


### Bench-scale studies to facilitate the use of pre-formed chloramines for biofouling control in ocean water desalination



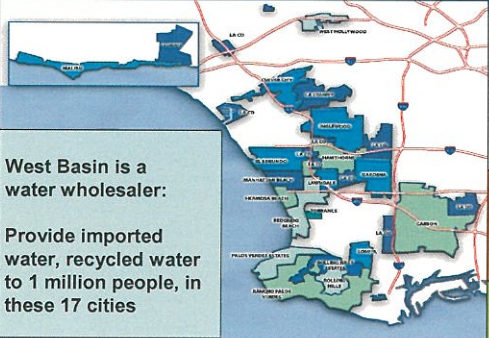
May 20, 2009

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West Basin  
Municipal Water District

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### Who is West Basin MWD?

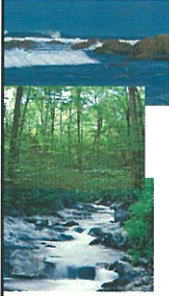


West Basin is a water wholesaler:

Provide imported water, recycled water to 1 million people, in these 17 cities

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### West Basin: Environmental Model



- Recycle 30 MGD going to 70 MGD
  - Five designer waters
  - Indirect potable reuse for seawater barrier
  - Investigating direct potable
- Conserve 1 billion gallons going to 2 billion gallons
- Water conservation & environmental education programs being expanded
- Brackish water desal
- Working with WRD to put recycled water into groundwater basin
- Investigating storm water reuse in Dominguez Channel
- Investigating ocean desalination as part of overall diverse water supply portfolio
- Programs reduce wastewater to Bay

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### Water Reliability 2020

- By 2020, we will take control of our water future & make our water more reliable by doing:
  - Double water recycling
  - Double conservation
  - More water education
  - Start ocean-water desalination


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### Water Reliability 2020

- Many benefits from local control:
  - Improved reliability for sustainable cities
  - Prevention of water rationing
  - Drought protection
  - Emergency supply
  - Guaranteed water for industry/economy
  - Reduced energy use
  - Costs same as importing water
  - Helps MWD
  - Helps Bay Delta & environment
  - Improves water quality

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### Doubling Water Recycling



- We are water recycling experts!
- Have only plant that produces 5 types of "designer" water - Irrigation water to distilled water
- Save industrial customers 20-30% on water, and dependable supply
- Produce 30 million gallons a day (mgd) going to 70 mgd
- 70 miles irrigation pipe going to 130 miles
- Irrigation saves 2,200 kWh of electricity for each acre foot over importing water
- Reduces wastewater to Santa Monica Bay

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## Executive Summary

1. Previous work: Chloraminating seawater made bromamines that oxidized the membranes
2. This work:
  - a. Confirmed bromamines when conventional methods are used
  - b. Showed pre-formed chloramines do not make bromamines

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## Biofouling has been solved in WW reuse

1. Precede RO with membrane filtration
  - Eliminates the seed
2. Carry a chloramine residual through both membranes
  - Inhibits growth

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## West Basin tried to extend the concept to SWRO

1. MF/SWRO
2.  $\text{Cl}_2 + \text{NH}_3$ , later  $\text{NH}_3 + \text{Cl}_2$
3. Residual attacked membranes
4. DPD showed "Free Chlorine"

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## Problem attributed to bromamines

1. SW is high in bromide (~ 65 mg/L)
2. Chlorine takes bromide to bromine
  - a.  $\text{HOCl} + \text{Br}^- = \text{HOBr} + \text{Cl}^-$
3. Result: bromamine, not chloramine
  - b.  $\text{HOBr} + \text{NH}_3 = \text{NH}_2\text{Br} + \text{H}_2\text{O}$
4. Bromamines act like free chlorine

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## Solution: preformed chloramines

1.  $\text{HOCl} + \text{Br}^- = \text{HOBr} + \text{Cl}^-$  *FAST*
2.  $\text{HOBr} + \text{NH}_3 = \text{NH}_2\text{Cl} + \text{H}_2\text{O}$  *FAST*
3.  $2\text{NH}_2\text{Cl} + \text{Br}^- = \text{NHBrCl} + \text{Cl}^- + \text{NH}_3$  *SLOW*

### Therefore:

- 1) Preformed chloramines can be used
- 2) Free chlorine test can be used to check

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## Project Goals: Phase 1

1. To find a way to make pre-formed chloramines for pilot, demo and full-scale
2. Use free chlorine test to confirm that pre-formed chloramines in seawater do not produce "free chlorine"

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## Project Tasks

- Task 1: Manufacturing chloramines
- Task 2: Selecting residual measurement method & characterizing its response
- Task 3: Confirm "free chlorine" is not formed

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## Task 1 - Making preformed chloramines

- 1. Two alternatives:
  - a. Batching
  - b. Continuous
- 2. Batching:
  - a. Would have to be stable
  - b. Would have to be 5 to 10%

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## Batching Experiments

- 1. Lots of published bench-top work
  - a. Usually 100 to 1000 mg/L (.01 to 0.1%)
  - b. Trick is to add NH<sub>3</sub> to NaOCl, not visa versa
- 2. Stability dependent on pH, Cl<sub>2</sub>/N, & concentration

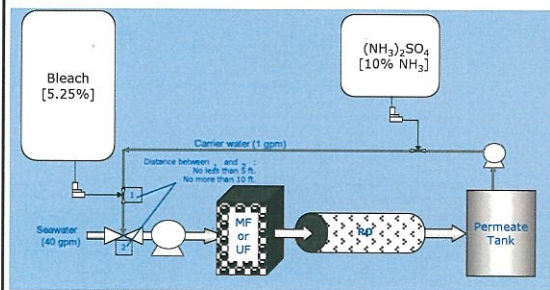
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## Batching Experiments

- 1. Tried full-strength NaOCl & NH<sub>4</sub>OH first
  - a. Combined them with no incident
  - b. But solution effervesced and lost strength rapidly
  - c. Suspected hydrazine formation:  
$$\text{NH}_2\text{Cl} + \text{NH}_3 = \text{N}_2\text{H}_4(\text{gas}) + \text{HCl}$$
- 2. Switched to NaOCl & NH<sub>4</sub>Cl
  - a. Tried various pHs
  - b. Tried various Cl<sub>2</sub>/N ratios
  - c. All concentrated solutions were unstable
- 3. Conclusion: must use continuous process (like those used for O<sub>3</sub> and ClO<sub>2</sub>)

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## Possible Design for Manufacturing pre-formed chloramines



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## Task 2A - Selecting a method to measure the residual

- 1. No Standard Methods for bromamines
  - a. AwwaRF, bromamines appear as free Cl<sub>2</sub>
  - b. Earlier WBMWD work DPD showed free Cl<sub>2</sub>
  - c. Amperometric method is more widely respected than DPD (fewer interferences)
- 2. Began experiments using Amperometric,
  - a. method was too slow
- 3. Compared Amperometric and DPD for free and combined chlorine in seawater
  - a. Similar results obtained
  - b. Subsequent experiments use DPD

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### Task 2B - Characterizing the Response of the DPD Method to the Oxidants Important to this Study

1. Studied two waters
  - a. Buffered bromide water
  - b. Filtered seawater
2. Added Chlorine three ways
  - a. Chlorine only
  - b. Chlorine and, then, ammonia
  - c. Pre-formed chloramines
3. Looked at the response of the DPD methods for free and total chlorine on the freshly chlorinated water (before significant decay)

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### Task 2b Characterizing DPD Response

	Chlorine only	Chlorine + ammonia	Pre-formed Chloramines
Buffered bromide water	Scenario I	Scenario II	Scenario III
Filtered ocean water	Scenario IV	Scenario V	Scenario VI

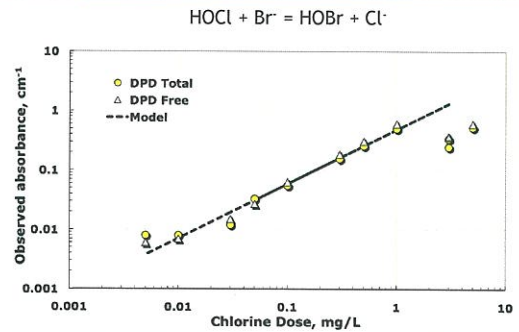
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### Task 2b Characterizing DPD Response

1. For all six Scenarios, we tested chlorine doses of 0.005, 0.01, 0.03, 0.05, 0.1, 0.3, 0.5, 1, 3, & 5 mg/L.
2. In each case, the residual was measured immediately after 5-minute mixing using the DPD colormetric method for free and total chlorine

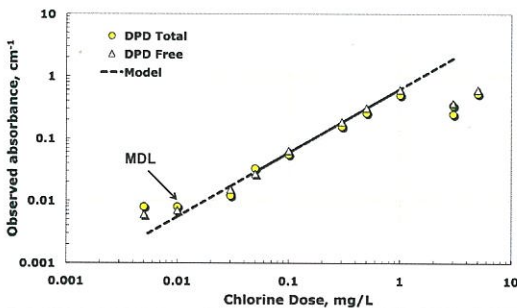
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### Scenario I: Bromide water + Chlorine



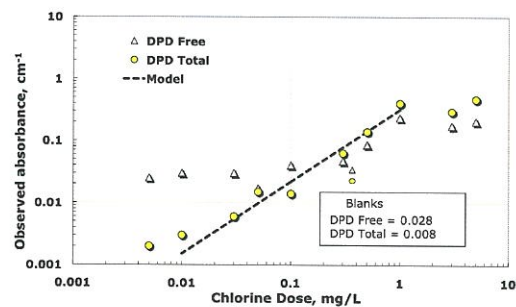
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### Scenario I: Bromide water and Chlorine



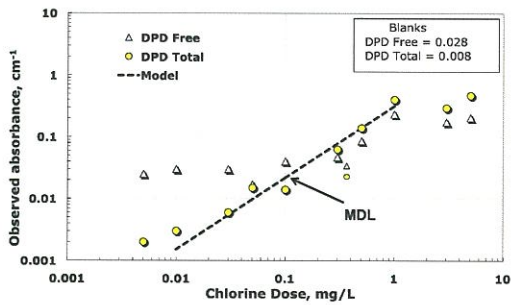
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### Scenario IV: Seawater + Chlorine



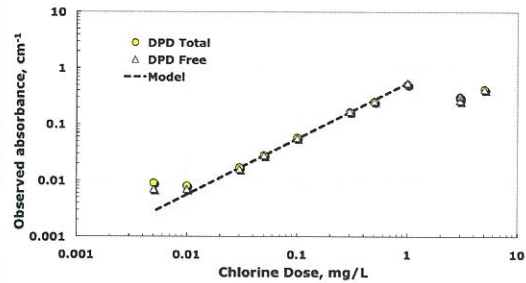
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### Scenario IV: Seawater and Chlorine



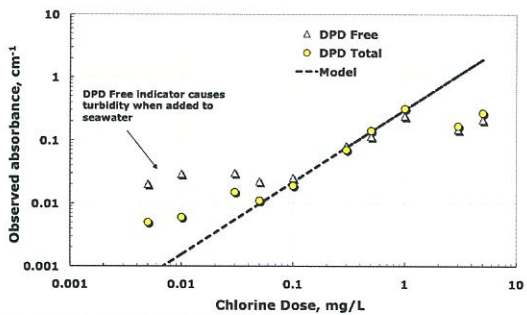
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### Scenario II: Bromide water + Chlorine & Ammonia



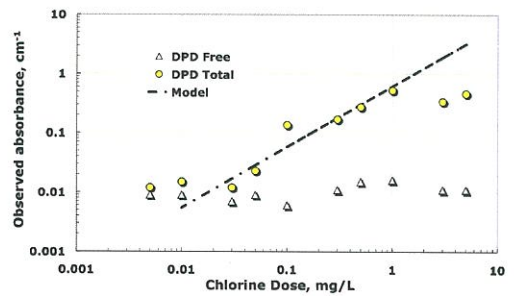
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### Scenario V: Seawater + Chlorine & Ammonia



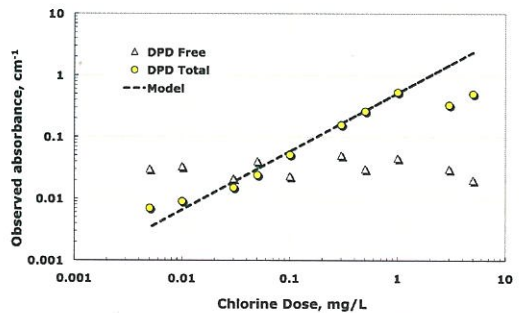
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### Scenario III: Bromide water + Pre-formed NH<sub>2</sub>Cl



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### Scenario VI: Seawater + Pre-formed NH<sub>2</sub>Cl



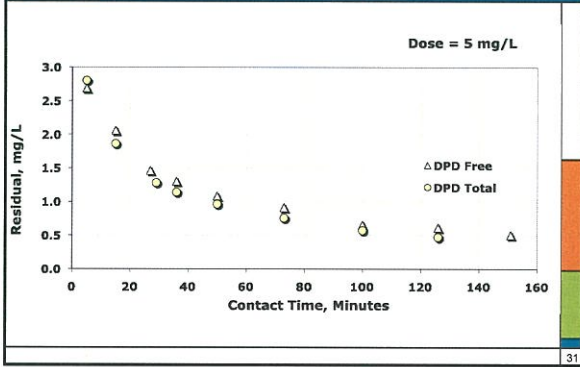
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### Task 3 - Confirming that Bromamines are not Formed When PRE-FORMED Chloramines are added to Ocean Water and a Short Contact Time is Maintained

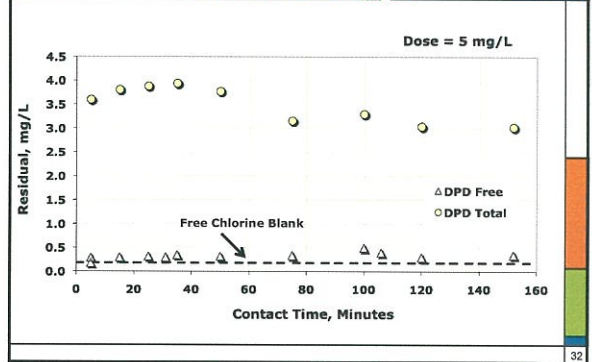
1. All the work done with filtered ocean water
2. Compared pre-formed chloramines with chlorine, then ammonia
3. Monitored the decay of the free and total chlorine residual for 150 minutes.

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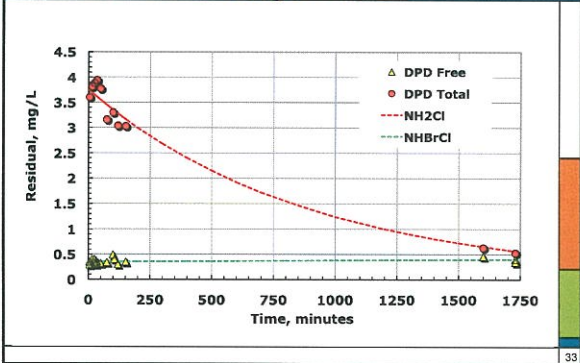
### Scenario V: Seawater + Chlorine & Ammonia



### Scenario VI: Seawater + Pre-formed NH<sub>2</sub>Cl



### Seawater + Pre-formed chloramines, long-term



Thank-You

Questions