Removal of magnetic resonance imaging contrast agents through advanced water treatment plants
Michael G. Lawrence, Jurg Keller and Yvan Poussade

ABSTRACT

Stable gadolinium (Gd) complexes have been used as paramagnetic contrast agents for magnetic resonance imaging (MRI) for over 20 years, and have recently been identified as environmental contaminants. As the rare earth elements (REE), which include Gd, are able to be measured accurately at very low concentrations (e.g. Tb is measured at 7 fmol/kg in this study) using inductively coupled plasma mass spectrometry (ICP-MS), it is possible to determine the fate of this class of compounds during the production of purified recycled water from effluent.

Coagulation and microfiltration have negligible removal, with the major removal step occurring across the reverse osmosis membrane where anthropogenic Gd (the amount of Gd attributable to MRI contrast agents) is reduced from 0.39 nmol/kg to 0.59 pmol/kg, a reduction of 99.85%. The RO concentrate has anthropogenic Gd concentrations of 2.6 nmol/kg, an increase in concentration in line with the design characteristics of the plant. The increased concentration in the RO concentrate may allow further development of anthropogenic Gd as a tracer of the fate of the RO concentrate in the environment.

Key words: advanced water treatment, anthropogenic gadolinium, ICP-MS, rejection efficiency, reverse osmosis

INTRODUCTION

Areas of South East Queensland in Australia recently experienced the worst drought (as measured by both duration and the accumulated rainfall deficit) in recorded history (Queensland Government 2007). As a result, surface water supply dams dwindled, extreme water restrictions were introduced, and residential water consumption reduced by well over 50% (from > 300 to < 120 L person$^{-1}$ day$^{-1}$). The severity of the drought brought water supply security to the forefront of political discussions, and highlighted the problems associated with an increasing population and potential reduction in rainfall run-off in South East Queensland catchments as a result of climate change. The Western Corridor Recycled Water Project in South East Queensland is the largest indirect potable water reuse schemes in the Southern Hemisphere (Traves & Davies 2008), and currently the third largest worldwide; it has a capacity of up to 182,000 m$^3$ day$^{-1}$ of purified recycled water, which is produced in three treatment facilities. A proportion of manufactured water is being used by industry to reduce their reliance on drinking water, and the remainder is intended to supplement regional water supply dams.

Purified recycled water will be produced in Advanced Water Treatment Plants (AWTPs) that form three of the seven barriers in a system-wide multi-barrier approach to water reuse. The barriers within the AWTPs include, in series, microfiltration, reverse osmosis, and advanced oxidation (UV irradiation and peroxide) and produces water of sufficient standard to augment drinking water supplies (Australian Government 2008). Micropollutants are primarily separated from the product stream at the reverse osmosis (RO) step, followed by advanced oxidation.
(UV/peroxide) to oxidize any residual that may pass through the RO barrier. However, the effectiveness of the RO barrier in removing micropollutants in full-scale operation is difficult to quantify directly at normal organic micropollutant concentrations. Many organic micropollutants can be measured using LC–MS–MS, but despite the success of this technique, the major limitation is that most micropollutants, even after a 1,000 fold pre-concentration, are present at concentrations similar to their limits of detection e.g. (Richardson 2006). As a result, a 10-fold reduction in concentration will render most analytes undetectable, and prevent effective quantification of the effectiveness of the various barriers. In this paper, we describe how, by using a different analytical approach, it is possible to efficiently quantify the rejection of a specific class of micropollutants across the RO barrier.

Gadolinium is a rare earth element (REE), and shares many characteristics with the remainder of the REE series. Gadolinium can be directly quantified at the sub-pmol/kg level by inductively coupled plasma mass spectrometry (ICP-MS) (Lawrence et al. 2006b, 2009). From a geochemical perspective, Gd is normally present in natural matrices at concentrations proportional to the remainder of the REE series, (except for a small positive anomaly in saline water). As a result, the naturally occurring concentration of Gd [Gd\textsubscript{nat}] in fresh water samples can be calculated by applying a third order fit to the shale-normalised REE concentrations (Lawrence et al. 2009). However, for municipal wastewater, the shale normalised REE pattern (for an example, see Figure 3) has a distinct concentration spike, or anomaly, at Gd.

Stable Gd-complexes have found a use as contrast-agents in magnetic resonance imaging (MRI) as they are strongly paramagnetic. Because large amounts of Gd (≈3 g per adult patient) are utilized in each MRI investigation, and the complexes are unreactive in the human body, they enter municipal wastewater, where they are detectable as a large positive Gd anomaly (Bau & Dulski 1996). The difference between the measured and the predicted concentration is defined as anthropogenic Gd,

\[ [\text{Gd}_{\text{Anth}}] = [\text{Gd}_{\text{Measured}}] - [\text{Gd}_{\text{Natural}}] \] (1)

which is an indirect measure of the concentration of contrast agents that have been added. Anthropogenic Gd is a ubiquitous micropollutant in wastewater effluent in regions where magnetic resonance imaging is available, and has been detected in Europe, Japan, the USA, and Australia (Bau & Dulski 1996; Moller et al. 2000; Zhu et al. 2004; Knappe et al. 2005; Verplanck et al. 2005; Lawrence et al. 2006b). Concentrations of [Gd\textsubscript{Anth}] in the effluent from wastewater treatment plants (WWTPs) in Berlin, Germany have reached levels as high as 7 nmol/kg (Bau & Dulski 1996; Knappe et al. 2005), approximately 2,000 times higher than the geogenic, or natural Gd concentration. In South East Queensland, [Gd\textsubscript{Anth}] encompasses the range of 0.1–1.5 nmol/kg, approximately 10–100 times the natural abundance (Lawrence et al. 2009). In this study, we quantify the rejection of [Gd\textsubscript{Anth}] across the various barriers of an AWTP. Anthropogenic Gd was removed by the RO barrier to concentrations at or below the detection limit of the direct analysis method, therefore, we preconcentrate the RO product water by evaporation to accurately quantify specific rejection rates.

**GENERAL DESCRIPTION OF THE ADVANCED WATER TREATMENT PLANTS**

The AWTPs that are constructed, or under construction, as part of the South East Queensland water grid follow the same general design path, as illustrated in Figure 1. The treated effluent from wastewater treatment plants (WWTPs), with effluent total N typically <3 mg/L, and total P concentration ranging between 1 mg/L and 10 mg/L, is pretreated by flocculation and sedimentation, and held in the raw water tank for up to 20 hours. The hydraulic retention time in the raw water tank, coupled with the retention time within the upstream wastewater treatment plants has the effect of homogenizing the water, and dampening the expected daily concentration cycles in the wastewater treatment plant effluent. While there are likely to be variations in the weekly concentration profiles of Gd\textsubscript{Anth}, the >40 hours hydraulic retention time (including retention time in both the wastewater treatment plant and advanced treatment plant) suggests that grab sampling is an appropriate approach for a study of this type. Flocculation and sedimentation is followed, in sequence, by microfiltration (MF) through hollow fiber membrane filters with
nominal pore sizes of 0.1–0.2 micron, reverse osmosis (RO), and advanced oxidation using UV/H₂O₂ (Post UV). The product, purified recycled water, is stabilized by addition of lime and chlorine, before being pumped for industrial use, or ultimately, to supplement water supply dams. The concentrate stream from the reverse osmosis process is further treated prior to discharge to the environment.

**METHODS**

**Sample collection**

Samples for REE analysis were collected in duplicate or triplicate in rigorously acid cleaned 30 or 60 mL low density polyethylene (LDPE) bottles using trace metal clean techniques. Water samples were collected from two full-scale and one pilot-scale AWTP. For the initial investigations, the full-scale plant was sampled at all locations specified in Figure 1. After the initial investigations, both the full-scale AWTPs (using different reverse osmosis membranes) and a pilot-scale AWTP were sampled at locations 1, 3, 4 and 7 in order to better quantify rejection across two different RO membranes. Throughout all sampling regimes, the samples were filtered using Millipore Millex GV 0.22 μm syringe filters, with the exception of the samples collected immediately after the microfiltration, reverse osmosis and UV-oxidation steps (samples 3–5) for which filtration was unnecessary. Samples of reverse osmosis permeate required for the pre-concentration experiments were collected in rigorously acid cleaned 10 L LDPE carboys. Upon return to the laboratory, all samples were immediately acidified to pH 1.5 with double quartz-distilled nitric acid (for the initial experiments) or, subsequently with triple distilled nitric acid (where the double quartz distilled acid had been further purified by sub-boiling Teflon distillation). Samples were transferred to acid cleaned test tubes and spiked with 1 ppb In and Rh to act as an internal standard prior to analysis using a Thermo X-series ICPMS (Lawrence et al. 2009).

**Analytical method**

Samples were analysed using a Thermo X-series ICP-MS housed in a clean facility at the University of Queensland.
Instrumental conditions are similar to those previously described (Lawrence et al. 2006a, 2009). Briefly, the instrument was tuned for maximum sensitivity using the high performance sample introduction system, while maintaining oxide production below 2% (measured using CeO/Ce). The raw instrument data was corrected for variations in internal standard, external drift, and interfering oxides (Eggins et al. 1997). Instrument response was then calibrated against hotplate digests for the US Geological Survey (USGS) dolerite reference material W-2, using REE concentrations listed in Table 1. A similarly prepared hotplate digest of the USGS basalt reference material BIR-1 was used as a primary quality control. The National Research Council of Canada (NRCC) River Water Reference material SLRS-4 was used as an external drift monitor, and secondary quality control.

Initial results indicated that the RO permeate had REE concentrations at or below the method detection limit. In order to increase our ability to quantify the rejection factor, it was necessary to introduce a preconcentration step for the RO permeate. Two options were evaluated: evaporation, and extraction. Extraction techniques (either solid phase extraction or liquid–liquid extraction) each involve contact of the sample with other reagents, and it would be very difficult to maintain process blanks below the levels required to quantify the REE accurately. However, as the sample in question was RO permeate; it has an exceptionally clean matrix relative to most other sample types. Therefore, evaporation (sub-boiling, under an ULPA clean hood in a trace metal clean laboratory) was considered to be the most suitable method.

The ability to perform the evaporation without contamination was first investigated by evaporating six replicates of MilliQ in 500 mL FEP bottles in an ISO class-4 ULPA laminar flow hood. After evaporation, the residual (not visible) was redissolved in 2–3 mL of 2% triple distilled nitric acid, resulting in concentration factors of 40–250. The solution was quantitatively transferred to an acid cleaned test-tube where it was spiked with 1 ppb Re prior to analysis. The REE concentrations measured for pre-concentrated MilliQ were compared to an internal-standard-spiked MilliQ water blank (Figure 2). The instrumental results in Figure 2 are compared without blank subtraction. The shale-normalized REE patterns for the concentrated MilliQ samples plot well below the Milli-Q blanks, indicating that the instrumental analysis step is the major contributor to the measured blank. Reverse osmosis permeate was subsequently treated identically to pre-concentrated MilliQ.

Eight replicates of reverse osmosis permeate were concentrated in the same manner, and resulted in a visible residual that dissolved completely upon addition of 2–3 mL of 2% triple distilled nitric acid. Despite the pre-concentration of all dissolved constituents, the internal standard signal suppression was minimal, a smooth REE pattern is resolved, and the measured concentrations are sufficiently above the detection limit to ensure accurate quantification. Interestingly, the REE pattern of the RO permeate has a measurable Gd Anth component. Therefore, the RO barrier must be slightly permeable to one or more of the contrast agents. As indicated in Table 1, both the full-scale AWTP (twice) and the pilot AWTP have detectable Gd Anth in the RO permeate following pre-concentration. Samples taken from a second AWTP in January 2009 had sufficient anthropogenic Gd to enable quantification of Gd Anth in the RO permeate without preconcentration.

**RESULTS AND DISCUSSION**

The measured REE concentrations, and calculated anthropogenic Gd concentrations are presented in Table 1. The shale-normalised REE patterns of water samples through the treatment train in the full-scale AWTP are presented in Figure 3.

**Removal of Gd Anth through the treatment process**

The feed water to the first full-scale AWTP consists either of the combined stream from 3 separate WWTPs, or from a single WWTP, in separate pipes, thus samples 1a and 1b represent the two separate feed-waters. The source water was sampled and analysed 3 times over a 3-month time period encompassing sampling throughout the weekly cycle. The source water to the AWTP had \([\text{Gd Anth}] = 115\) to 350 pmol/kg. The minimum measured \([\text{Gd Anth}]\) was 20 times the expected natural abundance.
Table 1 | Rare Earth Element concentrations (pmol/kg unless indicated otherwise) of water samples through the AWTP treatment train. Values are averages of at least 3 replicate samples. The Gd anomaly is calculated (Lawrence et al. 2009) from a third order fit of the MuQ normalised (Kamber et al. 2005) REE pattern after exclusion of potentially anomalous elements.

<table>
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<tr>
<th>Sample (pmol/kg)</th>
<th>La</th>
<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
<th>Sm</th>
<th>Eu</th>
<th>Gd</th>
<th>Tb</th>
<th>Dy</th>
<th>Ho</th>
<th>Er</th>
<th>Tm</th>
<th>Yb</th>
<th>Lu</th>
<th>Gd Anomaly (unitless)</th>
<th>Gd Anth (nmol/kg)</th>
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</thead>
<tbody>
<tr>
<td>W-2 (µmol/kg)</td>
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<td>165.69</td>
<td>21.47</td>
<td>89.51</td>
<td>21.72</td>
<td>7.20</td>
<td>23.58</td>
<td>3.87</td>
<td>23.43</td>
<td>4.87</td>
<td>13.28</td>
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<td>BIR-1 (µmol/kg)</td>
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<td>13.57</td>
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<td>7.31</td>
<td>3.45</td>
<td>11.83</td>
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<td>0.54</td>
<td>1.96</td>
<td>1.93</td>
<td>1.16</td>
<td>0.52</td>
<td>0.11</td>
<td>0.58</td>
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<td>0.23</td>
<td>0.06</td>
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<td>3σ</td>
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<td>0.18</td>
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<td>0.25</td>
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<td>0.03</td>
<td>0.06</td>
<td>0.01</td>
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<td>0.004</td>
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<tr>
<td>3σ</td>
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<td>0.001</td>
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<td>0.004</td>
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<td>0.036</td>
<td>0.016</td>
<td>0.655</td>
<td>0.007</td>
<td>0.042</td>
<td>0.012</td>
<td>0.049</td>
<td>0.010</td>
<td>0.068</td>
<td>0.012</td>
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<tr>
<td>3σ</td>
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<td>0.107</td>
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<td>0.002</td>
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AWTP treatment train ($n = 3$)

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<th>Sample</th>
<th>La</th>
<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
<th>Sm</th>
<th>Eu</th>
<th>Gd</th>
<th>Tb</th>
<th>Dy</th>
<th>Ho</th>
<th>Er</th>
<th>Tm</th>
<th>Yb</th>
<th>Lu</th>
<th>Gd Anomaly (unitless)</th>
<th>Gd Anth (nmol/kg)</th>
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<tr>
<td>Inlet 1a</td>
<td>16.0</td>
<td>21.7</td>
<td>5.3</td>
<td>22.4</td>
<td>8.5</td>
<td>3.3</td>
<td>260.8</td>
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<td>17.0</td>
<td>5.0</td>
<td>18.5</td>
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<td>23.1</td>
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<td>Inlet 1b</td>
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<td>16.7</td>
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<td>5.0</td>
<td>2.1</td>
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<td>8.2</td>
<td>2.4</td>
<td>7.8</td>
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<td>10.1</td>
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<td>33.1</td>
<td>116</td>
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<td>MF feed</td>
<td>1.0</td>
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<td>1.9</td>
<td>17.2</td>
<td>4.5</td>
<td>1.9</td>
<td>234.5</td>
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<td>6.9</td>
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<tr>
<td>RO concentrate</td>
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<td>68.0</td>
<td>18.6</td>
<td>97.5</td>
<td>30.1</td>
<td>12.5</td>
<td>1,735.1</td>
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<td>86.5</td>
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<td>8.5</td>
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AWTP treatment train ($n = 3$)

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<th>Nd</th>
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<th>Eu</th>
<th>Gd</th>
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<th>Lu</th>
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Pilot AWTP ($n = 3$)

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<th>Tb</th>
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<th>Er</th>
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<th>Yb</th>
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<th>Gd Anomaly (unitless)</th>
<th>Gd Anth (nmol/kg)</th>
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<td>3.42</td>
<td>16.94</td>
<td>6.29</td>
<td>1.77</td>
<td>1,657</td>
<td>3.08</td>
<td>34.98</td>
<td>12.36</td>
<td>43.18</td>
<td>7.28</td>
<td>46.54</td>
<td>8.09</td>
<td>95.5</td>
<td>1,638</td>
</tr>
<tr>
<td>RO permeate</td>
<td>0.09</td>
<td>0.17</td>
<td>0.02</td>
<td>0.21</td>
<td>0.02</td>
<td>0.01</td>
<td>1.00</td>
<td>0.01</td>
<td>0.04</td>
<td>0.01</td>
<td>0.04</td>
<td>0.01</td>
<td>0.04</td>
<td>0.01</td>
<td>27.9</td>
<td>0.96</td>
</tr>
<tr>
<td>RO concentrate</td>
<td>24.2</td>
<td>71.8</td>
<td>23.3</td>
<td>108.7</td>
<td>37.9</td>
<td>13.3</td>
<td>10,759</td>
<td>24.7</td>
<td>220.6</td>
<td>78.5</td>
<td>269.1</td>
<td>45.3</td>
<td>302.2</td>
<td>52.2</td>
<td>106.6</td>
<td>10,665</td>
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</table>
The raw water holding tank (sample location 2 in Figure 1) effectively homogenizes water from the various WWTPs and is, therefore, a more relevant sample for tracing the fate of the Gd contrast agents through the AWTP. The \([\text{Gd}_{\text{Anth}}]\) immediately prior to microfiltration, is 230 pmol/kg, almost identical to the value of 240 pmol/kg determined after the MF membrane, but before RO. The lack of removal confirms that the measured Gd is in the dissolved phase, consistent with the interpretation of \(\text{Gd}_{\text{Anth}}\) as consisting of dissolved organometallic pharmaceuticals.

Reverse osmosis follows MF, but, without pre-concentration, the measured REE concentrations in the RO product water were analytically undetectable, preventing calculation of \([\text{Gd}_{\text{Anth}}]\). Nonetheless, the removal of all REE, including \(\text{Gd}_{\text{Anth}}\), to concentrations at or below the detection limit suggests a removal factor approaching or exceeding 1,000.

The REE patterns of the product water through the rest of the AWTP stream were also determined. The sample taken immediately following the advanced oxidation step has a detectable, smooth REE pattern indicating addition of REE. Industrial grade hydrogen peroxide is added at a concentration of 3–5 mg/L immediately prior to sampling, suggesting the bulk chemical is the REE source. The REE concentrations increase further in the stabilized product water (following addition of lime and hypochlorite), most likely due to the presence of REE in the lime. The component was undetectable in either the post-advanced-oxidation or the final purified recycled water samples.

As expected, there is a strong \(\text{Gd}_{\text{Anth}}\) signal in the RO concentrate stream with \([\text{Gd}_{\text{Anth}}]=1.7 \text{ nmol/kg}\), (Figure 3). This represents a concentration factor of \(\approx 7\) (in the initial sampling protocol, sample 3 was taken in front of the RO feed tank, so a more accurate calculation is not possible), closely in line with the design concentration factor for the AWTP of approximately 6.8:1. The concentration factors (defined by the RO feed and RO concentrate samples) were subsequently remeasured at the full-scale and pilot plants as 6.70 and 6.51 respectively. The RO concentrate (ROC, open triangles) and the treated RO concentrate sample (ROC treated, open squares) have essentially identical \(\text{Gd}_{\text{Anth}}\) components, but there is a slight negative shift for the other elements in the REE pattern, indicates some removal during biological nitrification, denitrification and coagulation.
Quantification of contrast agent rejection across the reverse osmosis membrane(s)

If considered as a class of chemicals, it is possible to quantify the rejection of the MRI contrast agents. The rejection for the full-scale plant was determined, on two separate occasions, to be 99.83 and 99.85%, whilst the rejection through the pilot plant (which uses an RO membrane from a different manufacturer) was slightly higher at 99.94%. The rejection measured directly in a second full scale AWTP (using the same membranes as the Pilot Plant) was 99.84%. This corresponds to a log reduction, calculated as \( \log \left( \frac{[\text{RO feed}]}{[\text{RO permeate}]} \right) \), of 2.8 for both the full-scale AWTPs, and 3.2 for the pilot plant. The calculated reduction is an average for all chemicals in this class; however, this value may not be a true reflection of the removal of each of the individual contrast agents. There are at least 14 Gd-containing contrast agents licensed for use in Australia. Magnevist®, Primovist®, Gadovist® and OptiMARK® are all used (to some extent) in hospitals in South East Queensland, (personal communications, Gail Durbridge, UQ Centre for Magnetic Resonance, Ray Buckley, Qld Health). At neutral pH, Magnevist® and Primovist® are doubly charged cationic linear chain complexes, whereas the neutral OptiMARK® and Gadovist® complexes are linear and macrocyclic respectively. The differing charge and chemical structures of these complexes would be expected to affect their transport across the RO membrane, however, it is not possible within the constraints of the method, which only measures Gd concentrations, to determine the individual concentrations of each of these complexes. Further research is being conducted to directly identify which of the contrast agents is passing through the RO membrane.

Applications for the \( \text{Gd}_{\text{Anth}} \) measurement technique

The ubiquitous presence of \( \text{Gd}_{\text{Anth}} \) in wastewater provides an opportunity to investigate micropollutants using a technique other than LC–MS–MS. There are several potential applications of this tracer to environmental questions. For example, our own previous research (Lawrence et al. 2009) has demonstrated that there is currently no evidence for \( \text{Gd}_{\text{Anth}} \) in the potable water supply in South East Queensland. On the results obtained in this study, we would not expect this situation to change as a result of the addition of purified recycled water to the regional water supply. Future detection of \( \text{Gd}_{\text{Anth}} \) in the water supply dams would be an indicator of contamination; most likely from the addition of effluent upstream of the dams, but potentially also due to system failure within the advanced treatment plant.

In contrast, the detection of \( \sim 2 \text{nmol/kg} \text{Gd}_{\text{Anth}} \) in the reverse osmosis concentrate provides new research opportunities. As the SE Qld water grid expands, the discharge of wastewater to the environment will be minimized. As \( [\text{Gd}_{\text{Anth}}] \) is increased in the RO concentrate, essentially limited to 3 discharge points, and because \( \text{Gd}_{\text{Anth}} \) behaves conservatively during estuarine mixing (Kulaksiz & Bau 2007), \( \text{Gd}_{\text{Anth}} \) would be expected to co-occur with any wastewater sourced micropollutants in the marine environment. In this manner, \( \text{Gd}_{\text{Anth}} \) may be utilized as a cheaper, more sensitive, and more rapid alternative to assess the distribution of other more environmentally damaging micropollutants. Further, \( \text{Gd}_{\text{Anth}} \) could be developed to provide real data with which to test hydrological models, and as a prescreening tool to refine both field-based and modeled environmental risk assessments of the effect of micropollutants in these environments. We would expect that \( \text{Gd}_{\text{Anth}} \) should find similar applications in developed parts of the world where advanced medical technologies are common.

CONCLUSIONS

- Gadolinium based MRI contrast agents, determined as \( \text{Gd}_{\text{Anth}} \), are present at \( \sim 200 \text{pM} \) in the feed water of the AWTP, and are efficiently rejected during reverse osmosis, resulting in reverse osmosis concentrate concentrations 6.8 times higher, in line with plant design characteristics.
- It is nonetheless still possible to detect \( \text{Gd}_{\text{Anth}} \) in the reverse osmosis permeate, allowing for accurate quantification of rejection of these micropollutants in normal operation. The rejection of \( \text{Gd}_{\text{Anth}} \) exceeds

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log 2.8 for two full-scale plants (using different reverse osmosis membranes), and one pilot plant. The concentration of Gd\textsubscript{Anth} in the reverse osmosis permeate is close to the instrument detection limit, but the method detection limit can be lowered if the sample is preconcentrated. In these low-matrix waters, evaporation is the preferred preconcentration technique.

- The higher concentration of Gd\textsubscript{Anth} in the reverse osmosis concentrate provides further opportunities to determine the fate of the reverse osmosis concentrate in the environment.

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**REFERENCES**


