

*Sustainable Nanotechnology Conference 2015*

**Fate of Fullerenes (C<sub>60</sub>) during Peracetic Acid  
(PAA) Post Disinfection of Treated Alum  
Enhanced Combined Sewer Overflow (CSO)  
Primary Treatment**

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*UNIVERSITY OF ALBERTA*

*MARCH 9, 2015*

# Outline

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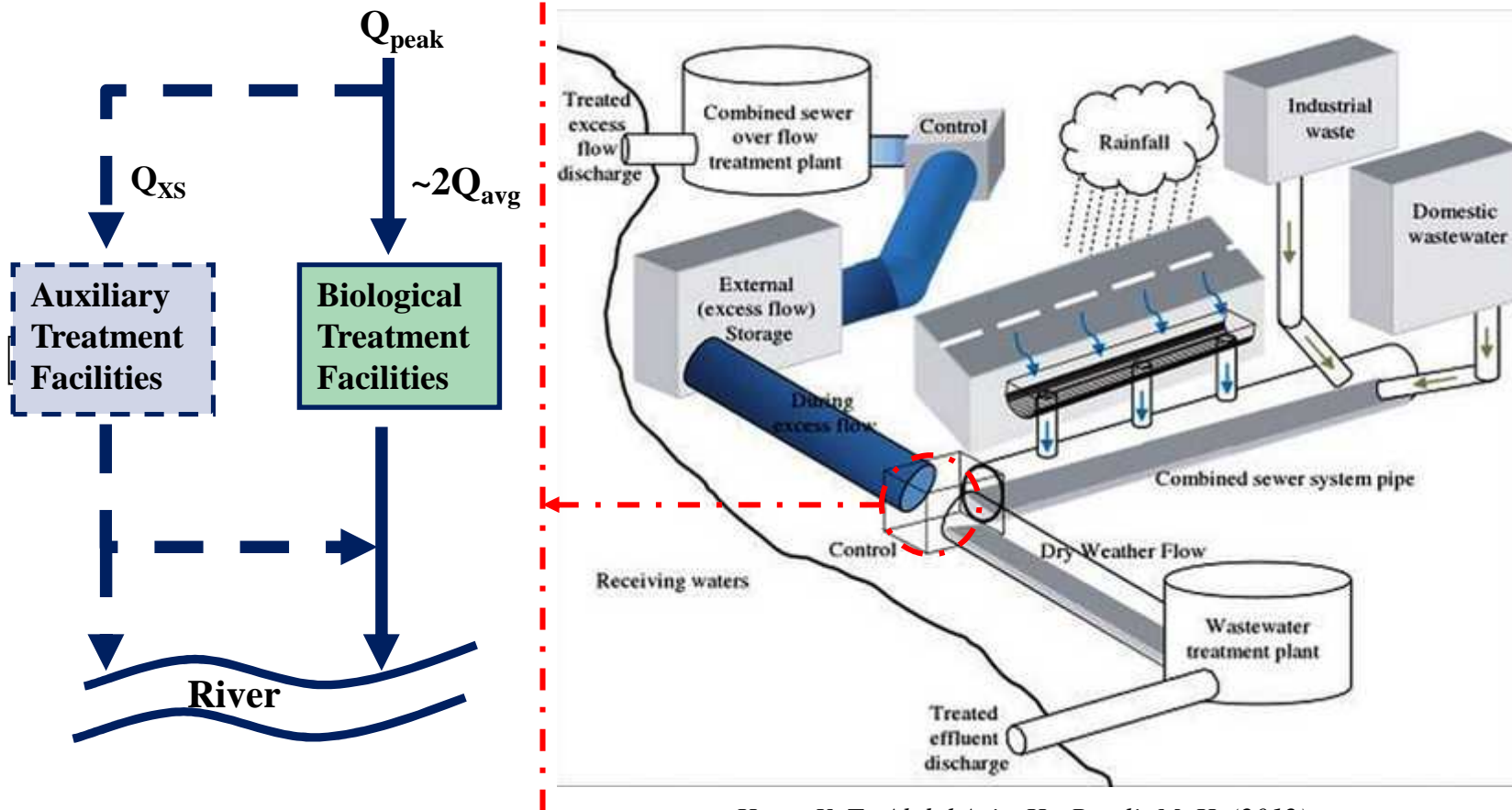
1. Introduction
2. Project Objectives
3. Selection of Unit Processes
4. Results and Discussion
5. Work Currently in Progress

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# Combined Sewer Overflow System

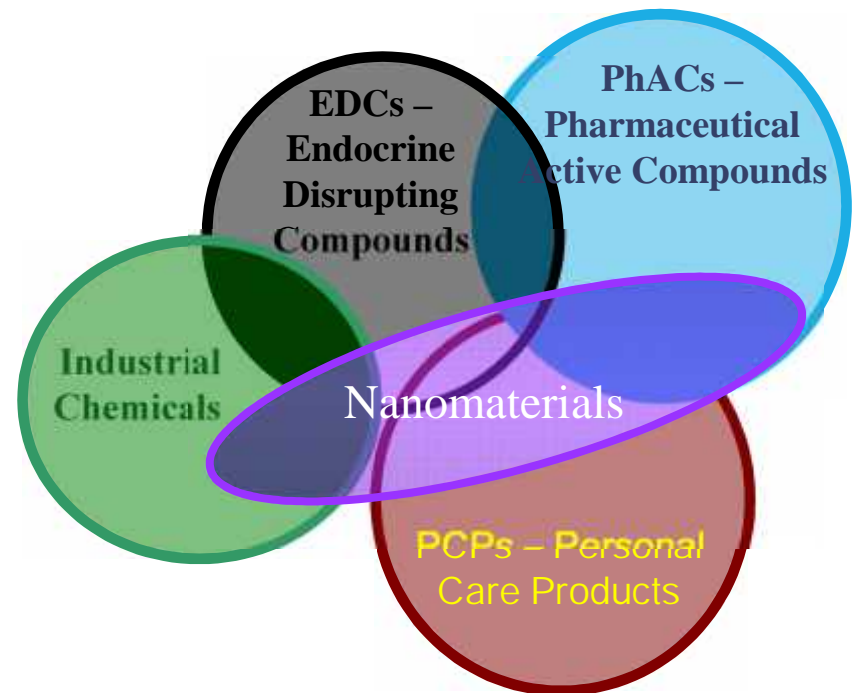


Hung, Y.-T.; Abdul Aziz, H.; Ramli, M. H. (2012)

# Emerging Contaminants

## “small IS DIFFERENT”

"existing regulatory approaches and risk management strategies are appropriate for the challenges presented by nanomaterials," however, it recommended that more investment be made in strategic risk assessment research.



Council of Canadian Academies  
Conseil des académies canadiennes

[Council of Canadian Academies, 2008, “Small is Different: A Science Perspective on the Regulatory Challenges of the Nanoscale”](#)

# Toxicity of Fullerenes C<sub>60</sub>

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## ➤ **Solvation Method**

(Solvent Exchange, Ultra-Sonication, Long Stirring)

## ➤ **Surface Modification**

(Adsorption of other Materials)

## ➤ **Functionalization or Derivatization**

(Fullerol, Oxo-derivatives)

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# Selection of Unit Processes

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## Enhanced Primary Treatment (Settling + Disinfection)

### ➤ **Coagulation/Flocculation/Sedimentation:**

Destabilization of colloidal impurities- Transferring small particles in to large aggregates – Adsorption of dissolved organic materials into the aggregates- Removal of aggregates by sedimentation

### ➤ **Disinfection:**

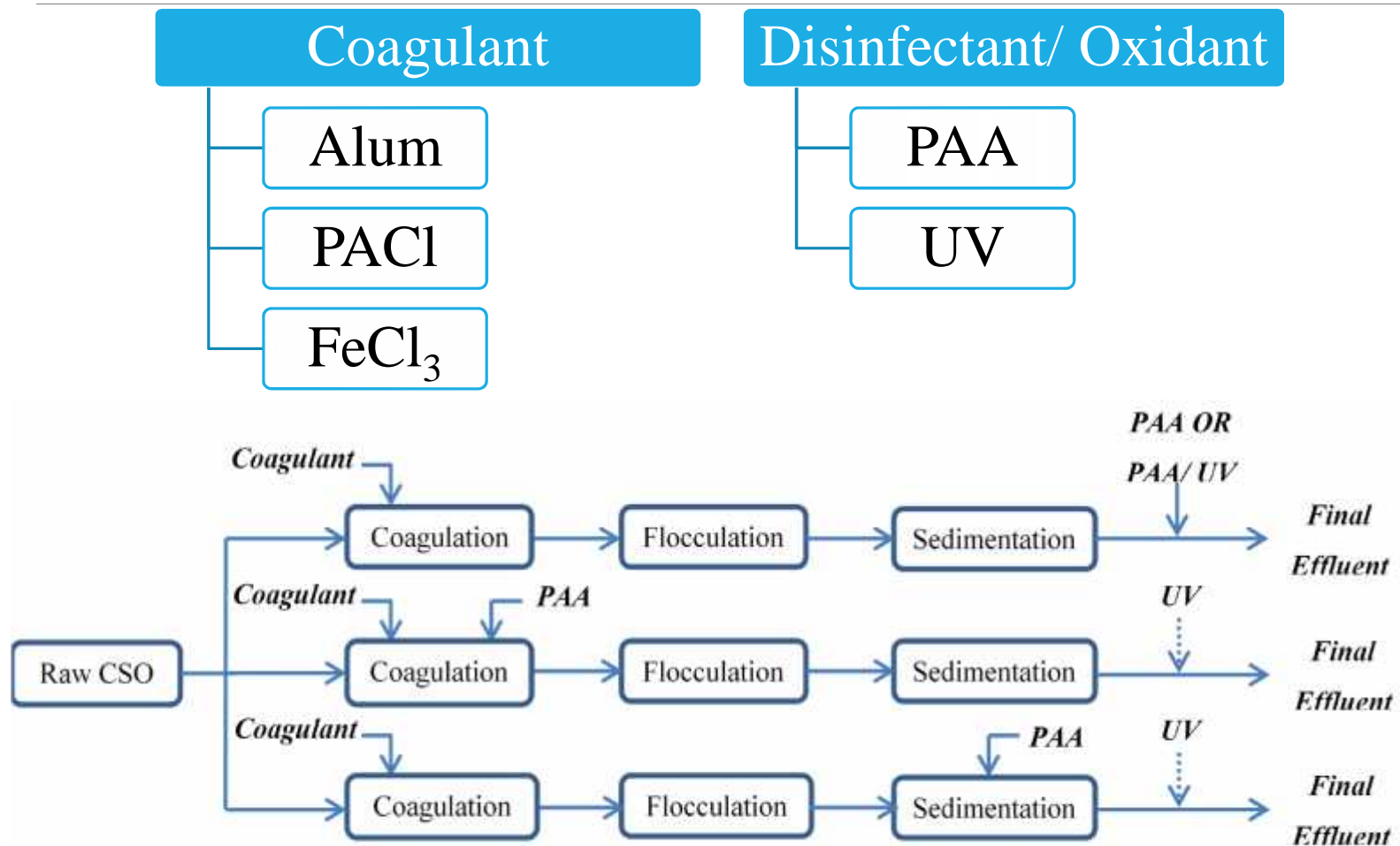
Kill/ Inactivate harmful organisms (bacteria and viruses) and control/ remove the odour precursors

## Hypothesis

Combinations of oxidants and coagulants will transform and mineralize the target pollutants and result in the reduction or elimination of their toxicity.



# PAA Study



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## Overall Objectives

- Enhancement of primary sedimentation process for the treatment of CSOs
- Assessment of the environmental impacts and mitigation measures of some NMs of emerging concern

## Short-Term Objectives

- Selection of the optimum operating conditions of the most effective chemicals and processes for CSO treatment
- Investigation of the role of using dual disinfection system
- Understanding the fundamentals of the selected processes in handling NPs
- Assessment of the effects selected coagulants and oxidants on the transformation of selected NPs.
- Investigation of the removal efficiency of the regulated parameters such as chemical oxygen demand (COD), nitrogen, phosphorus, *E. coli*, etc. with the increase of NMs.
- Toxicity reduction

## Long-Term Objectives

- Scientific foundation for the sustainable and integrated management of CSO
- Assisting decision-makers to adopt sustainable development strategies based on the simulation of actual conditions and the predictions of the impact of NPs on the environment
- Protection of environment and human health

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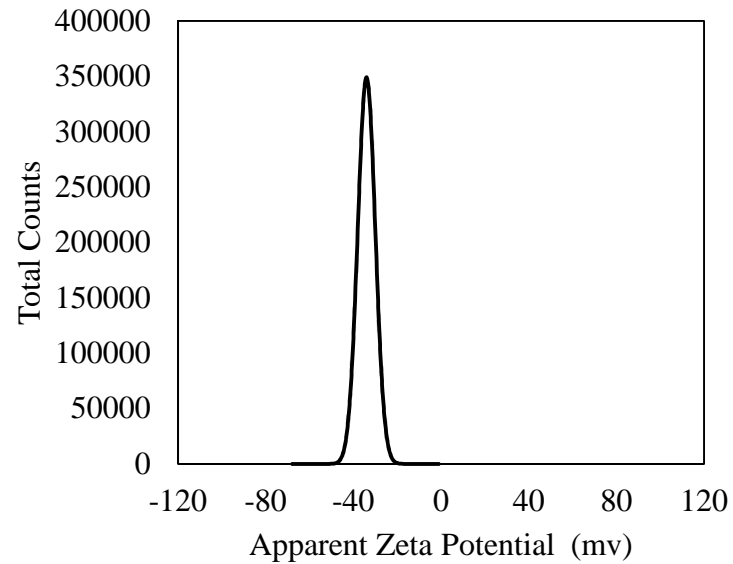
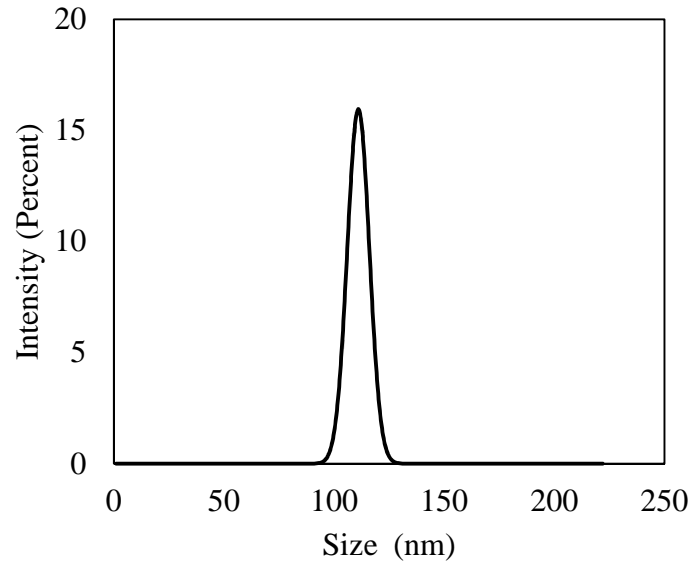
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**Sub Project#1: Fate of fullerenes (C<sub>60</sub>) during peracetic acid (PAA) post disinfection of treated alum-enhanced combined sewer overflow (CSO) primary treatment**

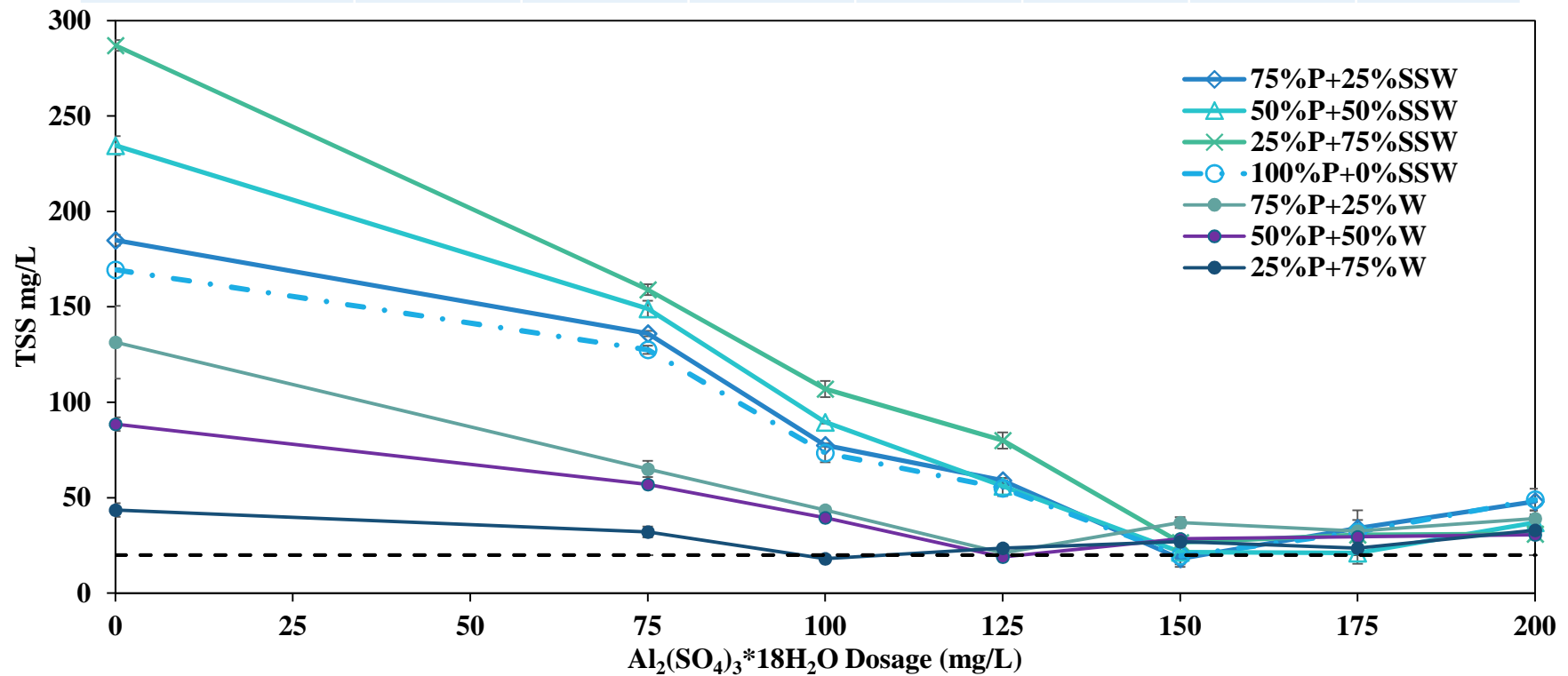
# Preparation of nC60

## ➤ Solvent Exchange (Toluene)



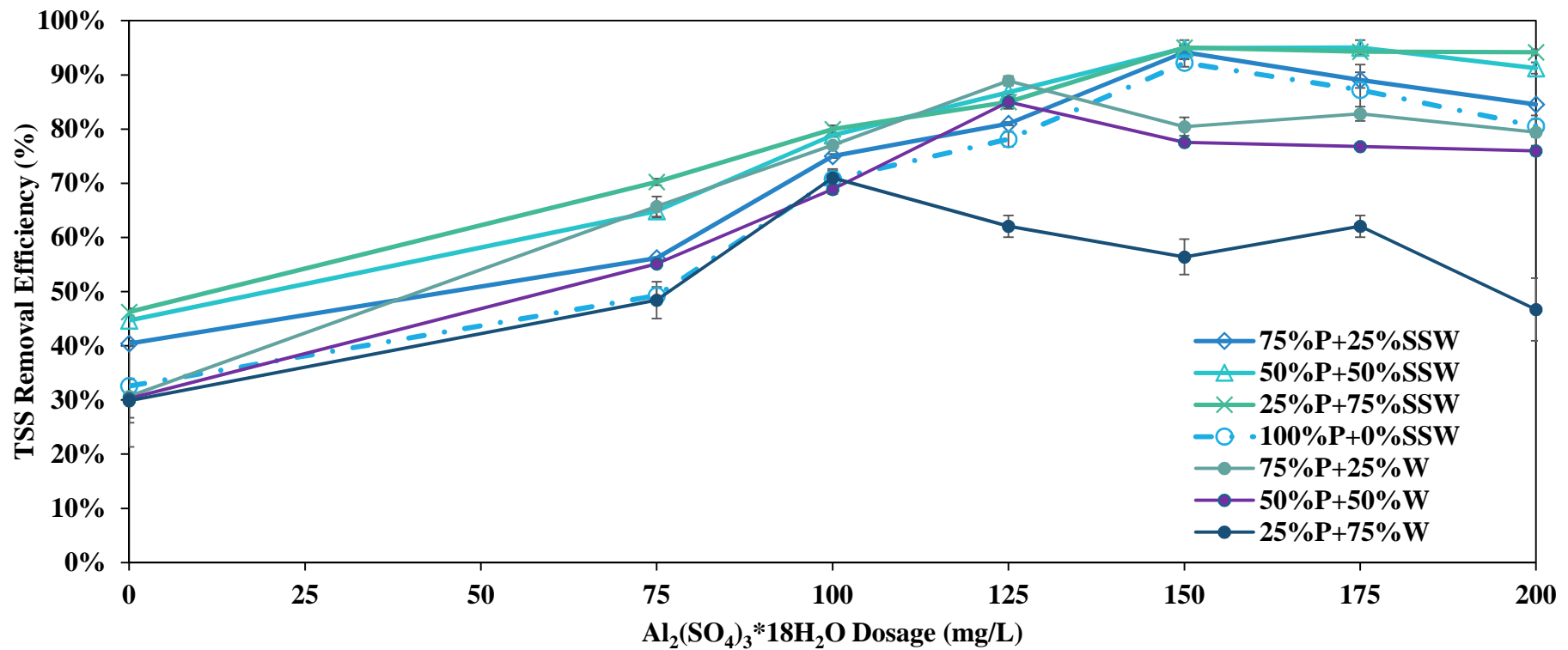
# CFS- Flushes Role

Sample Type	25%P+ 75%W	50%P+ 50%W	75%P+ 25%W	100%P	75%P+ 25%SSW	50%P+ 50%SSW	25%P+ 75%SSW
Avg. TSS (mg/L)	62	127	189.5	251.5	310.5	424	534



# CFS- Flushes Role

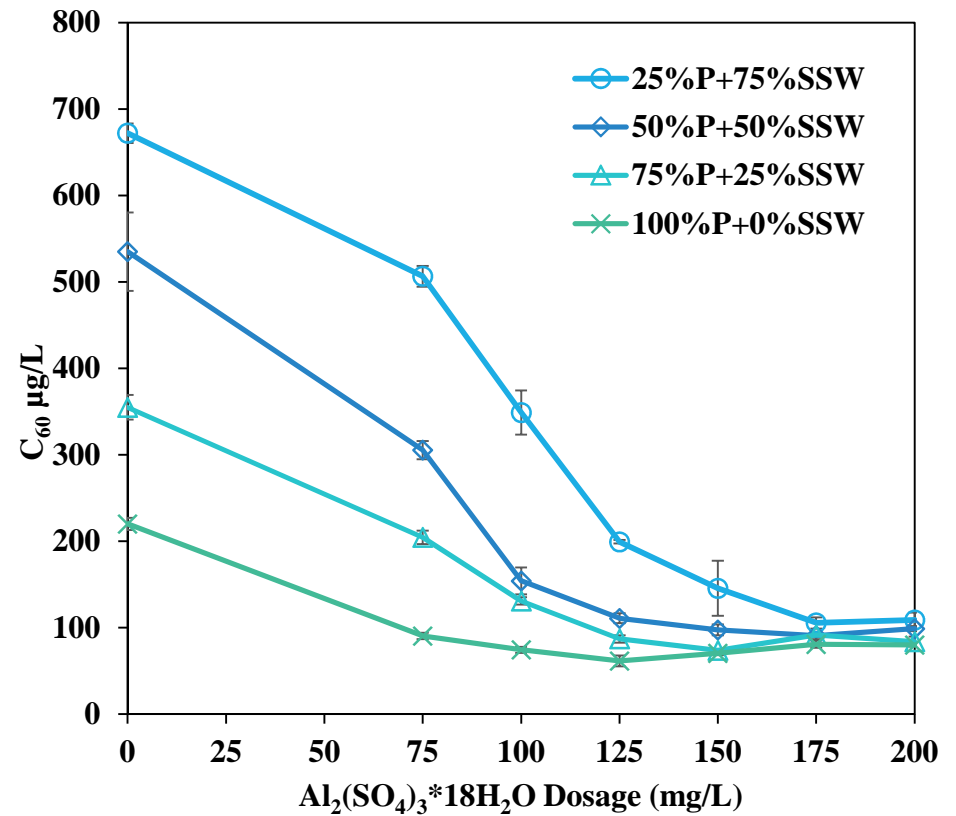
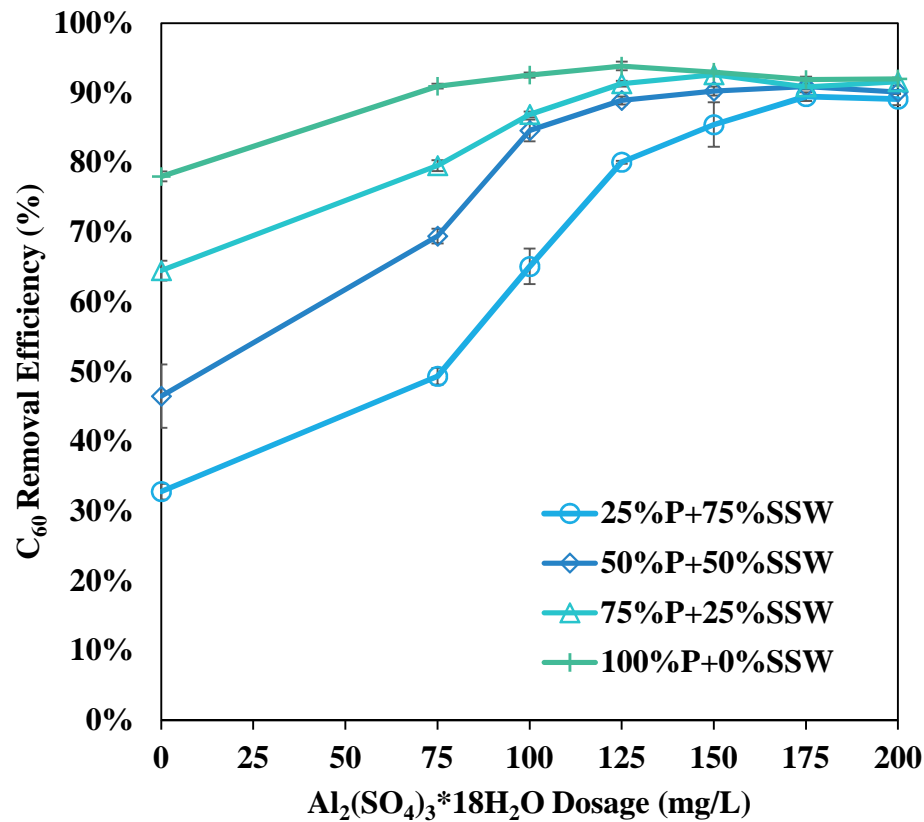
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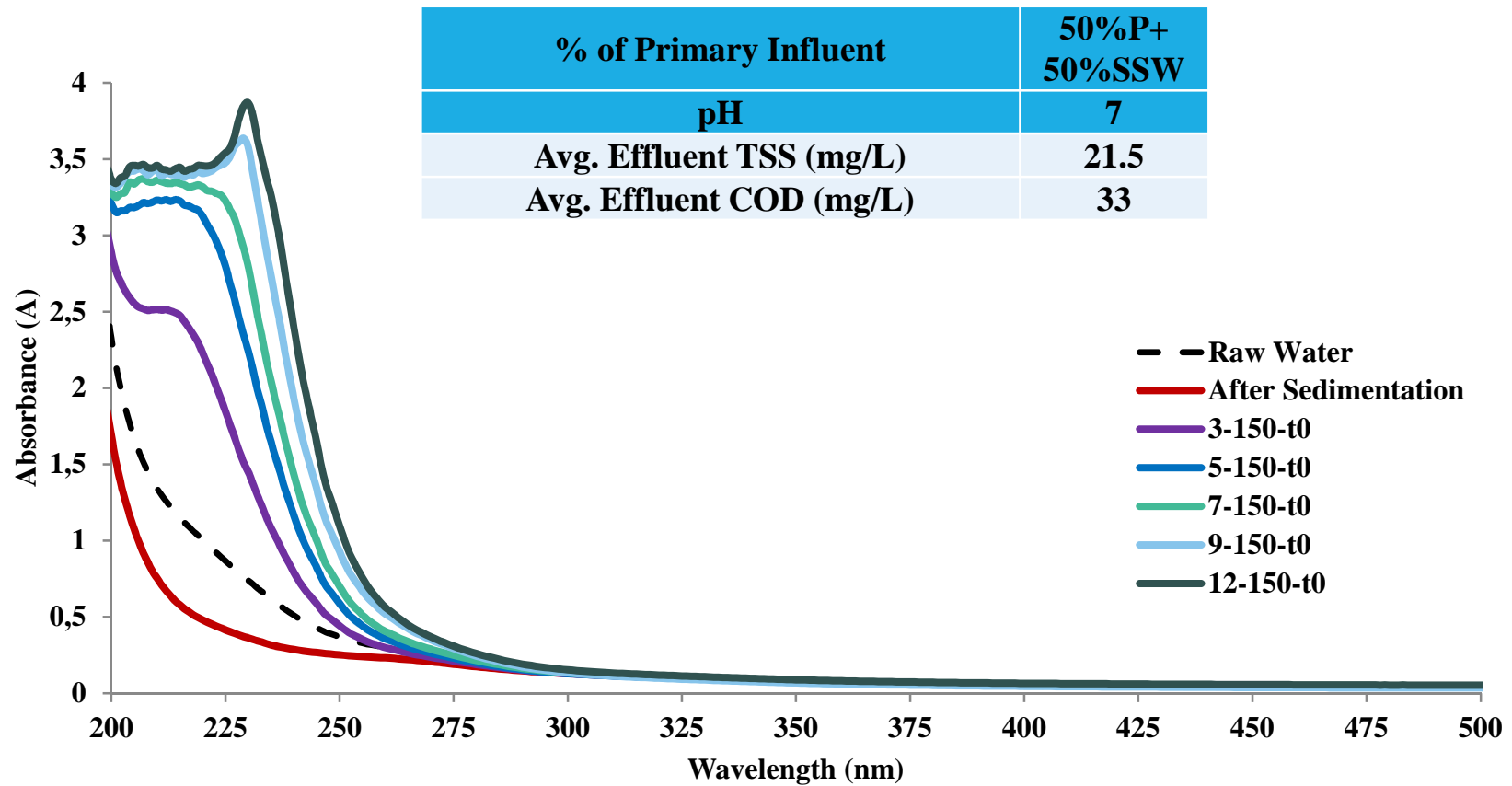
Spiked  $C_{60}$  in the Influent

1 mg/L



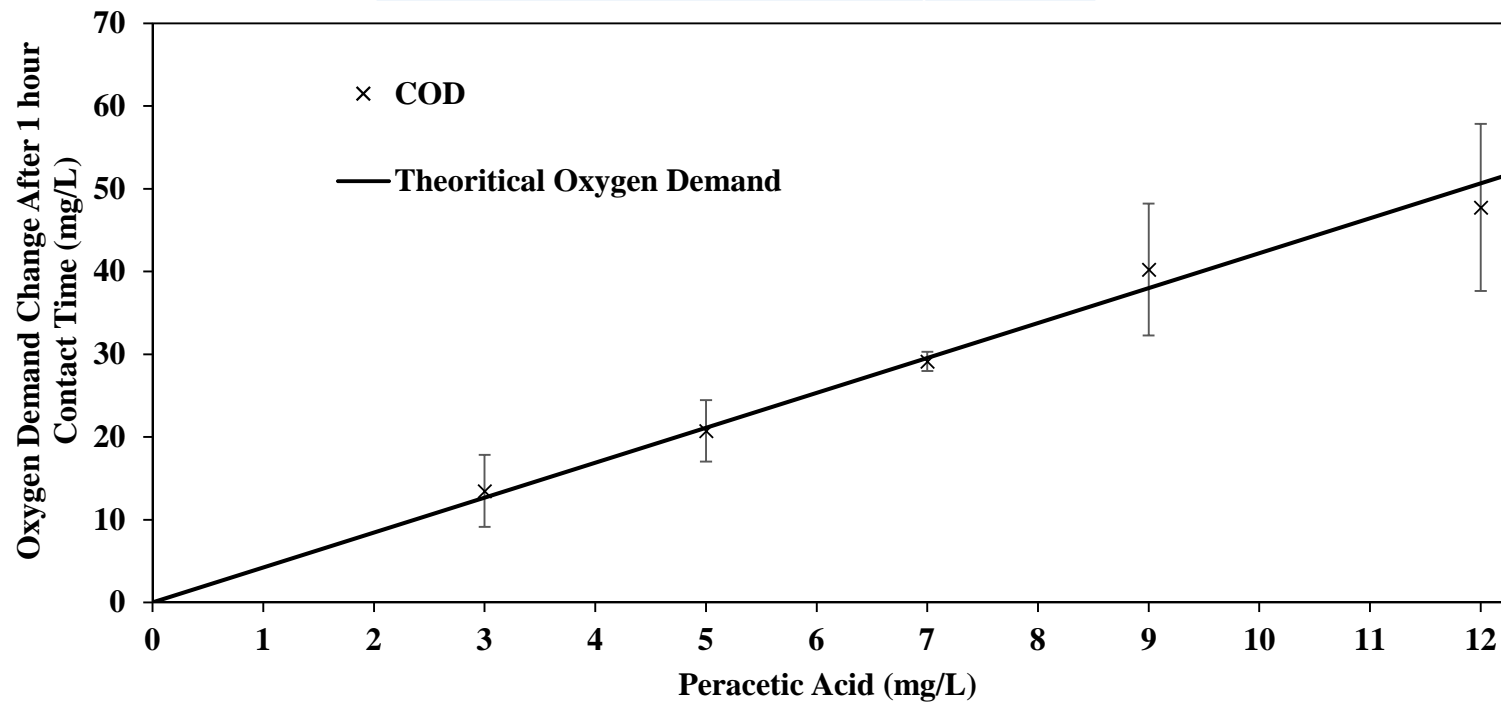


# PAA Post Disinfection

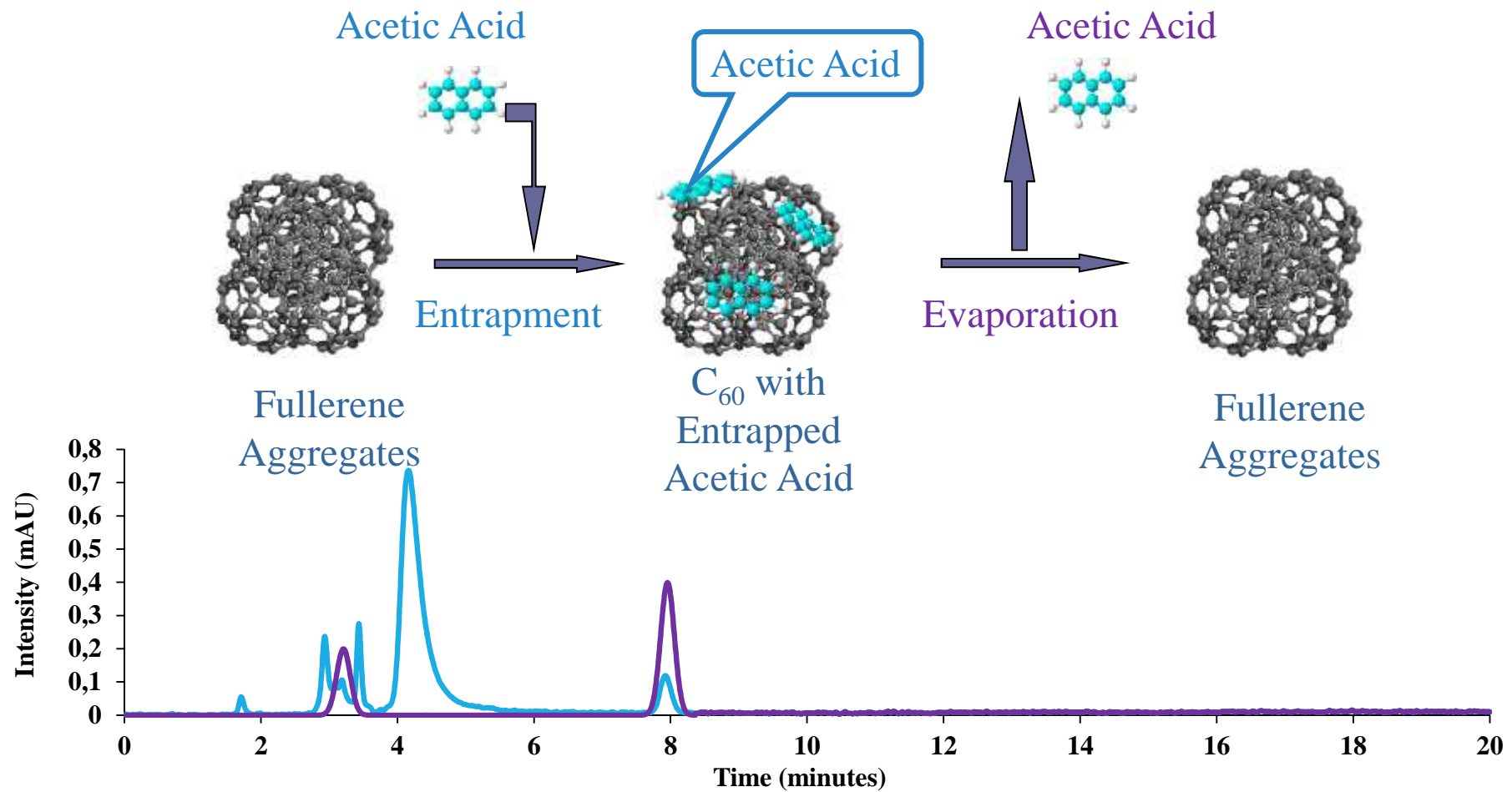


# PAA Post Disinfection

% of Primary Influent	50%P+ 50% SSW
pH	7
Avg. Effluent TSS (mg/L)	21.5
Avg. Effluent COD (mg/L)	33



# PAA Post Disinfection



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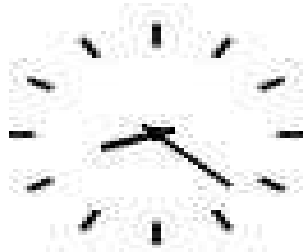
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# Work Currently in Progress (May 2015)

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1. Simultaneous Removal of *E.coli* and C<sub>60</sub>
2. Repeat Experiments at 5° Celsius
3. Kinetics
4. Toxicity Studies



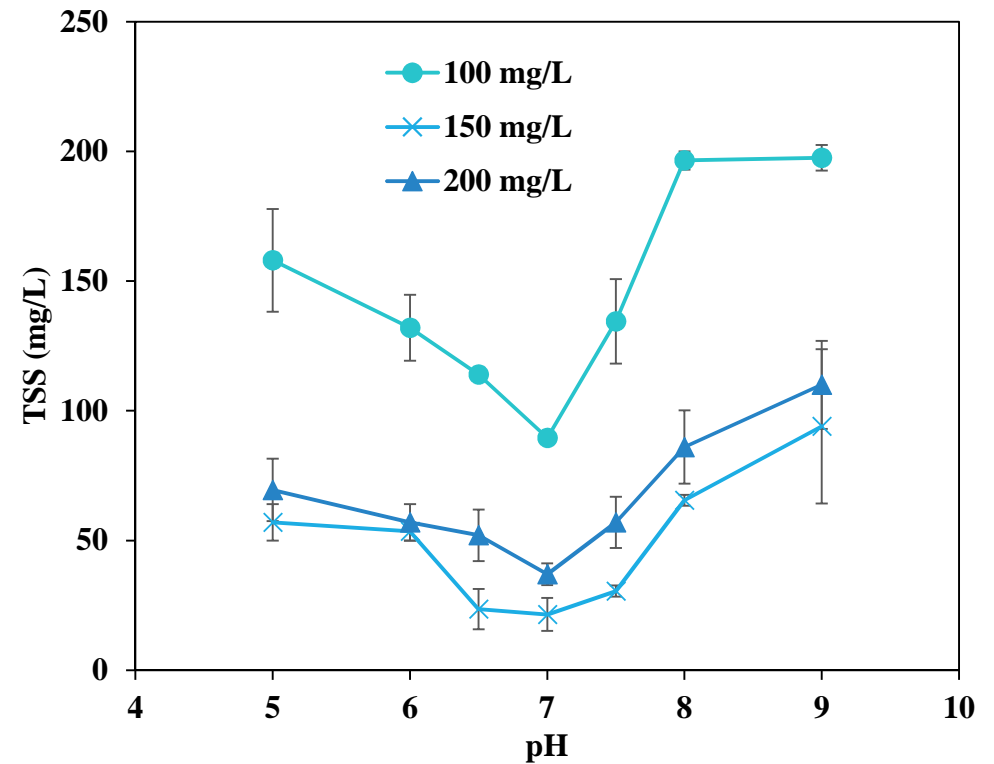
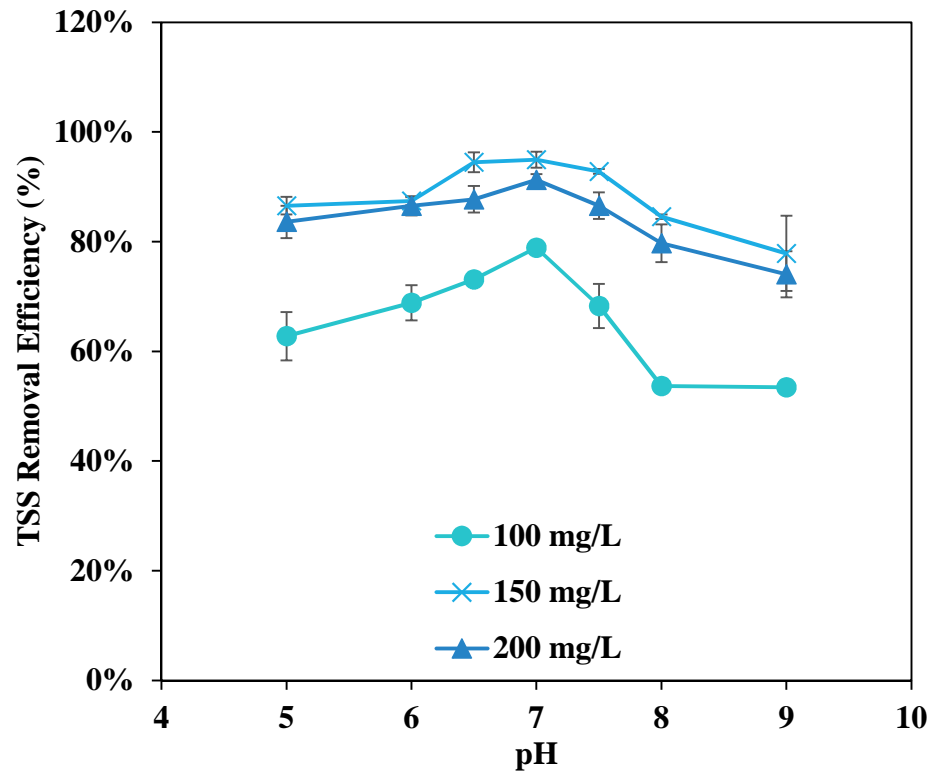
Q & A time



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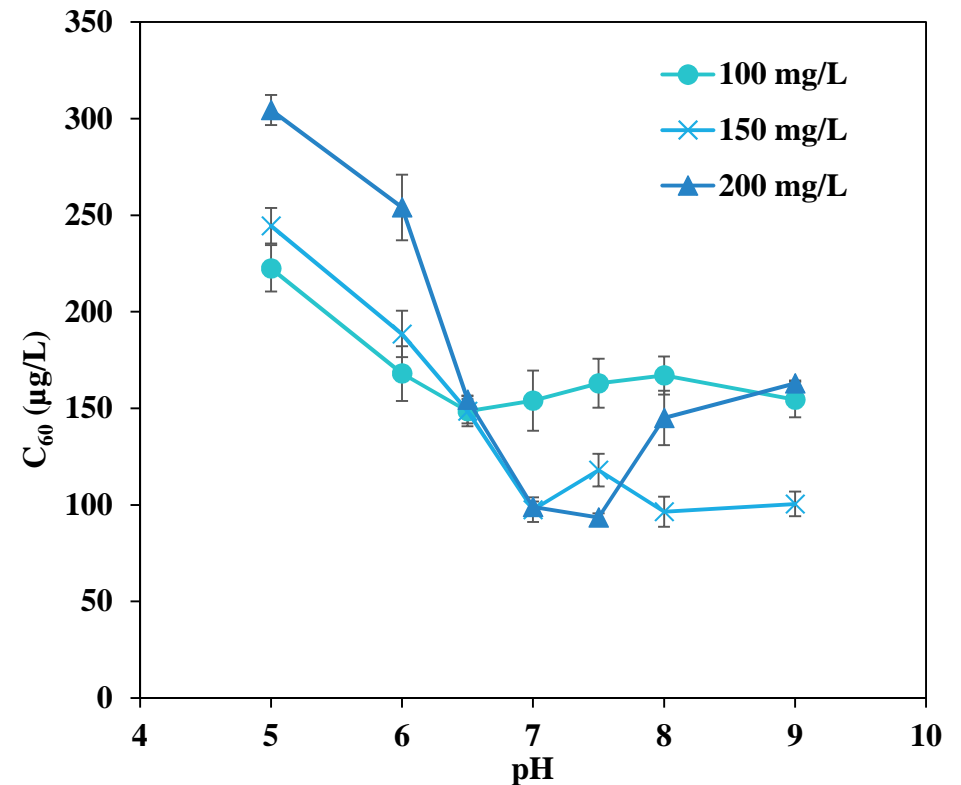
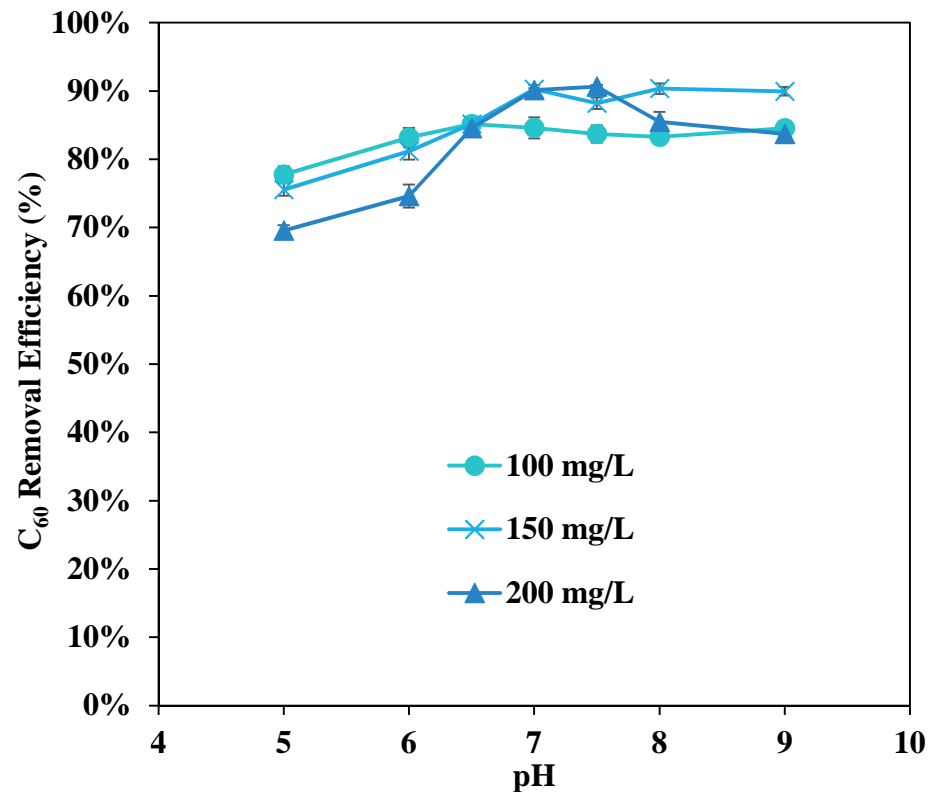
# Sub Project#1: CFS- pH Role

<b>% of Primary Influent</b>	<b>50%</b>
<b>Avg. TSS (mg/L)</b>	<b>424</b>



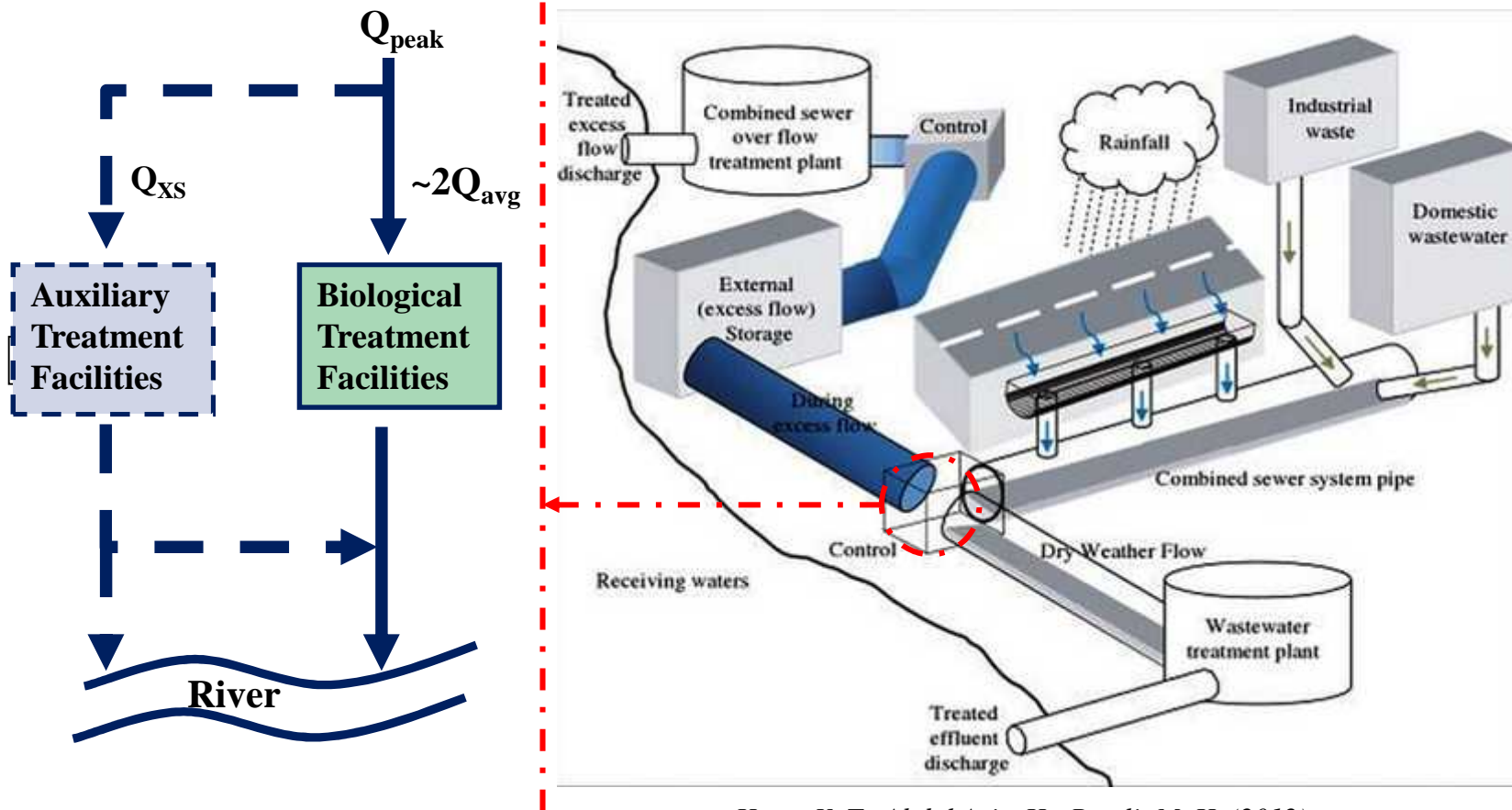
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<b>% of Primary Influent</b>	<b>50%</b>
<b>Spiked <math>C_{60}</math> in the Influent (mg/L)</b>	<b>1</b>





# Combined Sewer Overflow System



Hung, Y.-T.; Abdul Aziz, H.; Ramli, M. H. (2012)

# Typical Pollutant Concentrations Found in CSOs

*US EPA, 2001*

Contaminant Source	BOD <sub>5</sub> (mg/L)	TSS (mg/L)	Total N (mg/L)	Total P (mg/L)	Fecal Coliform (cfu/100mL)
Untreated Domestic Wastewater	100—400	100—350	20— 85	4—15	10 <sup>7</sup> —10 <sup>9</sup>
Treated Wastewater - Secondary	<5—30	<5—30	15— 25	<1—5	< 200
Urban Runoff	10—250	67—101	0.4—1.0	0.7—1.7	10 <sup>3</sup> —10 <sup>7</sup>
<b>CSO</b>	25 —100	150—400	3—24	1—10	10 <sup>5</sup> —10 <sup>7</sup>

# Yearly Flow and TSS Load to the NSR passing through Edmonton

*Gyurek, L.; Lodewyk, S.; Malesevic, L., 2010*

Source	Yearly flow (ML/Year)	Yearly TSS Load (Tones)
Storm water outfalls	67,000 (0.89% of NSR Yearly Flow)	8600 (82%)
Combined sewer overflows from Rat Creek outfall plus 17 smaller ones	1,500 (0.02% of NSR Yearly Flow)	760 (7%)
GBWWTP final effluent that utilized secondary treatment	94,000 (1.3% of NSR Yearly Flow)	650 (6%)
GBWWTP bypassed effluent that utilizes EPT only	3,000 (0.04% of NSR Yearly Flow)	560 (5%)

# GB WWTP- Approval to Operate

Parameter	Limit	Calculation Method	Sample Type
BOD <sub>5</sub>	20 mg/L	Monthly arithmetic mean	_____
TSS	20 mg/L	Monthly arithmetic mean	Daily composite samples
Total Phosphorus	1.0 mg/L	Monthly arithmetic mean	Daily composite samples
Ammonia-Nitrogen (December 1 to May 31)	10 mg/L	Monthly arithmetic mean	Daily composite samples
Ammonia-Nitrogen (June 1 to November 30)	5.0 mg/L	Monthly arithmetic mean	Daily composite samples
E. coli counts	200units/ 100mL	Monthly geometric mean	Daily grab samples
pH	6.5 –9.5 pH unit	_____	_____

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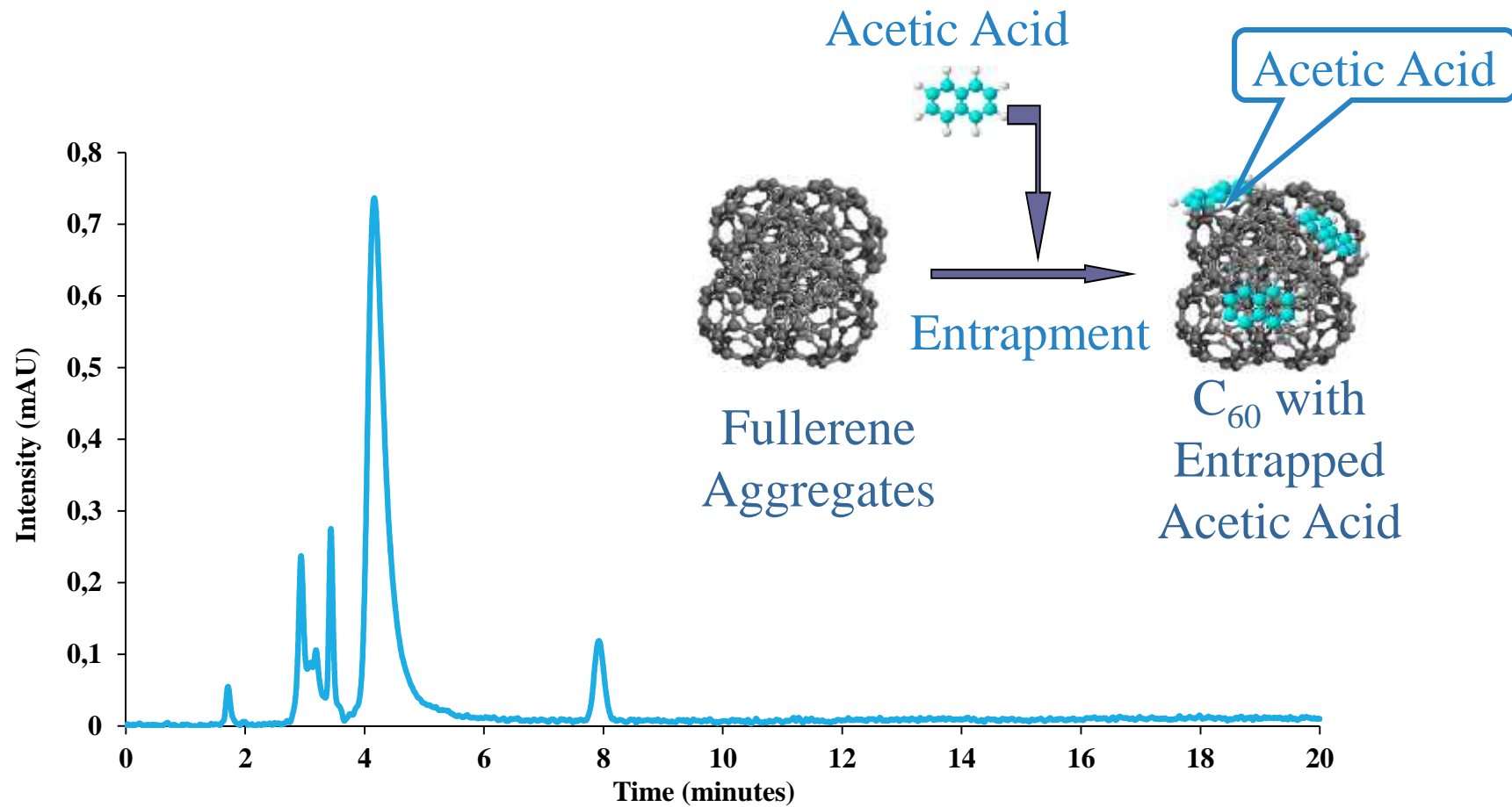
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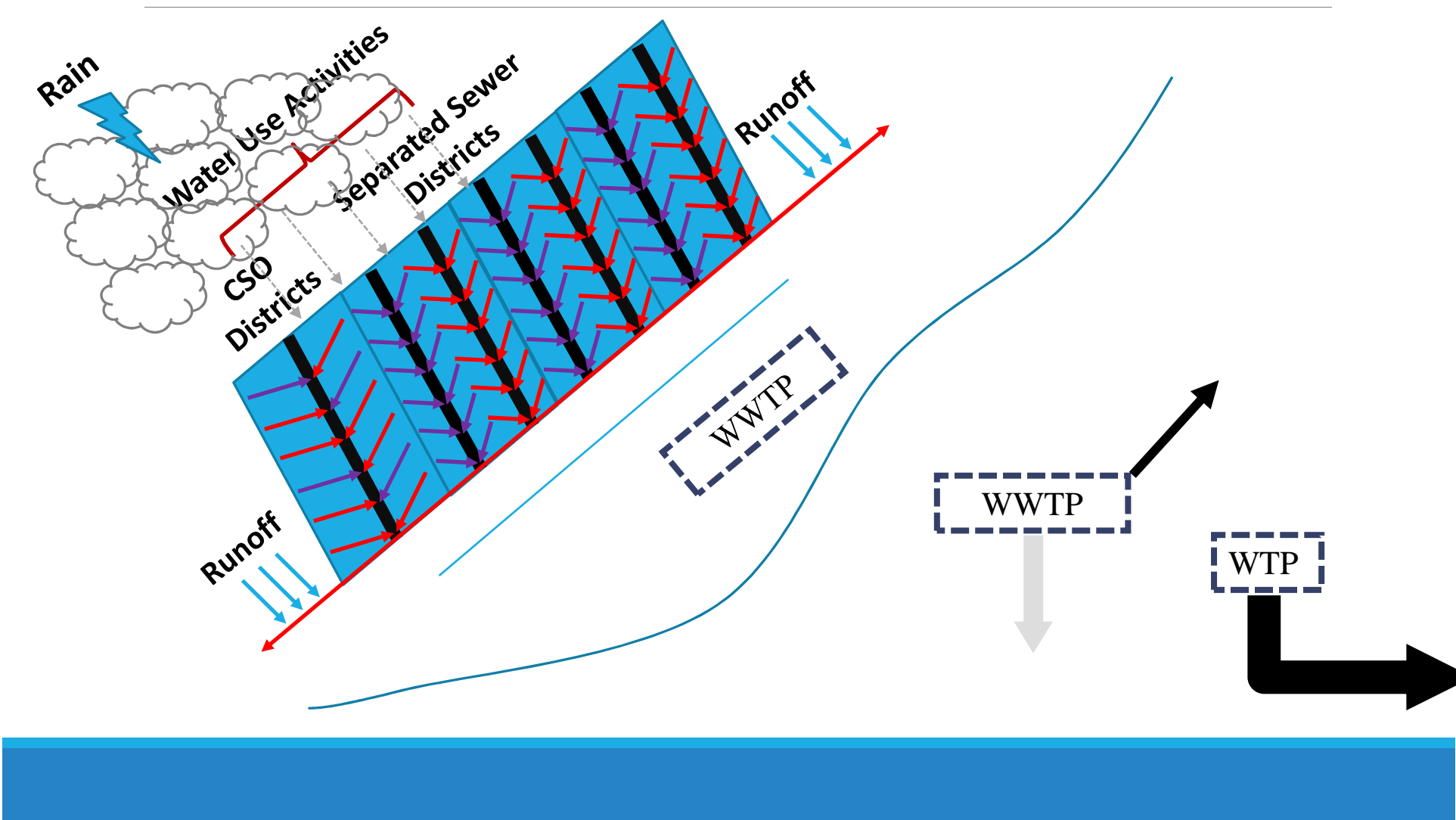
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# Research Plan

Activity		2015												2016												2017								
		1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4	5				
Literature Review and Experimental Design		█												█																				
Fullerenes	Different coagulants + Post Disinfection using PAA/ UV	█																																
	Pre Disinfection using PAA+Different coagulants+ Post Disinfection using UV					█																												
	Ferrate + Post Disinfection using UV									█																								
	Dissemination												█																					
Titanium Dioxide	Different coagulants + Post Disinfection using PAA/ UV													█																				
	Pre Disinfection using PAA+Different coagulants+ Post Disinfection using UV																	█																
	Ferrate + Post Disinfection using UV																					█												
	Dissemination																								█									
Dissimination of All Results																										█								
Thesis Writing																											█							

# Sub Project#1: PAA Post Disinfection





# Building Fugacity or Aquivalent Concentration Model

Lake/ Rivers

Primary Sedimentation Tank

Hydrologic and Limnologic Parameters  
Volume of Water  
Particles Present, entering, and leaving  
Evaporation and Precipitation rates  
Sediment Deposition and Resuspension Rates

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Volume of Water  
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Mass Transfer Coefficients and diffusion variables  
Although chemical dependent, a common value can be applied to all chemicals

Reaction Rate Constants (Metals= Zero unless a speciation change is considered)

Partitioning Properties of the chemical between various environmental media are treated (Z values)-  
Z values are dependent on both the chemical and the nature of the medium

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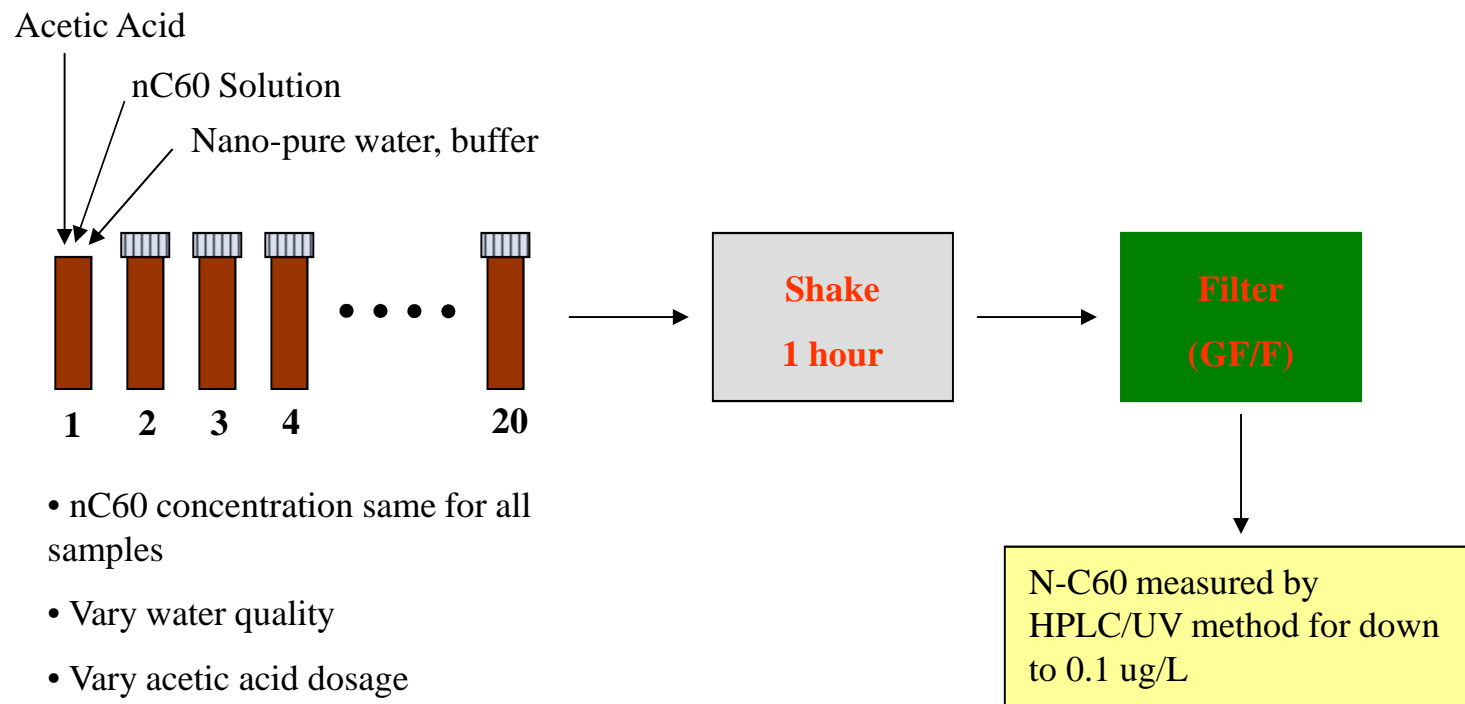
Volatile Chemicals

Fugacity Approach: Estimate is based on Air Phase then Partitioning Between Air and Water

Involatile Chemicals

Aquivalent Approach: Calculations begin with assigning the water phase  $Z$  a value of unity

# Batch Sorption Procedure





# Mass balance modeling at WWTP on nC60

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## Input Parameters

$$Q = 2.3 \text{ mgd}$$

$$\text{HRT} = 2.3 \text{ hours}$$

$$\theta = 5 \text{ days}$$

$$C_0 = 6 \text{ mg/L}$$

$$K = 3.1$$

$$1/n = 1.4$$

## Results

Predicted effluent C60 conc = 4.7 mg/L (78%)

22% of nC60 would go to biosolids

Model estimates must be validated with lab and field measurements

# Mass balance on nanoparticles in a WWTP operating at steady state

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Assume sorption to biological matter dominates over biodegradation or volatilization for engineered nanoparticles

Mass Balance Equation (mass NPs per time) at steady state:

$$\underline{QC_0 - QC - \frac{(KC_e^{1/n})XV}{\theta} = 0}$$

Terms are common WWTP parameters:  $Q$  = water flowrate,  $C_0$  &  $C_e$  are inlet and effluent nanoparticle concentrations,  $X$  is biomass concentration,  $\theta$  is sludge retention time,  $V$  is reactor volume,  $K$  and  $1/n$  are Freundlich isotherm parameters

42

Estimate  $K$  and  $1/n$  from batch isotherms



# Alkalinity Effect on Coagulation

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# Removal Mechanisms in CFS

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