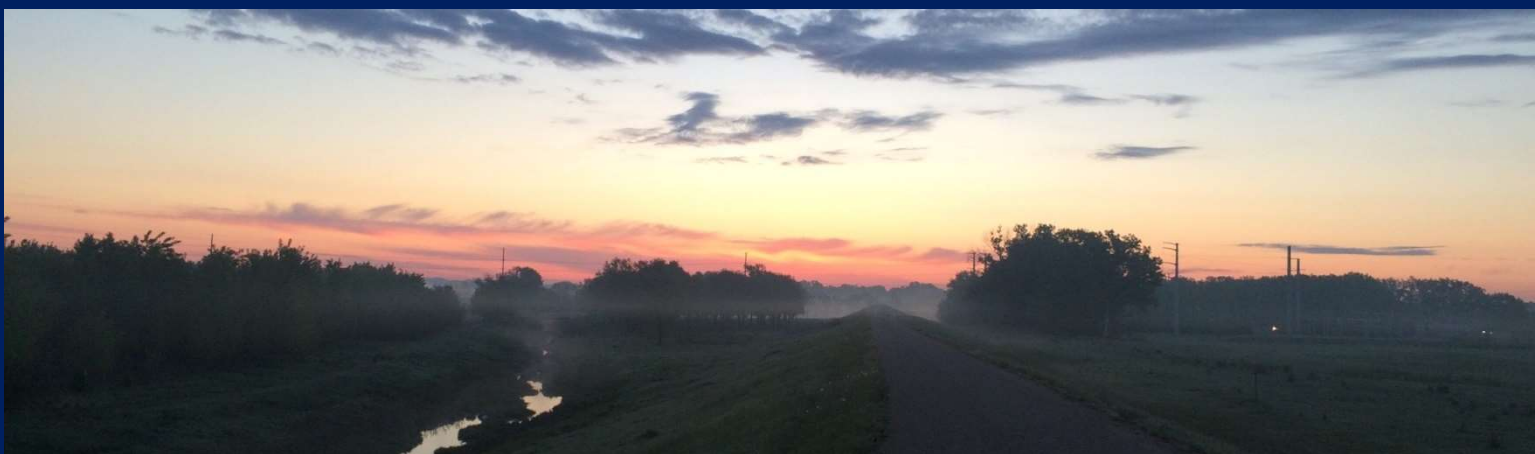


Advancements in Organics Monitoring Lead to Improved Jar Testing Optimization



National Environmental Monitoring Conference 2016

Topics in Drinking Water

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Outline of Presentation

1. What is total organic carbon (TOC) and why is it important
2. Importance of jar testing
3. Presentation of experimental data
4. Discussion on value of TOC and new monitoring advancements



What is TOC?

TOC, as defined in EPA Method 415.3, “is the gross amount of organic matter found in natural water.

Suspended particulate, colloidal, and dissolved organic matter are part of the TOC measurement.”

USEPA. Determination of Total Organic Carbon and Specific UV Absorbance at 254 nm In Source water and Drinking Water. EPA/600/R-05/055, February 2005.

What is TOC?

TOC = Total Organic Carbon

Total amount of **organic carbon** in natural water



Where does TOC come from?

Organic compounds come from plants, animals, etc. They can become bound to dissolved or suspended material in natural water sources

—————→ **Natural Organic Matter (NOM)**

What contributes to TOC?

Natural Organic Matter (NOM)

And also...

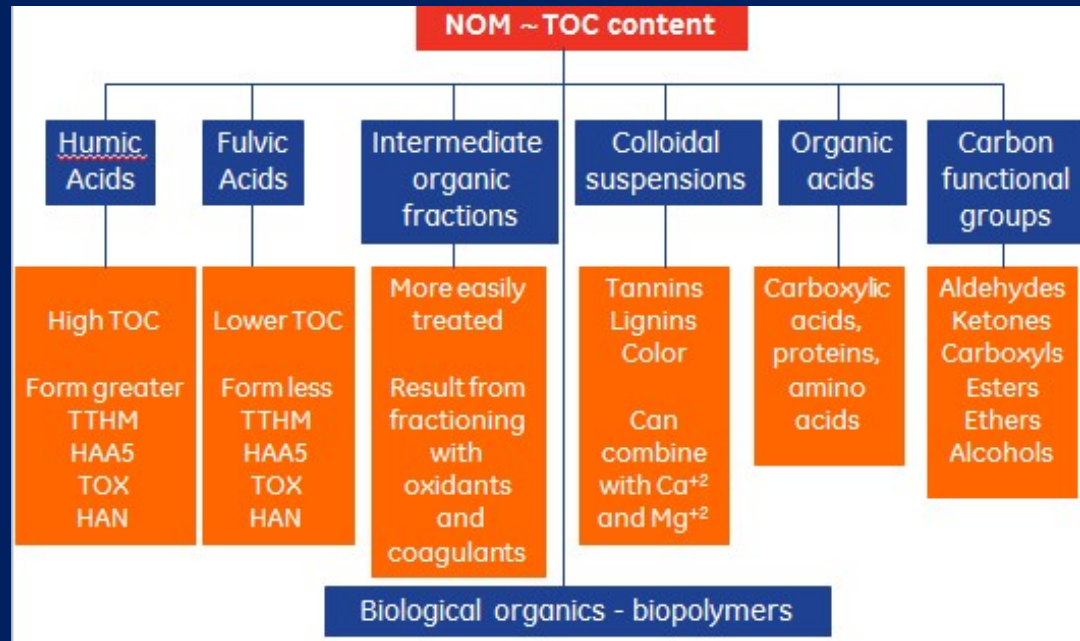
Taste and Odor

Microbes and bacteria

Reclaim

Waste

Industry (Oil, Gas, Pharmaceutical...)



TOC Defined and Compared

TOC

- Measures gross amount of organic matter found in natural water.
- Includes suspended particulate, colloidal, and dissolved organic matter.
- Doesn't Include settleable solids, inorganic sediments, organic particulate.

DOC

- Measures soluble and/or colloidal organic matter filtered through 0.45- μm .

Turbidity

- Measures water clarity—how much the material suspended in water decreases the passage of light through the water.
- Doesn't have health criteria. Doesn't distinguish between inorganic, organic, color, etc.

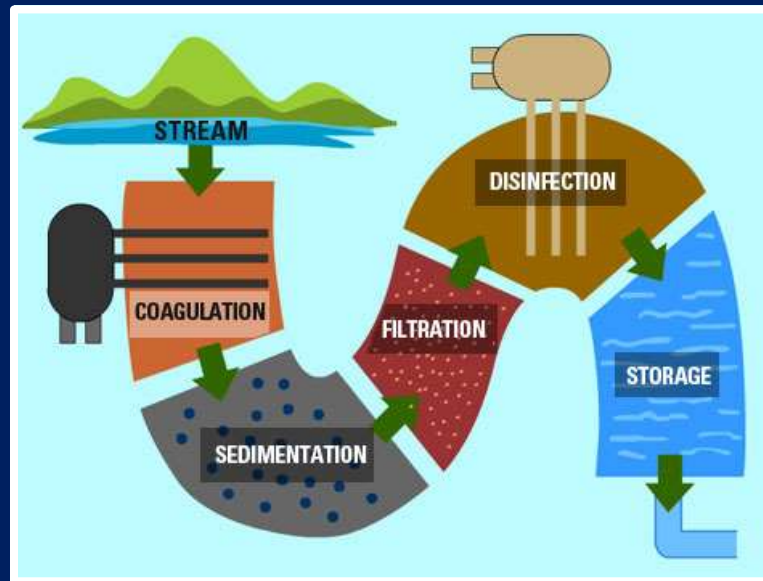
SUVA- Specific absorbance UV254 nm

- Measures DOC aromatic content—calculated by DOC and UV254 as alternative EPA compliance. Requires DOC and UV254.
- Several interference at 254nm.

Why is TOC important?

Conventional Water Treatment: TOC removal is regulated

Influent TOC



Effluent TOC

Why is TOC important?

Conventional Water Treatment: TOC removal is regulated

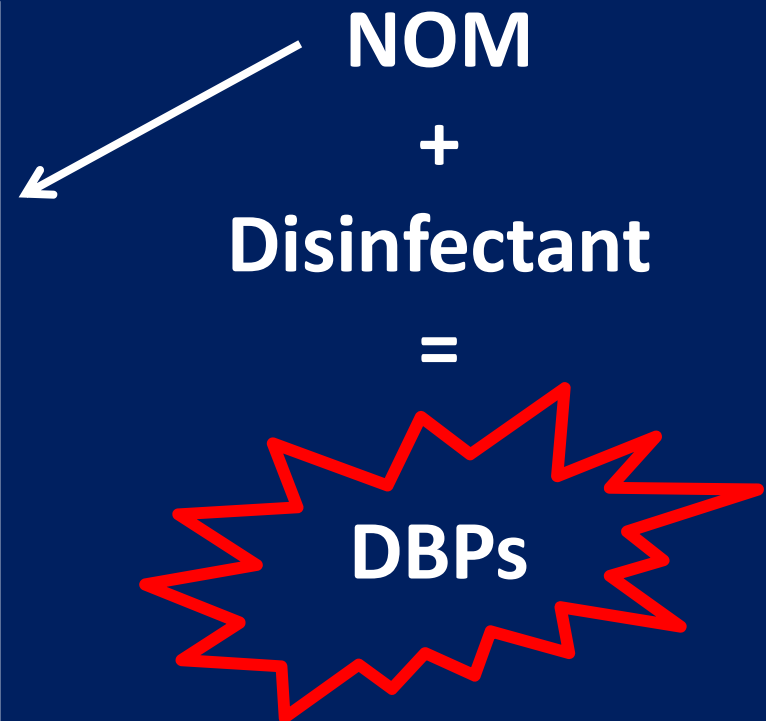
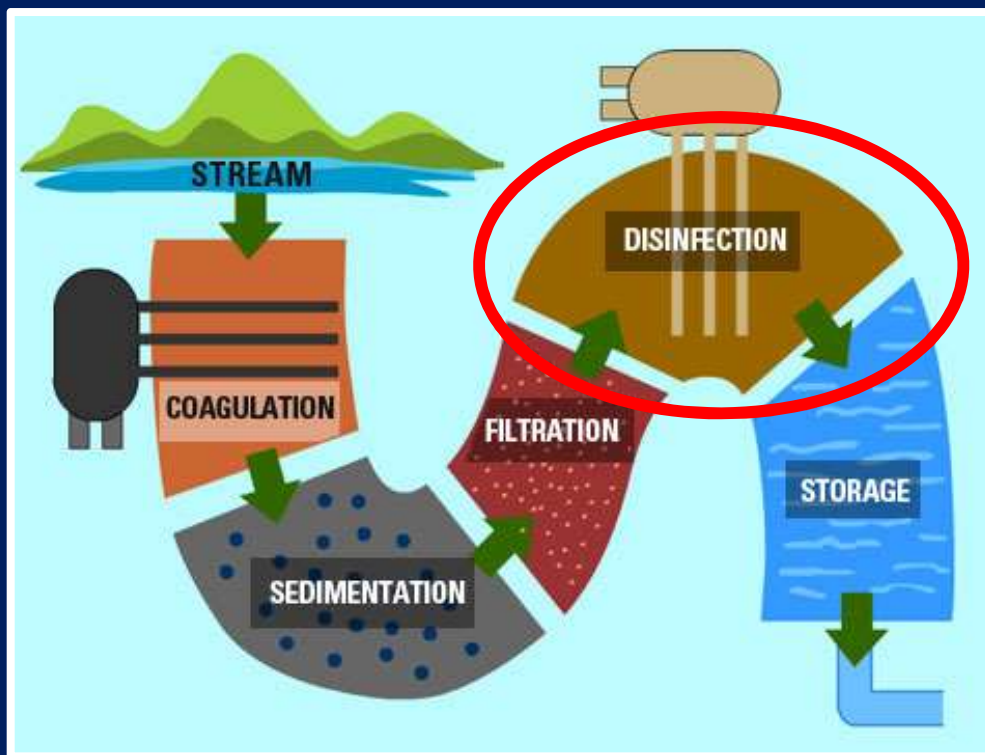
Source Water TOC (mg/L)	Source Water Alkalinity, mg/L as CaCO ₃		
	0-60	>60-120	>120
> 2.0 to 4.0	35.0%	25.0%	15.0%
> 4.0 to 8.0	45.0%	35.0%	25.0%
> 8.0	50.0%	40.0%	30.0%

Drinking water plants required to remove a certain percentage of the influent TOC based on the alkalinity of the water and the incoming concentration of TOC

Why is TOC important?

Disinfection By-Products (DBPs)

All water treatment plants

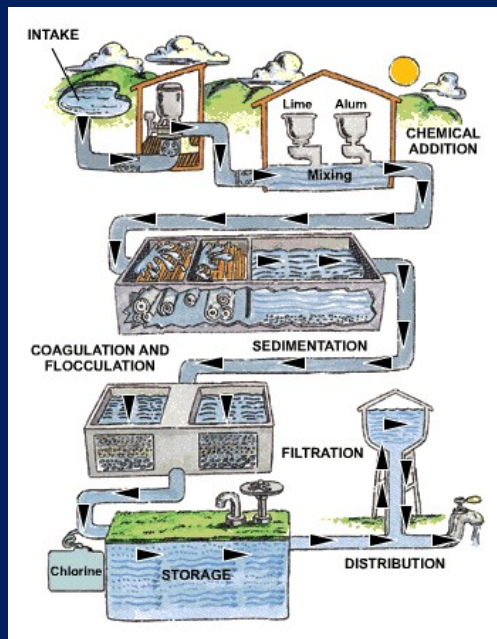


Why is TOC important?

Disinfection By-Products (DBPs)

DBP Formation is dependent on:

- ✓ Temperature
- ✓ pH
- ✓ Time



Currently regulated DBPs:

- Trihalomethanes (THMs)
- Haloacetic Acids (HAAs)
- Chlorite
- Bromate

...more are coming...

Why is TOC important?

Disinfection By-Products (DBPs)

Water treatment plants want to minimize microbial growth
AND DBP formation

Lowering TOC is the best solution for both!



Why is TOC important?

Regulated TOC removal

&

Regulated DBP levels

...sometimes even meeting the regulated TOC percent removal doesn't mean that you will meet the DBP regulation limits for the furthest point in the distribution system...

Why is TOC important?

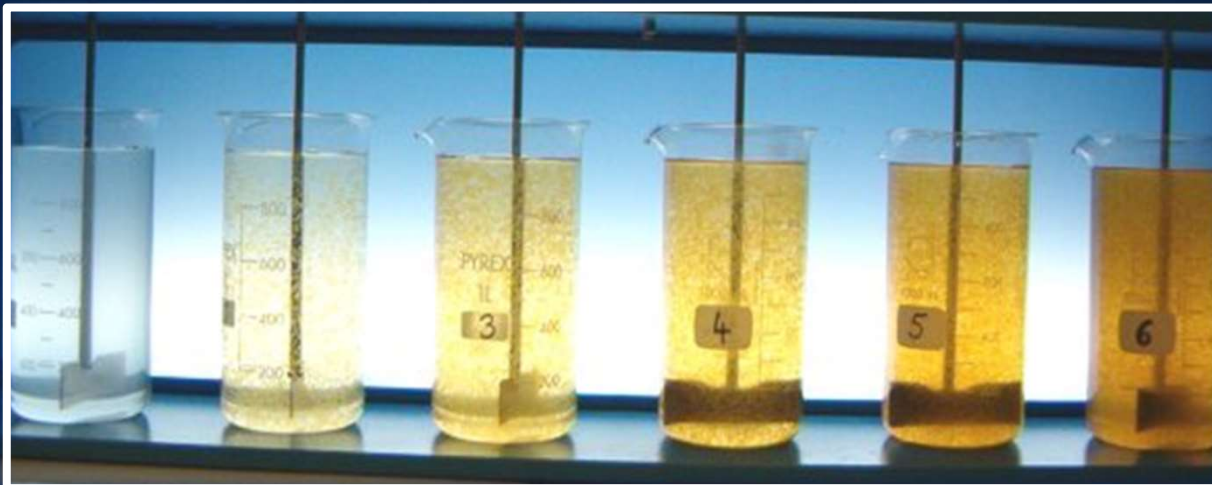
- Process control and optimization
- Data driven treatment decisions
- Monitor overall health of the system
- Meet effluent quality goals

Jar Testing

Jar testing is beneficial for plants so that they can optimize their treatment process

Plants want to pick the right coagulant dosage and treatment so that they can:

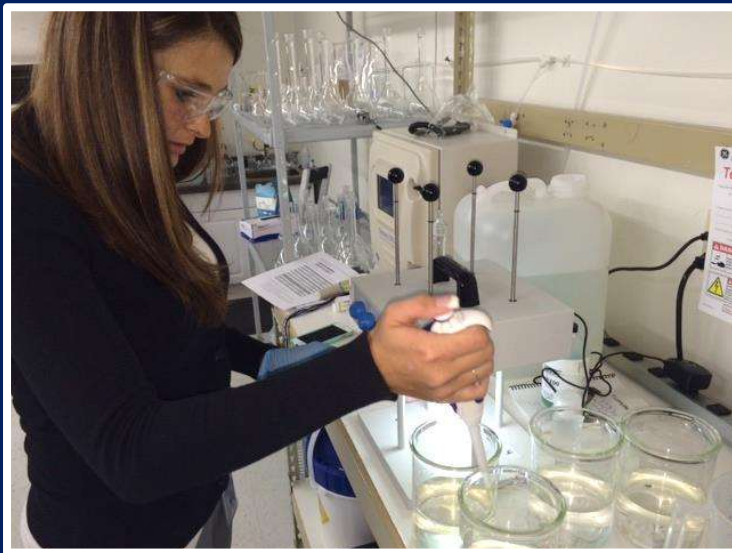
- ✓ Maximize TOC removal to meet regulations
- ✓ Minimize sludge production
- ✓ Minimize costs



Jar Testing

Simulation of the coagulation and flocculation steps in the water treatment process

Important for determining the optimal coagulant and dosage for a plant's raw water



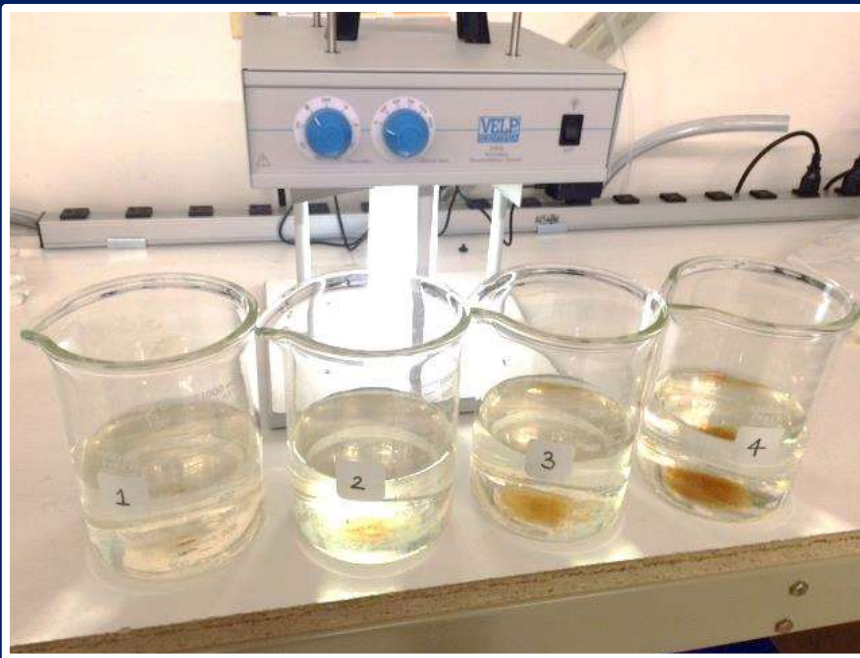
Add coagulant at different doses to raw water



Replicate plant contactors with flocculation simulator

Jar Testing

Simulation of the coagulation and flocculation steps in the water treatment process



Let the water settle

After flocculation and settling, sample the settled water to determine which coagulant dose was best

Jar Testing

Parameters typically measured:

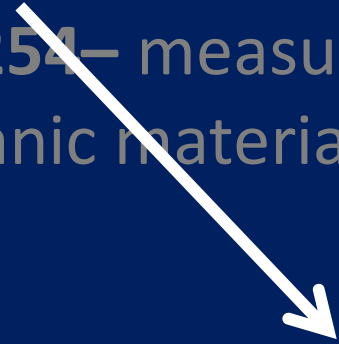
- ✓ **Turbidity** – measure of water clarity
- ✓ **UV254**– measure of the aromatic content of the organic material in the water



Jar Testing

Parameters typically measured:

- ✓ **Turbidity** – measure of water clarity
- ✓ **UV254** – measure of the aromatic content of the organic material in the water

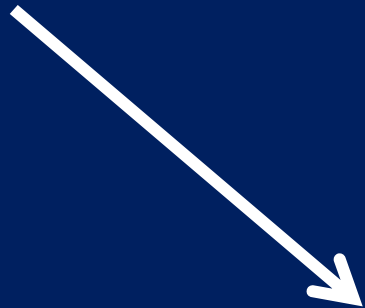


Issues: Doesn't distinguish between inorganic, organic, particulates. Is only a measure of how much light passes through water.

Jar Testing

Parameters typically measured:

- ✓ **Turbidity** – measure of water clarity
- ✓ **UV254** – measure of the aromatic content of the organic material in the water

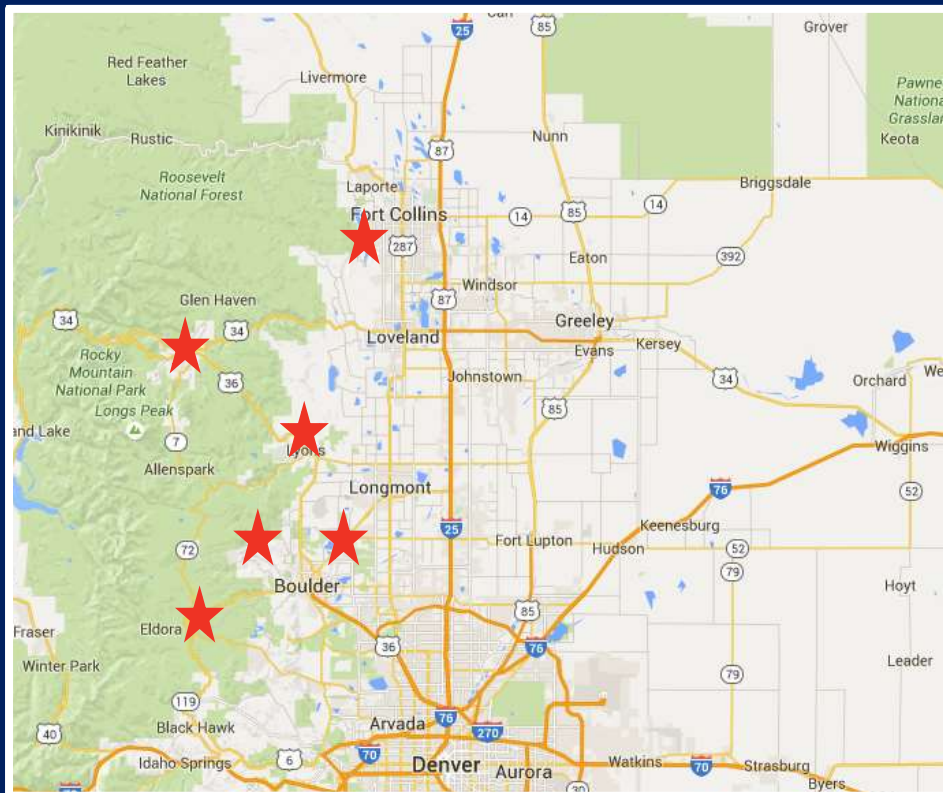


Issues: Not all organic molecules absorb in the UV spectrum, multiple interferences at 254 nm wavelength.

Jar Testing Experiment

Collected natural surface water from 10 sites

Water samples were representative of surface water feeding local water treatment plants



6 sites in Colorado

- ✓ river
- ✓ reservoir
- ✓ lake
- ✓ mountain
- ✓ plains

Jar Testing Experiment

Collected natural surface water from 10 sites

Water samples were representative of surface water feeding local water treatment plants

Wyoming: reservoir



Arizona: canal

Texas: river and lake

Jar Testing Experiment

Tested two different coagulants:

- ✓ **Ferric Chloride (Ferric)**
- ✓ **Aluminum Sulfate (Alum)**

Measured Parameters

Raw Water:

- Alkalinity
- pH
- TOC
- Turbidity
- UV254

Settled Water:

- TOC
- Turbidity
- UV254

Jar Testing Experiment

Tested two different coagulants:

- ✓ Ferric Chloride (Ferric)
- ✓ Aluminum Sulfate (Alum)

Goal: To investigate how turbidity, UV254, and TOC all were influenced by different coagulant dosages

Spoiler alert: turbidity and UV were not always the best indicator of optimum TOC removal

- pH
- TOC
- Turbidity
- UV
- Turbidity
- UV

Jar Testing Experiment

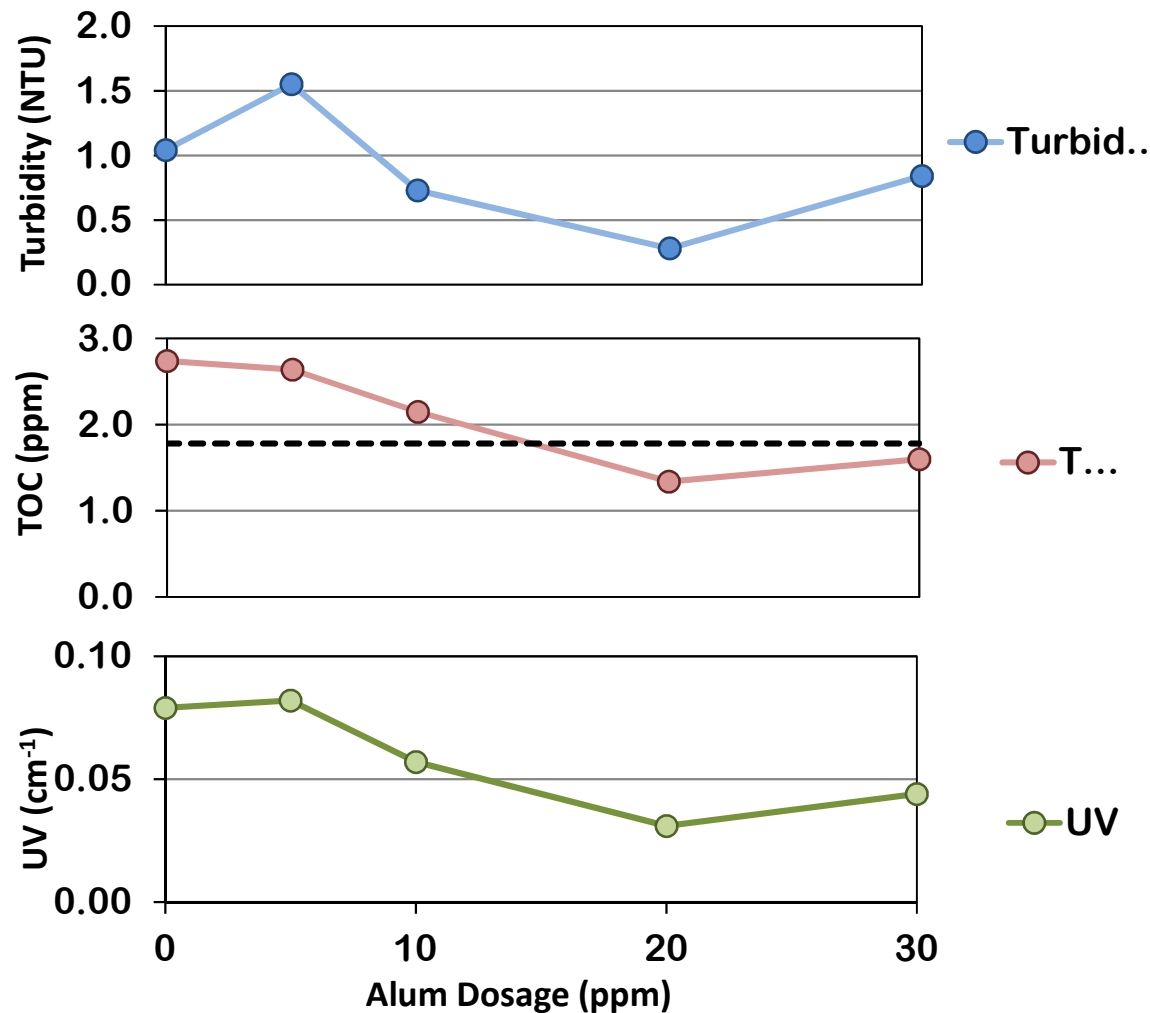
TOC Method:

UV persulfate oxidation
with membrane
conductivity detection
on a Sievers M9 TOC
Analyzer



Experimental Data

Site 1: Saint Vrain River in Lyons, CO

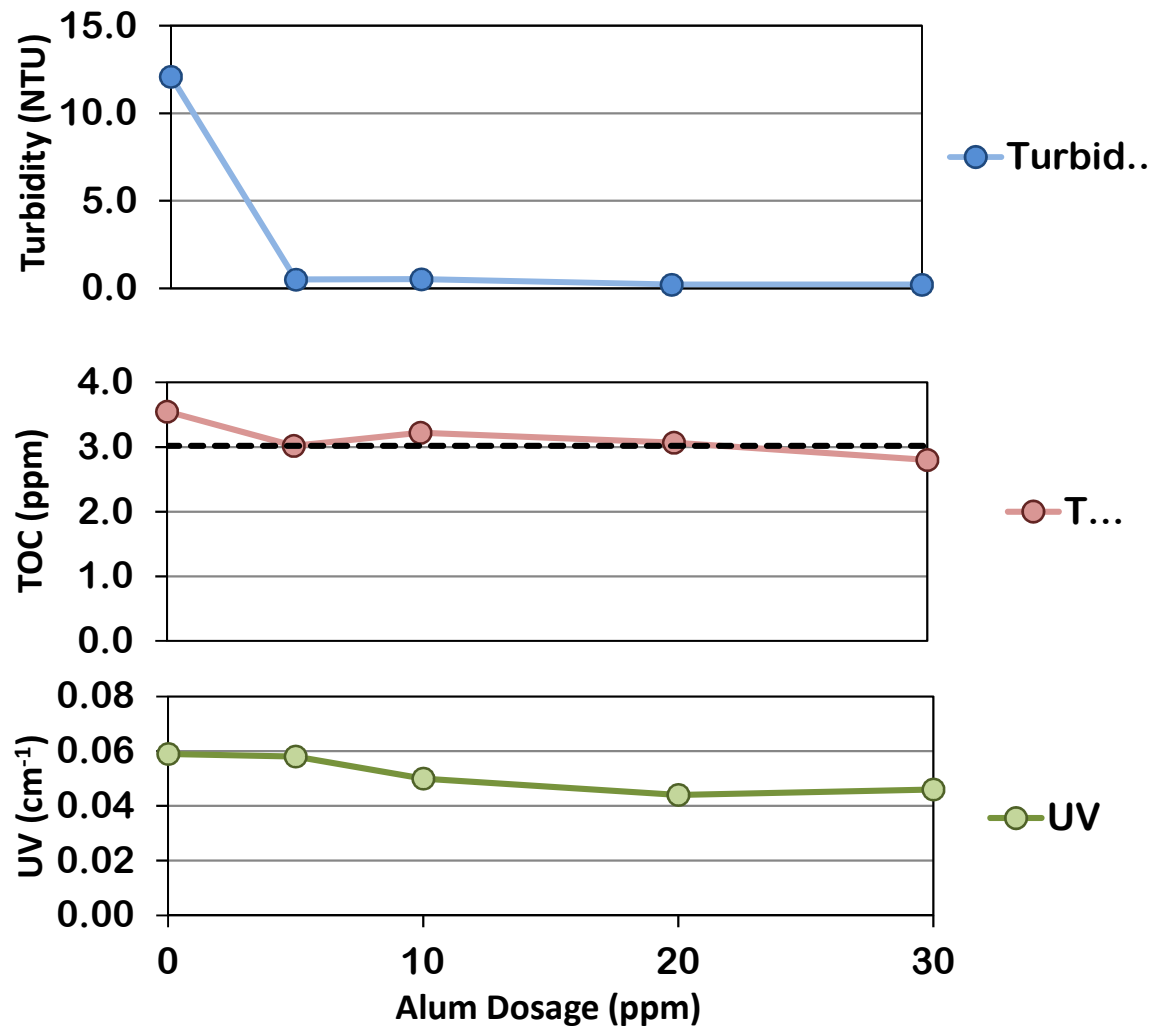


Lowest Turbidity was also lowest TOC and lowest UV

Adding more coagulant did not improve TOC or turbidity removal

Experimental Data

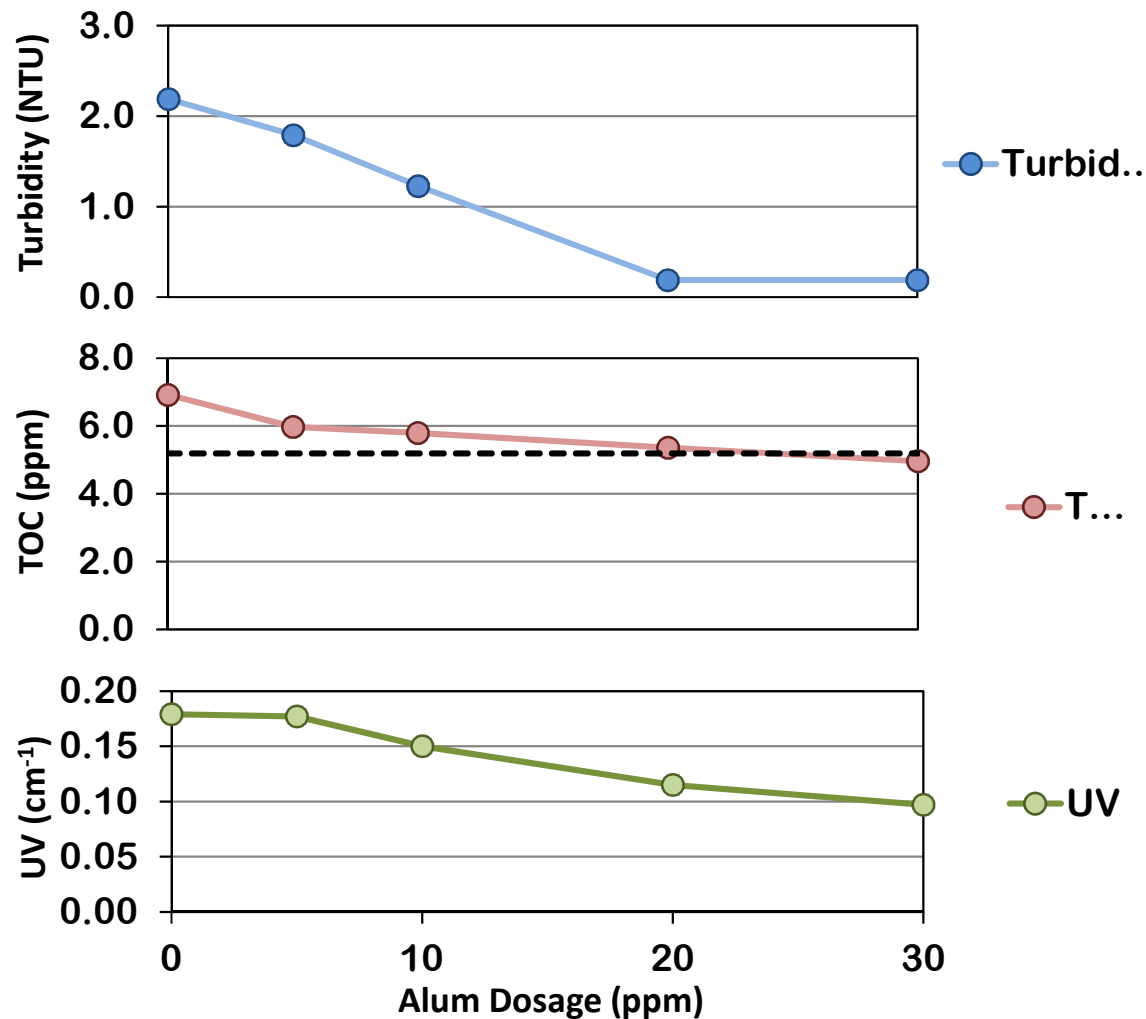
Site 3: Canal water from Gilbert, AZ



20 and 30 ppm Alum dosage had the same turbidity, but the TOC went down with the 30 ppm (even though UV went up)

Experimental Data

Site 4: San Gabriel River from Austin, TX

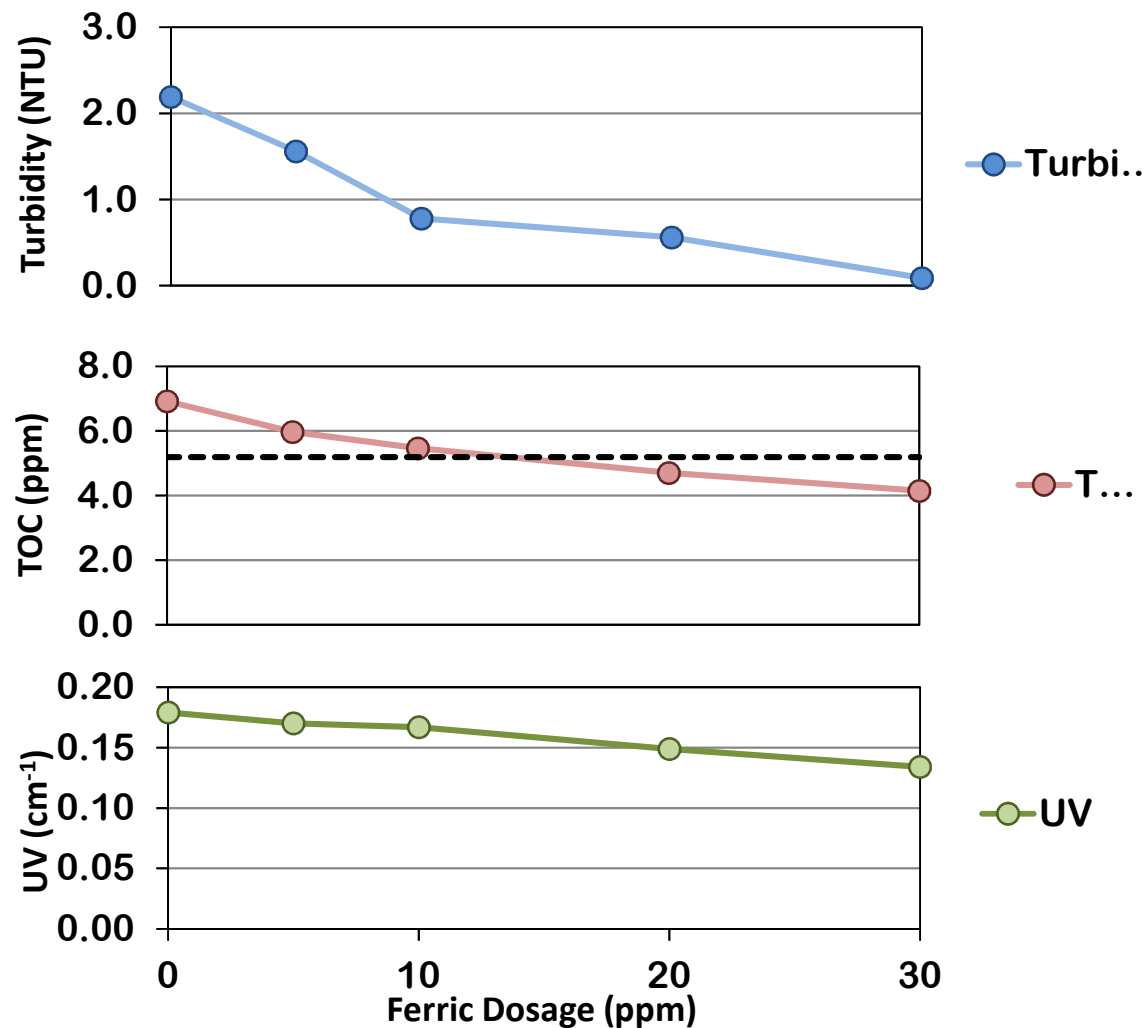


20 and 30 ppm Alum dosage had the same turbidity, but there was slightly better TOC removal with the 30 ppm

But...

Experimental Data

Site 4: San Gabriel River from Austin, TX



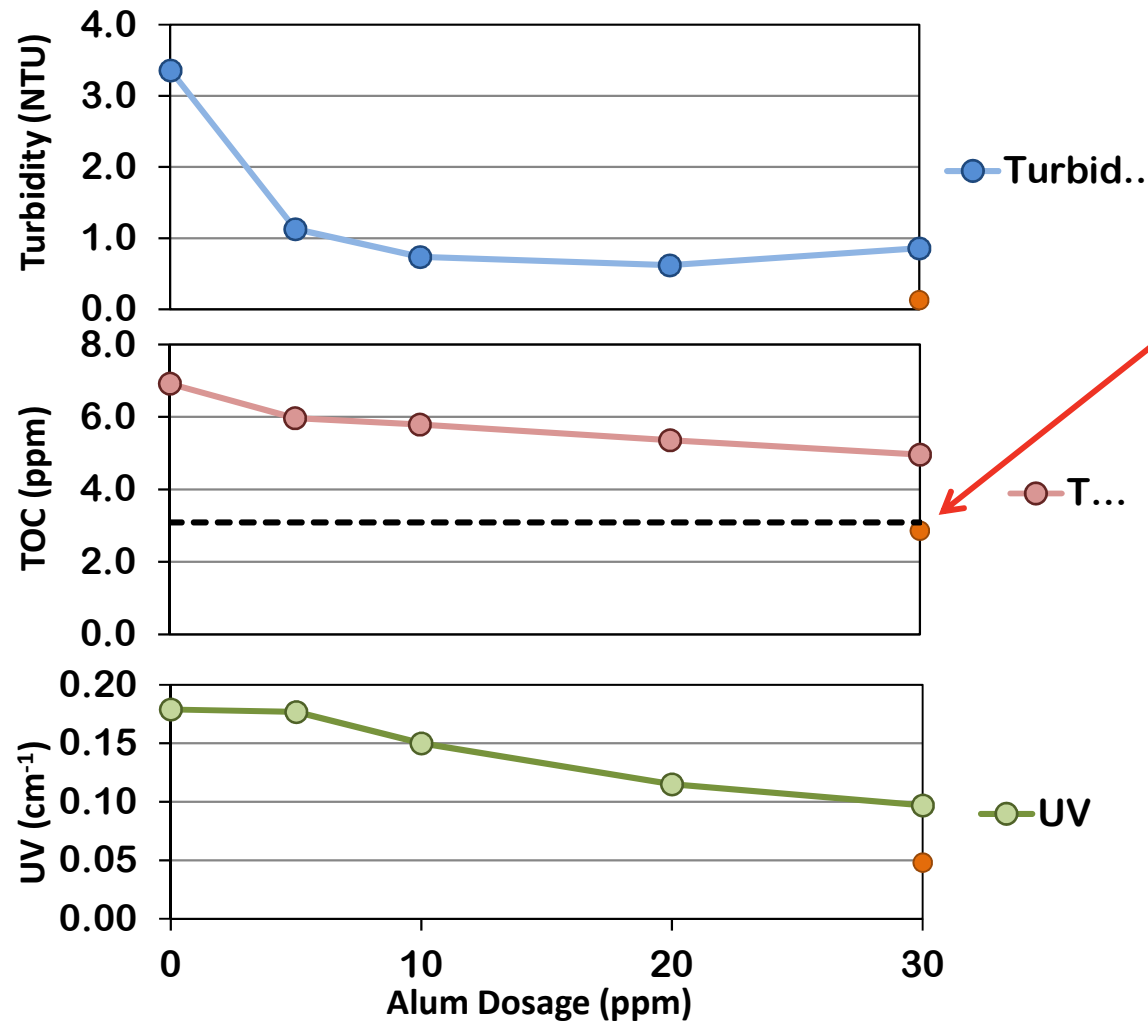
The Ferric was actually a better coagulant than Alum for TOC removal

Could potentially dose less with the Ferric (20 ppm) than the Alum (30 ppm) based on TOC removal

UV with Ferric has interferences, would have picked wrong chemical

Experimental Data

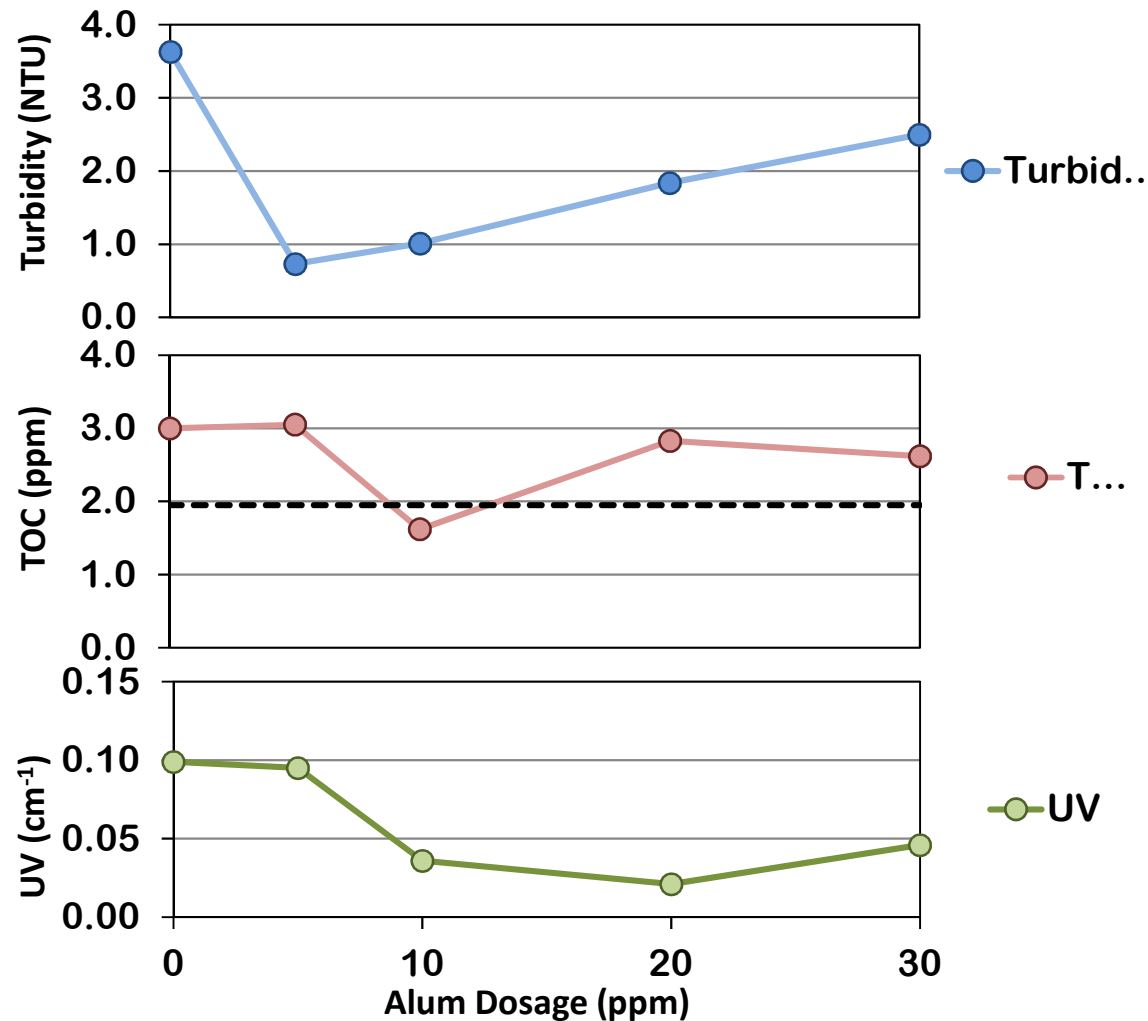
Site 5: Lady Bird Lake in Austin, TX



Adjusting pH to 6.2 on this water with the 30 ppm alum was the only way to remove enough TOC (the turbidity also went down with pH adjustment)

Experimental Data

Site 7: Lake Estes in Estes Park, CO

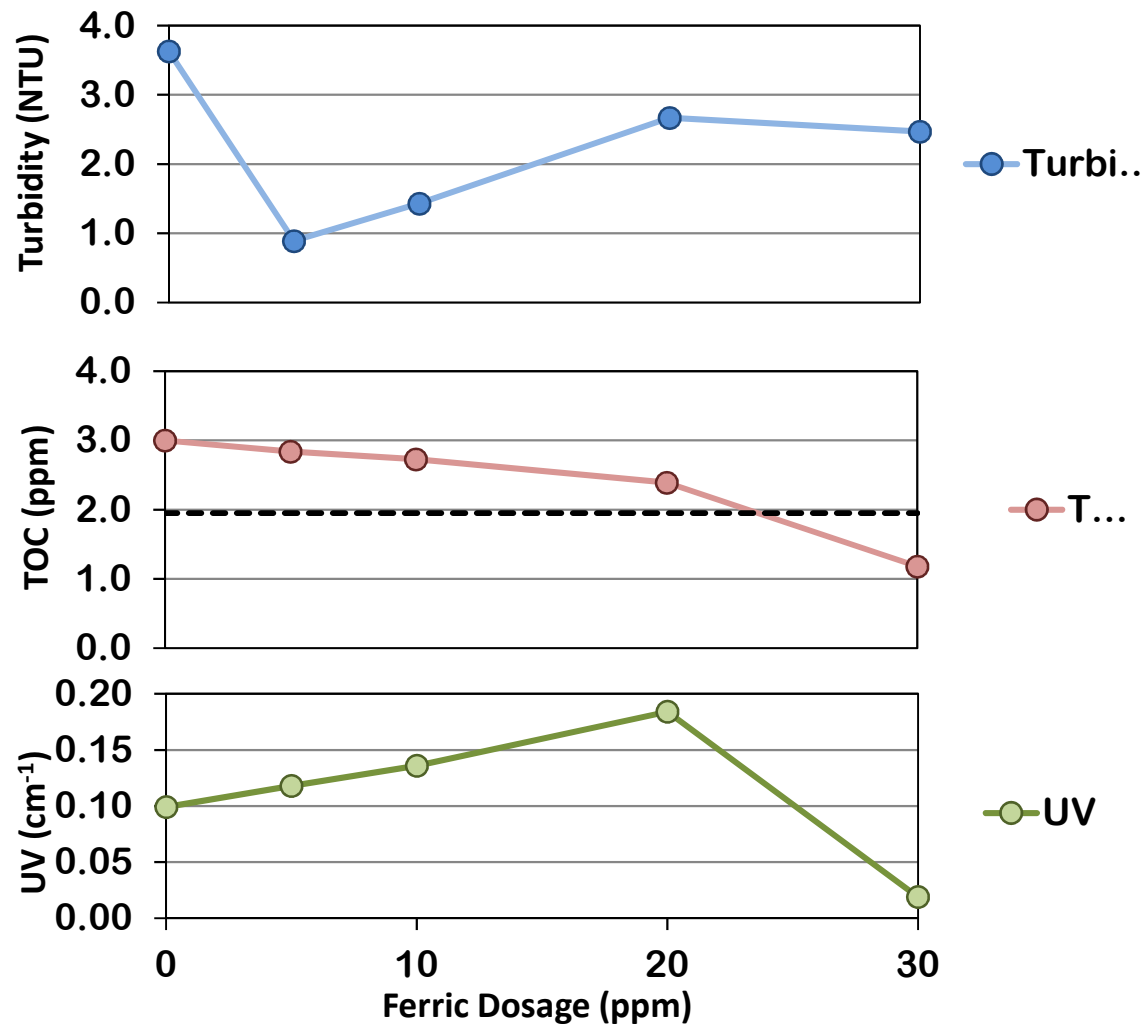


With the Alum, the lowest turbidity (5 ppm Alum) had no TOC removal

And...

Experimental Data

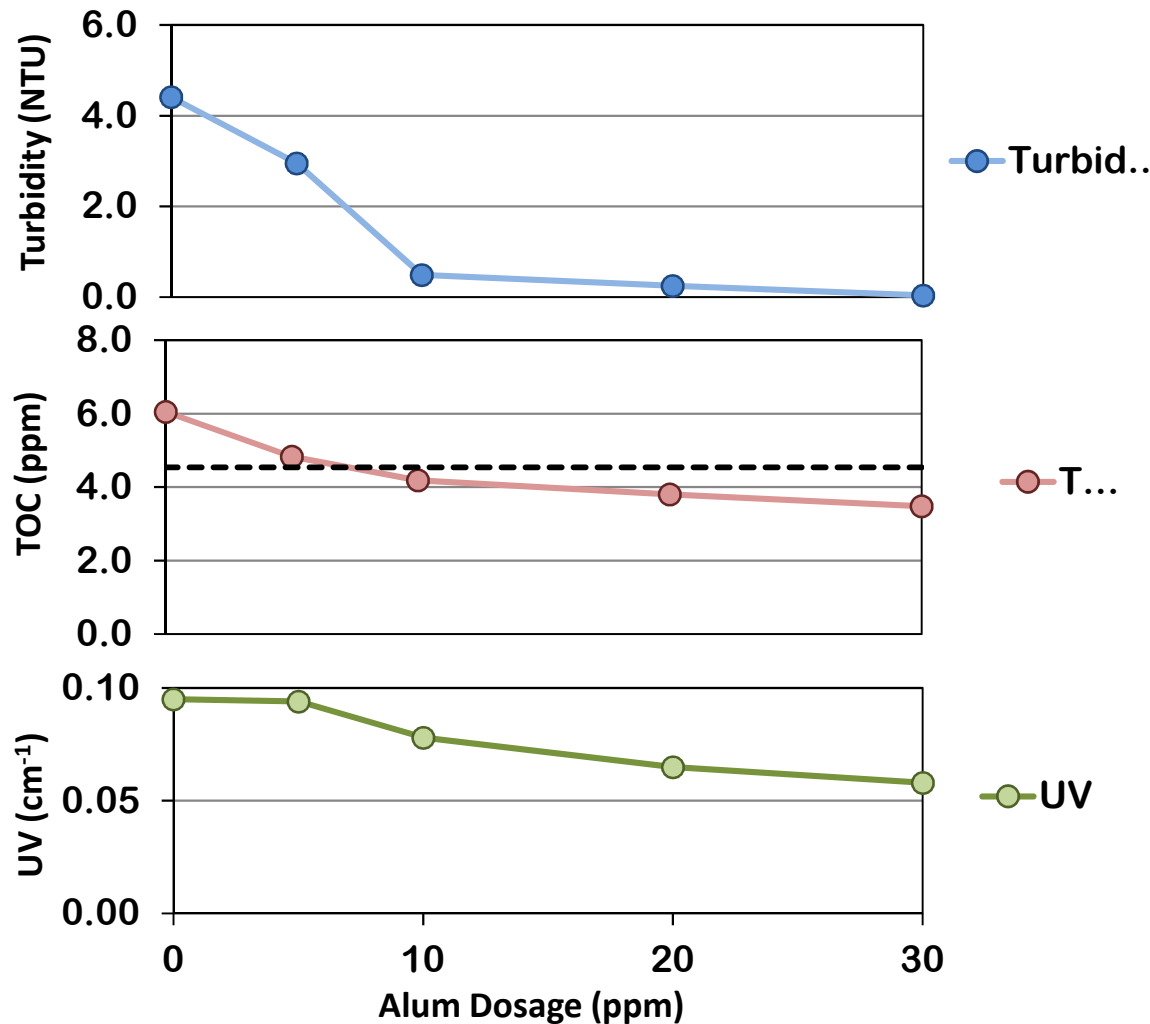
Site 7: Lake Estes in Estes Park, CO



Even the lowest
turbidity with the
Ferric had almost no
TOC removal

Experimental Data

Site 10: Pine Brook Reservoir in Boulder, CO



The lowest turbidity corresponded to the best TOC removal... but it isn't low enough (2.8 ppm) to meet the DBP regulations for this plant

Enhanced Coagulation

Jar Testing – Taking it a Step Further

Enhanced Coagulation and THM Formation Potential Test

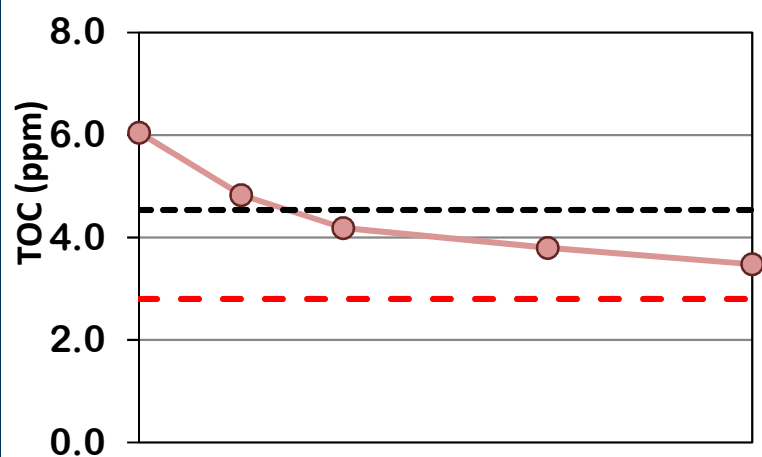
Enhanced Coagulation

Removing more TOC than required for TOC removal to ensure DBP limits are met everywhere in distribution system

THM Formation Potential Test

1. Filter samples through a 5 um syringe filter
2. pH adjust all samples to the same pH
3. Add 5 parts bleach
4. Incubate samples for 24 hours at 25C
6. Measure for residual Chlorine
(lower residual can indicate higher THM FP)

Pine Brook Reservoir



Arkansas 2.2 MGD Plant

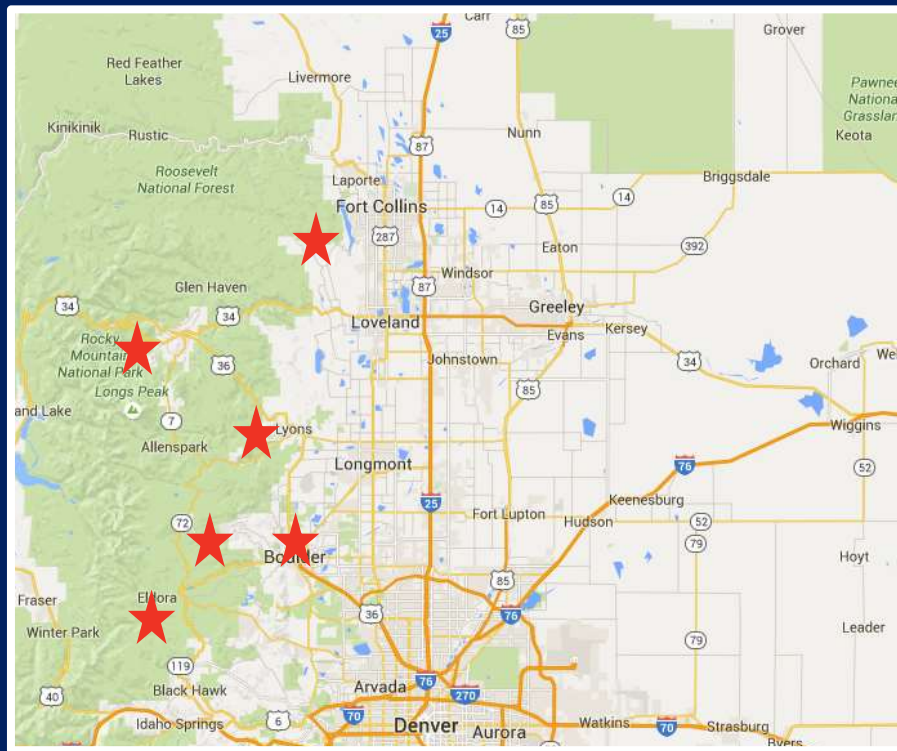
JAR	Settled NTU	TOC	TOC % removal	Residual Cl (THM)
1	0.223	1.47	27%	0.8ppm
4	0.169	1.59	21.3%	0.3ppm (57ppb)
5	0.171	1.63	19%	0.1ppm (75ppb)

Data Summary

- The lowest turbidity and lowest UV corresponded to the greatest TOC removal in **less than half of the sites**
- Sometimes a slightly higher turbidity corresponded to better TOC removal
- At some sites, less chemical dosage is better for TOC removal (but was slightly worse for turbidity)

Value of Using TOC

Every plant is different AND every plant changes throughout the year



✓ Even the six sites in Colorado all showed great diversity in the optimal water treatment

Site	TOC (ppm)	Alkalinity
Coot Lake	3.7	175
Pine Brook Res.	6.1	135
Barker Res.	2.3	25
Lake Estes	3.6	20
Horsetooth Res.	4.9	40
St Vrain River	2.7	40

Value of Using TOC

Choosing the right chemical and proper dosage

Not all chemicals will work best for any given source water

Not all optimal treatment steps (pH adjustment) make the most sense in a process environment

Best to balance cost and treatment options for the long term



Some chemical companies will do blends and/or help optimize chemical dosages for a plant's source water (many of these chemical companies use TOC)

Value of Using TOC

Process Control & Optimization

- Use data to save time and money
- Proactive testing helps operators react to security or weather events
- Real-time data allows for immediate changes without waiting for lab results
- Understand process from start to finish
- Continually improve for optimal performance

Value of Using TOC

Case Study: City of Englewood, CO



Problem: too much sludge and too much money spent on chemicals

Goal: Reduce chemical costs and sludge production

Value of Using TOC

Case Study: City of Englewood, CO



Before: only using turbidity with jar testing

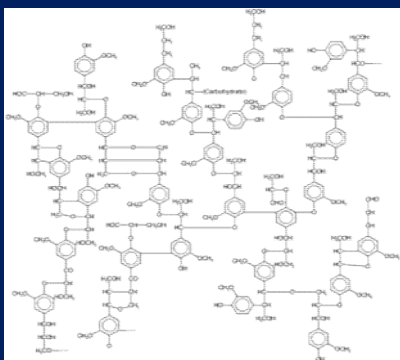
After: expanded jar testing to include TOC and then scaled it up to the whole treatment process

Plant saw a significant reduction in chemicals needed and sludge production

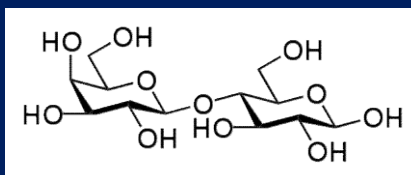
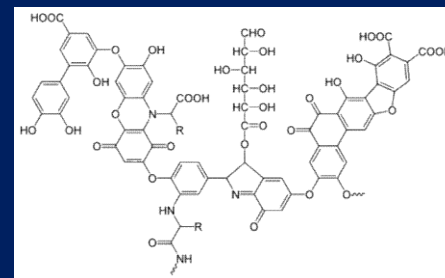
1 year savings of > \$100k in chemical and disposal costs

Size Distribution of Organics

TOC is highly diverse and knowing what compounds make up that TOC can be useful in treatment



Larger molecules tend to be removed better with lower doses of coagulant than smaller molecules

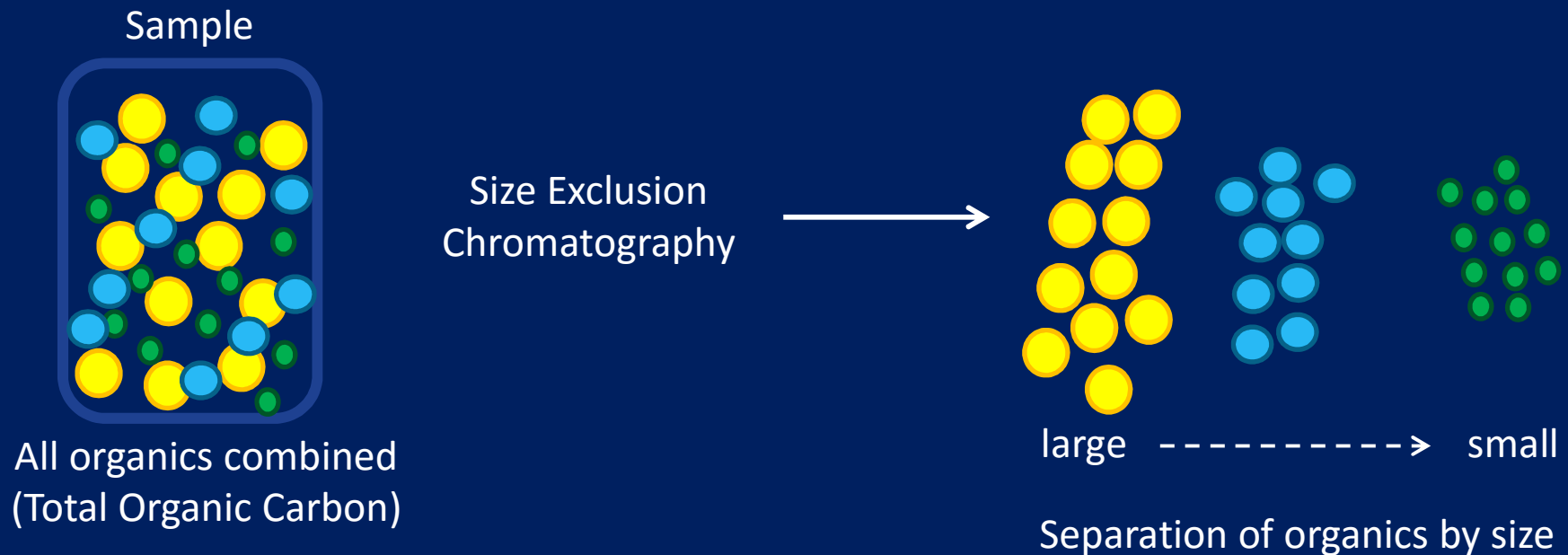


How do you know what is in your TOC?

Size Distribution of Organics

Technology to determine size distribution of organics in water

Size Exclusion Chromatography with both UV and DOC detection

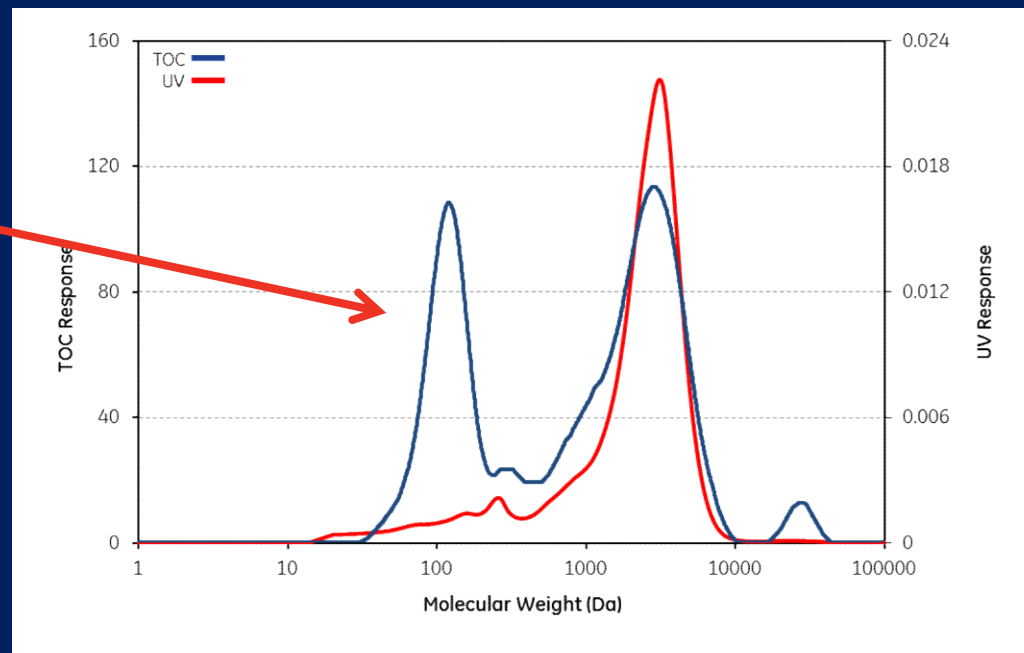


Size Distribution of Organics

Why is this important?

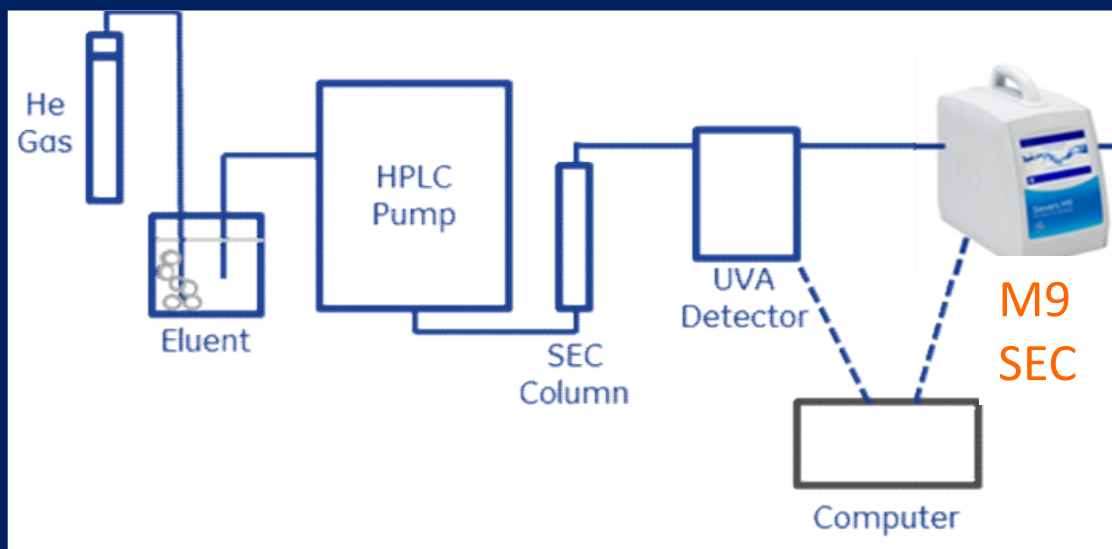
- ✓ DOC detection because not all organics will be detected by UV
- ✓ Organics in some size fractions produce more DBP's (humic acids, etc.)
- ✓ Complete picture or “**footprint**” of the organics to optimize treatment
- ✓ Shows changes in organic characteristics throughout the year

This whole size fraction of organics is not detected by UV!



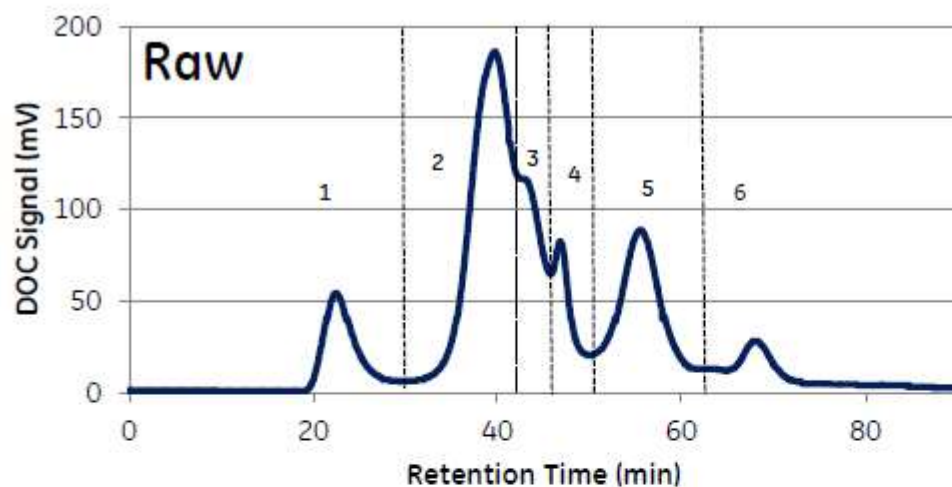
Introduction to the M9 SEC

- Size Exclusion Chromatography (SEC) plus compact, fast, DOC Detector
- HPLC SEC-UVA + DOC detector = better understanding of organics
- HPLC drives sample through the DOC Detector
- Detects aromatic & nonaromatic fractions as a function of MW
- Easily integrated with the HPLC SEC to measure DOC along with UVA

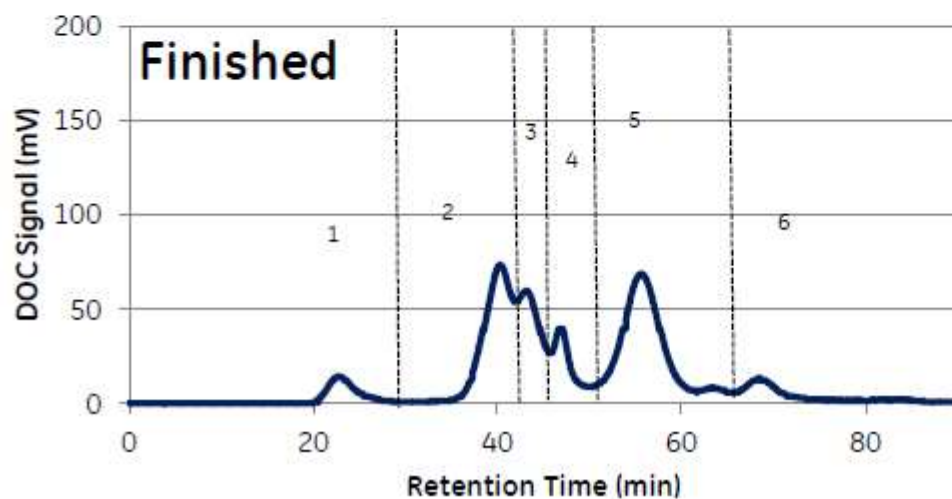


Results give insight into hard-to-remove substances & water treatment efficiency

Size Distribution of Organics

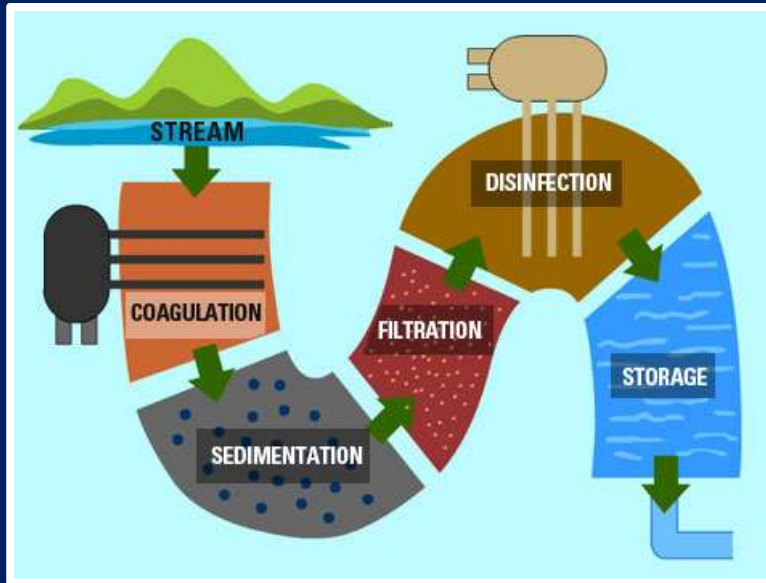


Raw	
Peak #	DOC
1	0.6 ppm
2	2.7 ppm
3	1.0 ppm
4	0.6 ppm
5	1.4 ppm
6	0.6 ppm
Total	6.9 ppm

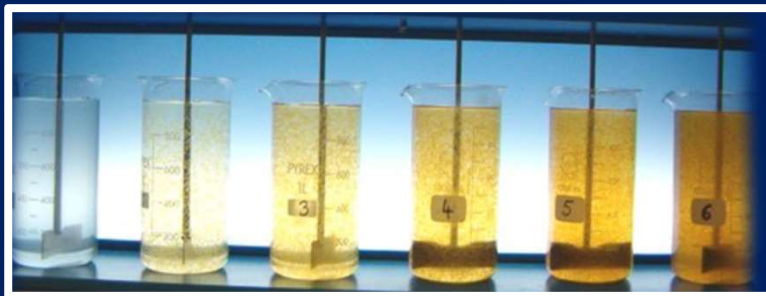


Finished	
Peak #	DOC
1	0.2 ppm
2	0.8 ppm
3	0.5 ppm
4	0.3 ppm
5	1.1 ppm
6	0.3 ppm
Total	3.2 ppm

Summary



- ✓ TOC is important for regulatory requirements (DBP limits and %TOC removal).
- ✓ Jar testing that includes TOC as a measured parameter gives the most comprehensive information on optimizing the treatment process.
- ✓ Every plant has different water that can change throughout the year.
- ✓ Understanding and characterizing organics through a plant can help determine optimal treatment strategies.



Questions?

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