Novel Treatment to Reduce Bromide and Iodide in Drinking Water Sources

ARC Linkage Project LP100100285

WaterRA Science Talks to Industry

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Some Challenges in WA Drinking Water Supply

- high concentrations of bromide and iodide in many source waters
- WA groundwaters and surface waters [bromide] : < 0.05 mg/L (LOD) to ~3 mg/L
- Perth Seawater Desal Plant RO-treated water [bromide] < 0.2 mg/L
- WA groundwaters and surface waters [iodide] < 0.01 mg/L (LOD) to ~0.1 mg/L
- some iodide concentrations as high as ~0.5-0.6 mg/L

Significance of Bromide and Iodide – Australian Drinking Water Guidelines

- Bromide not subject to guideline value
- Iodide
  - ✓2011 [iodide] ≤ 0.5 mg/L
  - ✓2004 [iodide] ≤ 0.1 mg/L

Other Significance of Bromide and Iodide

- Potential to form brominated and iodinated disinfection by-products (DBPs) upon disinfection
- Br-DBPs and I-DBPs are usually of greater health concern than corresponding Cl-DBPs

E.g. Iodoacetic acid is the most genotoxic DBP known

- Some Br-DBPs and I-DBPs known to induce tastes and odours

E.g. CHI_3 organoleptic threshold concentration: 0.03 - 1 µg/L

For Improved Water Quality

Need to develop effective and economical methods of removal of bromide and/or iodide during drinking water treatment

Very few practical methods currently available

- ❑ Membrane techniques: expensive, energy intensive, not suitable for waters with high concentrations of DOC
- ❑ Ion exchange processes inefficient due to competing anions (e.g. sulfate, chloride)

ARC LP Project Objectives

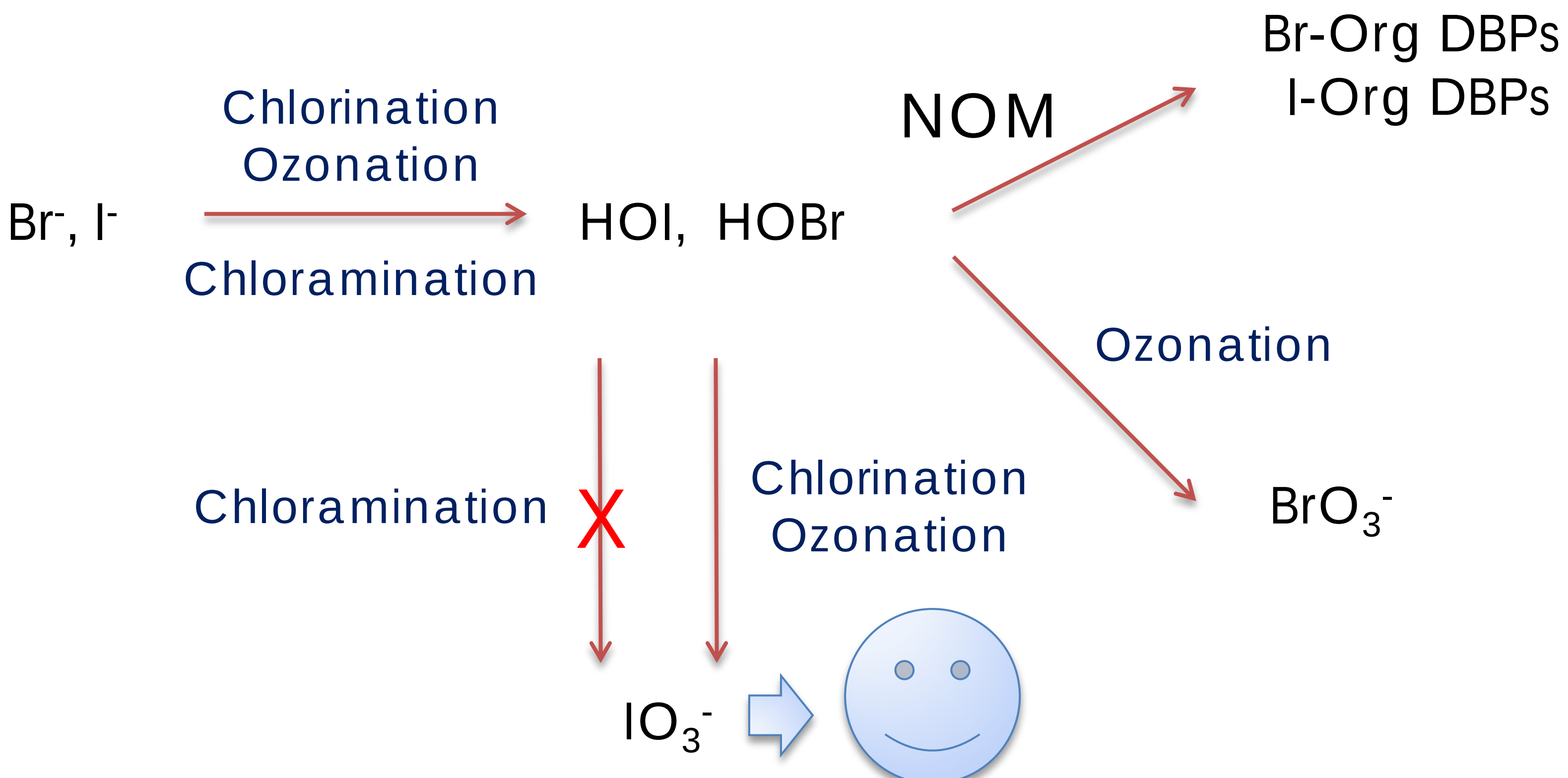
- To better understand the impact of high concentrations of bromide and iodide in source waters

- To develop *innovative new water treatment processes* to selectively remove both bromide and iodide from potable water sources

Project Objective 1

- To better understand the impact of high concentrations of bromide and iodide in source waters

Transformation Pathways of Bromide and Iodide During Water Treatment



Impact of High Bromide/Iodide Study

Two source waters chosen with:

- High bromide and iodide concentrations
- Minimal water treatment (only chlorination) before distribution

GW: chlorination 4 mg/L
SW: chlorination 2 mg/L

Water Quality Characteristics

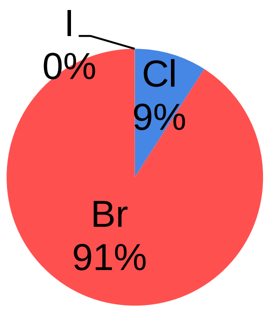
Samples		Parameters			
		DOC (mg/L)	Bromide, Br^- (µg/L)	Iodide, I^- (µg/L)	Iodate, IO_3^- (µg/L)
GW	Raw Water	1.2	677	72	9
	Distribution System	1.2	662	<10	125
SW	Raw Water	3.5	399	87	5
	Distribution System	3.5	60	<10	141

- ❑ Initial bromide concentration decreased after chlorination
  - ❑ More significantly where DOC conc higher → Br-Org DBPs
- ❑ Majority of initial iodide converted to iodate upon chlorination (we have found bromide catalyses this conversion)

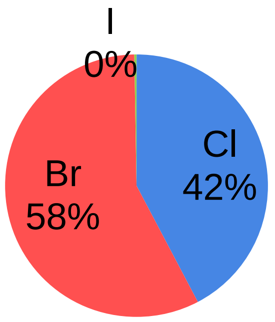
Organic DBP Formation in Distribution System Samples

Formation of Br-, I- and Cl-Org DBPs: Molar Proportions of Trihalomethanes

GW Distribution System



SW Distribution System



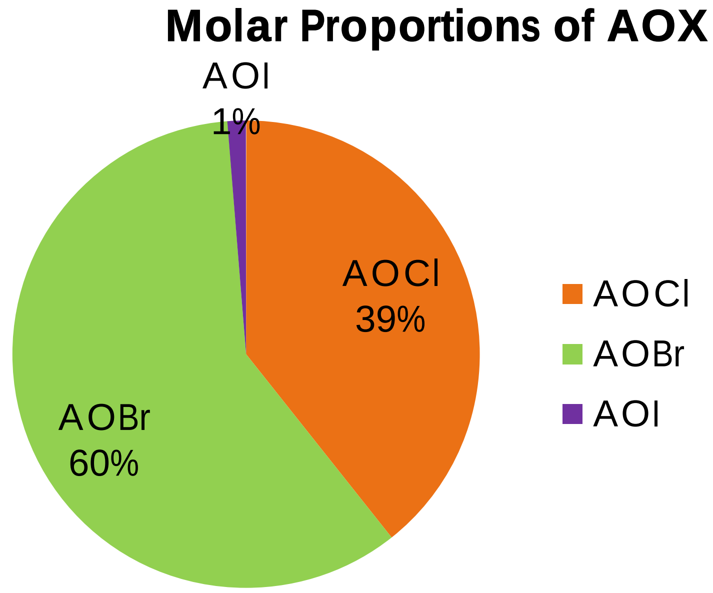
- ❑ Molar Ratio $Cl_2 : Br^-$ was approx. 6 : 1
- ❑ Despite much higher relative amount of chlorine to formed bromine in the system, bromine incorporation into THMs dominated over chlorine incorporation
- ➢ Much higher reactivity of bromine for reactions with NOM leading to THM formation than chlorine

AOX: Adsorbable Organic Halogen

- Measurement of major fraction of all Cl-, Br- and I-organic DBPs

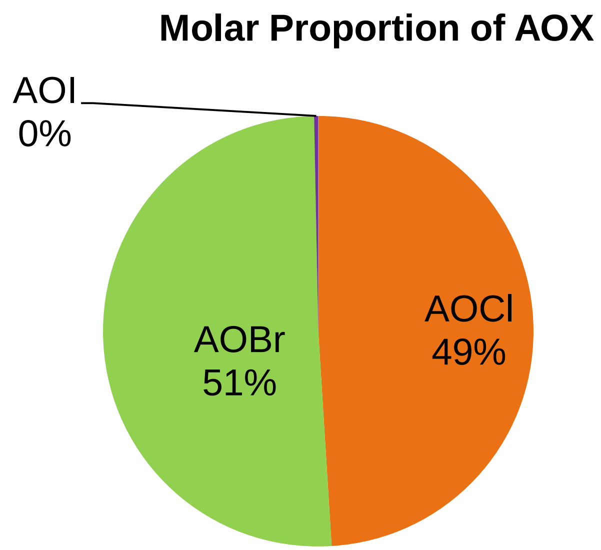
AOX → Known DBPs + Unknown organic halogens

Formation of Br-, I- and Cl-Org DBPs: AOX in GW



- ❑Br-Org DBPs (AOBr) predominate, even though ratio of Cl_2:Br^- is high
- ❑Much higher reactivity of bromine for reactions with NOM leading to bromine incorporation than chlorine

Formation of Br-, I- and Cl-Org DBPs: AOX in SW



- ❑Br-Org DBPs (AOBr) and Cl-Org DBPs formed in similar abundance, even though ratio of Cl_2:Br^- is high
- ❑Much higher reactivity of bromine for reactions with NOM leading to bromine incorporation than chlorine

Chlorinous Odours in Distribution System Samples

Odours When Free Cl_2 Concentration Above Free Cl_2 Odour Threshold Concentration

- All panellists agreed that a chlorinous odour was present for all distributed waters

Odours When Free Cl_2 Concentration Below Free Cl_2 Odour Threshold Concentration

- Chlorinous odour was still present in GW Distribution System & SW Treatment Plant Outlet samples

- i.e. Chlorinous odour still experienced even when there was not enough chlorine to cause a chlorinous odour

- This chlorinous odour may *possibly* be due to presence of bromine above its OTC

Impact of High Bromide and Iodide: Relevance to Water Industry

When bromide is high, Br-Org DBPs will predominate over Cl-Org DBPs.

This is important because Br-Org DBPs are a greater health issue than Cl-Org DBPs.

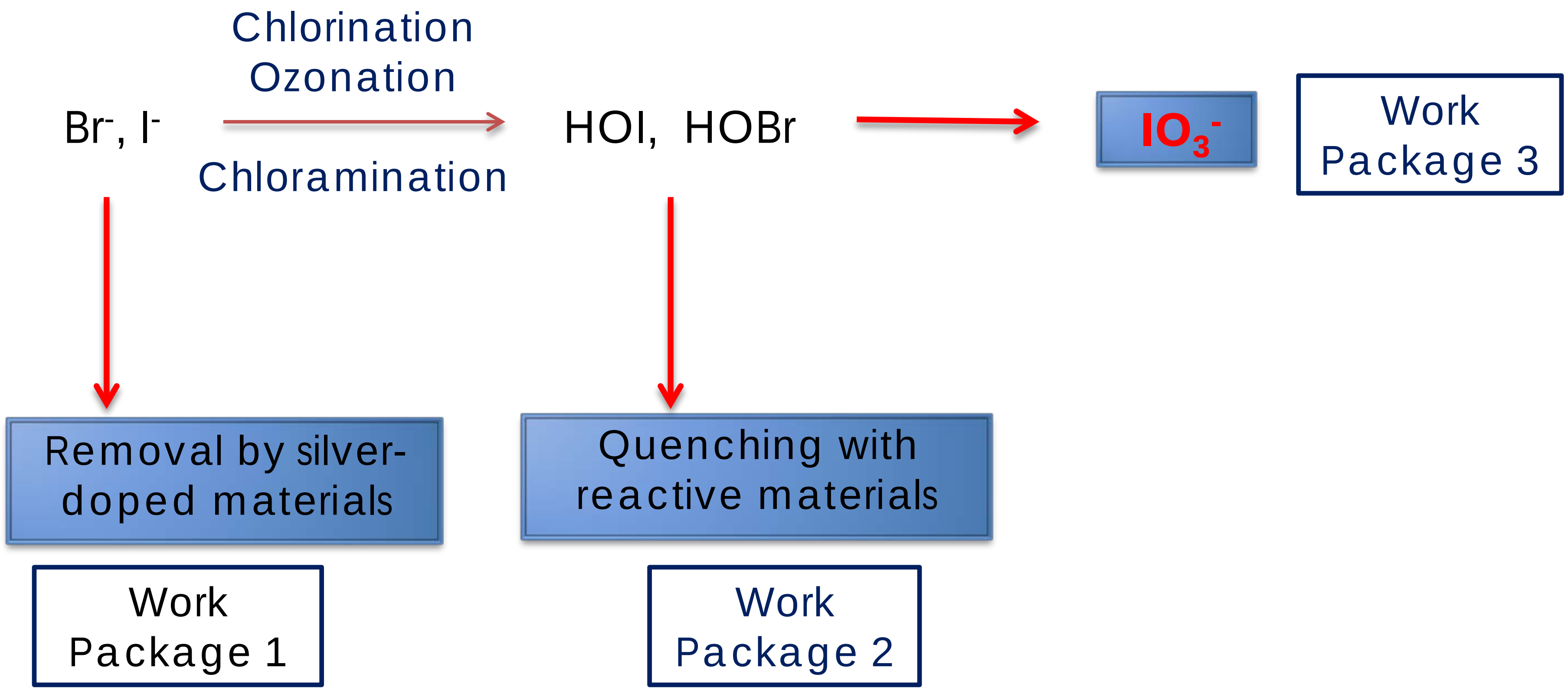
If chlorine is used, most of the iodide will be converted to harmless iodate

High bromide may play a role in chlorinous odours present when free chlorine concentration is below its OTC

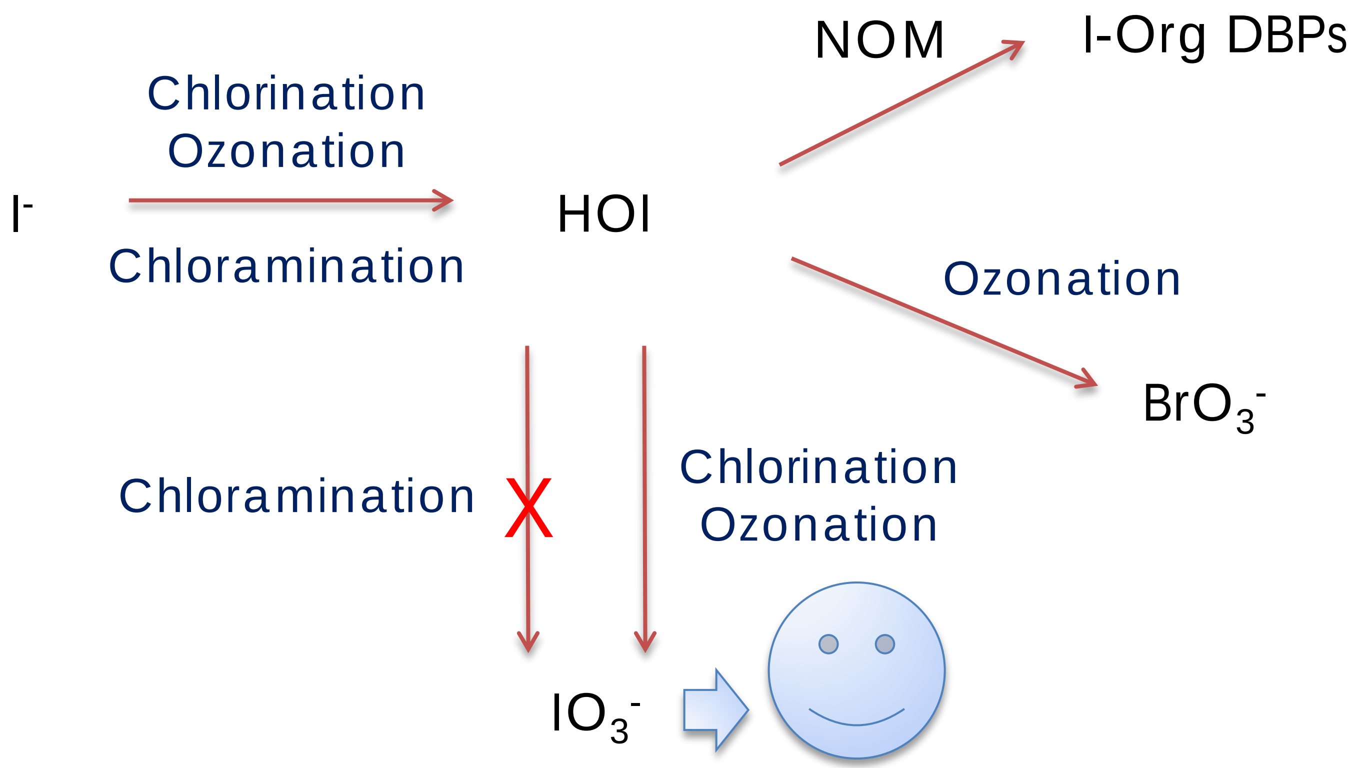
Project Objective 2

- To develop *innovative new water treatment processes* to selectively remove both bromide and iodide from potable water sources

Innovative New Water Treatment Processes



Transformation Pathways of Iodide



- **High iodide is an issue in chloramination since I-Org DBPs are favoured because iodate can't be formed**
- **Bromide is an issue in ozonation because bromate can be formed**

Key Project Objectives of Work Package 3

Develop **treatment options** to:

mitigate the formation of potentially harmful **I-Organic DBPs** during disinfection by chloramination by **maximising conversion of iodide into non-harmful inorganic iodate**,

while also **minimizing formation of bromate**

Mitigation of I-Organic DBP Formation

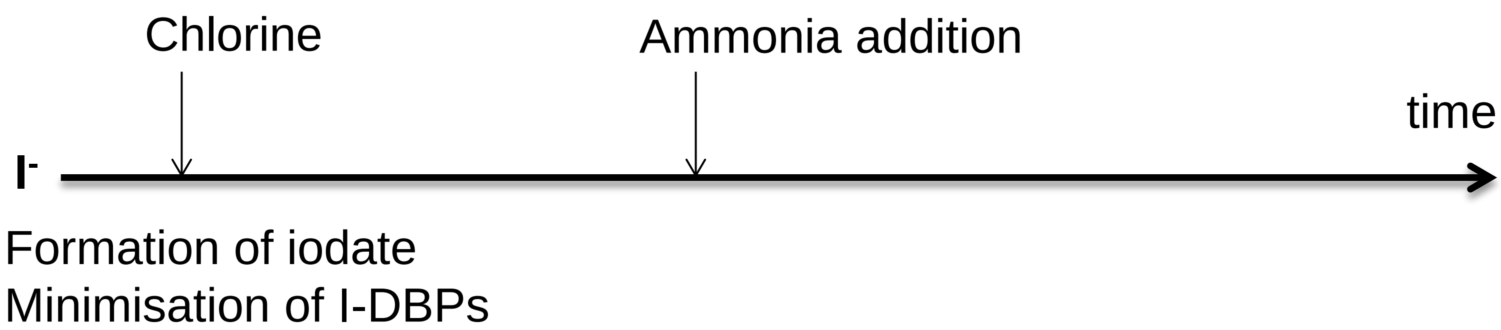
Strategy 1

- Pre-chlorination/post-chloramination

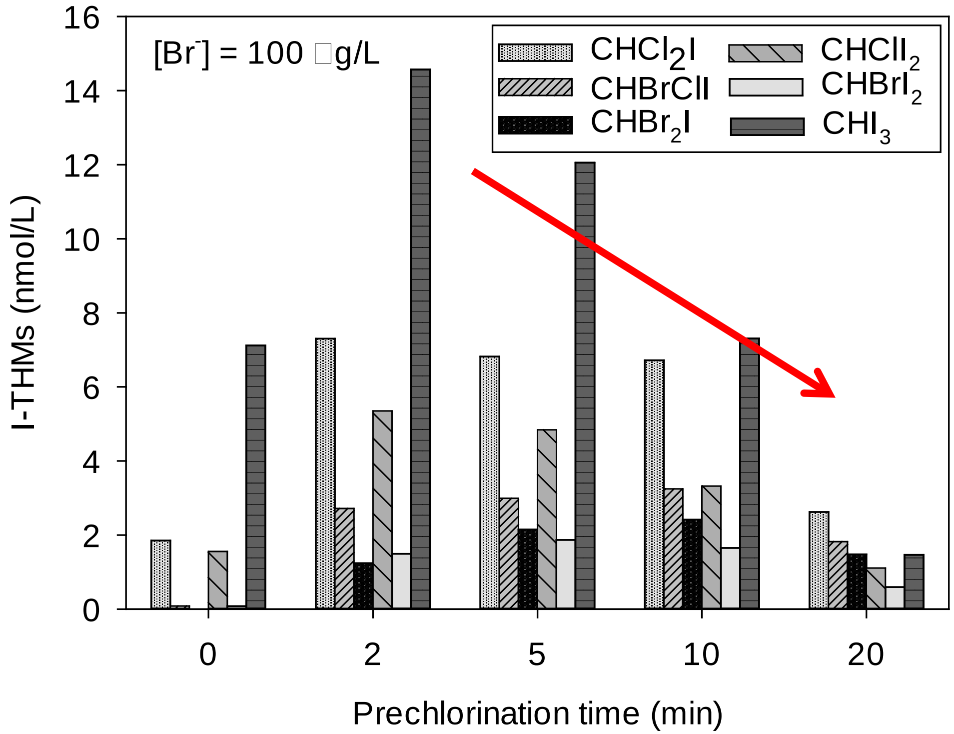
- Pre-ozonation: selective oxidation of I^- to IO_3^-

Strategy 2

Strategy 1:
Pre-chlorination / Post-chloramination



Effect of Pre-chlorination Time on I-Org DBP (here I-THM) Formation



- ❑ Chlorination (different contact times) followed by ammonia addition, with analysis of I-THMs after 24 h
- ❑ Low prechlorination times increase I-THM formation
- ❑ Longer prechlorination times limit the formation of I-THMs, especially more iodinated THMs like CHI_3

Criquet et al., 2012

Pre-chlorination during Chloramination to reduce I-THM Formation: Relevance to Water Industry

Having a longer pre-chlorination contact time can reduce formation of I-THMs

Chlorine followed by ammonia addition for chloramination can be useful for reduction of problems arising from high iodide in source waters

Strategy 2:
Pre-ozonation:
Selective Oxidation of Iodide to Iodate

with simultaneous bromate and I-THM minimization

Reaction Rates of Oxidation of Iodide and Bromide by Ozone

$$I^- \xrightarrow{O_3} HOI \xrightarrow{O_3} IO_3^-$$

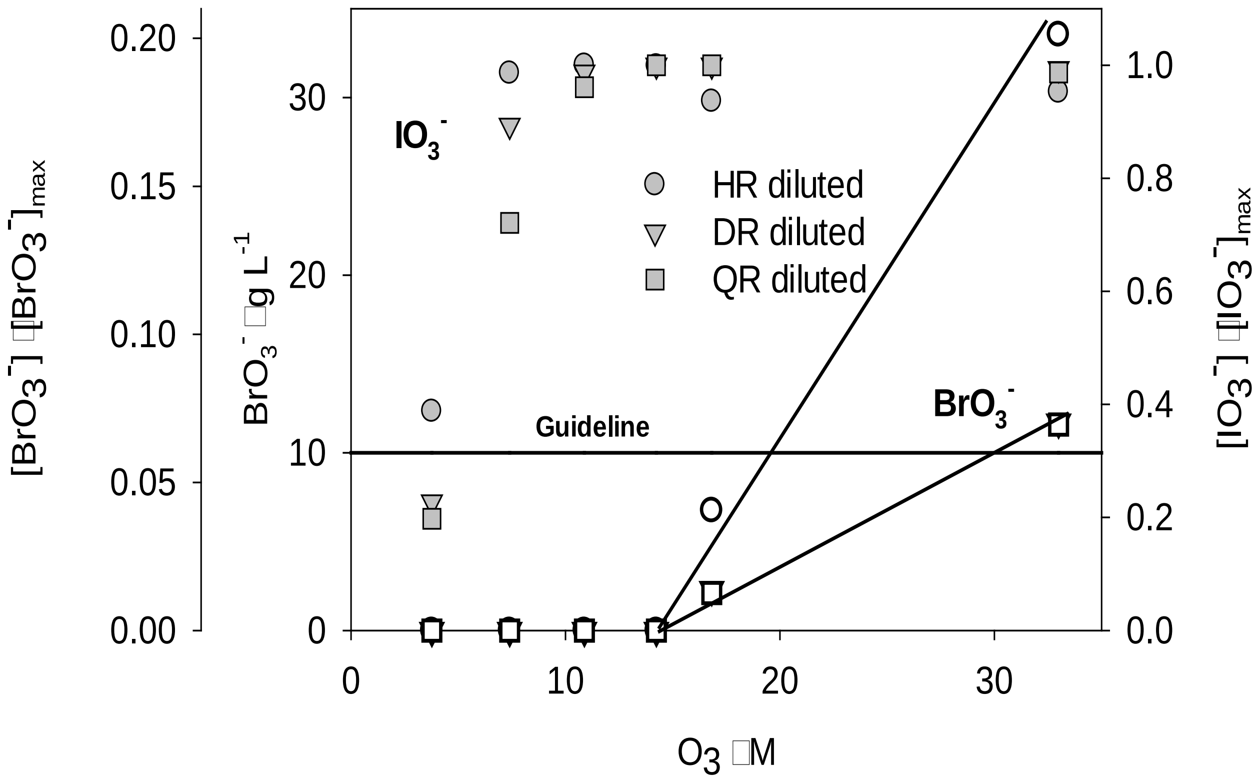
very fast | fast

$$Br^- \xrightarrow{O_3} HOBr \xrightarrow{O_3} BrO_3^-$$

moderate | moderate

Oxidation of iodide by ozone really fast compared to the oxidation of bromide

Formation of Iodate and Bromate during Ozonation of Raw Waters



Experimental conditions:
[DOC]= 1.3 mgC/L
[I-]= 50 µg/L
[Br-]= 100 µg/L
pH=8

❑100% conversion of iodide into IO_3^- without BrO_3^- formation is possible

I-Org DBP (I-THM) Formation during Ozonation

- Formation of two I-DBPs, $CHCl_2I$ and CHBrClI, reduced by increasing ozone dose

- Ozonation treatment reduces the formation of I-THMs

Pre-ozonation before Chloramination to reduce I-THM Formation: Relevance to Water Industry

Ozone can quickly oxidise iodide to iodate (so I-DBPs aren't formed), without formation of bromate, if correct ozone dose used

Pre-ozonation before chloramination can be useful for reduction of problems arising from high iodide in source waters

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