Removal of Hydrogen Sulfide from Groundwater by Granular **Activated Carbon** 

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# Co-authors and Acknowledgements

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- Acknowledgements
  - Steve Styles, Chris Cassotta, Derek Smith City of Huntington Beach





## Introduction

- Project locations: City of Huntington Beach's three potable wells
  - ► Well 3
  - Well 6
  - Well 9
- Design Capacity: 3,000 to 3,500 GPM each
- Current treatment
  - Chlorination (Free Cl<sub>2</sub> with gaseous Cl<sub>2</sub>)
  - Fluoridation (HF)



### Project Objective

Utilize the groundwater to maximize the local water resources in the current drought situations

- Historically the wells haven't been run at their full speed (50% to 60%)
- Water quality concerns at the design production rates
  - ▶ Color (NOM): <5 CU  $\rightarrow$  up to 15 CU
  - ►  $H_2S$ : non-detect → up to 0.2 mg/L
- Addition of treatment facilities has been considered
  - Granular activated carbon (GAC)
  - Chlorine-bisulfite-chlorine
  - Ozone
- GAC-based treatment has already been selected for one of the wells
  - Being considered at the other wells

# Pilot Study Objectives

GAC-based treatment has been tested by the City of Huntington Beach and a full-scale demo filter has been installed and used at Well 9 since 2010

- The demo filter has a design capacity of 250 gpm
- Coconut shell-based media
- No backwash
- A series of pilot studies have been carried out
  - ▶ To evaluate the feasibility of the GAC-based treatment
  - To identify H<sub>2</sub>S removal mechanisms
  - To ensure no odor or other unexpected water quality issues in the distribution system
  - To determine full-scale design parameters



# History of On-site Pilot Studies

- > 2006: Initial pilot study (up to 30 gpm) at Well 9
- 2009: Demo GAC filter vessel (250 gpm, sidestream) at Well
  9
- 2014: Demo GAC filter monitoring (with chlorine) at Well 9 (Up to 350 gpm)
- 2014: Small pilot GAC at Well 9 (0.25 gpm)
- 2014: Demo GAC filter monitoring (without chlorine) at Well 9 (Up to 400 gpm)
- 2014-2015: Small pilot GAC at Wells 6 and 3 (Up to 0.6 gpm, reduced filter bed depth)
- 2015: Demo GAC filter monitoring (reduced filter bed depth) at Well 9 (ongoing)
- 2015: Small pilot GAC and non-GAC at Well 9 (Up to 0.6 gpm)

#### NOTE: Full-scale filters are being designed for Well 9

# **General Methodologies**

Pilot filters: Two scales

Demo GAC filter at Well 9 (250 to 400 gpm)

10' diameter

- Surface loading rate: 3.5 to 5.6 gpm/ft<sup>2</sup>
- Pilot filtration skid (0.25 to 0.6 gpm)
  - Five 2' filter columns (3" ID clear PVC), in series or in parallel
  - Surface loading rate: 5.1 to 12.8 gpm/ft<sup>2</sup>
  - ▶ GAC media and non-GAC media
- Study periods
  - 4 to 8 weeks each
- Water quality parameters monitored
  - $\blacktriangleright$  H<sub>2</sub>S, color
  - pH, DO, ORP, TDS, temperature, turbidity, nitrate, odor, HPC, TOC
    - ► A flow cell was used to measure DO and ORP accurately



## Coconut Shell GAC Media Specifications

- Mesh size: 12 x 30
- NSF 61 certified
- Carbon tetrachloride #: 60%
- Iodine #: 1,100 min
- Ash, weight %: 3 max
- Hardness %: 98 min
- Moisture as packed wt%: 3 max
- Apparent density g/cc: 0.45-0.52

# Head Loss in GAC Filters (0.25 gpm, 5 Filters in Series)



# H<sub>2</sub>S Removal in GAC Filters (0.25 gpm, 5 Filters in Series)



# Color Removal in GAC Filters (0.25 gpm, 5 Filters in Series)



# H<sub>2</sub>S, DO, Nitrate-N, and ORP (0.25 gpm, 5 Filters in Series)



# Head Loss in GAC Filters (0.25 gpm, 5 filters in Series)



#### Colonization at the Surface of Filter 1 (0.25 gpm, 5 Filters in Series)



## H<sub>2</sub>S Removal Mechanisms

#### Physicochemical

- Adsorption/catalytic oxidation
  - Only at the start up (a few days)
- Chlorine/Mn-mediated oxidation
  - No chlorine

#### Biological

- Thiobacillus spp.
  - Autotrophic denitrifier
- ▶ Thiothrix spp.
  - Gram-negative, microaerobic sulfide oxidizer



# 16S rRNA Analysis

Filter Filter Filter Filter

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	– Sulfur Oxidizers	Quantity	Anaerobe/ Facultative anaerobe	Aerobe
		0-10		
		10-100		
		100-1000		
		1000-10000		
		10000-30000		

Sulfate Reducers

Denitrifying Bacteria (Certain species)

- Aerobic sulfur oxidizer in the top 2'
  - e.g., Thiothrix
- Anaerobic/facultative sulfur oxidizers in the middle
  - e.g., Sulfuricella, Thiobacillus
- Sulfate reducers at the bottom 2'
  - e.g., Desulforegula, Desulfurivibrio

# Microbial Oxidation of H<sub>2</sub>S (Hypothesis)

Aerobic sulfur oxidizer Thiothrix Anaerobic/Facultative sulfur oxidizer *Thiobacilus* 

#### **Oxygen Consumption**





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## Byproducts and Odor

#### Elemental sulfur

- Polysulfides
  - Products of elemental sulfur and H<sub>2</sub>S
  - ► HS<sub>n</sub>H
  - Matchstick odor
- Elemental sulfur was detected in the Demo GAC filter effluent
- Polysulfide was non-detect
  - However, a very slight matchstick odor was present in some of the filter effluent samples
  - Need more sensitive sulfur analysis methods

Odor Test GAC + Chlorination							
Incubation Time	Raw	Chlorinated- Fluoridated Raw	GAC Treated	Chlorinated- Fluoridated GAC Treated			
<30 min	Strong rotten egg	Strong smoky/match stick	No odor	Strong bleach			
3 hours	Weak rotten egg	Strong smoky/match stick	No odor	Bleach			
6 hours	No odor	Strong smoky/match stick	No odor	Bleach			
Implications	Hydrogen sulfide was present, dissipated during the incubation	Polysulfide was present, very persisting odor	No hydrogen sulfide/ polysulfide was present	No hydrogen sulfide/ polysulfide was present			

# High Flow Rate, Short EBCT (12.8 gpm/ft<sup>2</sup>, 1.2 min, Parallel)



### Conclusions

 GAC-based H<sub>2</sub>S removal is feasible, repeatable, consistent and almost instantaneous

- Coconut-shell based GAC
- Worked at all three well sites
- No odorous byproducts before/after chlorination
- The primary removal mechanism is microbial
  - DO, ORP and nitrate are important parameters to monitor
  - Sulfate reduction may occur if the EBCT is too long
- Service flow rate can be as high as 13 gpm/ft<sup>2</sup>
- EBCT can be as short as 1 min
  - Bed depth: Minimum 2'
  - Huge savings in capital and O&M costs
- The filters can be run for at least 3 to 4 weeks
  - Up to a few years (the demo filter at Well 9)
  - Backwash will remove excess biomass and elemental sulfur

# THANKS

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