

# Removal of PAHs Compounds from Aqueous Solution with Modified Zeolites

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# Agenda

- \* Background (PAHs & Surfactants)
- \* Research questions
- \* Modifications of zeolite
- \* Batch test for PAHs adsorption
- \* Effect of contact time, adsorbent dosage, pH & temperature
- \* Conclusion

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What Are PAHs Compound?

# PAHs Compound

- \* **Polycyclic aromatic hydrocarbons (PAHs)**

- \* **Sources**

- \* **1) Natural**

- \* Forest fires or volcanoes

- \* **2) Anthropogenic**

- \* Incomplete burning of organic matter

- \* Vehicle traffic, tobacco smoking, cooking

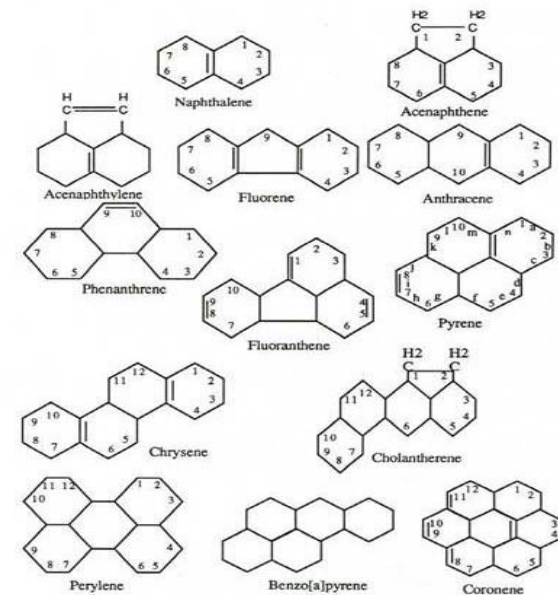
- \* **Properties**

- \* Non-polar; hydrophobic

- \* Slightly soluble in water

- \* Very volatile (2- 3 ring)

- \* Higher molecular weight, less water soluble

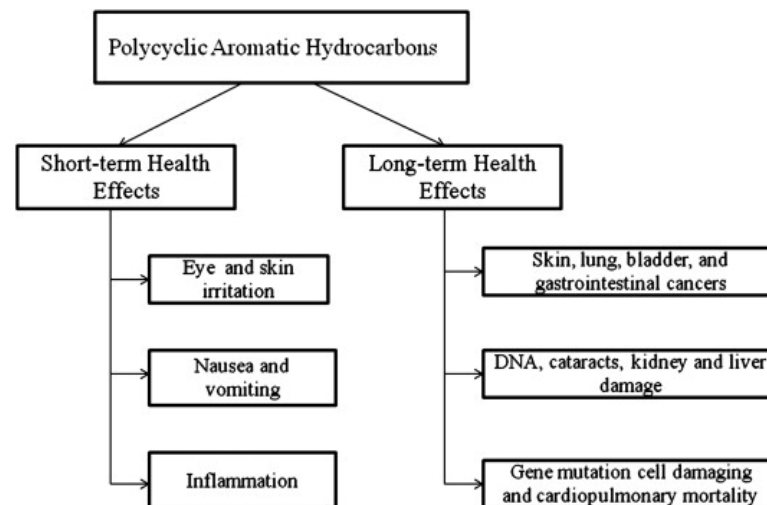




# Why Are PAHs a Concern?

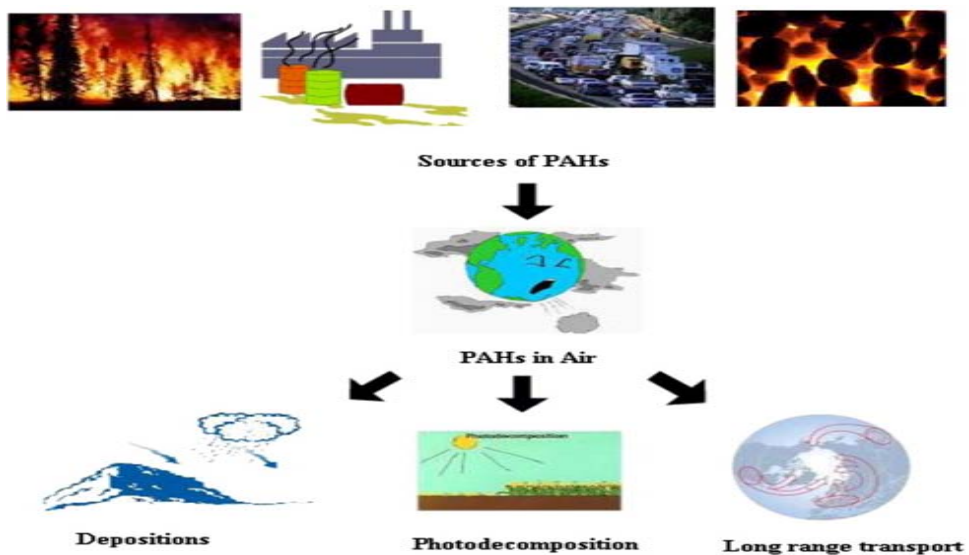
# Environmental Concerns with PAHs

- \* **Resistant to Degradation**
- \* **Toxic**
  - \* Significant acute toxicity to aquatic organisms
  - \* Naphthalene, fluorene, phenanthrene, and anthracene
- \* **Mutagenic & Carcinogenic**
  - \* PAHs have been known to be carcinogenic
  - \* Benz(a)anthracene & benzo(a)pyrene
- \* **Included in the US-EPA priority pollutants lists**



Source: Ki-Hyun Kim, Shamin Ara Jahan, Ehsanul Kabir, Richard J.C. Brown, Environment International, Vol. 60, 2013, p. 71-80

# What Are PAHs Occurrences in the Environment?



Source: Ki-Hyun Kim, Shamin Ara Jahan, Ehsanul Kabir, Richard J.C. Brown, Environment International, Volume 60, October 2013, Pages 71-80

# PAHs Concentrations in the Environment

Reference/PAHs	Anthracene	Fluoranthene	Fluorene	Phenanthrene	Pyrene
<b>Water (ng/L)</b>					
(Luo, et al. 2004) Pearl River Delta, China	3.14	4.1	2.3	10.7	1.8
(Zhang, et al. 2004) Tonghui River, Beijing, China	14.98 (5.9-46.7)	34.75 (14.78-80.7)	58.19 (20.7-141)	122.9 (49-312)	28.30 (12.7-71.5)
<b>Air</b>					
(Albinet, et al. 2007) Marseilles, France (pg m <sup>-3</sup> )	767 (3-4 343)	3 488 (2 104-4 826)	1 098 (272-2 707)	8 470 (3 482-15 287)	5 832 (379-18 69)
(Wang, et al. 2011) Beijing Tianjin region, China (ng/m <sup>3</sup> )	19.9 (1.58-62.4)	48.2 (6.3-282.4)	116.1 (16.9-281.5)	153.5 (16.6-427.9)	24.99 (3.4-138.9)
<b>Simedent (ng/g)</b>					
(Zhang, et al. 2004) Tonghui River, Beijing, China	16.2 (2.94-143.3)	93.8 (16.25-462.4)	21.9 (4.70-39.75)	87.2 (2.16-572.2)	80.3 (12.6-625.4)
(Navarro-Ortega, et al. 2010) Ebro River Basin, Spain	14.7 (0.17- 175.85)	147.5 (0.90- 4931.01)	28.0 (0.54- 194.2)	45.5 (0.77- 255.75)	117.9 (1.02- 4139)



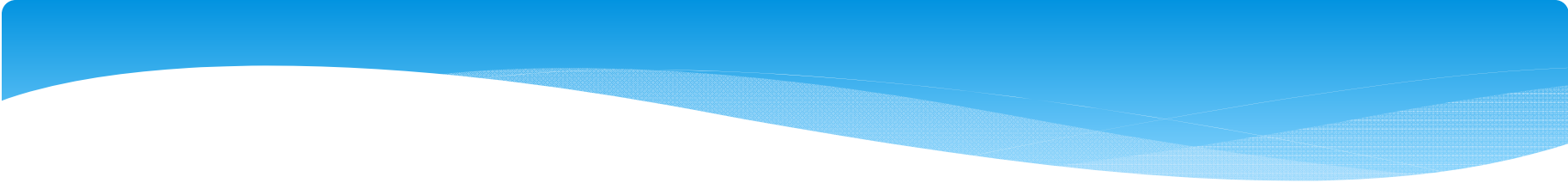


Are There any Water Quality Criteria for PAHs?

# Water Quality Criteria in BC

PAHs	Freshwater (long-term) (µg/L)	Marine water (µg/L)	Sediments (Fresh Water) (µg/g)	Sediments (Marin Water) (µg/g)
Naphthalene	1	1	0.01	0.01
Fluorene	12	12	0.2	0.2
Anthracene	4	NR	0.6	NR
Phenanthrene	0.3	NR	0.04	NR
Fluoranthene	4	NR	2	NR
Pyrene	NR	NR	NR	NR
Benzo[a]pyrene	0.01	0.01	0.06	0.06

Source: Ministry of Environment, Lands and Parks Province of British Columbia, N.K. Nagpal, 1993, Water Quality Branch Water Management Division

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What is the best method to Remove  
PAHs from Water?

# PAHs Removal Methods

**Oxidation**

**Biodegradation**

**Adsorption**

**batch method**

# Research Questions

- \* What method is best to remove PAHs from aqueous solution?
- \* Are there any adsorbents available to remove PAHs?
- \* What would be the adsorption kinetic of PAHs?
- \* What would be the effects of pH and temperature on PAHs adsorption?

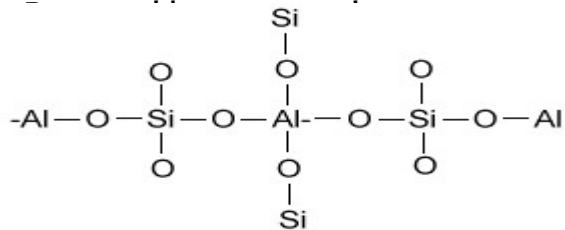
# PAHs Removal from Water

- \* **Activated Carbon**

- \* High price
- \* Not environmentally friendly

- \* **Zeolite**

- \* Having large open spaces
- \* Allow ions and molecules to easily pass in and out
- \* Negatively-charged minerals





What Are the Cationic Surfactants ?

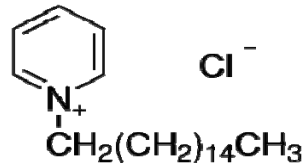
# Cationic Surfactants

Quaternary ammonium cations: structure ( $\text{NR}_4^+$ )

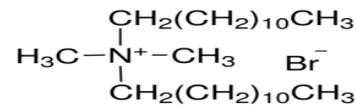
Removal of bisphenol, chromate and BTEX

HDTMA-Br and HDTMA-Cl

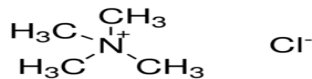
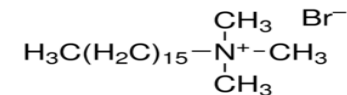
Cetylpyridinium chloride (CPC)



Didodecyldimethylammonium bromide (DDAB)



Hexadecyltrimethylammonium bromide (HDTMA)



Tetramethylammonium chloride (TMA-Cl)

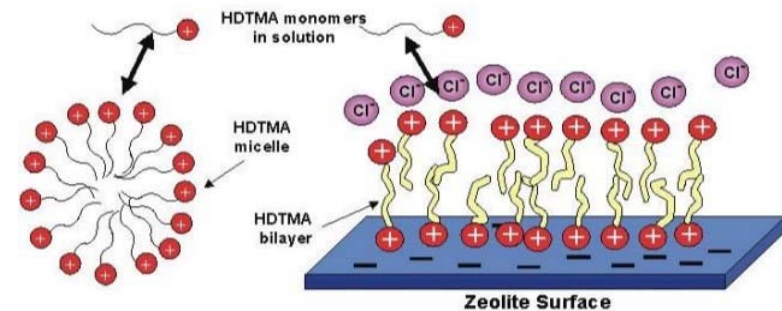




What is the method to *Modify Zeolite with Surfactants*?

# Modification of Zeolite with Surfactants

- \* **Modification**
- \* Mix
- \* Stir
- \* Separate
- \* Wash
- \* Dry
- \* Modified zeolite with
- \* CPC (CPC-MZ),
- \* DDAB (DDAB-MZ),
- \* HDTMA (HDTMA-MZ),
- \* TMA (TMA-MZ)



Source: <http://www.ees.nmt.edu/bowman/research/SMZ/ZeoSurfInt.html>



# What Is PAHs Adsorption Test

# Batch Adsorption Test

- \* **Adsorbents: Modified zeolite with CPC, DDAB, HDTMA, TMA and NZ**
- \* **Mixture solution: Fluoranthene and Fluorene**
- \* Mix & Rotate
- \* Centrifuge & separate
- \* Perform liquid-liquid extraction
- \* Evaporate the solvent to 3mL
- \* Evaporate the solvent under a gentle stream of nitrogen to dryness
- \* Add toluene & internal standard
- \* Inject to GC/MS



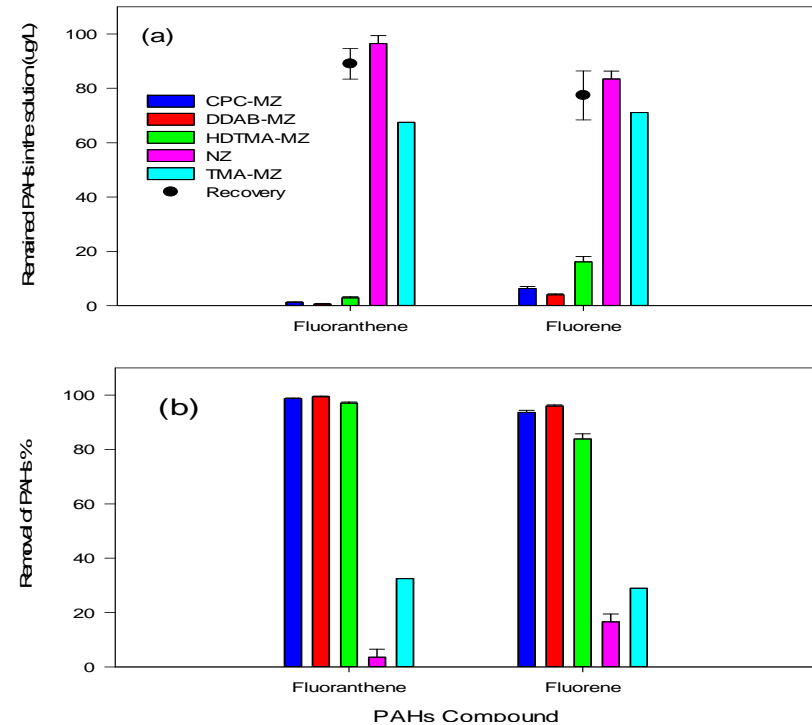
# Adsorption of PAHS

Highest to lowest PAHs removal  
using modified zeolites  
DDAB>CPC>HDTMA>TMA>NZ

PAHs adsorption on each modified zeolite  
Fluoranthene > Fluorene

octanol-water partition coefficient,  $K_{ow}$ ,  
Higher  $K_{ow}$  indicates more hydrophobicity

FLA(4.90) > FLU (4.18)





What Is the Adsorption Kinetic of PAHs?

# PAHs Adsorption Kinetics

Adsorption on CPC-MZ

Fluoranthene > Fluorene

Adsorption on DDAB-MZ

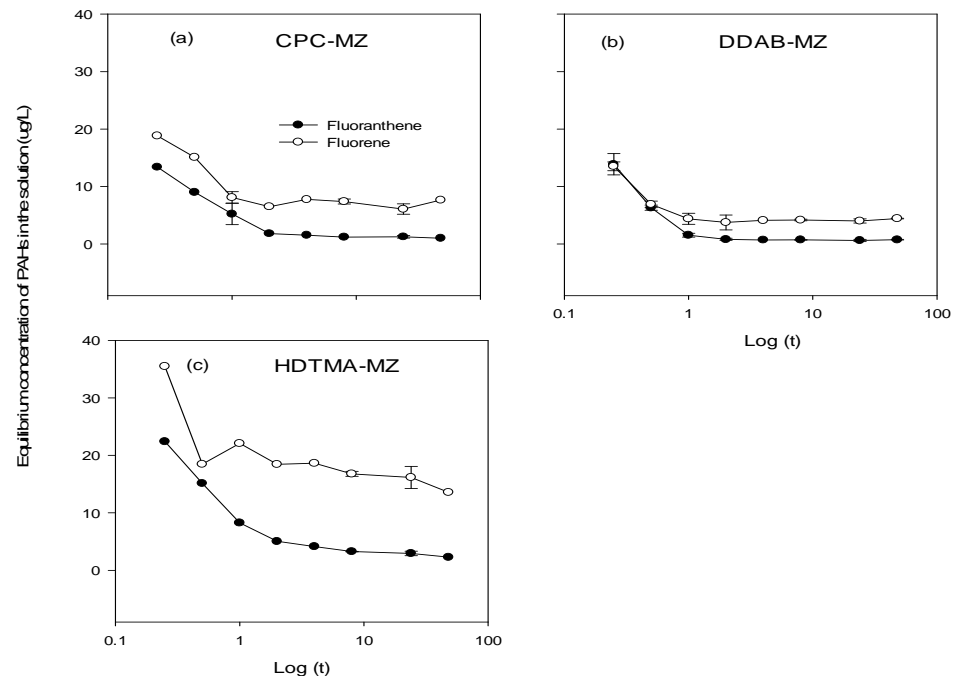
Fluoranthene > Fluorene

Adsorption on HDTMA-MZ

Fluoranthene > Fluorene

Adsorption rate on modified zeolites

DDAB-MZ > CPC-MZ > HDTMA-MZ



# Parameters of PAHs Adsorption Kinetic

Pseudo-First order equation

$$q_t = q_e[1 - \exp(-k_1 t)]$$

Pseudo-Second order equation

$$q_t = k_2 q_e^2 t / 1 + k_2 q_e t$$

Intra-particle diffusion equation

$$q_t = k_{int} t^{1/2}$$

$K_2$ : the adsorption rate constants of the second-order kinetic  
 $q_e$  ( $\mu\text{g/g}$ ): equilibrium adsorption uptake (at time  $t = \infty$ )  
 $q_t$  ( $\mu\text{g/g}$ ): adsorption uptake (at time  $t$ )

	First-order	Second-order	Intra-particle		
	$R^2$	$R^2$	$K_2^a$	$q_e^b$	$R^2$
<b>CPC-MZ</b>					
Fluoranthene	0.009	1	115	9.9	0.7
Fluorene	3E-05	1	9	9.4	0.6
<b>DDAB-MZ</b>					
Fluoranthene	0.034	1	59	9.9	0.5
Fluorene	0.18	1	16	9.6	0.4
<b>HDTMA-MZ</b>					
Fluoranthene	0.006	1	54	9.8	0.7
Fluorene	0.003	0.999	18	8.6	0.6





What is the Adsorbent Dosage to Meet the Water Quality Criteria?

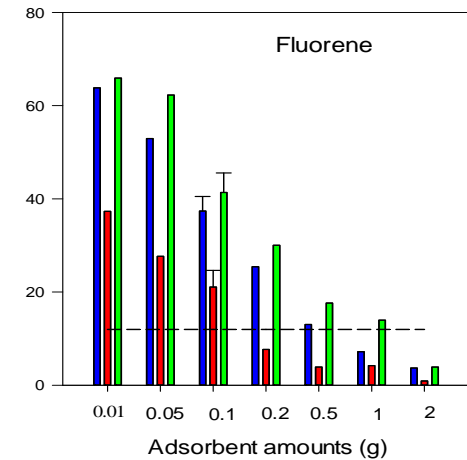
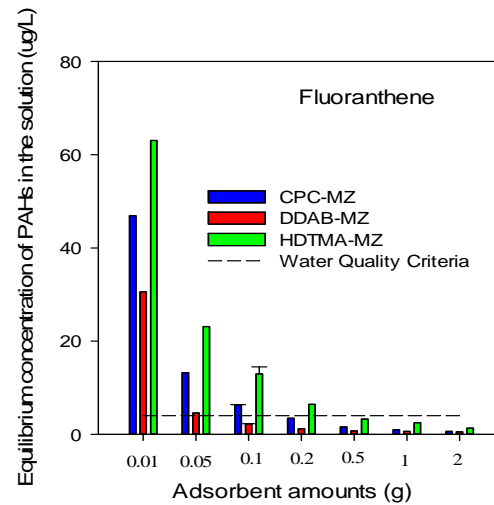
# Effect of Adsorbent Dosage

## Fluoranthene

Solid : Liquid Ratio  
1:1000 for DDAB-MZ  
1:500 for CPC-MZ  
1:200 for HDTMA-MZ

## Fluorene

Solid : Liquid Ratio  
1:500 for DDAB-MZ  
1:100 for CPC-MZ  
1:50 for HDTMA-MZ





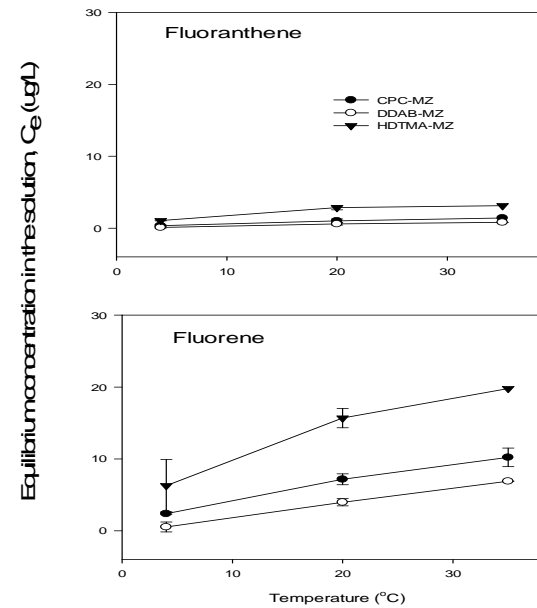
Does Temperature or pH Affect the PAHs Adsorption ?

# Effect of Temperature

Vapor Pressure at 298 K

Fluorene > Fluoranthene

$(6.58 \times 10^{-2}) > (1.2 \times 10^{-3})$  Pa



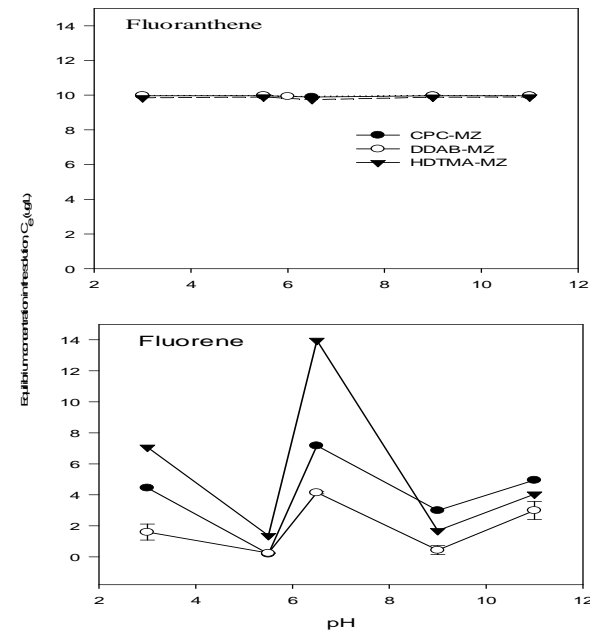
# Effect of pH

pH effect on PAHs adsorption  
Fluorene > Fluoranthene

pH effect on modified zeolite  
HDTMA-MZ > CPC-MZ > DDAB-MZ

Fluorene  $pK_a = 22.6$

The C<sub>9</sub>-H sites of the fluorene ring are weakly acidic



# Conclusion & Recommendations

- \* More than 95% PAHs removal by using CPC-MZ & DDAB-MZ
- \* No effect on fluoranthene adsorption by applying different temperatures and pH on CPC-MZ, and DDAB-MZ, unlike fluorene
- \* Great potential alternative to Activated carbon
- \* Good Potential adsorbent to remove the PAHs from stormwater runoff, landfill leachate and WWT effluent
- \* Test to remove other PAHs or organic pollutants from water

# Acknowledgment

- \* Thankful to
- \* Professor Loretta Li (UBC)
- \* My Parents
- \* My family

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Thank You  
Questions ?

