Chemical monitoring strategy for the assessment of advanced water treatment plant performance
J. E. Drewes, J. A. McDonald, T. Trinh, M. V. Storey and S. J. Khan

ABSTRACT
A pilot-scale plant was employed to validate the performance of a proposed full-scale advanced water treatment plant (AWTP) in Sydney, Australia. The primary aim of this study was to develop a chemical monitoring program that can demonstrate proper plant operation resulting in the removal of priority chemical constituents in the product water. The feed water quality to the pilot plant was tertiary-treated effluent from a wastewater treatment plant. The unit processes of the AWTP were comprised of an integrated membrane system (ultrafiltration, reverse osmosis) followed by final chlorination generating a water quality that does not present a source of human or environmental health concern. The chemical monitoring program was undertaken over 6 weeks during pilot plant operation and involved the quantitative analysis of pharmaceuticals and personal care products, steroidal hormones, industrial chemicals, pesticides, N-nitrosamines and halomethanes. The first phase consisted of baseline monitoring of target compounds to quantify influent concentrations in feed waters to the plant. This was followed by a period of validation monitoring utilising indicator chemicals and surrogate measures suitable to assess proper process performance at various stages of the AWTP. This effort was supported by challenge testing experiments to further validate removal of a series of indicator chemicals by reverse osmosis. This pilot-scale study demonstrated a simplified analytical approach that can be employed to assure proper operation of advanced water treatment processes and the absence of trace organic chemicals.

Key words | advanced water treatment plant, chemical monitoring strategy, reverse osmosis, trace chemical contaminants

INTRODUCTION
To maintain river health in the Hawkesbury Nepean River system and replace more than 12 billion litres of drinking water currently released from Sydney's major water source, Warragamba Dam, Sydney Water is currently constructing an advanced water treatment plant (AWTP) that will produce up to 18 billion litres of highly treated recycled water annually. Termed the ‘Replacement Flows’ project, this initiative will collect and treat municipal effluent from three major sewage treatment plants (STPs) (St Marys, Penrith and Quakers Hill) in north western Sydney.

A pilot plant simulating the processes of the proposed AWTP was constructed and operated at St Marys STP for a 3-month period. This pilot was used to refine and validate the operational parameters of the AWTP process and to define a monitoring approach for chemical and microbiological constituents for the Replacement Flows Project (RFP). A screening-level risk assessment (SLRA) undertaken for the RFP identified a number of downstream users of the Hawkesbury-Nepean river system, including the North Richmond Water Filtration Plant that supplies potable water meeting the
Australian Drinking Water Guidelines to customers in North Richmond and surrounding areas (Khan et al. 2007). The primary aim of this chemical monitoring program was therefore to validate many of the assumptions made in the SLRA and furthermore:

1. Confirm that key chemicals of potential toxicological concern (including pharmaceuticals, endocrine disrupting chemicals, and emerging disinfection by-products) in the product water are either absent or present at trace concentrations that do not present a source of human or environmental health concern.

2. Establish and validate a series of indicator chemicals and surrogate measures (bulk water parameters) that can confirm proper performance of individual AWTP unit operations.

The monitoring program developed for this project incorporates appropriate chemical indicator compounds and surrogate parameters that address validation of treatment process performance as well as operation and verification requirements described in relevant Australian Guidelines for Water Recycling (AGWR 2008).

The tailored employment of appropriate surrogates and indicator chemicals within predefined boundary conditions developed by Drewes et al. (2008) results in a monitoring regime aiming at obtaining information that provide certainty in proper treatment performance at minimal costs. In the context of this study and consistent with the AGWR, a surrogate is a quantifiable parameter that can serve as a performance measure of treatment processes that relate to removal of specific hazards. For example, conductivity is commonly used as a surrogate for the removal of chemical hazards by reverse osmosis. Similarly, an indicator chemical is a specific chemical that can be used to measure the efficacy of a treatment process. Chemical indicators are selected to represent characteristics of a family or group of chemicals, all of which are assumed to have comparable properties that determine their fate, transport, and removal during treatment.

Physicochemical properties (e.g., molecular size, pK_a, log K_{ow}, volatility, and dipole moment) often determine the fate and transport of a compound during various treatment processes such as high-pressure membranes (Bellona et al. 2004). Thus, the judicious selection of multiple indicators, representing a broad range of properties, enables the assessment to account for compounds that may not be currently identified (“unknowns”), as well as new compounds synthesised and entering the environment in the future (e.g., new pharmaceuticals), provided they fall within the range of the properties covered by the indicators. The underlying assumption is that absence or removal of an indicator compound during a treatment process would also ensure absence or removal of other compounds with comparable physicochemical properties. Proper removal is ensured as long as the treatment process of interest is operating according to its technical specifications. It is therefore necessary to define, for each treatment process, the operating conditions under which proper removal is to be expected (Drewes et al. 2008).

MONITORING PROGRAM

The advanced treatment train proposed for the RFP will utilise tertiary-treated wastewater (<6 mg/L total nitrogen) as source water and consist of chemical dosing (chloramination, pH adjustment), an integrated membrane system (IMS) consisting of ultrafiltration (UF) followed by reverse osmosis (RO) (ESPA2, Hydranautics, Oceanside, CA), a carbon dioxide scrubber and final chlorine disinfection and dechlorination. Of these unit processes, only RO will provide an effective treatment barrier for most chemical contaminants potentially present in the source water (Snyder et al. 2007, Bellona et al. 2008). Thus, the monitoring program developed in this study is designed to assure proper performance of the key treatment barrier, reverse osmosis, for these chemical contaminants.

According to the AGWR (2008), monitoring may be used to:

- obtain baseline information (to underpin the risk assessment process),
- determine whether recycled water systems will be safe and not represent a risk to human health or have detrimental effects on the environment (validation, i.e. ‘Will it work?’),
- ensure that preventive measures are working (operational monitoring, i.e. ‘Is it working now?’),
- determine whether the recycled water system has operated effectively, achieved compliance with management requirements and has not represented a risk to public health or had detrimental effects on the environment (verification, i.e. ‘Did it work?’).
Following this logic, performance assessment of individual unit processes comprising an overall treatment train are distinguished into two phases: validation monitoring during piloting/commissioning and compliance monitoring during full-scale operation (defined as operational and verification monitoring). The monitoring approach in this study identified suitable surrogate parameters for ongoing process validation as well as chemical indicator compounds to assure absence of chemical contaminants in the product water. In addition, challenge tests of the treatment system were conducted by spiking selected indicator chemicals at concentrations above background levels. The individual steps followed in tailoring such a monitoring program are outlined in Table 1.

Piloting of the RO process at the proposed AWTP allowed both validating that operational parameters are within technical specifications and quantifying the removal (differential) of surrogate parameters ($X_i$) within these conditions ($\Delta X_i = (X_{i,\text{in}} - X_{i,\text{out}})/X_{i,\text{in}}$). In parallel, an occurrence study was undertaken to confirm the presence of viable indicator compounds in the final effluent of the three STPs (St Marys, Penrith and Quakers Hill) representing the source water feeding the AWTP. During piloting of the RO process, challenge tests were conducted with selected indicator compounds ($Y_i$) spiked at elevated concentrations to determine their removal differential $\Delta Y_i$ under normal operating conditions. The meaningful use of all of these measures requires that suitable process boundary conditions regarding

<table>
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<tr>
<th>Table 1</th>
<th>Application of the surrogate/indicator framework to an overall treatment train (adapted from Drewes et al. (2008))</th>
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<tr>
<td><strong>Surrogate Parameters</strong></td>
<td><strong>Indicator Compounds</strong></td>
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<td><strong>Validation Monitoring: Piloting or/and Commissioning</strong></td>
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</table>
| Step 1 Define and verify operational boundary conditions for each unit process comprising the overall treatment train after operating the system assuring steady-state conditions. Do operational boundary conditions meet design criteria within an acceptable range?  
If yes, proceed to step 2.  
If not, determine cause for deviation. | Baseline Monitoring:  
Conduct occurrence study to confirm presence of viable indicator compounds in the feedwater of each unit process |
| Step 2 Quantify surrogate, e.g., conductivity rejection of overall system. Is conductivity rejection within previously observed range and does it meet performance specification of manufacturer?  
If yes, proceed to step 3  
If not, determine cause for deviation, for example by quantifying conductivity rejection of individual pressure vessels | Identify 5–10 suitable indicator compounds for spiking study (challenge test) at pilot-scale |
| **Step 3 Validation Monitoring:**  
Quantify removal differential of viable surrogate parameter $\Delta X_i = (X_{i,\text{in}} - X_{i,\text{out}})/X_{i,\text{in}}$ | Validation Monitoring:  
Conduct spiking study with select indicator compounds (5–10) to determine the removal differentials under pre-determined operating conditions: $\Delta Y_i = (Y_{i,\text{in}} - Y_{i,\text{out}})/Y_{i,\text{in}}$  
Select 3–6 indicator compounds from categories classified as “Good removal” |
| Step 4 Select viable surrogate and operational parameters for each unit process |  |
| **Compliance Monitoring: Full-scale Operation** |  |
| Step 5 Confirm operational boundary conditions of full-scale train and removal differential $\Delta X_i$ for selected surrogate and operational parameters |  |
| Step 6 **Operational Monitoring:** Monitor differential $\Delta X_i$ of select surrogate and operational parameters for each unit process or/and the overall treatment train on a regular basis (daily, weekly) | **Verification Monitoring:** Monitor differential $\Delta Y_i$ of selected indicator compounds for each unit process or/and the overall treatment train regularly, but less frequently (semi-annually, annually). |
plant design and operation are maintained. For the proposed RO process, both at pilot- and full-scale, these boundary conditions were defined as a source water quality equivalent to UF-treated secondary effluent, pH adjusted to 6.3–6.7, addition of scale inhibitors, and operation at a recovery of 80 to 85%, and a permeate flux of approximately 20 L m⁻²h⁻¹.

**Surrogate parameters**

The removal of the surrogate parameter selected for performance assessment of the RO process should correlate with the removal of indicator compounds occurring at nanograms-per-litre (ng.L⁻¹) concentrations. Thus, a partial or complete removal of a surrogate parameter can demonstrate the proper operation of a unit operation or treatment train regarding the removal of trace organic chemicals. Total organic carbon (TOC), conductivity, and boron rejection were identified in previous research (Drewes et al. 2008) as sensitive measures for the timely identification of performance deficiencies, which may (or may not) result in a diminished removal of chemical contaminants by RO treatment. In this case, conductivity was selected due to its high sensitivity to indicator compound rejection (Drewes et al. 2005) and its suitability for continuous online monitoring.

**Indicator compounds**

Significant research has been conducted to understand the performance of IMS, employing UF followed by RO, in removing select chemical contaminants (Bellona & Drewes 2007; Snyder et al. 2007; Bellona et al. 2008). Building upon this knowledge-base and results revealed from pilot- and full-scale experiments, Drewes et al. (2008) have defined treatment removal categories for indicator compounds of RO systems.

The vast majority of indicator chemicals are efficiently rejected by RO membranes exceeding 90% removal (Snyder et al. 2007; Drewes et al. 2008). Compounds that are non-ionic (neutral) and small can exhibit a partial removal, as observed for nitrosamines, such as NDMA or 1,4-dioxane (Bellona et al. 2004). Indicator chemicals that are small but exhibit hydrophobic properties can adsorb to the polymeric structure of thin-film composite membranes and partition through the active layer of the membrane into the permeate. For example, one compound meeting these properties is chloroform, which usually exhibits only moderate removal during RO treatment (Drewes et al. 2005). The highly efficient rejection of wastewater-derived contaminants by RO membranes limits the number of available indicator compounds representing intermediate removal to a few. None of the indicator compounds considered in this study exhibited poor removal (<25%).

In order to identify a series of suitable indicator chemicals for this project, the presence of viable indicator compounds needed to be confirmed. This was accomplished through an occurrence survey undertaken at the influent of the pilot plant as well as final effluents from the Penrith STP and the Quakers Hill STP. Table 2 shows the full suite of 48 trace organic chemical contaminants that were monitored in the pilot plant. The chemicals that were previously identified as potential suitable indicator compounds including their expected degree of removal by Drewes et al. (2008) are marked by asterisks. The target chemicals present in the influent water at levels five times above the method detection limit are marked with a triangle.

Samples were collected from the three tertiary treated effluents (St Marys, Penrith, Quakers Hill), the UF feed after chloramination, UF permeate (prior to RO balance tank), RO Feed (after RO balance tank), concentrates and permeates, and the final effluent (post chlorination tank).

**Challenge testing**

The objective of the challenge test was to validate the performance of the reverse osmosis membrane process in rejecting trace organic constituents and to correlate removal to the attenuation of surrogate parameters. For the tests of this study, 7 indicator compounds from the treatment categories “good removal (>90%)” and “intermediate removal (50–25%)” as defined by Drewes et al. (2008) were selected as shown in Table 3. In addition to these established indicator compounds, two further chemicals were tested. These were N-nitrosodiethylamine (NDEA) and N-nitrosodipropylamine (NDPA).

The test required elevating the concentration for the select target compounds in the RO feed to approximately 100 times of the concentrations observed during baseline
monitoring for a period of approximately 90 minutes. During this time, samples of the elevated feed water after the high-pressure pump, permeates and concentrates of each stage, and the combined permeate were collected. Samples were collected in pre-cleaned amber glass bottles with preservative and quenching agents added. Two sets of samples were collected for analysis after 60 and 90 minutes from initiating the spike. Samples were extracted within 24 hours and analysed by LC/MS-MS.

A one litre stock solution was prepared containing 30 mg/L of each of caffeine, carbamazepine, ibuprofen, NDPA, NDEA, NDMA and TCEP. Chloroform was not included in the spiking solution since the on-going monitoring of the plant had confirmed that chloroform was measurable at all stages of the treatment process (including RO permeates) at background concentrations of less than 20 ng/L. The one litre stock solution was then diluted into a 120 L plastic drum to give a final challenge test solution concentration of approximately 0.25 mg/L. This solution was then pumped into the RO feed line at a flow rate of approximately 70 L/hr (Figure 1).

Prior to and during the challenge tests, online pH, temperature, permeate flux, recovery and conductivity measurements were recorded. The challenge test was executed only after confirming that the system was achieving a conductivity rejection as previously observed during piloting and was operating within the above mentioned boundary conditions (recovery: ~80%; permeate flux: ~20 LMH; pH = 6.5).

For each indicator compound, rejection was calculated (average concentration of combined permeate divided by average feed water concentration) and compared to the removal categories reported for indicator compounds for RO systems (Drewes et al. 2008). Observed removal percentage similar or larger than the expected removal percentage

Table 2 | Trace organic chemical contaminants monitored during the pilot plant study

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<tr>
<th>Compound</th>
<th>Concentration</th>
<th>Removal Category</th>
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<tr>
<td>Linuron</td>
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<tr>
<td>Atrazine</td>
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<tr>
<td>Atenolol</td>
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<tr>
<td>Sulfamethoxazole</td>
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<tr>
<td>Paracetamol</td>
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<td></td>
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<tr>
<td>Caffeine</td>
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<tr>
<td>Trimethoprim</td>
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</tr>
<tr>
<td>Enalapril</td>
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<tr>
<td>Dilantin</td>
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<tr>
<td>Risperidone</td>
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<tr>
<td>Fluoxetine</td>
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<td>Naproxen</td>
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Compounds detected in pilot plant influent at levels at least five times above the detection limit of usually 5 ng/L.

Compounds detected in pilot plant influent, but at levels less than five times the detection limit.

*Potential suitable indicator compounds for RO processes identified by Drewes et al. (2008) and their degree of expected removal (*: >90%, **: 25–50%)

Table 3 | Selected indicator compounds for performance validation and expected degree of removal as suggested by Drewes et al. (2008)*

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration</th>
<th>Removal Category</th>
</tr>
</thead>
<tbody>
<tr>
<td>Caffeine</td>
<td></td>
<td>Intermediate Removal</td>
</tr>
<tr>
<td>Carbamazepine</td>
<td></td>
<td>Poor Removal</td>
</tr>
<tr>
<td>NDPA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TCEP</td>
<td></td>
<td></td>
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<tr>
<td>NDEA</td>
<td></td>
<td></td>
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<tr>
<td>NDMA</td>
<td></td>
<td></td>
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<tr>
<td>Chloroform</td>
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Operating conditions: recovery: ~80%; permeate flux: ~20 LMH; pH = 6.5.

Removal of compounds was verified through peer-reviewed literature data or experimental data generated during this study.
(Table 3) indicated that proper performance of the RO system could be assumed. For the surrogate parameter conductivity, the removal differential ($\Delta X_i$) between the RO feed and the various stages of RO permeates were calculated. The mean calculated values were Stage 1 permeate (0.99), Stage 2 permeate (0.98), Stage 3 permeate (0.96) and combined permeate (0.98), all relative to the Stage 1 RO feed water (as opposed to subsequent concentrates).

During commissioning of the full-scale RO operation (compliance monitoring), the operational boundary conditions and removal differentials $\Delta X_i$ for selected surrogate parameters must be validated (Table 1). To ensure proper performance of the full-scale RO process, the selected surrogate (e.g., conductivity) should be monitored on a regular basis to confirm compliance with the recycled water quality management plan (operational monitoring). While it is implied that proper performance of the full-scale treatment train will ensure appropriate removal of chemical contaminants, additional monitoring should be conducted to provide confidence for the end users and regulators in the quality of water supplied and functionality of the system as a whole. This verification monitoring which might include selected 3–6 indicator compounds (e.g., atenolol, carbamazepine, dilantin, TCEP, chloroform) for the RO process and/or the overall treatment could occur at frequencies in the order of several months to annually.

Monte-carlo analysis

In order to describe removal of contaminants by reverse osmosis rejection, the concentrations of each contaminant was assessed as a ‘stochastic’ variable taking into account the inherent variability as well as the uncertainty associated with sampling and analysis. A useful way of dealing with a stochastic variable in mathematical models is by describing it, not as a ‘point value’, but as a distribution of values. A probability distribution function (PDF) is a mathematical function that represents a distribution in terms of the probability or frequency of occurrence of specific values within the distribution. The assumption of a lognormal distribution for contaminant variability has been recommended (Eisenberg et al. 2001). Water quality variability may then be characterised by the fitting of lognormal probability plots to available data.

Computing sums, multiplications and other transformations on multiple distribution functions is a mathematically challenging task and, in some cases, impossible. For this, Monte-Carlo techniques can provide a powerful alternative approach. Monte Carlo simulation is currently the most widely used method for probabilistic health risk assessment and exposure assessment (Paustenbach 2000; Lester et al. 2007).

Monte Carlo analysis was undertaken to simulate a distribution for percentage removal for each of the challenge test chemicals. The simulated removal distributions for three N-nitrosamines are provided in Figure 2 as illustrative examples. These PDFs predicted mean removals for NDMA (32%), NDEA (91%) and NDPA (98%) resulting in concentrations consistently below 5 ng/L for these compounds in this pilot study. Of these, only NDMA was assessed by Drewes et al. (2008) as a potential indicator compound with poor removal properties (25–50%). The PDF for NDMA in Figure 2 shows that most of the simulated distribution is indeed within this range.
CONCLUSIONS

The chemical monitoring strategy described in this paper was developed and implemented for the assessment of the performance of an AWTP. The monitoring program was undertaken over 6 weeks during pilot plant operation and involved the quantitative analysis of pharmaceuticals and personal care products, steroidal hormones, industrial chemicals, pesticides, N-nitrosamines, and halomethanes. Baseline monitoring of target compounds in AWTP influents revealed measurable concentrations of a number of potential indicator compounds. This monitoring was followed by a period of validation monitoring using potential indicator chemicals and surrogate measures suitable to assess proper process performance at various stages of the plant. This effort was augmented by challenge testing experiments to further validate removal of a series of indicator chemicals (and two additional N-nitrosamines) by a 3-stage reverse osmosis process.

This pilot-scale study demonstrated that a simplified analytical approach can be employed to assure proper operation of advanced water treatment processes and absence of trace organic chemicals. Verification monitoring of the full scale plant should include surrogate parameter (conductivity) monitoring and might include selected 5–6 indicator compounds for the RO process and/or the overall treatment process. This could occur at frequencies in the order of several months to annually.

REFERENCES


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