Radium-226 treatment 20 years post uranium mine closure

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Abstract

In Elliot Lake, Ontario, uranium mining occurred from the 1950's until the 1990's when decommissioning took place. Within the Elliot Lake area, Rio Algom Limited owns eight tailings management areas (TMAs) which are currently (since the mid-1990's to present day) in active care and maintenance with management focused on water management, treatment, and environmental monitoring. Of the eight TMAs, four are flooded.

Radium-226 is a parameter of concern associated with mine impacted water and monitored within the receiving environment. Raw water from the TMAs also contains sulphate due to the historical use of sulphuric acid to extract uranium as well as sub-aerial pyrite oxidation of tailings prior to flooding. The decommissioning environmental impact statement (EIS) predicted that within the flooded TMA basins, radium-226 and sulphate concentrations would decrease over time. As part of the closure and decommissioning process for the Elliot Lake mines, a focused and integrated performance monitoring framework was developed to monitor contaminants of concern at the source (within the TMAs), within the pathways (treated effluents and seepage), and within receiving environments.

Since decommissioning, the TMAs have exhibited a trend towards decreased radium-226 and sulphate concentrations as was predicted in the decommissioning EIS. However, effective (conventional) treatment for radium-226 has relied upon elevated sulphate concentrations that were present in the raw TMA water. Conventional radium-226 treatment involves barium chloride addition to raw TMA water to induce barite (barium sulphate) precipitation, which co-precipitates and/or adsorbs radium-226. These treatment solids settle out prior to discharge of the clarified water to the receiving environment.

Thermodynamically, barite will precipitate at the decreased sulphate concentrations currently (2022) observed within the basins. However, barite precipitation and settling prior to discharge has become increasingly challenging. Radium-226 monitoring has shown that treatment efficacy decreases during periods of high precipitation in the spring and fall. In this study, a combination of bench tests with field surveys were used to test the hypothesis that treatment challenges are caused by seasonal influx of organic acids, combined with the dilution of sulphate due to run-off. These tests were completed in two flooded TMAs at Elliot Lake, where each TMA responded differently with respect to the characteristics of organic acids and how they interfered with barite precipitation and particle settling. This phenomenon has the potential to affect other decommissioned TMAs where radium-226 is being treated using barite precipitation.

Keywords: *radium-226, sulphate, post-closure, water treatment, barite*

1 Introduction

1.1 Site background

Uranium mining was undertaken in the Elliot Lake area of northeastern Ontario for approximately forty years. Rio Algom Limited (RAL), a wholly owned subsidiary of BHP, maintains two decommissioned uranium tailings management areas (TMAs), the Stanleigh TMA and the Panel TMA which will be the focus of this paper.

The Stanleigh uranium mine operated from 1958 to 1960 and again from 1983 until closure in 1996. Twenty million tonnes of tailings were produced during mine operation and deposited in the TMA (Figure 1). The

TMA is a flooded basin located in the lake formerly known as Crotch Lake and contained by five low permeability dams. Water level management is required to ensure tailings saturation as well as dam stability, and the required water level was achieved by flooding the TMA basin which took place from 1998 to 2002.
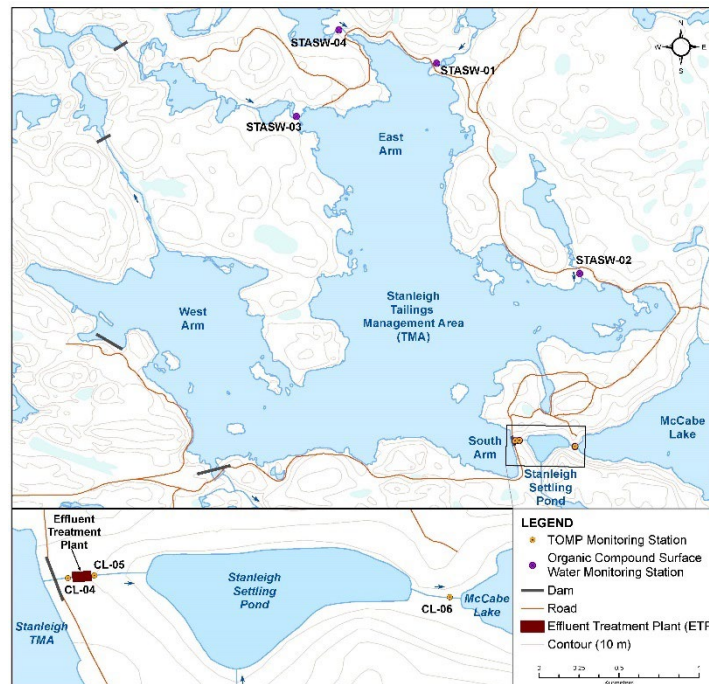

Figure 1   The Stanleigh TMA with field survey water collection stations

The Panel uranium mine operated from 1958-1961 and again from 1979 to closure in 1991. The 15 million tonnes of tailings in the Panel TMA were deposited in two principal areas. The 84 ha Main (north) Basin occupies the former location of Strike Lake, which flows into the 39 ha South Basin (Figure 2). Tailings and water are presently contained within a bedrock perimeter and four containment dams. The smaller South Basin contains a relatively small quantity of tailings deposited in the late 1950s. It is contained by two low permeability dams and berms. Similar to the Stanleigh TMA, water level management is required to ensure tailings saturation as well as dam stability.

At closure, a focused and integrated performance monitoring framework was developed to monitor contaminants of concern at the source (the TMA operational monitoring program; TOMP), within the pathways (source area monitoring program, SAMP i.e., treated effluents and seepage), and within receiving environments (the Serpent River Watershed Monitoring Program; SRWMP). The performance monitoring framework identified mine indicator parameters or parameters of concern associated with the TMAs and included radium-226 and sulphate for the flooded basins (Minnow Environmental Incorporated (Minnow) 2005). In addition, environmental impact statements for the Stanleigh and Panel TMA facilities predicted that both radium-226 and sulphate concentrations would decrease over time (RAL 1995a and RAL 1995b).

Both facilities utilised conventional treatment for radium-226 in water, involving taking raw TMA water, adding lime for pH and dissolved metals control, and barium chloride for radium-226 control. The barium chloride is intended to react with the sulphate that is already present in the TMA water, to precipitate barium sulphate (barite), which also co-precipitates and/or adsorbs radium-226. Co-precipitation/adsorption of radium-226 removes it from the dissolved phase. This water (from the effluent treatment plant) then flows into settling ponds, where barite particles settle (along with radium-226), prior to being discharged into the receiving environment.
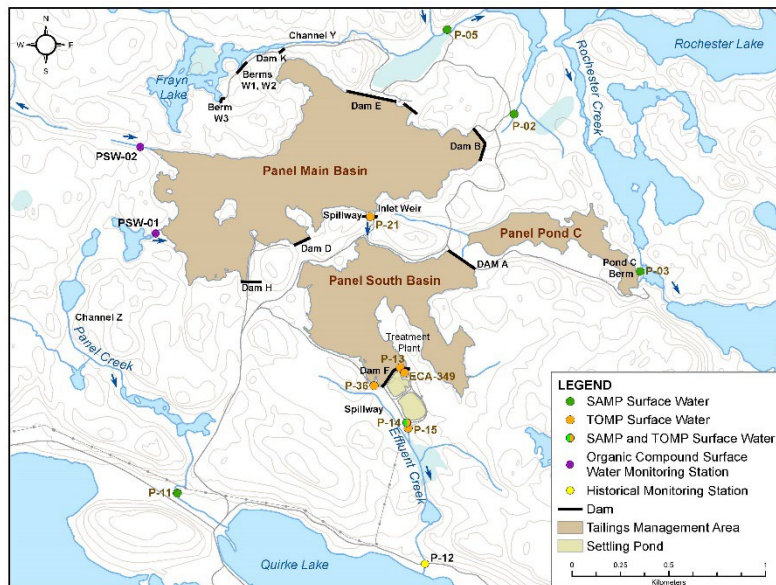
Figure 2   The Panel TMA with field survey water collection stations

1.2   Study objectives

Despite ongoing monitoring showing decreases in sulphate and radium-226 within flooded basin raw water as predicted in the EIS's, spikes in radium-226 in treated effluent have been observed seasonally (spring and fall) at the Stanleigh TMA starting in 2008, and more recently at the Panel TMA starting in 2017. Thermodynamically, barite will precipitate at the decreased sulphate concentrations currently (e.g., in 2022) observed within the basins. However, barite precipitation and settling prior to discharge has become increasingly challenging. Periods where radium-226 treatment using the conventional methodology becomes more difficult have been termed 'refractory'. In this study, a combination of two discrete pieces of work, bench tests and field surveys, were used to test the following hypotheses:

1. The cause of radium-226 treatment inefficiency is organic compounds.

2. The cause of radium-226 treatment inefficiency is an unidentified analyte that is present at a concentration sufficient to interfere with milligram-per-litre concentrations of barium.

3. The cause of radium-226 treatment inefficiency at the Stanleigh TMA is the same for the Panel TMA.

4. Decreasing sulphate concentrations in the TMAs are a contributing factor to the occurrence of refractory radium.

The bench testing scope of work involved a series of laboratory tests to investigate ways of removing or adding organic carbon, investigating if water from the two TMAs responded to tests in the same way, and using settling tests to investigate how changing sulphate and barium concentrations may change settling efficacy of barite particles. This work occurred over two phases (2020 and 2022). The first phase provided several approaches to testing the hypotheses, and the second phase allowed for the refinement of experimental methods and to test reproducibility.

The field survey scope involved weekly sampling at the two TMAs to determine if there were changes in water chemistry that may correlate to the occurrence of refractory radium, and potentially identify a source of the interference (e.g., a tributary to the TMA or the TMA itself). Both approaches (bench-scale testing and field survey) were conducted during two cycles of refractory radium. The intention of this was to verify findings and establish reproducibility from the first period of refractory radium, using a second period of refractory radium.

2   Methodology

2.1   Identifying refractory conditions

When treated water is exhibiting refractory radium conditions, barite particle growth is adequate for particle settling in comparison to non-refractory conditions, where settling is effective. For the purpose of this and other investigations, refractory radium was defined as when the total radium-226 concentration was equal to dissolved above a critical threshold of 0.2 Bq/L (Minnow 2022). Typically, refractory conditions are detected upon review of laboratory results for total and dissolved radium-226. As laboratory results can take days to weeks to receive, a field test was required to detect refractory conditions on a daily, if not hourly, timescale as refractory conditions are transient in nature. Therefore, a timed turbidity test was developed whereby temperature controlled (8 to 12°C) influent water was tested for refractory nature by adding reagents (barium chloride similar to the conventional treatment) to simulate treatment and then testing for turbidity (measured in NTU). Low turbidity test results (<10 NTU) were indicative of refractory conditions (poor treatment efficacy), whereas high turbidity test results (>10 NTU) were indicative of chemical precipitation and suggested less refractory to non-refractory conditions (normal treatment efficacy). Very low turbidity test results (<2 NTU) were considered to be 'severely' refractory conditions.

The bench-scale investigation used the turbidity test exclusively to determine if the raw TMA water used in the bench tests would be expected to give a refractory response under conventional treatment. The field survey used the turbidity test to detect if the Stanleigh TMA would be categorised as refractory if conventional treatment had been in operation. The Stanleigh TMA no longer uses barium chloride addition (conventional treatment) at the ETP, instead additions of pre-formed barite are used. However, the field survey refractory indicator at the Panel TMA was total and dissolved radium-226 concentration in the treated water.

2.2   Bench test investigation

2.2.1   Overview

The bench tests were designed to investigate Hypotheses 1, 3, and 4.

The premise of the experimental design for the bench tests was based on an observation that treatment solid barite particles are smaller during periods of treatment inefficiency (refractory radium) compared to when treatment was efficient and barite particle size was observed to be larger (Minnow 2022). Bench testing was conducted from 16th to 24th November 2020 and from 20th April to 1st May 2022, which captured a refractory period each in the spring and fall. Raw TMA water used for bench testing was tested for refractory response daily using the turbidity test.

The potential for organic compounds to be the cause of refractory radium was tested using several approaches:

- Commercially available organic acids were added to sulphate-spiked distilled water.

- Attempts were made to remove organics from sample (TMA) water using:

  ○ ozone (irreversible extraction) and ion exchange resins (reversible extraction) 1;

  ○ activated carbon (irreversible extraction);

  ○ hydrophobic resin (reversible extraction).

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[1] Treatment was not successful when using ozone or two ion exchange resins (Amberlite[TM] IRA 958 and IRA 410 resins) to attempt to remove the refractory response from Stanleigh TMA (CL-04) water and compared to control (distilled) water. Therefore, these methods will not be discussed further.

- Following their removal from sample water, extracted organic compounds were re-introduced to sulphate-spiked distilled water to determine if it is the substance causing the interference (reversible extraction only; Figure 3).
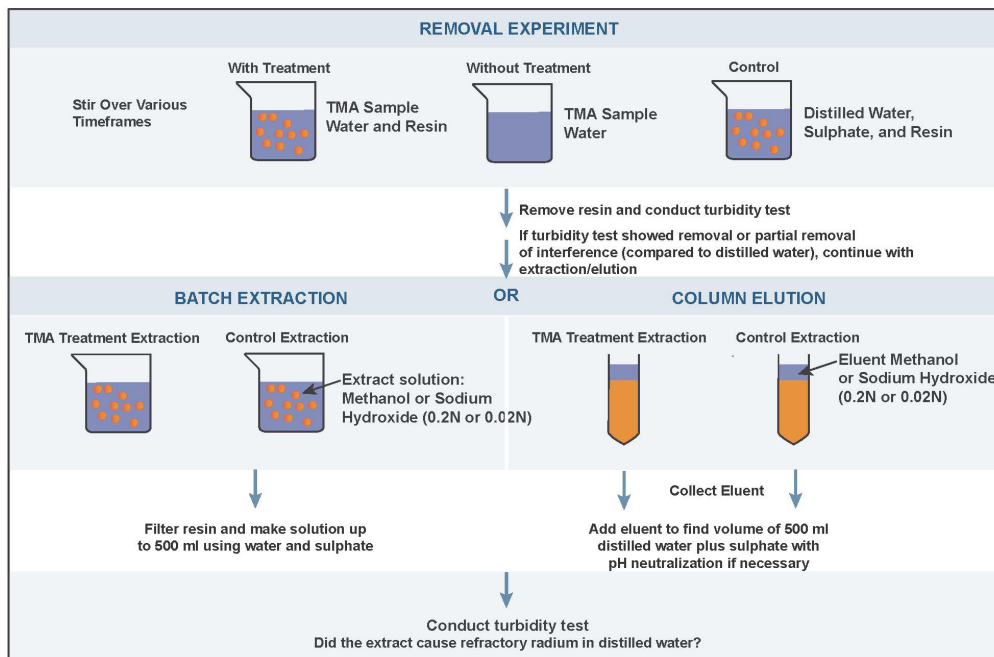

Figure 3   Schematic outlining extraction and re-introduction of interference hypothesised to cause refractory radium

Each experiment was based on changing water quality (i.e., sulphate concentration, addition of commercially available organic compounds, removal of natural organic compounds from the raw TMA water, or addition of TMA-extracted organics to distilled water) and using distilled water spiked with TMA-level sulphate concentrations for control experiments.

2.2.2   Addition of commercially available organic acids

Artificial organic acids (humic acid and fulvic acid) were added to sulphate-spiked distilled water at environmentally relevant concentrations. Humic acid (≥98% purchased from Thermo Scientific Chemicals) was used to create an 8 g/L stock solution using distilled water, and laboratory analysis of organic carbon content was used to verify this concentration. A stock solution of 10 mg/L fulvic acid (a fungal metabolite, CAS No. 479-66-3, purchased from Caymen Chemicals) was made in the same way. The resulting test water was then subjected to the turbidity test to determine if these artificial organic compounds could cause refractory conditions in the water. If so, this would provide weight of evidence that organic acids can cause refractory radium.

2.2.3   Activated carbon to remove organic compounds

Activated carbon was used to remove organic acids from TMA water under various experimental conditions. A sulphate-spiked distilled water method blank was tested alongside the first experiment water as a control. Powdered activated carbon (Norit® GSX powder, steam activated, acid washed) was more effective than granular (Norit® ROW 0.8 mm pellets) likely due to increased surface activity. Some experimental conditions were changed to attempt to improve organic extraction, these were pH (testing conditions of pH 3 and raw TMA water pH), ionic strength, extraction temperature, and extraction time. After the extraction period, the activated carbon was removed from the experiment water by vacuum filtration (polyether sulfone filters, 0.45 µm pore size, 47 mm diameter), and the experiment water was subjected to the turbidity test.

2.2.4   Hydrophobic resin to remove and re-introduce organic compounds

2.2.4.1   Removal of organic compounds

A hydrophobic resin (Amberlite® XAD®-16) was tested for use in organic extraction from experiment water (raw TMA water CL-04 and P-13, and control [distilled] water). Prior to use, the resin was cleaned according to Lepane (1999). Each water type was treated with resin under varying conditions, to attempt to improve the ability of the resin to remove the interference that causes refractory radium. Briefly, test water (500 mL) was measured and transferred to a borosilicate glass test beaker (1L). Using a centrifuge tube, 30 mL of loosely packed XAD-16 resin was added to each test beaker. For tests with a pH adjustment, hydrochloric acid was added to the test beaker to decrease the pH to 2.0 and the samples were then stirred for 4 hours at room temperature.

After the treatment period, the resin was removed by vacuum filtration. Sodium hydroxide was added to the test water to adjust the pH back to 6.5, the test water was then tested for turbidity (at a controlled temperature). The resin was collected into a labelled sample vial (50 mL metal-free centrifuge tube) using a plastic utensil and dilute hydrochloric acid added (0.01 M) according to Lepane (1999), in case it could be used for extraction experiments.

2.2.4.2   Addition of extracted organic compounds to sulphate-spiked distilled water

If successful in removing the interference, various experimental conditions were trialled to elute the organic compounds that had been extracted from the TMA water. This most successful method involved loading the resin as a slurry (with dilute hydrochloric acid) into glass columns (Bio-Rad Glass Econo-Column® Columns) to a bed volume of 20 mL. Once filled, the column was connected to a glass reservoir (Bio-Rad Econo-Column® Reservoir). The reservoir was loaded with dilute hydrochloric acid (100 mL of 0.01M) and allowed to gravity-flow through the column at an average rate of 3.3 mL/min. The weak acid rinse was discarded and 100 mL of 0.2M NaOH was used to elute the column over approximately 20 minutes, until it ran dry. Distilled water was added to the eluent for a total volume of 500 mL. This test water was then brought back to pH 6.5 to 7 using hydrochloric acid and spiked with sulphate to 45 mg/L and 78 mg/L for tests that contained organic extract from Stanleigh TMA water and Panel TMA water respectively. The sample was then tested for a refractory response using the turbidity test, at a controlled temperature.

2.3   Settling tests

Settling tests were designed to prove or disprove Hypothesis 4 'Decreasing sulphate concentrations in the TMAs are a contributing factor to the occurrence of refractory radium'. The experimental design varied (1) concentrations of barium and sulphate; and (2) molar ratios of barium to sulphate. The outcome of these variations was then investigated with respect to the particle size distribution of barite, whether it could be expected to settle in the Stanleigh Settling Pond, and whether TMA water contained interferences that influenced particle size or settling (using settling as an approximation for 'treatment efficacy').

The settling test chambers were in-house constructed plastic polycarbonate columns that were 50 cm in length, allowing for any particulate to settle through a distance of 45 cm during a test time of 11 hours[2]. The distance was considered the conservative distance necessary for a particle in the Stanleigh Settling Pond to settle through the surface mixed layer such that it will ultimately settle to the pond bed. This distance was estimated, based on a calculated vertical mixing depth of 20 cm (assuming the low turbulent diffusivity that is typical of a small water body; Chowdhury et al. 2015), as well as the spillway invert depth of 15 cm, which was multiplied by three to introduce conservatism.

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[2] The settling time (11 hours) was the shortest seasonal hydraulic retention time empirically determined in the Stanleigh Settling Pond during the spring (Calder Engineering Limited 2017).

Test water for the settling chambers was spiked to the required sulphate and barium concentrations and then stirred at room temperature for one hour, half of this solution was collected as a time-zero (t_0) sample, and the remaining half was poured into the settling chamber. After 11 hours in the settling chamber, the water sample from the top 45 cm of the settling chamber was collected by syphon. The t_0 and t_{11} samples were shipped in coolers with ice packs overnight to the University of Northern British Columbia for analysis of particle size distribution using a Malvern Mastersizer 3000, and to ALS, Waterloo, ON for analysis of total suspended solids (TSS), and total dissolved solids.

Time-zero and t_{11} samples of TSS were used to calculate a 'settling efficacy' for each of the settling tests. Knowing the barium and sulphate concentrations in the TMA water, as well as the known spike concentrations (depending on the experiment), PHREEQC[3] modelling was conducted to determine how much barite could be expected to precipitate on a thermodynamic basis. The concentration of TSS that remained in the settling chamber at t_{11} was subtracted from the TSS at t_0 and the result was assumed to be the amount of barite that had settled.

2.4 Field survey investigation

A field survey was completed whereby weekly water samples were collected at each TMA, the treatment plant influent and effluent, as well as the major tributary to the flooded basin of the TMA. The weekly field survey took place during treatment plant operation only and took place from 7th December 2021 to 3rd May 2022 at the Stanleigh TMA and from 13th December 2021 to 24th May at the Panel TMA.

To test Hypothesis 2, laboratory analysis included use of high-performance liquid chromatography electrospray ionisation tandem mass spectrometry (HPLC-ESI-MSMS)[4] to investigate if changes in the occurrence of refractory radium coincided with changes in the organic compounds (mass spectrum fingerprints), as well as a suite of supporting analytes (metals, organic carbon, anions, pH) that are present in water. Results from the HPLC-ESI-MSMS were visualised and analysed through a gridded approach where each mass spectrum was converted to a two-dimensional grid representing HPLC retention time (y-axis) and mass-to-charge ratio (m/z; x-axis).

The resulting laboratory data (HPLC-ESI-MSMS intensity grids and other supporting analytes) were compared to indicators of refractory radium in each TMA to determine if any analytes, particularly organic compounds, positively correlated with refractory radium events. The strength and direction of associations between indicators and water quality parameters were tested using a Spearman rank correlation analysis. Spearman's rank correlation was used so as not to assume that correlations should be linear or take any other specific mathematical form. All data screening and compilation, and subsequent analyses were conducted using R (R Core Team, 2021).

The approach to categorise the refractory status at each TMA was different. At the Stanleigh TMA, where treatment used pre-formed barite (i.e., no longer using conventional treatment with barium chloride), a turbidity test (Section 2.1) on raw TMA water was used to predict if treatment solids would precipitate. At the Panel TMA where conventional treatment was used for the majority of the field survey, total and dissolved radium-226 concentrations were used, and followed the definition of a refractory status as per Minnow (2022).

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[3] PHREEQC software is a thermodynamic equilibrium geochemical speciation/mass transfer model (Parkhurst & Appelo 1999). Input data for PHREEQC modelling used anion and cation concentrations of analytes using date-matched monitoring data for stations CL-04 and P-13 depending on whether settling tests were conducted in 2020 or 2022.

[4] Method developed in association with Testmark Laboratories with acknowledgement and thanks to Laurentian University.

3 Results

3.1 Bench test investigation

3.1.1 Determining refractory status

In 2020, raw Stanleigh TMA (station CL-04 [Figure 1] with sulphate concentration 45 mg/L) water daily turbidity test results were consistently low with turbidity ranging from 0.01 to 2.5 NTU, compared to the control (distilled water spiked with sulphate at 45 mg/L) with turbidity ranging 8 to 13 NTU. Thus, Stanleigh TMA water remained in the refractory state throughout the 2020 bench-testing period. In 2022, raw Stanleigh TMA (CL-04) water daily turbidity test results were low (i.e., less than 6 NTU) and therefore refractory for the respective sulphate level (36 mg/L).

In 2020, daily raw Panel TMA (P-13) water turbidity test results remained in the refractory state throughout. Although, the turbidity results increased towards the non-refractory boundary (i.e., towards 10 NTU) with the last four days of the 2020 test period. Similarly, in 2022, daily Panel TMA (P-13) water turbidity test results remained in a refractory state throughout and the turbidity results increased towards the borderline boundary (i.e., towards 8 NTU) near the end of the test period.

3.1.2 Addition of artificial organic acids

The turbidity test results showed that the introduction of both artificial organic acids induced a 'refractory' status in sulphate-spiked distilled water once the organic acids reached a sufficient concentration, 6 mg/L for humic acids and 3 mg/L for fulvic acids (Figure 4), note fulvic acid experiments were conducted in small (50 mL) sample vials due to a limited sample amount. This provided weight of evidence that organic compounds may cause poor chemical precipitation and/or settling at a treatment plant using conventional treatment (addition of barium chloride) and was consistent with scientific literature (e.g., Smith et al. 2004).

3.1.3 Removal of organics using activated carbon

Additions of activated carbon to Stanleigh TMA (CL-04) water showed a compelling increase in turbidity (approximately 7 NTU) compared to Stanleigh TMA water without the activated carbon (the control experiment; Figure 5). This suggested that treatment of Stanleigh TMA water with activated carbon removed the interference that causes 'refractory' test results (low turbidity). The greatest reduction of the refractory response (i.e., increase in turbidity) occurred when powdered activated carbon was added with no other additions (i.e., no change in pH or ionic strength).

Treatment of Panel TMA (P-13) water with activated carbon did not improve the turbidity compared to the untreated TMA water, unless the water had been acidified (to pH 3; Figure 5).

3.1.4 Hydrophobic resin to remove and reintroduce organic compounds

3.1.4.1 Removal of organic compounds

Stanleigh TMA water (CL-04) treated with XAD-16 resin had a higher turbidity than the untreated CL-04 water (without resin) such that it was closer to the turbidity of the control (sulphate-spiked distilled) water with resin (Figure 6, left pane). This suggested that XAD-16 hydrophobic resin was able to remove the interference that causes refractory radium from CL-04 water.

Panel TMA water (P-13) that was treated with XAD-16 resin showed an increase in turbidity compared to the untreated P-13 water and was closer to the turbidity of the control water with resin, however, only when the treatment was adjusted to pH 2 (Figure 6, right pane). The improvement in turbidity result after treatment of Panel TMA water with XAD-16 resin indicated that the interference that causes refractory was removed.

Stanleigh and Panel TMA water (CL-04, and P-13 respectively) were successfully treated with XAD-16 resin to remove the interference that causes refractory radium under different treatment conditions. Treatment of

raw Panel TMA water was adjusted to pH 2, while the Stanleigh TMA water treatment was more successful when treated with no pH adjustment.
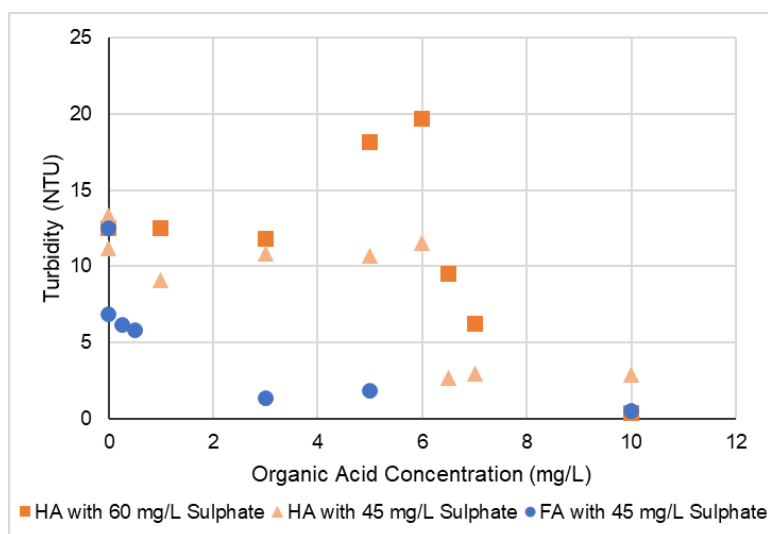

Figure 4   Addition of humic acid (HA) and fulvic acid (FA) to sulphate-spiked distilled water
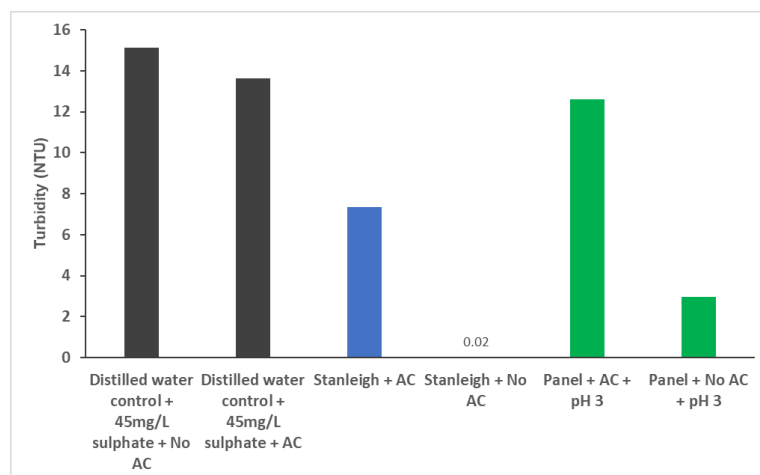

Figure 5   Changes in turbidity test result after treatment with and without activated carbon (AC)

3.1.4.2   Addition of raw TMA water extract to sulphate spiked distilled water

Hydrophobic XAD-16 resin samples that had been used to successfully remove the interference that causes refractory radium from TMA water were then eluted to extract the interference from the resin and reintroduce it to sulphate-spiked distilled water. The XAD-16 resin treated water had higher turbidity test results when treated at circumneutral pH with Stanleigh TMA water, but at pH 2 for Panel TMA water. Dilute sodium hydroxide (0.02 N) eluent from XAD-16 resin that had been used to treat Stanleigh TMA water was added to sulphate spiked (45 mg/L) distilled water and adjusted to pH 6.5 to 7. Turbidity testing showed that the sample eluents from the Stanleigh TMA water (CL-04) resin were consistently 3 NTU lower than the eluents from the control resin, as individual tests (data not shown) as well as when averaged (Figure 6, left pane).

The sodium hydroxide (0.2 N) eluent from resin that had been used for Panel TMA (P-13) water was added to sulphate-spiked (78 mg/L) distilled water adjusted to pH 6.5 to 7. Turbidity testing of this water showed that the sample eluent from the Panel TMA (P-13) resin was consistently lower compared to the eluent from the control resin when assessing individual tests (data not shown), as well as when averaged (Figure 6, right pane). Additional pH adjustment controls were tested for turbidity to ensure that the addition of salts (from additions of hydrochloric acid and sodium hydroxide) during pH adjustment did not confound the results.
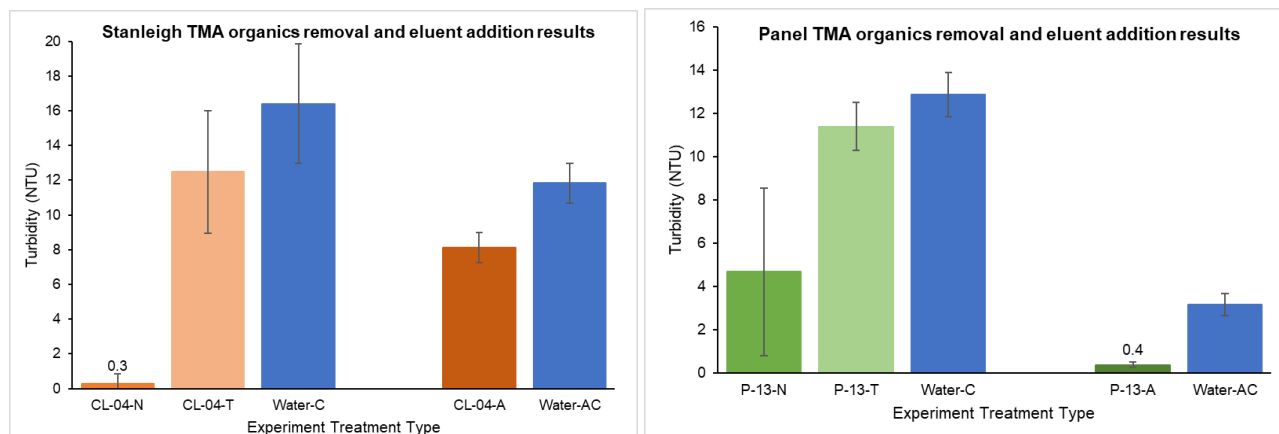
Figure 6   Turbidity test results of organics removal from raw Stanleigh TMA water (CL-04; left pane) and from raw Panel TMA water (P-13; right pane) with (T) and without (N) treatment using XAD-16 resin, and from control distilled water (C; both panes), and of eluent addition from TMA-treated XAD-16 resin (A) or distilled water-treated resin (AC) into sulphate-spiked distilled water

These results suggested that both TMA resin eluents (in sulphate-spiked distilled water) reintroduced the interference that causes refractory radium. Given that the XAD-16 resin is hydrophobic, it was inferred that the extract was likely a mixture of organic compounds, neutral (hydrophobic) compounds at the Stanleigh TMA and likely weak organic acids in Panel TMA water (on the basis that Panel TMA water needed pH adjustment to remove the interference and Stanleigh TMA water did not).

3.2   Settling efficacy

In total, 108 (of 131) settling tests fell within the analytical window of the Malvern Mastersizer 3000, the instrument used to determine particle size distribution. Settling tests that were below the detection of the Malvern Mastersizer (i.e., that had too few particles to be counted) were under conditions of very low reagent concentration (4.5 and 45 mg/L sulphate and/or 10mg/L barium). During the period when settling tests were conducted, the Panel TMA was categorised as refractory and did not transition to non-refractory, while the Stanleigh TMA did. Therefore, comparisons of refractory compared to non-refractory could be made for raw Stanleigh TMA water only.

Tests showed that particle size increased with saturation index, but Stanleigh TMA water always exhibited smaller particle size, compared to Panel TMA water and distilled water, and Stanleigh TMA water generally exhibited even smaller particle size when the water was categorized as refractory (Figure 7).
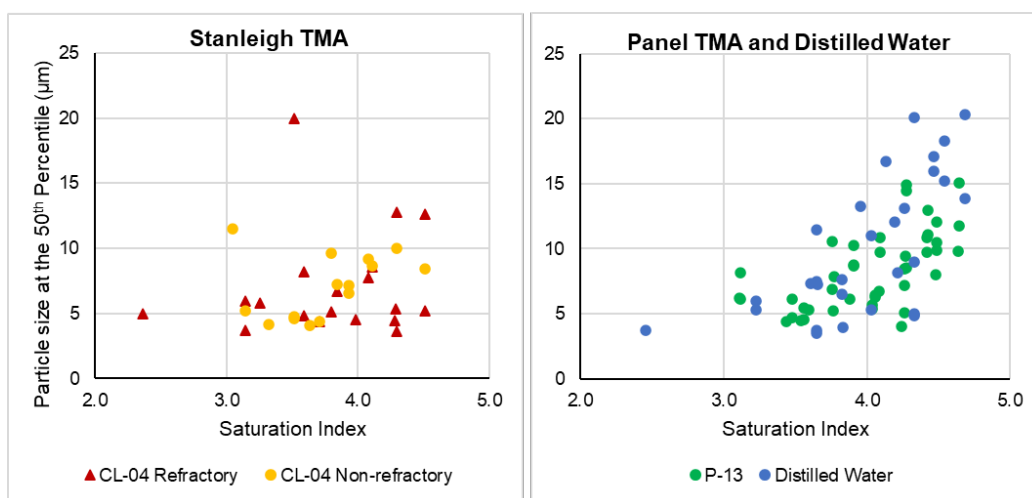

Figure 7   Changing particle size at the 50th percentile with barite saturation index for settling tests using raw Stanleigh TMA water (CL-04), raw Panel TMA water (P-13), and distilled water

Settling tests showed that particle size was not the major influencing factor for settling efficacy (Figure 8). When particle size at the 10th percentile was lower than the required particle size for settling (i.e., 2.44 μm, according to Stokes Law; Stokes 1851) there was dependency of settling efficacy and particle size. At around this same particle size, settling efficacy increased in Stanleigh and Panel TMA water when compared to distilled water, suggesting that the TMA water had greater agglomeration (evidenced by the higher settling efficacy) compared to tests using distilled water. This same phenomenon (higher settling efficacy starting at particle sizes equal to or greater than 2.5 μm) was also decreased somewhat in Stanleigh TMA water that had been categorised as refractory.
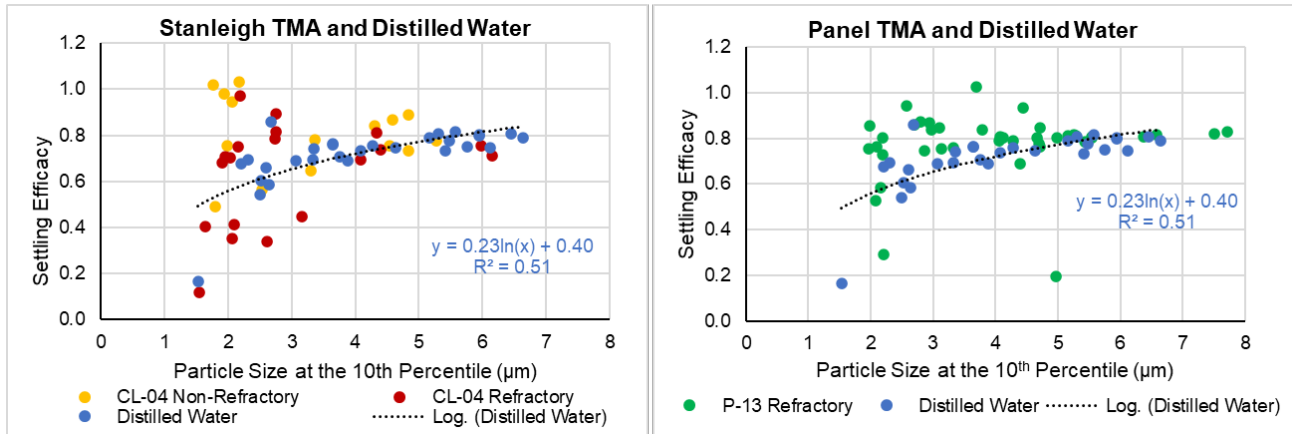

Figure 8   Changing settling efficacy with particle size at the 10th percentile, in settling tests with raw Stanleigh TMA water (CL-04; left pane), and raw Panel TMA water (right pane) compared to distilled water

In general, when sulphate concentrations were high (450 mg/L) settling tests using raw Panel TMA water agreed well with the distilled water tests, despite being categorised as refractory. While Stanleigh TMA water showed lower settling efficacy when water was categorised as refractory (data not shown). When Stanleigh TMA water was not categorised as refractory there was less difference between results for distilled water and Panel TMA water with Stanleigh TMA water. A comparison of a single set of conditions, (sulphate at 70 mg/L and barium at 111 mg/L resulting in a molar ratio of 1), showed that all three water-types generally showed a similar settling efficacy except when the Stanleigh TMA was categorised as refractory (Figure 9). This suggested that settling efficacy in Stanleigh TMA water is more strongly dependent on factors other than sulphate and barium concentration (i.e., potentially the presence of organic compounds that interfere with barite settling) compared to the Panel TMA.
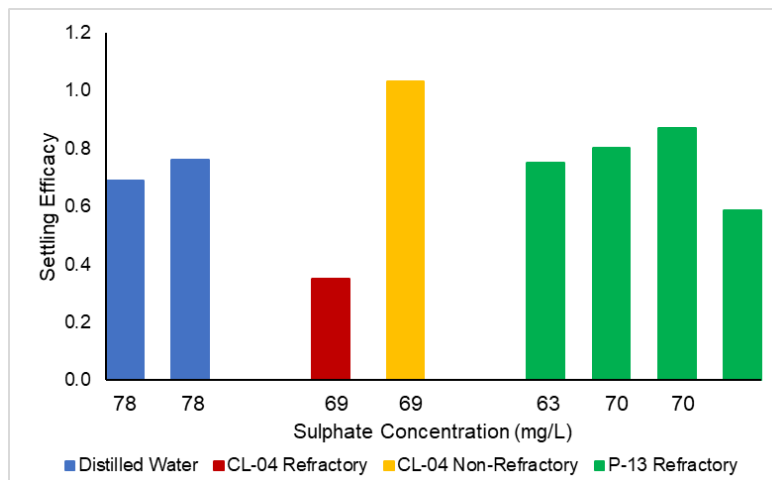

Figure 9   Comparison of settling efficacy among water types in settling tests at the same sulphate (63 to 78 mg/L) and barium (111 mg/L) concentrations

Settling efficacy was optimal in distilled water when the molar ratio was around 3.5 (either ion could be in excess to achieve similar settling efficacies; Figure 10). However, when raw Stanleigh TMA water was tested, when sulphate concentrations were low (i.e., at 36 to 45 mg/L, the current sulphate concentration in raw Stanleigh TMA water), the highest settling efficacies were achieved with highly excess barium concentrations (with barium to sulphate molar ratios of 2 to 8; Figure 10). While Panel TMA water showed good settling efficacy (i.e., 0.8) across a range of sulphate (starting at 70 mg/L) and barium concentrations and at barium to sulphate molar ratio around 1 (data not shown).
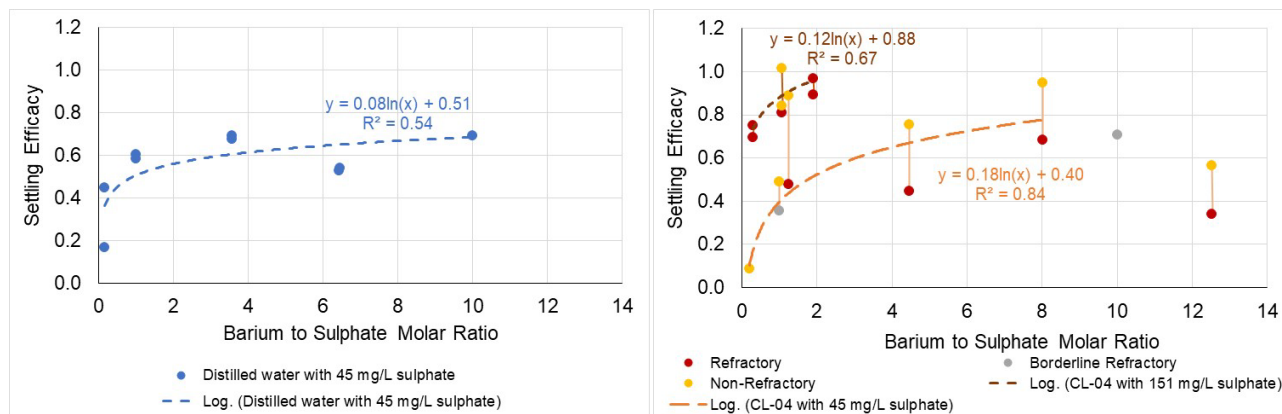

Figure 10   Changing settling efficacy with the barium to sulphate molar ratio in distilled water (left pane) at the same sulphate concentration as raw Stanleigh TMA water (CL-04; 45 mg/L sulphate) and with raw Stanleigh TMA water spiked to 151 mg/L (right pane)

3.3   Field survey results

Weekly sampling during treatment plant operation was conducted at each TMA to capture two cycles of refractory. This resulted in a total of 34 weeks of sampling at the Stanleigh TMA, with 27 of those weeks categorised as refractory; and 36 weeks of sampling at the Panel TMA, with 12 weeks categorised as refractory.

At the Stanleigh TMA, there was a significant ($p < 0.05$) difference in the organic compound mass spectrum fingerprints during refractory periods compared to non-refractory (Figure 11). When other supporting analytes were correlated with the refractory versus non-refractory category, no other significant correlations were found (data not shown).
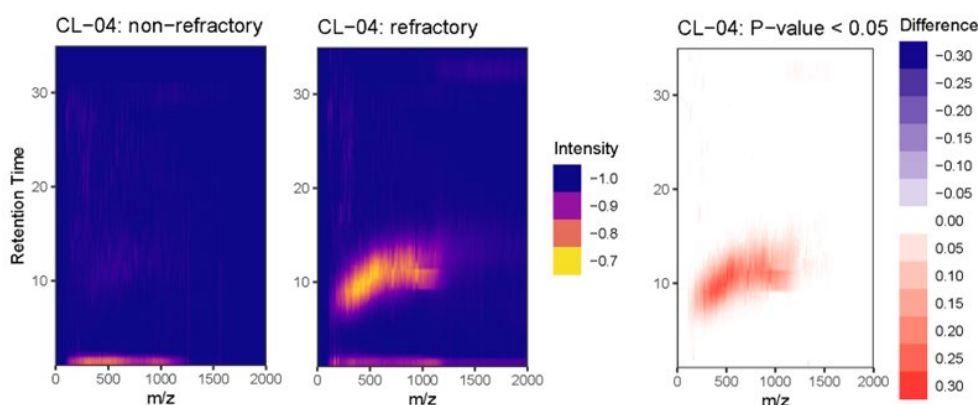

Figure 11   Stanleigh TMA influent (Station CL-04) HPLC ESI MS average data grouped by refractory status with significant difference ($p < 0.05$)

At the Panel TMA, there was a difference in organic compound mass spectrum fingerprints when weeks categorised as refractory compared to weeks that were non-refractory. The organic fingerprint that was correlated with refractory radium at the Panel TMA was similar to the fingerprint that correlated with

refractory radium at the Stanleigh TMA (data not shown). However, the difference in organic compound fingerprint during refractory compared to non-refractory at the Panel TMA was not significant (p>0.05). It is possible that while sulphate concentrations in raw TMA water at Panel are high (higher than at the Stanleigh TMA), this concentration of sulphate is sufficient to combat the interference of the organic compounds present at the Panel TMA. In addition, bench testing has shown that organic compounds in the raw Panel TMA water were likely weakly acidic, while at the Stanleigh TMA likely neutral, and this difference in hydrophobicity may also contribute to organic compounds at Panel having less of an influence on treatment efficacy.

There was a significant (R^2 of 0.73, p<0.05) correlation of increasing dissolved radium-226 concentration with increasing total aluminium in treated effluent (P-14; Figure 12) and a weaker correlation (R^2 of 0.49, p<0.1; data not shown) of total barium concentration with aluminium in treated effluent.
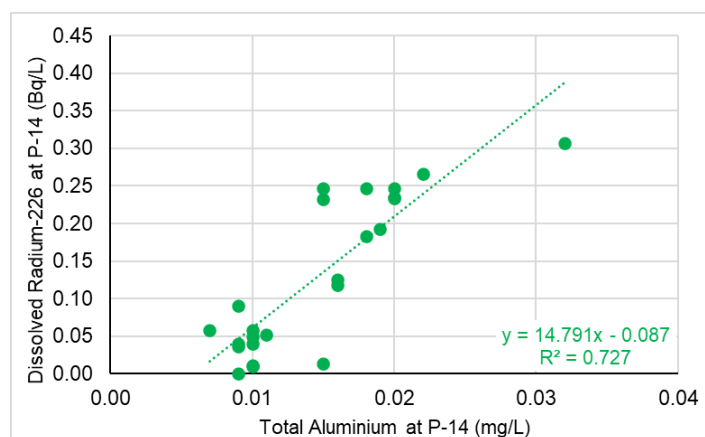

Figure 12 Weekly survey total aluminium and dissolved radium-226 concentrations in treated Panel TMA water

However, the role of aluminium is currently (i.e., in 2022) unclear, the solubility of aluminium oxides is highly variable at circumneutral pH (Appelo & Postma 2005), and thus aluminium may be transitioning between the dissolved and solid phase due to lime additions at the treatment plant. Though concentrations of aluminium were not at equivalent molar concentrations to barium, aluminium sesquioxides can have large surface areas and may present a colloidal interference. Thus, it may be of interest to monitor dissolved and total aluminium concentrations in treated effluent.

4 Conclusion

Hypothesis 1: 'dissolved organic compounds cause refractory radium' was proven correct. Evidence was provided through treatments to remove organics from sample water as well as re-introduce extracted organics into distilled water to determine that this could be the interference that contributes to the occurrence of refractory radium. Additionally, purchased organic acids were added to control (distilled) water spiked with two different sulphate concentrations that resulted in a refractory response to the turbidity tests.

Hypothesis 2: 'The cause of radium-226 treatment inefficiency is an unidentified analyte that is present at a concentration sufficient to interfere with milligram-per-litre concentrations of barium' was disproven for the Stanleigh TMA (several lines of evidence that point towards organic compounds being the interference), however may be correct for Panel as it was observed that increasing total aluminium concentrations correlated with increasing radium-226 concentrations. Further study would be required to fully ascertain the role of aluminium in supporting refractory conditions.

Hypothesis 3: 'the interference that causes refractory radium at the Stanleigh TMA is the same as that which causes refractory radium at the Panel TMA' was disproven through the parallel experimentation of Stanleigh and Panel TMA water. The cause of poor treatment results at the Stanleigh TMA (low sulphate in combination with organic compounds) may not be the cause at the Panel TMA, where sulphate concentrations are

potentially sufficiently high to overcome the interference caused by organic compounds. Sulphate concentration is clearly important when it comes to treatment efficacy, and although there were organic compounds that likely reduce treatment efficacy, at the time of this study (i.e., in 2022) this effect was surmounted by the higher concentration of sulphate at Panel ETP influent Station P-13 (when compared to the Stanleigh ETP influent Station CL-04), and there may be other factors that influence effective treatment at the Panel TMA such as aluminium.

Hypothesis 4: that 'decreasing sulphate concentrations in the TMAs as a contributing factor to the occurrence of refractory radium' was shown to be true through changing sulphate concentrations in specific experiments. Settling tests were used to investigate how changing sulphate and barium concentrations and molar ratios may influence settling efficacy. The results showed that when sulphate was limiting (as is the case at the Stanleigh TMA) the barium molar concentration would ideally be in excess by two to eight times.

Settling tests also showed that a saturation index of at least 3.5 resulted in the best settling efficacies, and assuming a barium concentration of 10 mg/L, this index was not achieved in either TMA. When Stanleigh TMA water was categorised as refractory, settling efficacies were lower (compared to when it was not refractory) particularly when one of the reagents was limiting (i.e., when sulphate was below 70 mg/L or barium was below 64 mg/L). Panel TMA water was categorised as refractory throughout the test period, however when compared to distilled water there was little difference in settling efficacies. Whereas bench testing showed that turbidity results were improved by the removal of organic compounds from Panel TMA water, therefore it is possible that while organics may not be influencing settling efficacy at the Panel TMA now, it may in the future (as sulphate concentration continue to decrease in the TMA). This also provided additional weight of evidence to disprove Hypothesis 3.

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