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Challenges – Radium Treatment Requires Sulphate in the Contact Water

- Conventional radium-226 treatment uses addition of barium chloride to raw TMA water, to precipitate barium sulphate (barite), as the TMA water contains sulphate.
- Barite is insoluble and will settle out of treated water co-precipitating/adsorbing radium-226 with it.
- Treated effluent is discharged to the receiving environment. However, seasonal peaks in radium-226 concentrations in treated effluent have been observed at both TMAs. These seasonal peaks typically occurred during spring and fall.
- These peaks were termed 'refractory radium'.





Study Plan

- 1. Create a simple beaker test to determine treatment efficacy (called the 'turbidity test')
- 2. Then conduct bench tests to:
 - Attempt to remove organic compounds and improve treatment efficacy,
 - Attempt to take the extracted organic compounds and reintroduce them to sulphate-spiked distilled water, and
 - Conduct settling tests to investigate how barium and sulphate concentrations affect settling and barite particle size distribution.
- 3. Conduct a field survey to:
 - Investigate the organic compound signature (mass spectrum fingerprint) in water over time, and how it may change during normal treatment efficacy compared to poor treatment efficacy, and
 - Determine if any other analyte may be interfering with barite particle settling other than organics (if not organics, then what?)



Turbidity Test

- Add Ba²⁺ and ferric sulphate to temperature-controlled water and test for turbidity after 20 or 30 minutes (generally mimicking treatment).
- Designed to determine if the treatment plant would have a problem. Allows real-time management decisions (rather than waiting for lab results to come back weeks later).
- Used for bench testing to determine if experiments had removed or added the interference that causes poor treatment efficacy.
- Used weekly on-site to determine if the treatment plant efficacy was 'poor' or 'normal' and to correlate to any observable changes in organic compound fingerprint in raw TMA water.









Activated carbon were 48hrs, Resins were 24 hours.



Turbidity tests showed that without treatment, after 48hrs 'poor' treatment efficacy persisted in TMA-S water.

TMA-P water showed treatment efficacy improvement in both tests. Daily batch testing suggest that the interference that causes 'poor' treatment efficacy may be transient at TMA-P.

Activated carbon will remove organic compounds irreversibly, but we wanted to be able to elute organics from a resin to be able to reintroduce them to distilled.



Bench Tests – Settling Efficacy

We conducted multiple column tests varying the amount of sulphate and barium, using TMA water for Stanleigh (when refractory and non-refractory) and Panel (refractory only), and distilled water. Data also suggested that, as barite saturation index increased, particle size increased.





Barium was at 111mg/L. Particle size also increased with saturation index.



Field Survey – Organic Mass Spectral Fingerprint

We collected organic fingerprint spectrum using HPLC-ESI-QQQ-MS* in raw Stanleigh and Panel TMA water and the TMA tributaries, weekly for 33 weeks. We categorized the results into 'poor' and 'normal' treatment efficacy by running synchronous weekly turbidity tests.



These 3D spectra represent several weeks of data overlaid for raw Stanleigh TMA water in negative ion mode.

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Summary

- Addition of humic and fulvic acids (at environmentally relevant concentrations) also caused poor turbidity test results in sulphate-spiked distilled water.
- The removal of the interference that causes poor treatment efficacy (barite particle settling) was achieved using activated carbon, and a hydrophobic resin.
- Particle size was improved with increasing saturation index.
- Settling tests showed that refractory water from Stanleigh influenced settling efficacy, while this was much less the case using water from the Panel TMA.
- There was evidence to suggest that organic compounds around 400 to 1,000 m/z (retention time 10 minutes) may be the cause. These ions were negatively charged.
- A comparison of Stanleigh TMA to Panel TMA suggested that the organic compounds have different acid dissociation constants among TMAs.
- These data provided weight of evidence to suggest that organic acids are the interference that causes poor treatment efficacy at the Stanleigh TMA, with something slightly different happening at the Panel TMA.



Hypotheses

The cause of refractory radium was:

- 1. The seasonal presence of organic compounds.
- → True at Stanleigh, not true at Panel
- 2. An unidentified analyte, present at concentrations sufficient to interfere with [Ba] at ppm levels.

 \rightarrow Possibly true at Panel (data not shown), but likely organics at Stanleigh, the difference may be the lower sulphate concentration at Stanleigh.

3. The same at both TMAs (Stanleigh and Panel TMAs).

 \rightarrow The cause appeared to be different at the two TMAs, however, this may change as sulphate concentrations decrease at Panel (towards lower existing sulphate concentrations at Stanleigh).

4. Decreasing sulphate concentrations in the TMAs are a contributing factor.

→ Settling tests showed that decreasing sulphate or barium would decrease settling efficacy. It is unclear if differences in sulphate concentration at Stanleigh and Panel TMAs could account for other differences in potential causes of refractory radium.

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