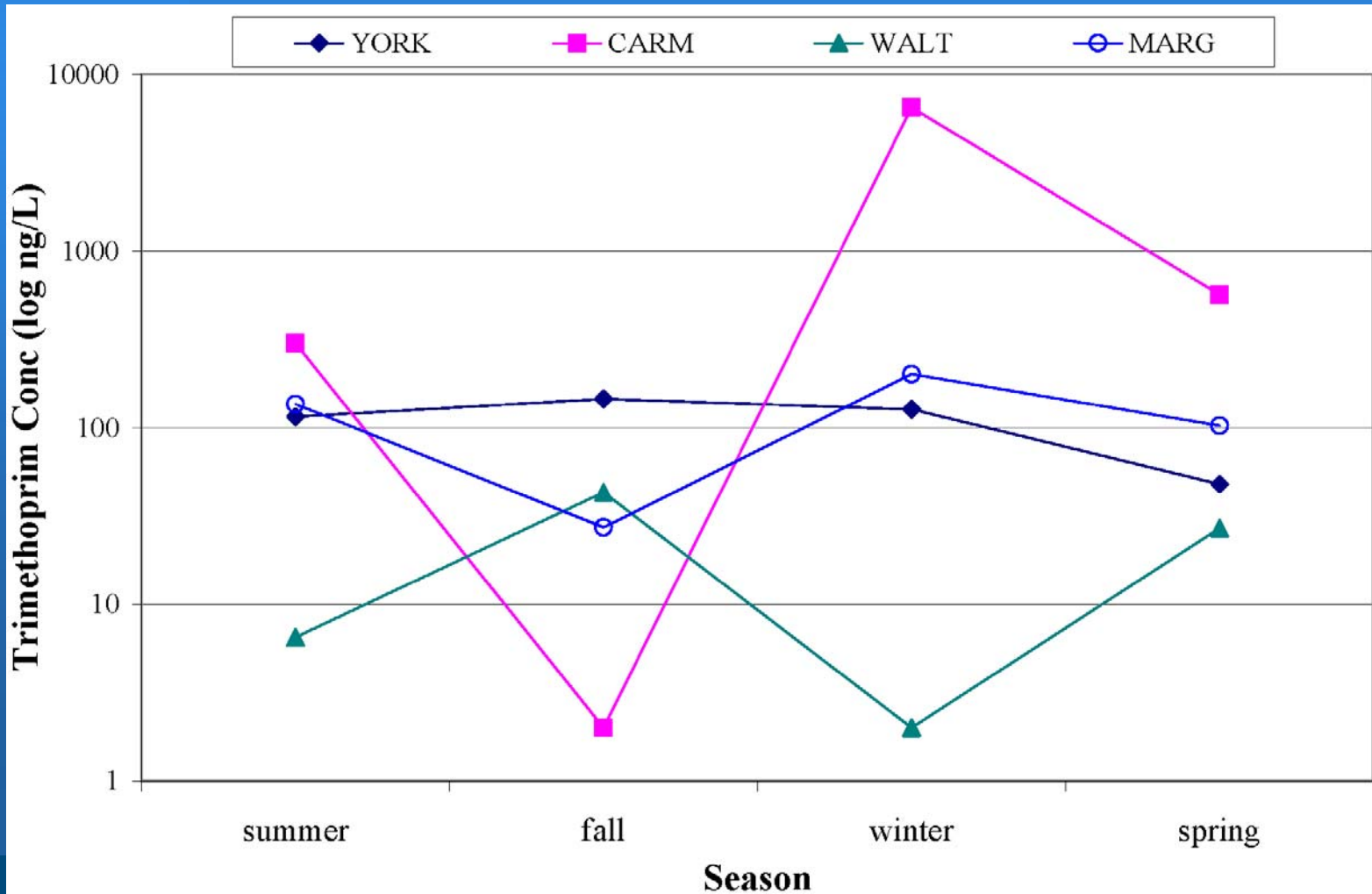
# Carbamazepine by Season

(Median Concentrations)



# Trimethoprim by Season

(Median Concentrations)



# 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)
- ◆ Higher atenolol and possibly carbamazepine concentrations at WWTPs in winter. Reduced biodegradation?

# Conclusions

- ◆ Very few detections in reservoir samples (and many not in duplicates), did see more frequent detections in EOH (caffeine in 17 samples and ibuprofen in 7 samples). Less dilution and/or higher WWTP effluent concentrations?
- ◆ Consistent with literature especially when considering detection limits.
- ◆ WWTP effluent concentrations (ng/L) are orders of magnitude lower than therapeutic doses (mg/day)

# Next Steps

- ◆ Improve analyte detection limits
- ◆ Sampling with tighter spatial resolution
- ◆ Sediment sampling
- ◆ Laboratory work to evaluate degradation