



Bromide Removal from Surface Waters Using Silver Impregnated Activated Carbon

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Bromide in Nature

- ▶ In aqueous condition, bromine exists primarily as anionic bromide (Br^-).
 - ▶ Br^- is ubiquitous in natural waters and concentrations range from 2 to 3000 $\mu\text{g/L}$
 - ▶ Natural source of Br^- (Geological sources):
 - ▶ magnesium and alkali metal bromide salts
 - ▶ seawaters
 - ▶ Anthropogenic source of Br^-
 - ▶ discharge of treated or untreated wastewaters
 - ▶ releases from coal-fired power plants and hydraulic fracturing operations
 - ▶ emission of 1,2 dibromoethane, a scavenger in leaded fuel
 - ▶ fertilizers, pesticides in agriculture
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Potential Impact of Bromide

- ▶ Br⁻ can lead to formation of brominated DBPs
 - ▶ Bromate (BrO₃⁻)
 - ▶ Brominated trihalomethanes (THMs)
 - ▶ Brominated haloacetic acids (HAAs)
 - ▶ Br⁻ may react with NOM to form organic halides, known as TOX.
 - ▶ Potential health concerns
 - ▶ Brominated DBPs are more cyto- and geno- toxic than their chlorinated analogues
 - ▶ Increasingly stringent regulations are imposed for some DBPs under the Disinfectants/Disinfection Byproduct Rule (D/DBPR)
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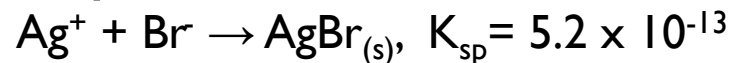


Bromide Removal Technologies

There is as yet no well established technology on bromide control.

We hypothesize a potential way to control Br by Silver Impregnated Activated Carbon (SIAC) due to:

Silver ions form insoluble precipitates with Br and enhance its adsorption by SIAC

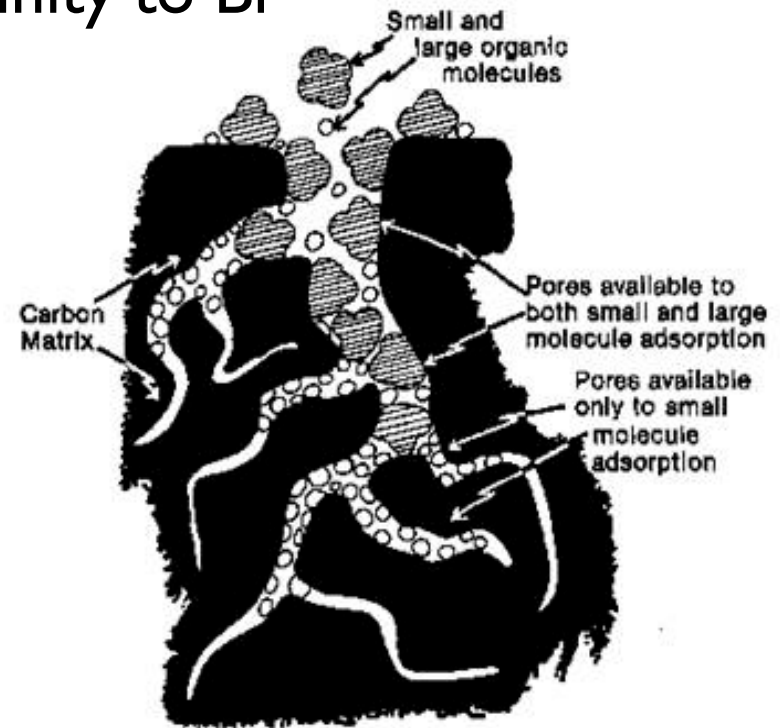


The porous structure and large surface area provide numerous adsorption sites

Can be easily applied in existing water treatment plants

Activated Carbons

- ▶ Activated carbon is a heterogeneous and porous adsorbent
- ▶ AC has been shown to effectively remove several organic substances
- ▶ AC does not show adsorption affinity to Br





Br removal by silver-loaded materials

- ▶ Sanchez polo et al. [2006, 2007] reported that the Ag-doped activated carbon aerogels remove Br, but decrease of Br removal was observed due to blocking of pores by dissolved organic matters, and the Cl⁻ competition.
- ▶ Gong et al. [2012] reported that the silver-loaded porous carbon spheres remove Br. They investigated the effect of competitive species, such as Cl⁻, I⁻, NO₃⁻, SO₄²⁻ and humic acid, on Br adsorption.





Main Objectives

Determine the optimum silver impregnation protocols and assess the role of carbon characteristics on material development.

Evaluate the applications of the developed materials at typical water treatment conditions.

Assess the developed materials in DBPs control.





Phases of the Study

- ▶ **Phase 1:** The effect of silver impregnation on carbon characteristics
- ▶ **Phase 2:** The effect of silver impregnation on Br removal
- ▶ **Phase 3:** The effect of background water chemistry (NOM and selected anions) on Br removal by SIACs
- ▶ **Phase 4:** The application of SIACs for THM control



Phase I

Phase I: To investigate the effect of silver impregnation on carbon characteristics

Phase I.1: The effect of pre-oxidation

Phase I.2: The effect of silver impregnation



Materials and Methods

- ▶ ACs used in this phase:
 - ▶ HD3000, 20B, WC800, F400 virgin PAC (200- 325 μm mesh size)
- ▶ Pre-oxidation (wet oxidation by HNO_3) technique:
 - ▶ Control (no oxidation)
 - ▶ by 10N HNO_3 at 160 $^\circ\text{C}$
 - ▶ by 15.7 HNO_3 at 160 $^\circ\text{C}$
 - ▶ by 15.7 N HNO_3 at 90 $^\circ\text{C}$
- ▶ Silver impregnation techniques:
 - ▶ Control (no silver impregnation)
 - ▶ with 0.1M AgNO_3
 - ▶ with 0.5M AgNO_3
 - ▶ with 1.5M AgNO_3



The effect of low vs. high oxidant concentration on pre-oxidation

Sample Name	Oxygen Content %	SSA m ² /g
HD 3000 raw PAC	4.4	642.0
HD3000 pre-ox PAC by 10N HNO ₃	18.6	528.4
HD3000 pre-ox PAC by 15.7N HNO ₃	19.1	<u>524.8</u>
WC 800 raw PAC	4.1	644.3
WC800 pre-ox PAC by 10N HNO ₃	10.9	569.3
WC800 pre-ox PAC by 15.7N HNO ₃	15.1	<u>438.6</u>

1. Increase in oxygen content and decrease in SSA after oxidation
2. Larger SSA decrease and oxygen content increase by 15.7N HNO₃
3. Larger SSA decrease for Microporous (WC800) than Mesoporous (HD3000) by 15.7 N HNO₃

The effect of low vs. high temperature on pre-oxidation

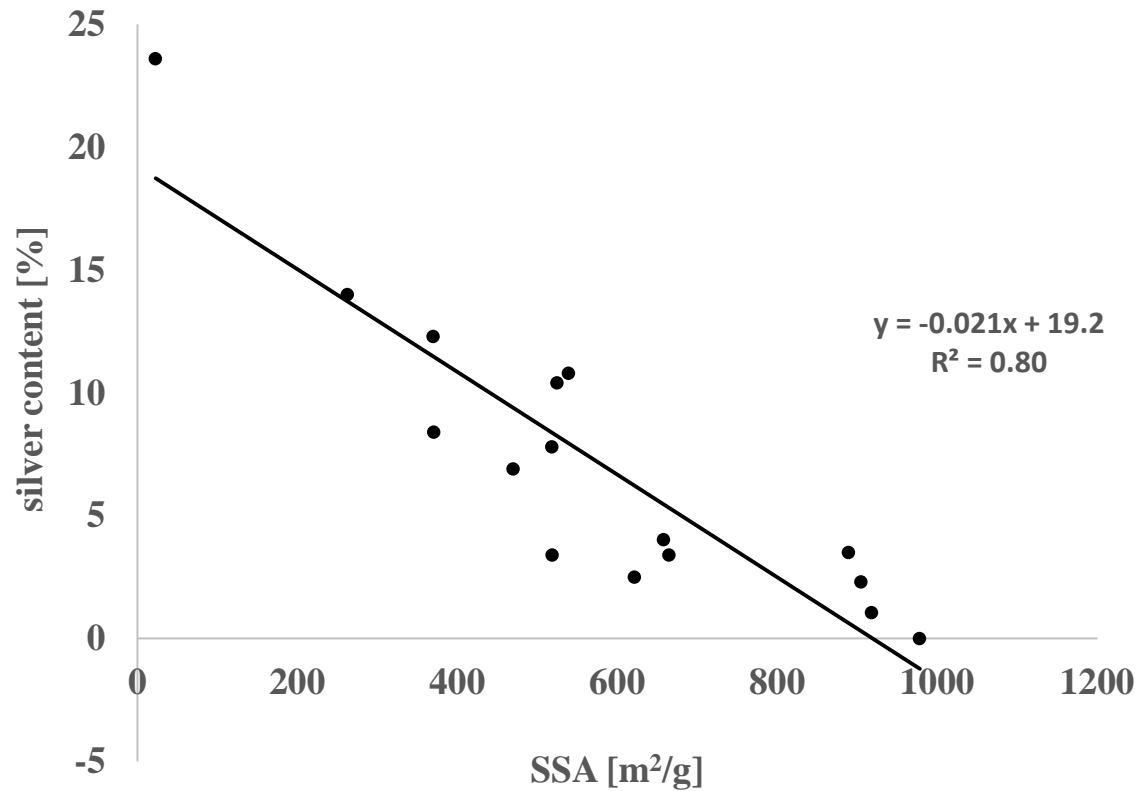
Sample Name	Oxygen Content %	BET Surface Area m ² /g
HD 3000 raw PAC	4.4	642.0
HD 3000 low T ox PAC by 15.7HNO ₃	15.9	530.1
HD 3000 high T ox PAC by 15.7HNO ₃	19.1	<u>373.6</u>
WC 800 raw PAC	4.1	644.3
WC800 low T ox PAC by 15.7HNO ₃	15.1	624.5
WC800 high T ox PAC by 15.7HNO ₃	18.9	<u>367.9</u>
F400 raw PAC	2.4	978.0
F400 low T ox PAC by 15.7HNO ₃	15.6	905.3
F400 high T ox PAC by 15.7HNO ₃	19.1	<u>472.3</u>

1. Higher oxygen content increase was observed at higher temperature oxidation
2. Larger SSA decrease was observed at higher temperature oxidation

Activated carbon characterization before and after silver impregnation

Sample Name	Oxygen Content	Surface Area	Silver Content
	%	m ² /g	%
HD 3000 raw PAC	4.4	642	-
HD 3000 raw SIAC by 0.5M AgNO ₃	4.3	635.3	2.1
HD 3000 10ox SIAC by 0.5M AgNO ₃	18.6	528.4	7.8
HD 3000 15.7ox SIAC by 0.5M AgNO ₃	19.1	524.8	10.4
HD 3000 low temp ox SIAC by 0.5M AgNO ₃	15.6	524.7	2.5
HD 3000 high temp ox SIAC by 0.5M AgNO ₃	18.9	370.8	8.4
WC 800 raw PAC	4.1	644.3	-
WC 800 raw SIAC by 1.5M AgNO ₃	3.9	621.6	2.5
WC 800 15.7ox SIAC by 1.5M AgNO ₃	17.4	<u>262.7</u>	14
WC 800 15.7ox SIAC by 0.1M AgNO ₃	13.7	518.6	3.4
WC 800 15.7ox SIAC by 0.5M AgNO ₃	14.6	539.1	10.8
WC 800 low temp ox SIAC by 0.5M AgNO ₃	14.5	664.5	3.4
WC 800 high temp ox SIAC by 0.5M AgNO ₃	18.5	369.7	<u>12.3</u>
20 B raw PAC	<u>0.93</u>	<u>1748</u>	-
20 B 15.7ox SIAC by 0.5M AgNO ₃	<u>19.6</u>	1681	3.6
F400 raw PAC	2.38	978	-
F 400 low temp ox SIAC by 0.5M AgNO ₃	15.0	904.8	2.3
F400 high temp ox SIAC by 0.5M AgNO ₃	18.7	469.8	6.9
1.05% commercial SIAC	N/A	918	<u>1.1</u>
4.03% commercial SIAC	N/A	658	4.0

Correlation of Silver Content and SSAs of SIACs



1. There was a negative correlation ($R^2 = 0.8$) between silver content and SSA
2. No correlations were observed between the oxygen and silver content



Conclusions of Phase I

- ▶ Relatively higher oxygen content and smaller SSA were observed after oxidation.
- ▶ The severity of oxidation was influenced by both HNO_3 concentration and oxidation temperature, the oxidation temperature was more influential.
- ▶ There was a negative correlation ($R^2 = 0.8$) between silver content and SSA of SIACs.





Phase II

Phase 2: To investigate the effect of silver impregnation on Br removal

Phase 2.1: The effect of pre-oxidation

Phase 2.2: The effect of silver impregnation

Phase 2.3: The effect of SIACs characteristics



Br⁻ Adsorption Experiments

- ▶ **Br adsorption experiments by SIACs were conducted:**
 - ▶ In completely mixed batch reactor (CMBRs, i.e. 50 mL plastic bottles)
 - ▶ At 25 mg/L carbon dose.
 - ▶ In DDW with Br initial spiked to ~300 ppb.
 - ▶ By tumbling bottles for 4 hours.
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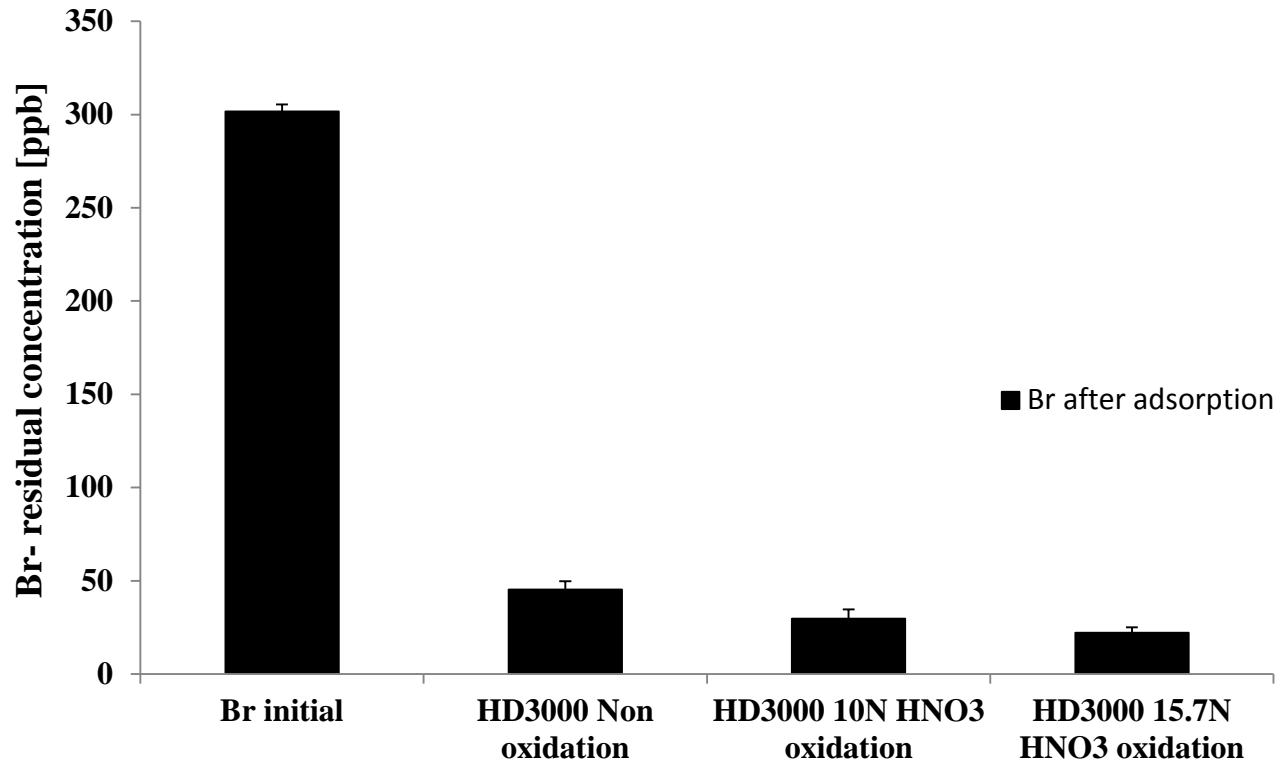


The Effect of Pre-oxidation

- ▶ **HD3000 virgin PACs were treated as:**
- ▶ (i). no pre-oxidation, impregnated with 0.5M AgNO₃, labeled as HD3000-05 raw SIAC.
- ▶ (ii). pre-oxidized by 10N HNO₃, then impregnated with 0.5M AgNO₃, labeled as 10 ox HD3000-05 SIAC.
- ▶ (iii). pre-oxidized by 15.7N HNO₃, then impregnated with 0.5M AgNO₃, labeled as 15.7 ox HD3000-05 SIAC.



Pre-oxidation Effect on Br Removal by SIACs in DDW



	HD3000 no oxidation	HD3000 by 10N HNO ₃ oxidation	HD3000 by 15.7N HNO ₃ oxidation
Silver content	2.1	7.8	10.4
SSA	635.3	528.4	524.8

- ▶ The pre-oxidation showed positive effect on Br uptake by SIACs over non pre-oxidation
- ▶ higher Br removal by SIACs by higher HNO₃ concentration (15.7N) pre-oxidation



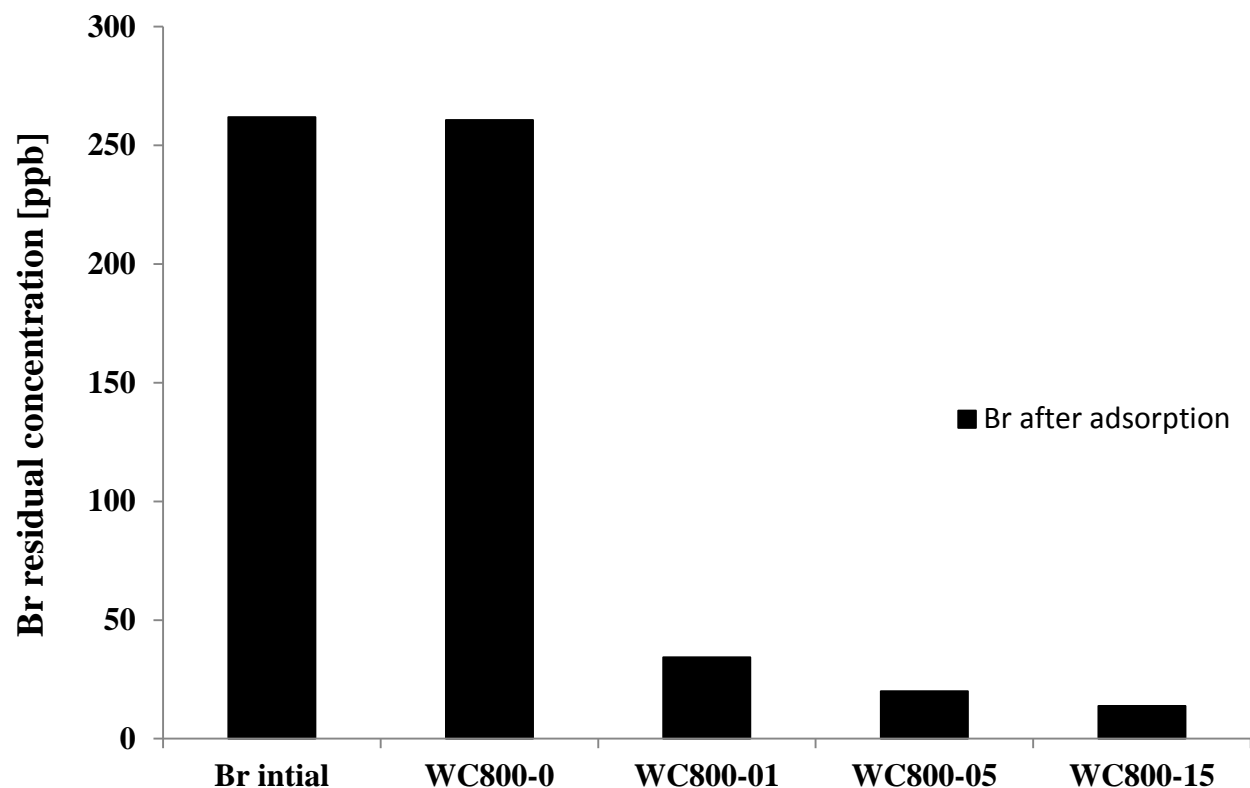
The Effect of Silver Salt Concentration

- ▶ **WC800 virgin PAC was pre-oxidized by 15.7N HNO₃ for all impregnation conditions, treated with silver as:**
- ▶ (i). no silver impregnation, labeled as WC800-0 ox PAC.
- ▶ (ii). impregnated with 0.1M AgNO₃ solution, labeled as WC800-01 ox SIAC.
- ▶ (iii). impregnated with 0.5M AgNO₃, labeled as WC800-05 ox SIAC.
- ▶ (iv). impregnated with 1.5M AgNO₃, labeled as WC800-05 ox SIAC.





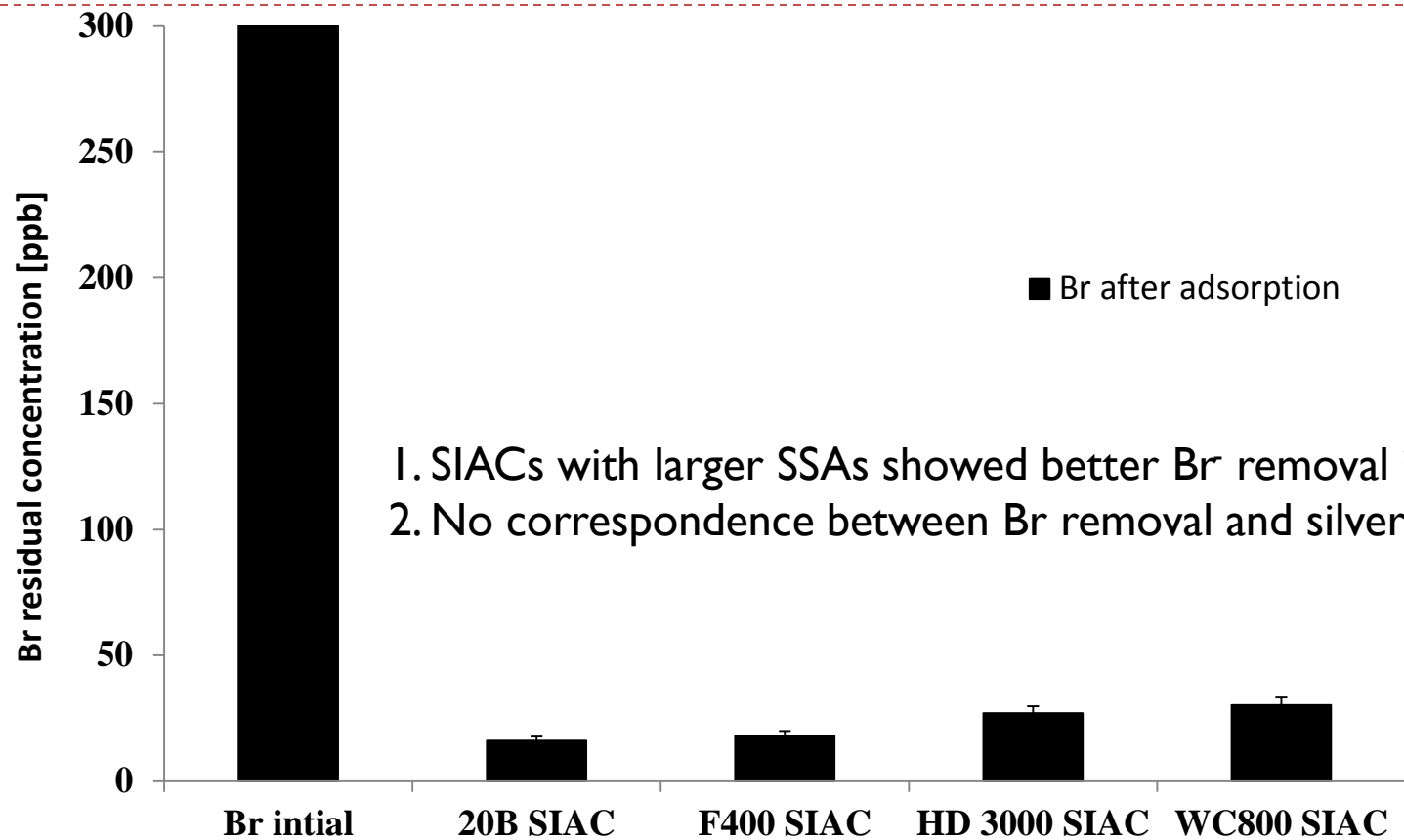
Silver Impregnation Effect on Br⁻ Removal in DDW



	WC800-01	WC800-05	WC800-15
Silver content	3.4	10.8	14
SSA	518.6	539.1	262.7

1. No Br uptake by WC800 AC with no silver impregnation
2. Better Br removal for AC impregnated by higher concentration AgNO₃

Br⁻ Adsorption Experiments in DDW by Different SIACs



	20B SIAC	F400 SIAC	HD3000 SIAC	WC800 SIAC
SSAs (m ² /g)	1680	889	539	525
Silver Content (%)	3.5	3.6	10.4	10.3

SSA from high to low

Conclusions of Phase II

Larger amount of Br was removed by SIACs which:

- ▶ were pre-oxidized by stronger HNO_3 (15.7N > 10N).
- ▶ were pre-oxidized at higher oxidation temperature (160°C > 90°C).
- ▶ were impregnated with higher concentration of AgNO_3 (1.5M > 0.5M > 0.1M > none).





Phase III

Phase 3: To investigate the effect of background water chemistry (NOM and selected anions) on Br removal by SIACs

Objective 3.1: The effect of chloride

Objective 3.2: The effect of NOM

Objective 3.3: The effect of source waters

Objective 3.4: The effect of alum coagulation (jar test)



Material and Methods

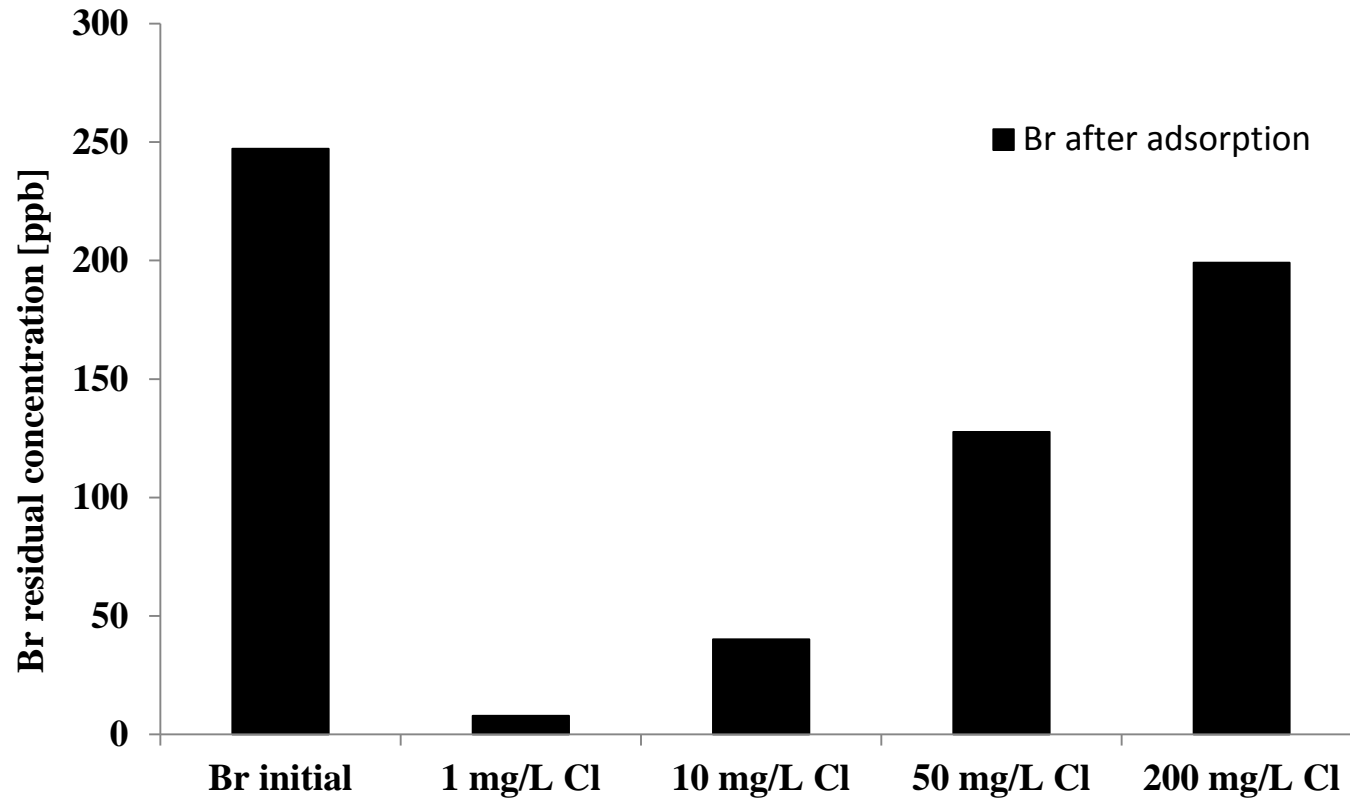
- ▶ Br adsorption experiments:
 - ▶ Same experimental protocol as in phase 2.

- ▶ Jar test:
 - ▶ Rapid mixing: 200 rpm for 1 min
 - ▶ Slow mixing: 25 rpm for 20 min
 - ▶ Settling: 2 hours
 - ▶ Alum dose: 30 mg/L (if applied)
 - ▶ SIAC dose: 10, 25, 50 mg/L





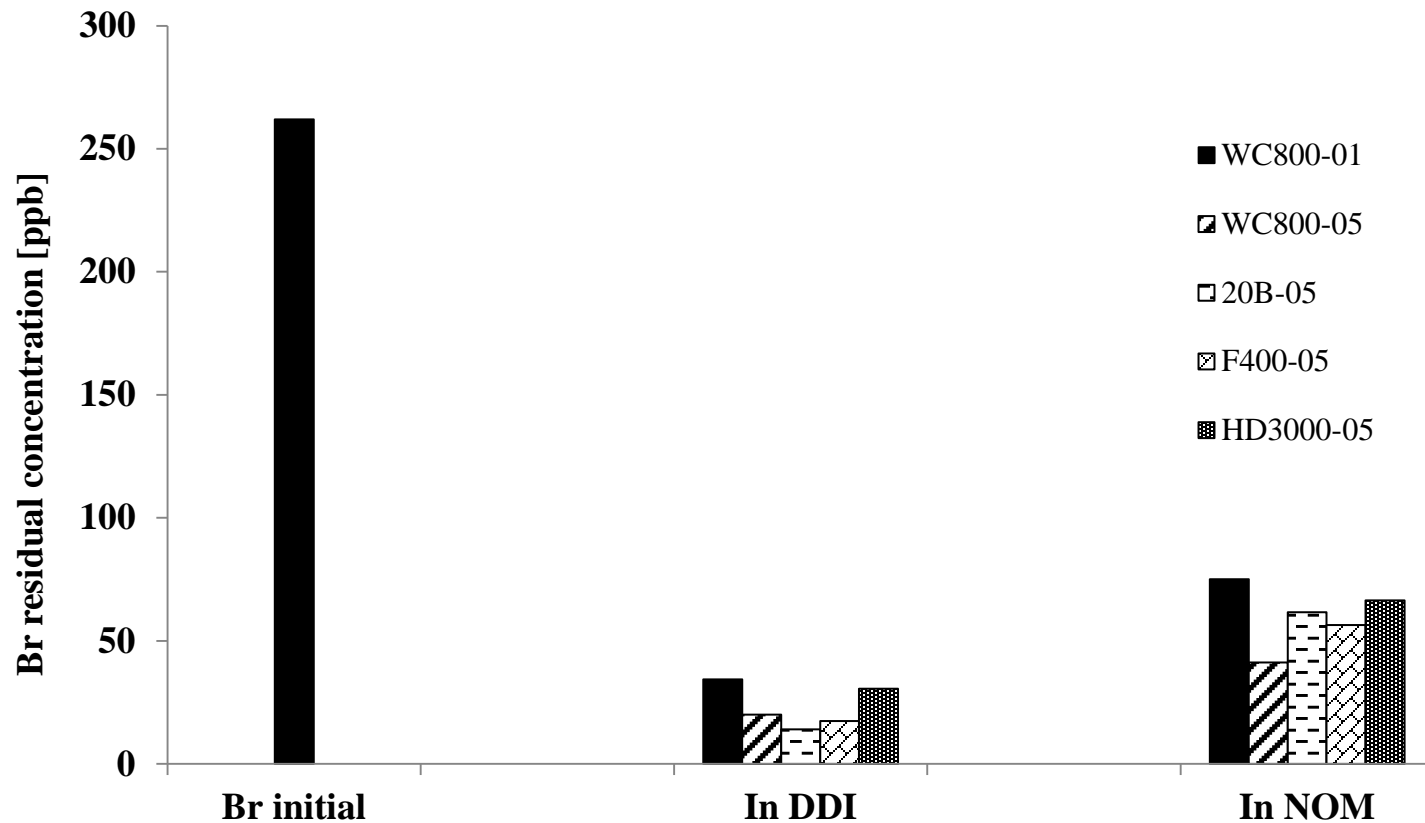
Chloride Effect on Bromide Removal



As Cl⁻ dose increase, the Br removal decreases



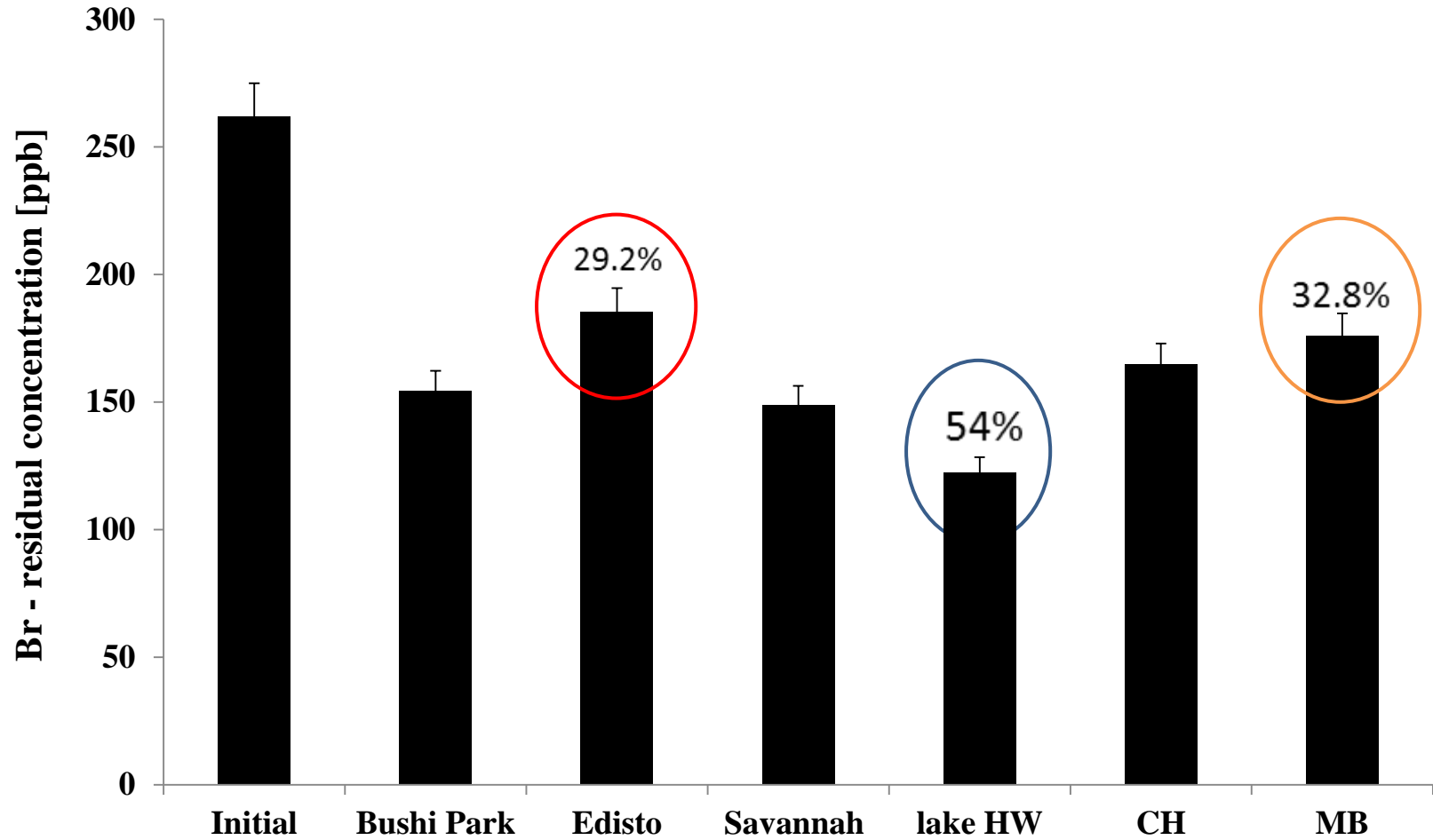
NOM Effect on Br removal



1. Br removal decreased in present of NOM, due to NOM competition
2. The mesoporous 20B SIAC has the largest decrease of Br removal due to NOM competition and pore blockage, because mesopore size is similar to NOM size (2 nm to 50 nm).



The Effect of Different Source Waters



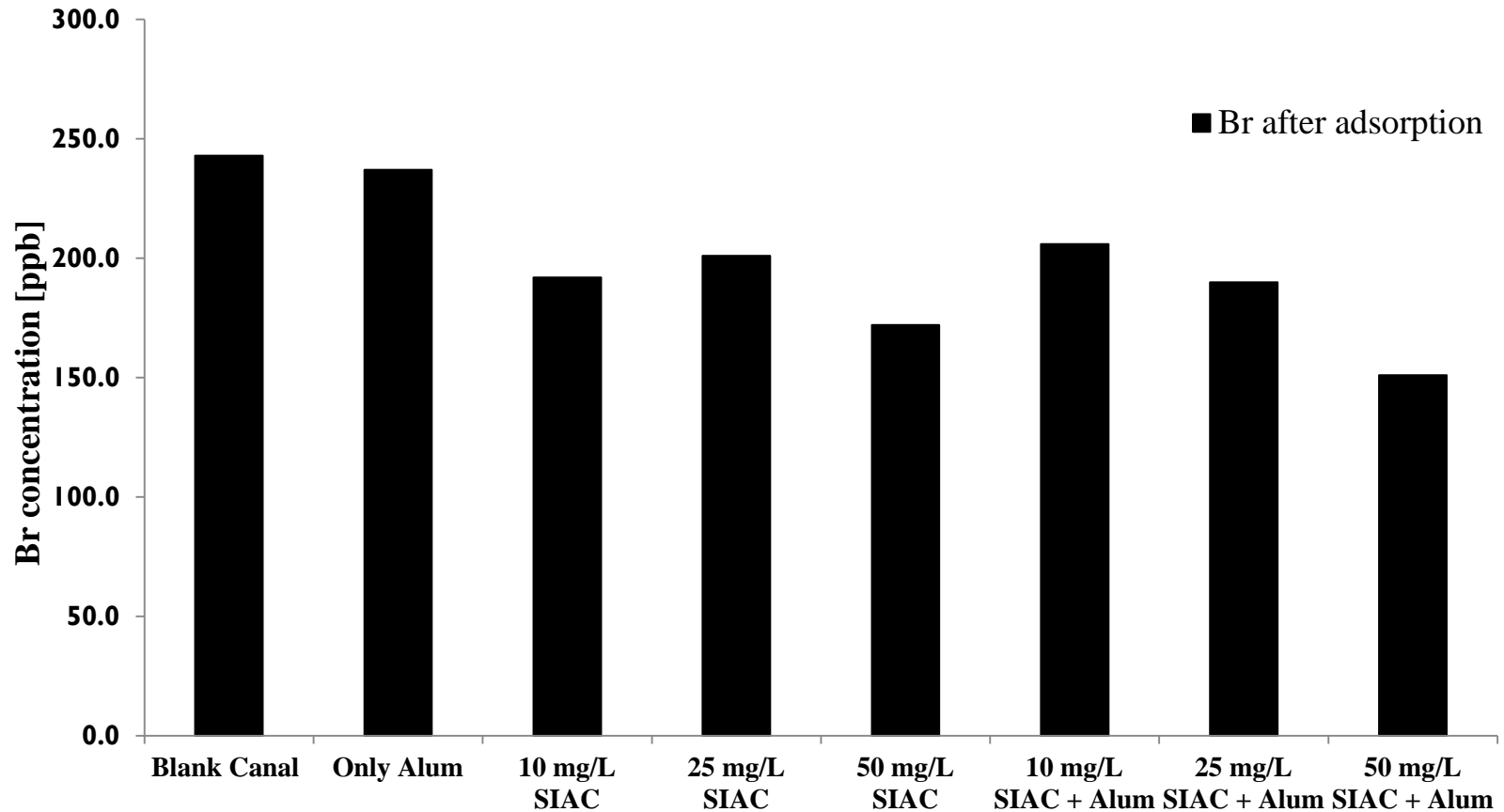
Selected Source Water Characteristics

	Br⁻ Concentration ppb	Cl⁻ Concentration mg/L	SO₄²⁻ Concentration mg/L	NO₃⁻ Concentration mg/L	TOC mg/L	UV cm ⁻¹	SUVA
MB Raw	100	19.5	5.7	0.53	27.6	1.203	4.4
CH Treated	81	14.5	35.2	0.09	3.4	0.045	1.3
Bushi Park	79.9	29.5	5.7	0.3	4.4	0.170	3.9
Edisto River	33.2	37.9	7.7	0.51	5.0	0.260	5.2
Savannah River	197.5	40.4	10.7	1.04	3.3	0.110	3.3
Lake Hartwell	20.1	2.6	2.0	0.61	2.1	0.038	1.8

Br removal is largely affect by Cl⁻ concentration and TOC



Jar test experiment of Br adsorption by SIAC



1. Alum itself does not remove Br
2. 30% to 40% Br removal was achieved with and without Alum + 50 mg/L SIAC

Conclusions of Phase III

- ▶ There was a decrease in Br removal with increasing dose of Cl^- due to Cl^- competition.
- ▶ Presence of NOM decreased Br removal, this decrease was attributed to pore blockage and NOM competition.
- ▶ Mesoporous SIACs are more likely to be influenced by NOM competition, because the carbon mesopore size is similar to NOM size (2 nm to 50 nm).



Conclusions of Phase III

- ▶ The Br removal by SIAC in HW was up to 56%, but was largely decreased (only ~30% removal) in high Cl⁻ (~40 mg/L) concentration and high TOC (27 mg/L) source waters.
- ▶ The Cl⁻ and NOM competition work as a combined interference for Br removal by SIACs.
- ▶ Br removal by SIAC was 30- 40% in jar test and alum did not make a notable difference.





Phase IV

Phase 4: To evaluate the application of SIACs for THM control

Phase 4.1: The THM formation and speciation before SIACs treatment

Phase 4.2: The THM formation and speciation after SIACs treatment



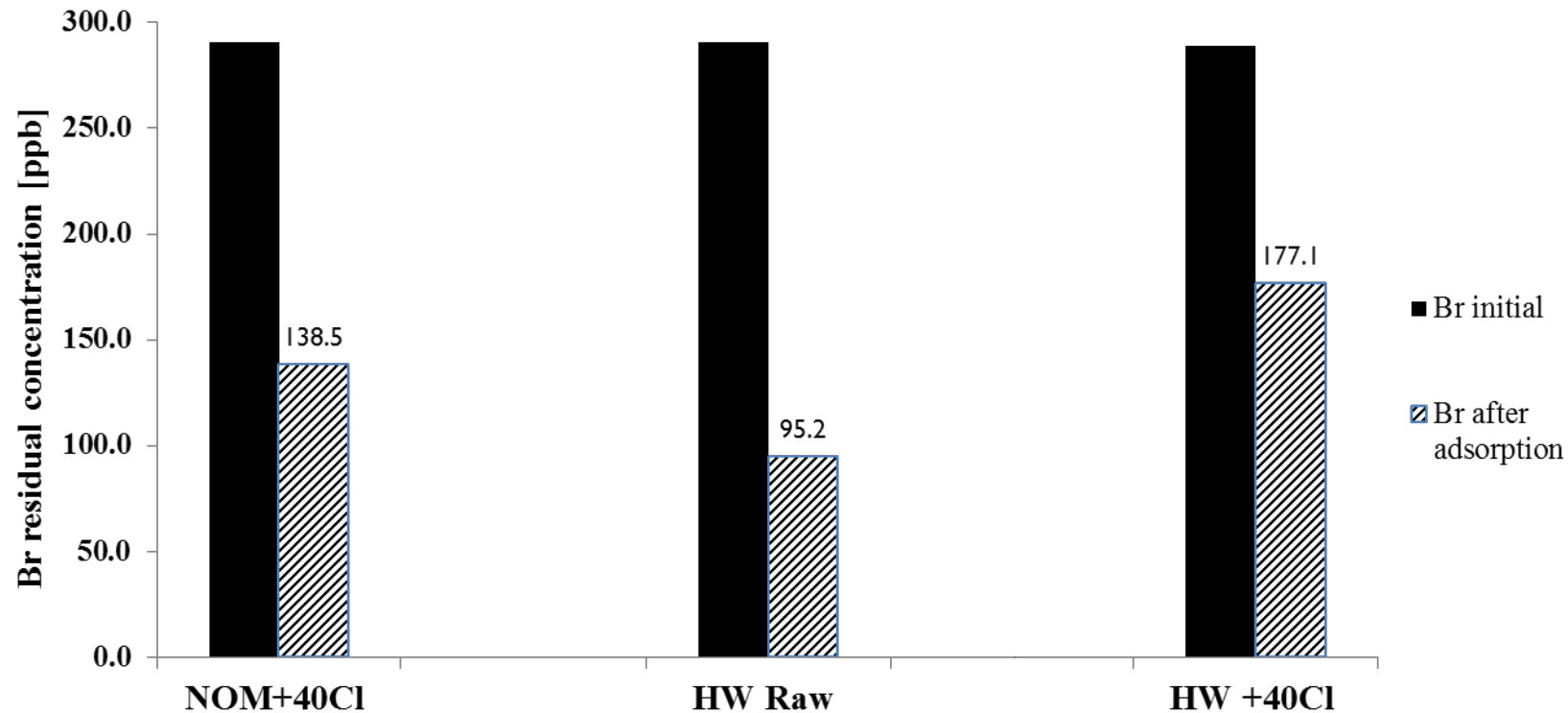
Material and Methods

- ▶ **THM formation experiments:**
 - ▶ Chlorine was used as the disinfectant to achieve higher than 0.4 mg/L residual after 1 day contact time.
 - ▶ pH was adjusted to 7.8 with phosphate buffer (20 mM).
 - ▶ The THMs formations were measured with GC.

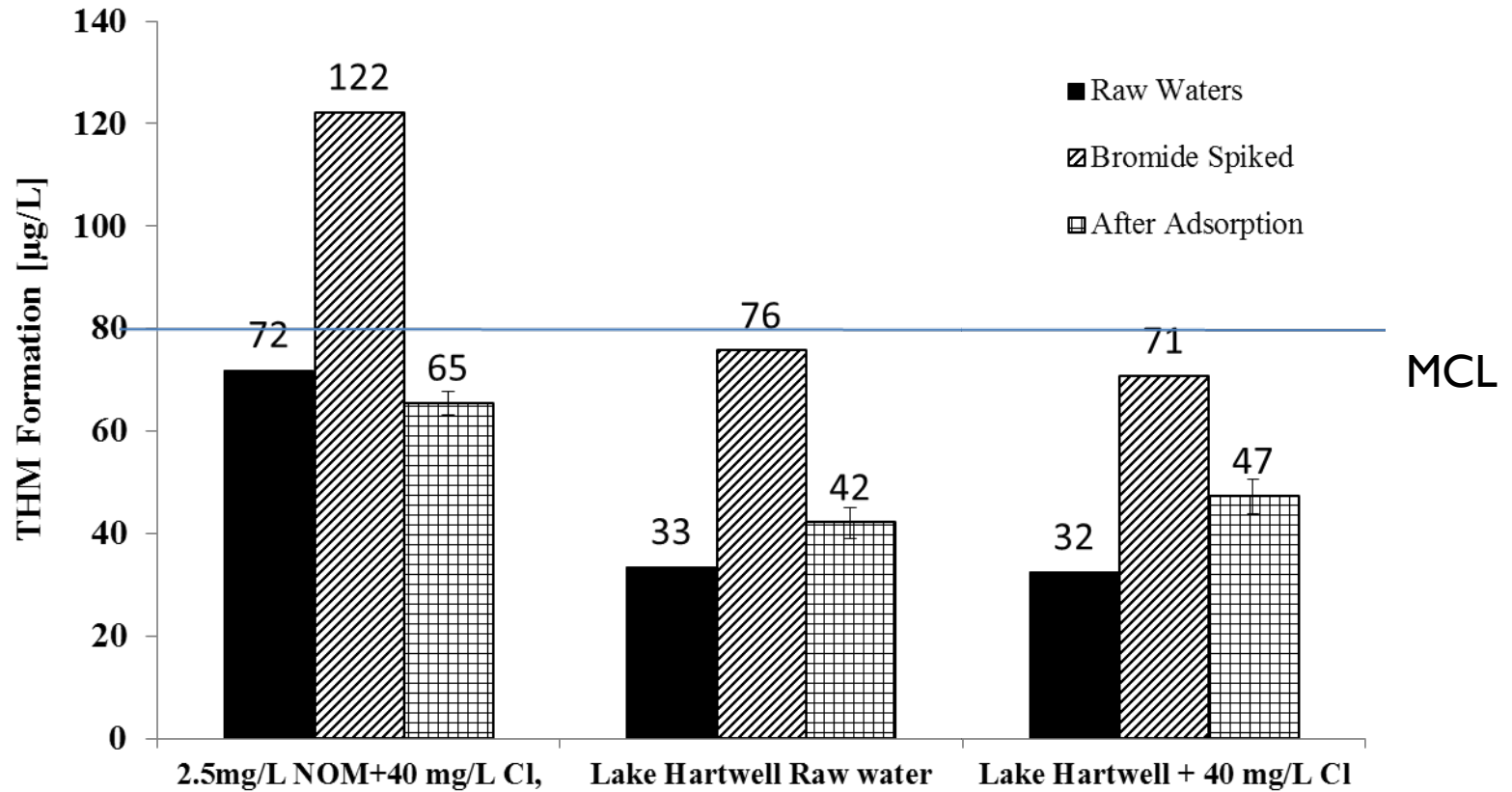
- ▶ The Br adsorption experiment was conducted in NOM+40Cl, HW, and HW+40Cl



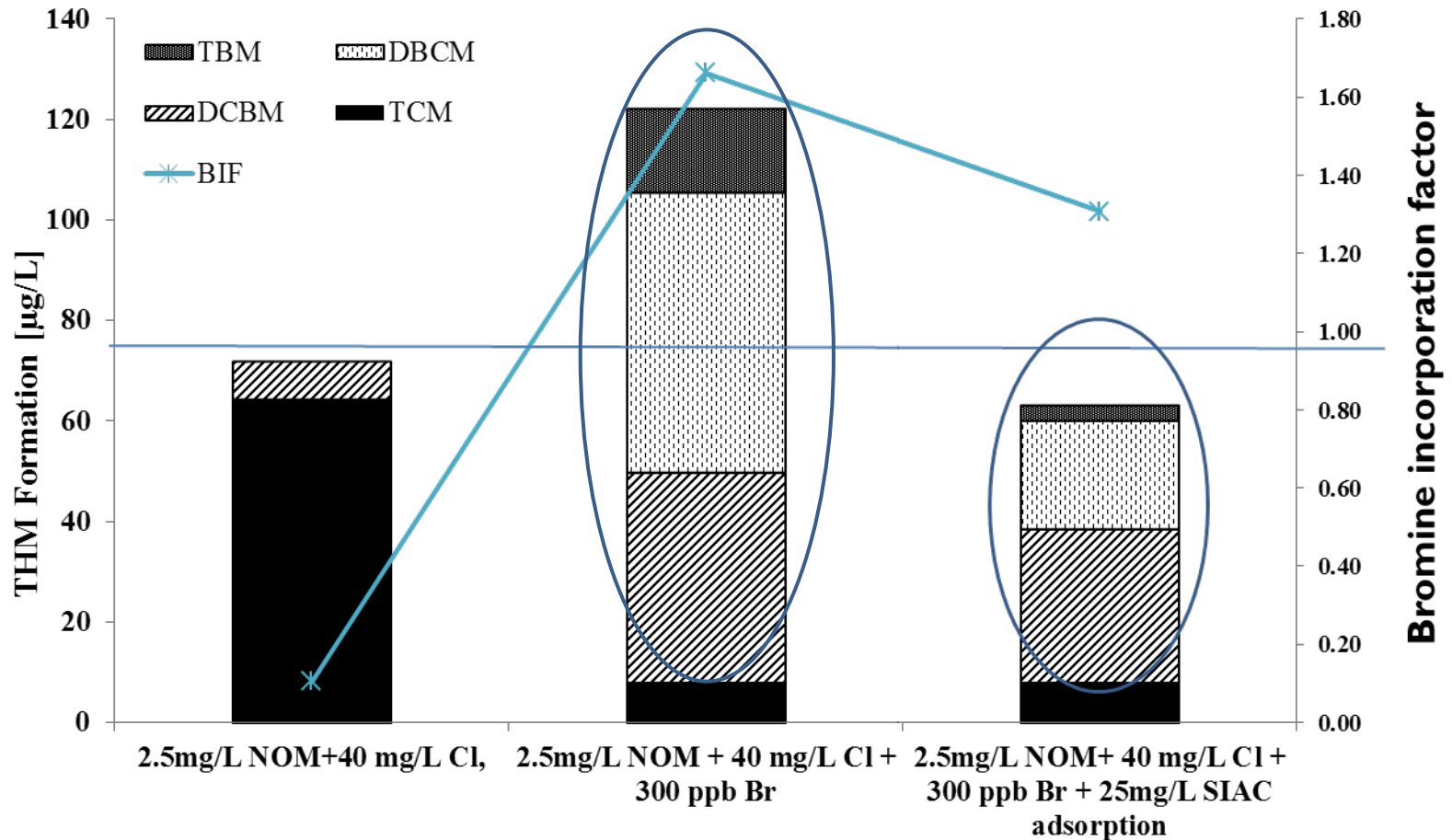
Br adsorption by WC800 low T ox SIAC in NOM and Lake HW spiked waters



Overall THM formation in raw water, Br⁻ spiked water, and SIAC treated water

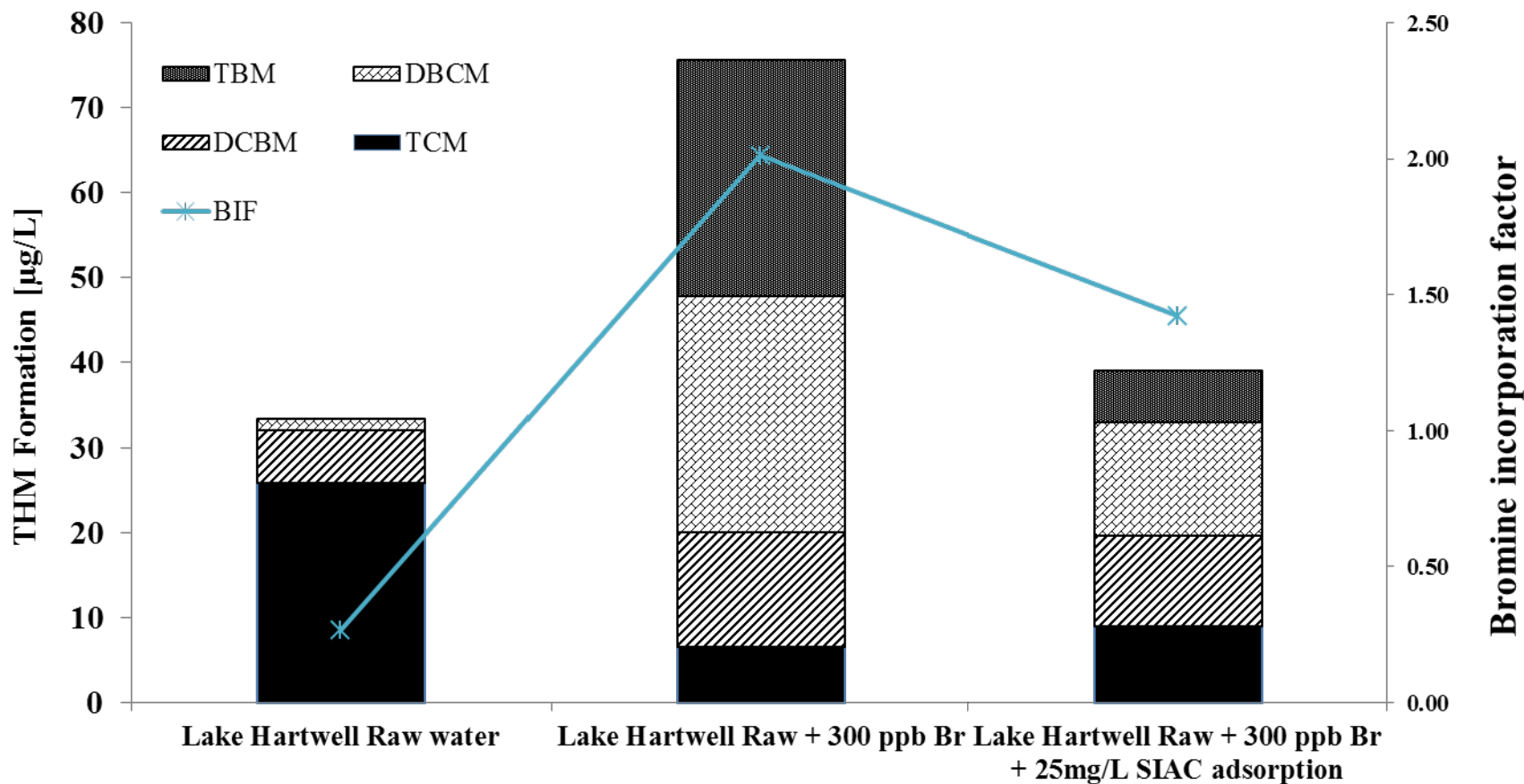


THM formation and speciation in NOM+40Cl



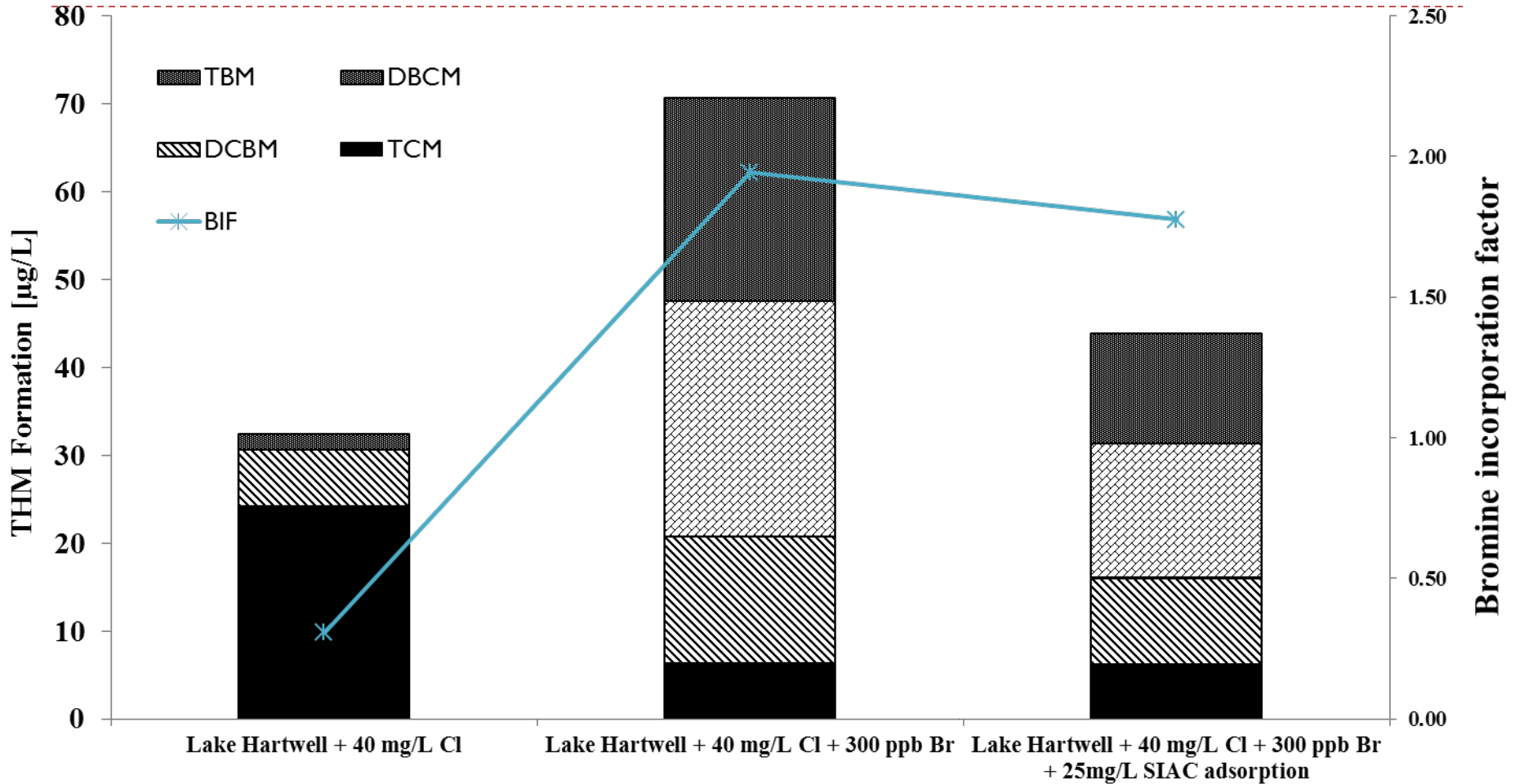
Almost half of the brominated species were removed due Br removal by SIACs

THM Formation and Speciation in Lake HW Raw Water



~half of the brominated species were removed due Br removal by SIACs

THM Formation and Speciation in Lake HW + 40 Cl



~40% of the brominated species were removed due Br removal by SIACs



Conclusions of Phase VI

- ▶ Br⁻ spiking largely shifted the THM species from chlorinated to brominated species, and the overall THM formation was increased.
- ▶ The large Br⁻ removal by SIAC adsorption played an important role in THMs formation control, especially for the control of brominated THM formation.





Summary of Important Findings & Future Research Recommendations

Summary of Important Findings

- ▶ The severity of oxidation was influenced by both HNO_3 concentration and oxidation temperature, the oxidation temperature was more influential.
- ▶ There was a negative correlation ($R^2 = 0.8$) between silver content and SSA of SIACs.
- ▶ SIACs pre-oxidized at higher HNO_3 concentration (15.7N) showed better Br removal.
- ▶ SIACs impregnated at higher AgNO_3 concentration showed better Br removal.
- ▶ SIACs with larger SSAs showed better Br removal.



Summary of Important Findings

- ▶ Mesoporous SIACs are more likely to be influenced by NOM competition, and the carbon mesopore size is similar to NOM size (2 nm to 50 nm).
- ▶ The Cl^- and NOM competition work as a combined interference for Br^- removal by SIACs.
- ▶ Br^- removal by SIAC was 30- 40% in jar test and alum did not make a notable difference.
- ▶ The large Br^- removal by SIAC adsorption played an important role in THMs formation control, especially for the control of brominated THM formation.



Future Research Recommendations

- ▶ Due to the low solubility product of Ag_3PO_4 ($K_{\text{sp}} \text{Ag}_3\text{PO}_4 = 8.9 \times 10^{-17}$, $K_{\text{sp}} \text{AgBr} = 5.2 \times 10^{-13}$), another potential competitive anion in water solution, PO_4^{3-} , although at low level of concentration in nature ($< 100 \mu\text{g/L}$), further experiment is recommended to investigate the anion completion effect between PO_4^{3-} and Br^- .
- ▶ Investigating the ionic strength effect of the background water may be useful in understanding how the soluble ions in the background water can influence the Br^- adsorption by SIACs.



Future Research Recommendations

- ▶ Pore-size distribution, SEM, EDX, and XRD measurements are needed to better determine the changes in the physical and chemical properties of SIACs as compared to the virgin ACs.
- ▶ Rapid small-scale column tests are recommended to undertaken to create a representative breakthrough profile for the SIACs.
- ▶ Adsorption of I^- experiments can be conducted by the developed SIACs.





Acknowledgements

- ▶ Dr. Tanju Karanfil
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- ▶ Karanfil Research Group Members
- ▶ EEES Family





Thank you

Questions?



	THM	TCM	DCBM	DBCM	TBM	TOC
	µg/L	µg/L	µg/L	µg/L	µg/L	mg/L
NOM+40Cl	72	64	8	0	0	2.2
NOM+40Cl Br spiked	122	8	42	56	17	2.2
NOM+40Cl Br spiked after	63	8	31	21	3	1.9
adsorption						
HW raw	33	26	6	1	0	1.7
HW raw Br spiked	76	7	13	28	28	1.7
HW raw Br spiked after	39	9	11	13	6	1.5
adsorption						
HW+40Cl	32	24	6	2	0	1.6
HW+40Cl Br spiked	70	6	14	27	23	1.6
HW+40Cl Br spiked after	43	6	10	15	12	1.4
adsorption						

Silver Impregnation of PAC

- ▶ The powdered activated carbon (PAC) was mixed in the silver nitrate (AgNO_3) solution and put in dark overnight for silver impregnation. The introduced Ag^+ from AgNO_3 associates with the graphitic surface of activated carbon and form either inner or outer sphere complexes. The hydroxyl groups in the carbon surface act as σ -electron donor ligands in the inner sphere complexation, and the counter ions form ionic complexes in the outer sphere complexation. Outer sphere complexes are less stable due to electrostatic (ionic) bonding instead of chemical bonding [Jia et al., 1998]. In addition, p-orbital electrons on the graphitic surface of activated carbon can also attract Ag^+ regardless of the surface charge. After attachment to carbon surface, Ag^+ is reduced from the donation of electrons from carbon surface to the metal ion. The reduced silver on carbon surface may form clusters that lessen the contact with anions, which in turn results in less Br removal [Davidson 1994].
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