PPCPs at a Point Source (Publicly Owned Treatment Works) Discharge Before and After Tertiary Disinfection by Chlorination

Jenny Pape,[a] Million Woudneh,[b] Richard Grace,[b] John Cosgrove,[b]

Greg Cavallo,[c] Ron MacGillivray,[c] Thomas Fikslin[c]

SETAC Portland

November 8th, 2010

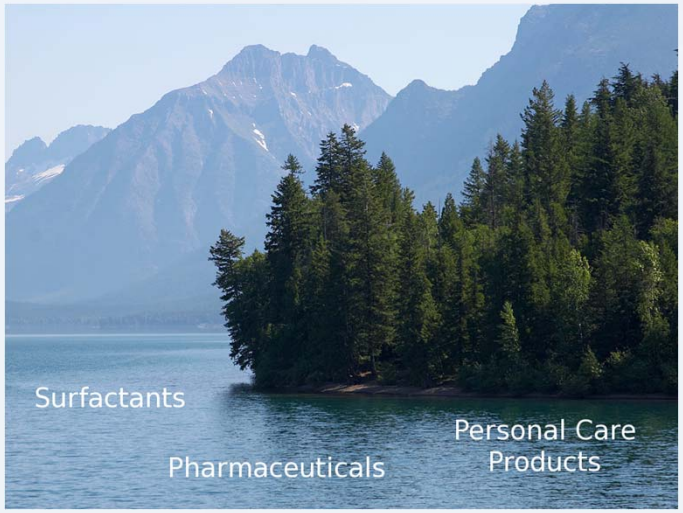
[a] University of Victoria

[b] AXYS Analytical Services

[c] Delaware River Basin Commission

Background

- PPCPs are being discovered and quantified in many water systems (surface, ground and to a lesser extent drinking water).
- PPCP methods are primarily focused on native analytes rather than transformation products.
- These analytes of emerging concern are termed “pseudo-persistent”.
- Current PPCP data may be misleading due to analyte speciation.



Project Objective & Approach

Does chlorination produce transformation products during wastewater treatment?

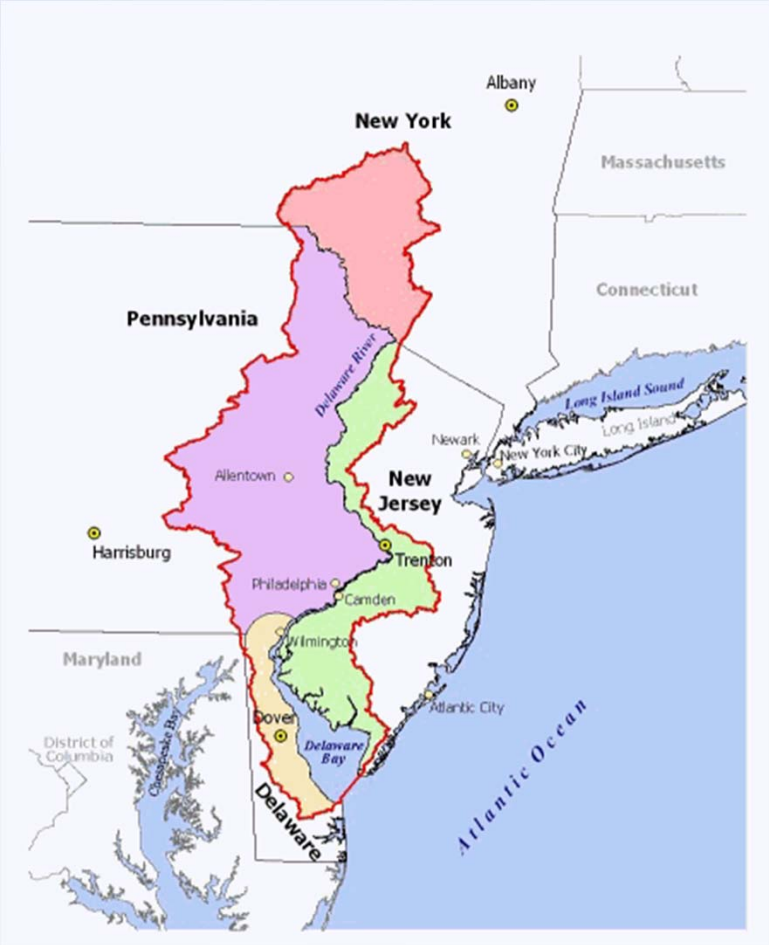
1. *Field Reconnaissance* – Extended EPA Method 1694 for occurrence in POTW effluent (3x for analyte consistency). Targets known to react with chlorine have been selected.

2. *Bench Chlorination* – a study of the chlorination of the selected analytes in reagent water to evaluate reactivity and the formation of transformation products was completed.

3. *Matrix Chlorination* – transformation products were demonstrated to form in a complex wastewater matrix.

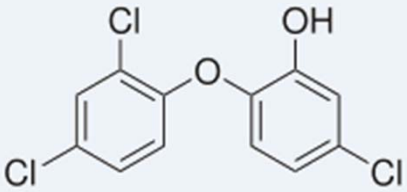
4. *Method Development* – analytical quantification of parent compounds and transformation products was developed. Wastewater samples were analyzed before and after chlorine treatment.

Site Selection & Design



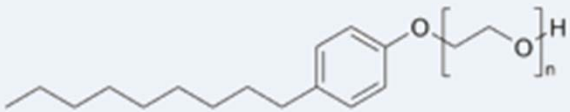
Triclosan

$C_{12}H_7O_2Cl_3$



Nonylphenol

$C_{15}H_{24}O$

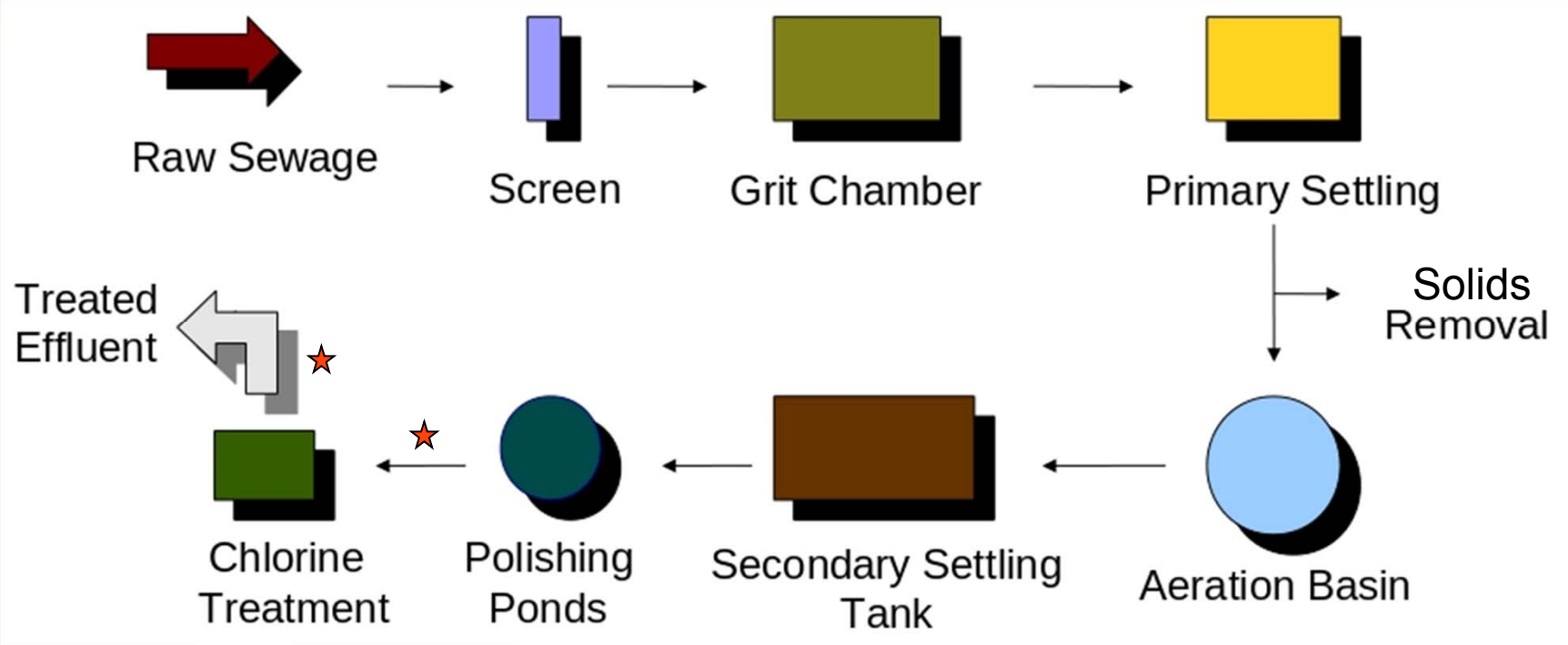


1. http://mapmaker.rutgers.edu/page1links.html.

Selected PPCPs Detected in Wastewater:

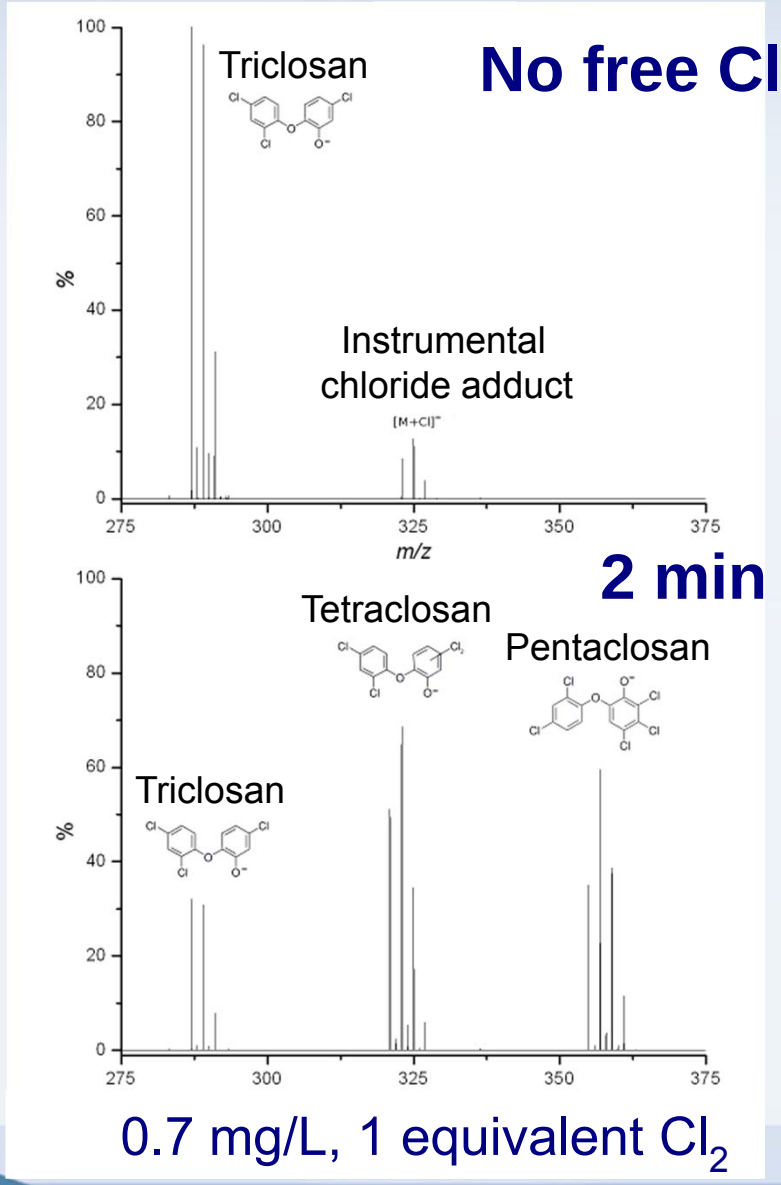
Compound	Use	Max (ng/L)	Mean (ng/L)
Triclosan	antimicrobial	340	280
Triclocarban	antimicrobial	130	110
Carbamazepine	anticonvulsant	340	300
Naproxen	antiinflammatory	750	410
Gemfibrozil	antilipidemic	1,000	830
Valsartan	antihypertensive	7,200	5,100
Meprobamate	antianxiety	760	640
Trimethoprim	antibiotic	330	330
Diphenhydramine	antihistamine	420	400
Nonylphenol	surfactant	21,000	13,000
Nonylphenol monoethoxylates	surfactant	2,900	2,800
Nonylphenol diethoxylates	surfactant	3,600	2,400

Wastewater Sampling



★ Triplicate wastewater samples obtained (June 25th, 28th, 29th)

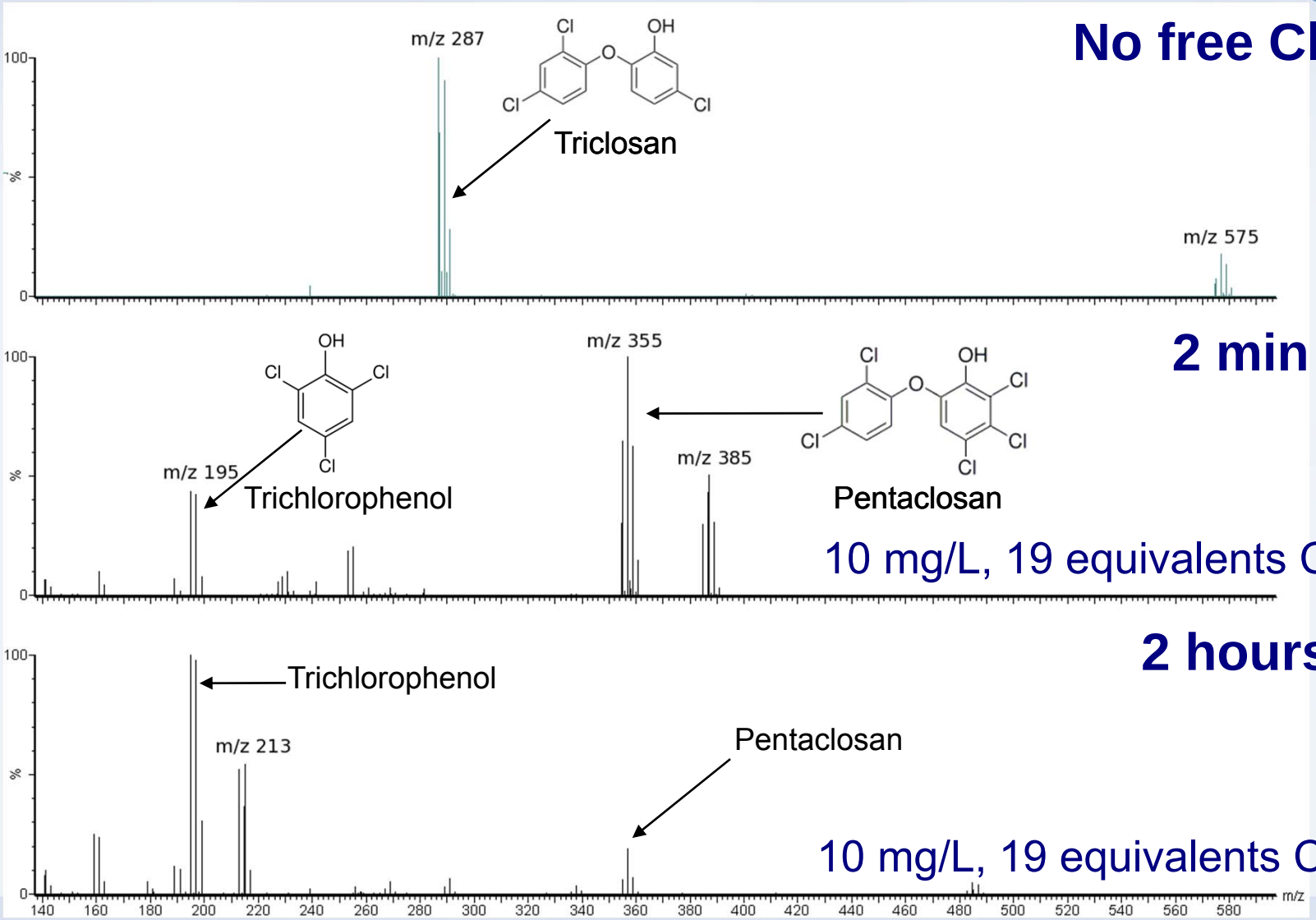
Bench Study – Reagent Water



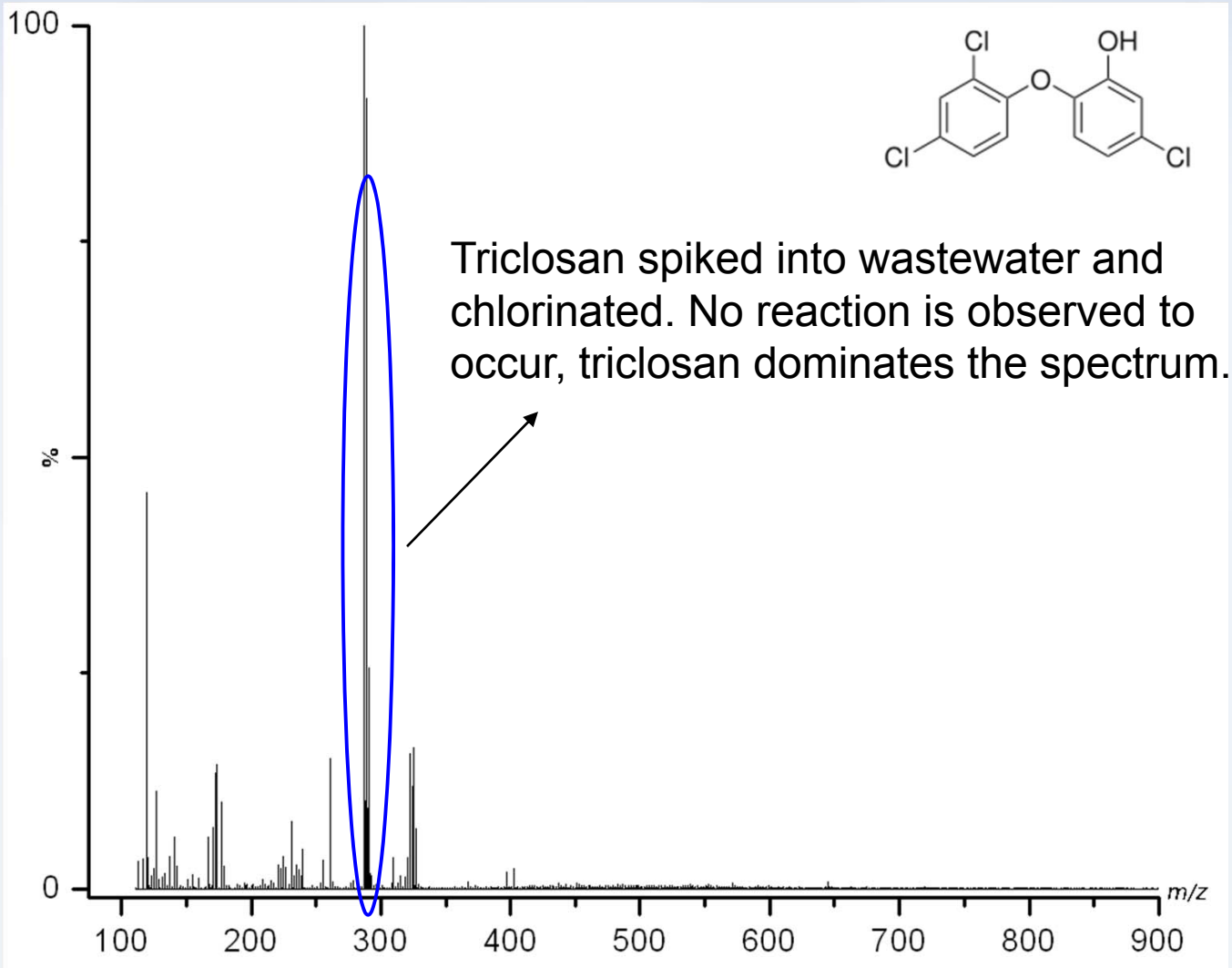
Triclosan (2.5 µg/mL) is stable in a reagent water matrix over the experimental window when no chlorine is present.

When free chlorine is provided triclosan reacts rapidly consuming the available chlorine.

Reagent Water – Increased Chlorination

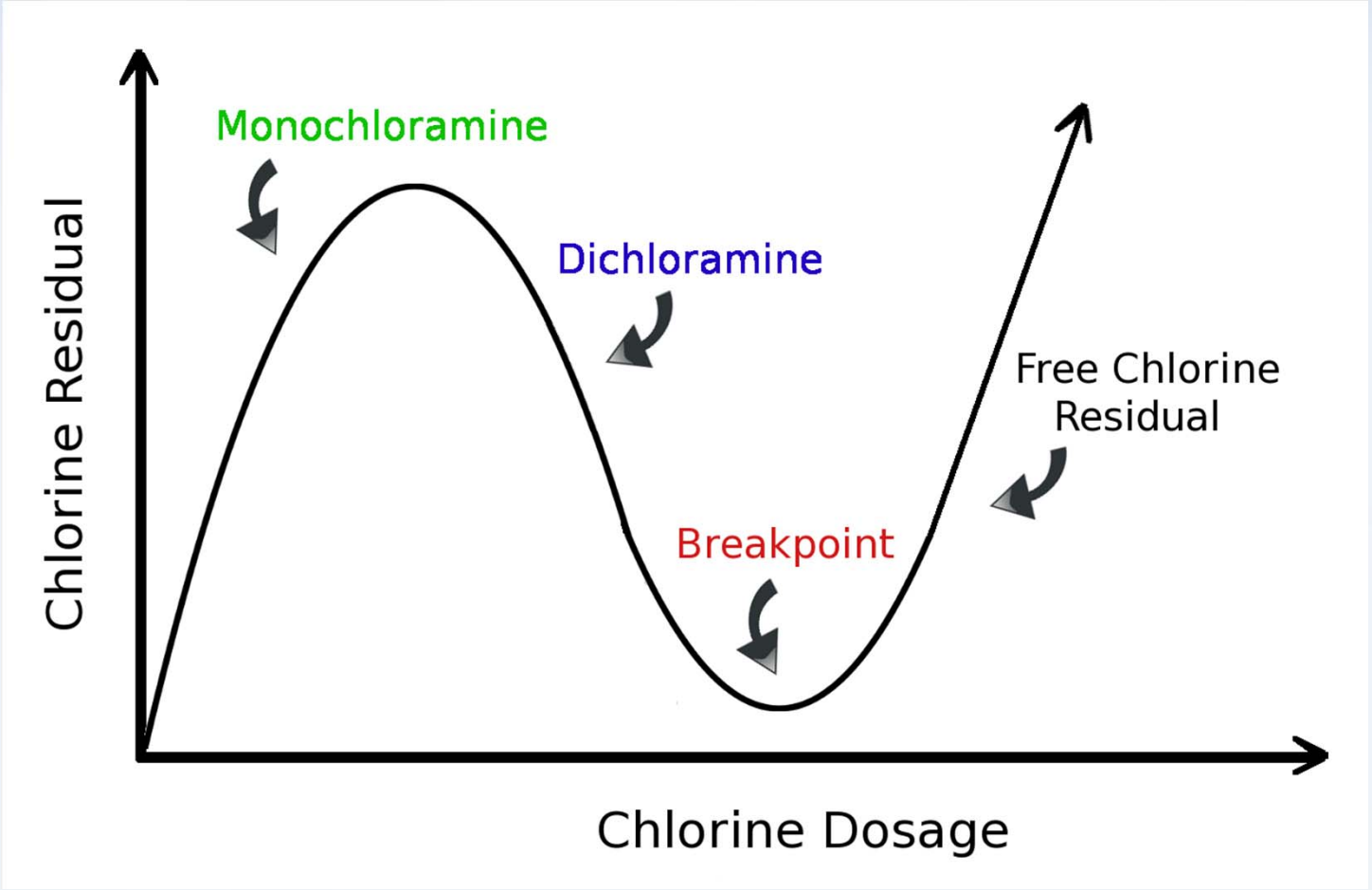


Bench Study – Wastewater



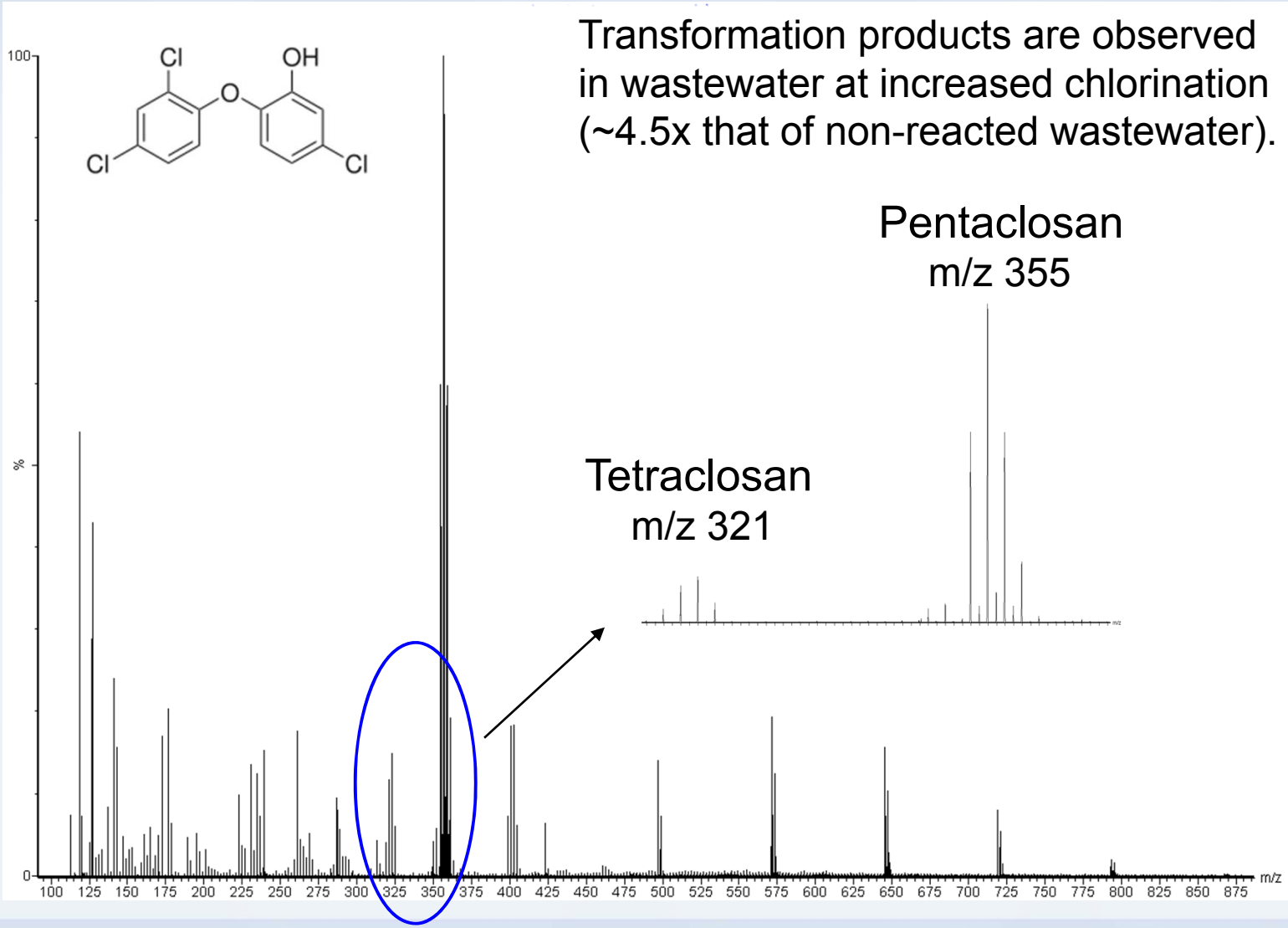
Triclosan spiked into wastewater and chlorinated. No reaction is observed to occur, triclosan dominates the spectrum.

Wastewater Breakpoint



Total Chlorine = Free Chlorine + Combined Chlorine

Wastewater – Increased Chlorination



Transformation products are observed in wastewater at increased chlorination (~4.5x that of non-reacted wastewater).

Pentaclosan
m/z 355

Tetraclosan
m/z 321

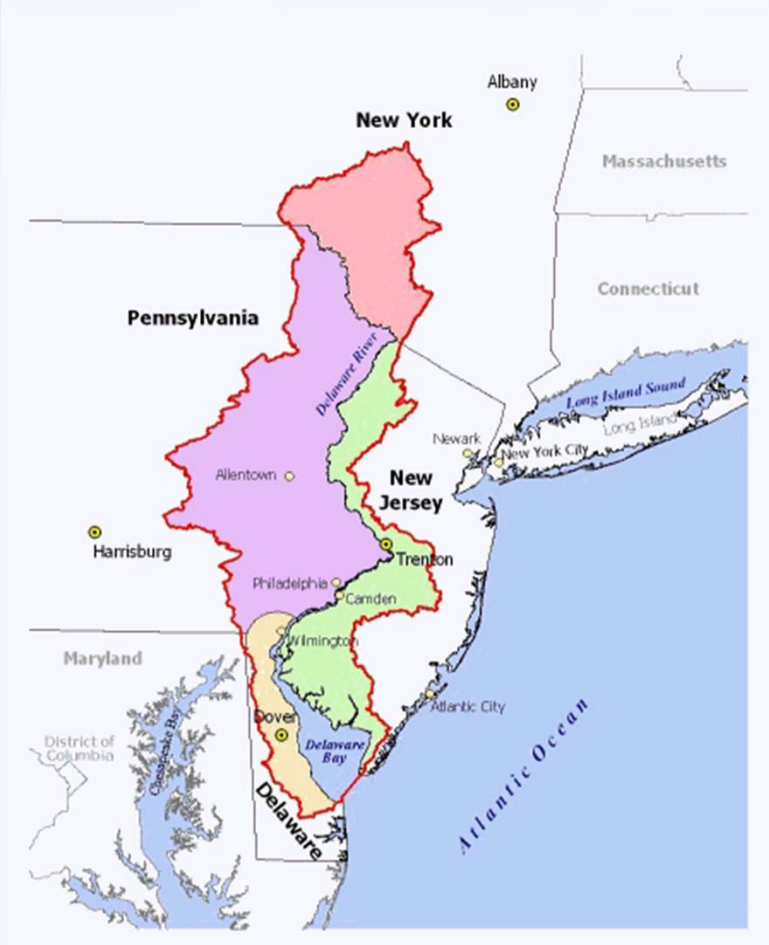
Quantitative Method Development

Analyte Target List	Surrogate Standard
Triclosan	$^{13}C_{12}$-Triclosan
Tetraclosan	$^{13}C_{12}$-Triclosan
Pentaclosan	$^{13}C_{12}$-Triclosan
Nonylphenol	$^{13}C_{6}$-Nonylphenol
Monochlorinated Nonylphenol	$^{13}C_{6}$-Nonylphenol
Dichlorinated Nonylphenol	$^{13}C_{6}$-Nonylphenol
2,4-Dichlorophenol	$^{13}C_{6}$-2,4-Dichlorophenol
Trichlorophenol	$^{13}C_{6}$-Trichlorophenol

Method Validation

Analyte	Mean (%)	Standard Deviation	Reporting Limit (ng/L)
Triclosan	100	7.4	5.0
Tetraclosan	89	6.7	5.0
Pentaclosan	74	6.6	5.0
Nonylphenol	130	15	46
Monochlorinated Nonylphenol	50	8.1	46
Dichlorinated Nonylphenol	76	18	46
2,4-Dichlorophenol	100	11	100
Trichlorophenol	110	26	5.4
$^{13}C_{12}$-Triclosan	90	6.9	
$^{13}C_{6}$-Nonylphenol	44	5.7	
$^{13}C_{6}$-2,4-Dichlorophenol	63	22	
$^{13}C_{6}$-Trichlorophenol	77	18	
$^{13}C_{6}$-2,4,5-T	98	4.4	

Wastewater Sampling



The selected publicly owned treatment works located near the Delaware River handles ~100 million gallons of sewage daily.

Samples were obtained on three separate days at both pre and post chlorination steps.

Sample chlorination was quenched prior to shipping using ascorbic acid. Samples were stored frozen in amber glass bottles upon receipt.

Wastewater Results

α = 0.05, n = 3

Analyte	Pre-chlorination Mean (ng/L)	Post-chlorination Mean (ng/L)	Reporting Limit (ng/L)	Significant Difference?
Triclosan	390	340	30	No
Nonylphenol	30,000	31,000	300	No
2,4-Dichlorophenol	130	320	100	No
Trichlorophenol	N. D.	N. D.	30	
Tetraclosan	N. D.	N. D.	30	
Pentaclosan	N. D.	N. D.	30	
Monochlorinated Nonylphenol	N. D.	N. D.	300	
Dichlorinated Nonylphenol	N. D.	N. D.	300	

Field Sample Results

- Pre and post chlorination wastewater samples were found to contain both nonylphenol (ppb) and triclosan (ppt).
- Statistical analysis at a confidence level of 95% indicates that the means of the nonylphenol and triclosan concentrations are not significantly different after treatment.
- Specific transformation products were not observed above the reporting limit.
- These results are consistent with the wastewater benchtop study which required increased amounts of sodium hypochlorite to observe transformation products.

Conclusions

Transformation products of triclosan and nonylphenol are not detected as a product of chlorine treatment in the studied publicly owned treatment works.

In situations where free chlorine is available, transformation products would be expected and could potentially comprise the entire analyte load, in particular for phenols.

Next Steps...

- Analysis of wastewater samples from a treatment plant employing nitrification processes (more likely to have free chlorine present).

- Expansion of the target list to include other relevant targets and transformation products, in particular those which are phenolic in nature.

- Use of the developed method in conjunction with dioxin analysis (EPA Method 1613B) to obtain further information about the occurrence and fate of triclosan transformation products.

Acknowledgements:

Million Woudneh
Georgina Brooks
Richard Grace
John Cosgrove

Greg Cavallo
Ron MacGillivray
Thomas Fikslin

Scott McIndoe