Target Screening of Chemicals of Concern in Recycled Water

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Abstract

The results of a characterisation study of water samples collected from an Advanced Water Recycling Plant (AWRP) operating in Perth, Western Australia are presented. The AWRP treats secondary wastewater by ultrafiltration, reverse osmosis (RO) and ultraviolet radiation (UV) to produce recycled water for groundwater replenishment. Water samples collected after RO and UV treatment were characterised by liquid chromatography-high resolution mass spectrometry, using an established protocol for target screening. The target screening of 291 compounds detected a total of 13 chemicals in post-RO and post-UV water, including 2 corrosion inhibitors (4+5-Methyl-1H-benzotriazole, benzotriazole), 3 pesticides (metolachlor, propiconazol, prosulfocarb), 3 pharmaceuticals (lamotrigin, metformin, tramadol), 1 personal care product (galaxalidone), 3 artificial sweeteners (saccharin, acesulfame, sucralose) and 1 flame retardant (triethyl phosphate). The corrosion inhibitors benzotriazole and 4+5-Methyl-1H-benzotriazole, and the pharmaceutical metformin were detected in hundreds of ng/L, while concentrations of the other compounds were present in low ng/L concentrations. Analysis of UV treated water samples showed that UV treatment also helped to reduced UV degradable compounds such as the corrosion inhibitors (>50% removal), triethyl phosphate (~50% removal) and the artificial sweetener acesulfame (~95% removal). Overall, the detection of 13 chemicals through target screening analyses did not account for the residual dissolved organic carbon (DOC) in post RO water, the majority of which is still an intriguing unknown. However, the target screening did show that there were no obvious “known” anthropogenic contaminants contributing to the majority of the DOC in post-RO and post-UV treated water. Calculated risk quotients (RQ) for all detected chemicals in UV treated water were 2 to 6 order of magnitude below 1, implying an high degree of safety associated with human consumption of recycled water. Overall the chemicals screening provided further evidence of the overall safety of the use of recycled wastewater treated by RO and UV as a potable water source.

Water Impact

While research into the chemical safety of recycled water has focussed on measuring chemicals in recycled water, it is not clear what percentage of residual dissolved organic carbon (DOC) in recycled water results from anthropogenic chemicals. Here we show that anthropogenic chemicals do not contribute significantly to residual DOC in recycled water after RO and UV treatment. A risk assessment of the chemicals detected in the recycled water also demonstrates the high degree of safety associated with human consumption of recycled water. However, the study also highlights that end-product compliance testing for all potential chemicals is time consuming and expensive. Further research into the use of bioassays as a monitoring tool for water recycling is recommended.

Introduction

In recent years, Western Australia has experienced a significant reduction in rainwater precipitation levels which has corresponded to a reduction in water available from dams and groundwater for drinking water production.[1] Use of treated wastewater as a drinking water source is becoming increasingly attractive, both in Australia and worldwide, and demonstrating that specific treatment technologies produce safe drinking water is of high importance, particularly focussing on chemical removal using reverse osmosis (RO) followed by ultraviolet irradiation (UV) for disinfection. Research into the safety of recycled water has focussed on monitoring and characterising residual concentrations of inorganic and organic micropollutants in the finished water.[2-4] Chemicals in wastewaters that potentially pose health concern include heavy metals, organic compounds with suspected carcinogenic properties (e.g. *N*-nitrosamines and halogenated disinfection by-products), pharmaceuticals and personal care products (e.g. endocrine disrupting compounds, cytostatics and antibiotics), pesticides and their degradation products, and other unregulated trace organic compounds (i.e. plasticisers, surfactants, musk fragrances, artificial sweeteners) derived from both domestic and industrial activities.[4,5] Therefore residual dissolved organic carbon (DOC) present in RO-treated wastewater may consist of anthropogenic organic compounds, in addition to residual organic matter originally present in drinking water and wastewater, or

chemicals used during RO treatment or leached from RO membranes.[6,7] Very few attempts to characterise this residual DOC have been reported to date,[8,9] although a recent assessment of 375 chemicals in recycled water suggested that only ~2-5% of DOC in the RO treated water could be attributed to regularly detected (>25% detection) anthropogenic chemicals.[10] In this work we present the results of a characterisation study of recycled water collected from an Advanced Water Recycling Plant (AWRP) located in Perth (WA) after both RO and UV treatment over four days. The water samples were extracted using mixed bed solid-phase extraction cartridges and then characterised by liquid chromatography-high resolution mass spectrometry.

While almost 400 chemicals were screened previously in RO treated wastewater from a Perth wastewater treatment plant,[5] particular emphasis in this work was given to polar chemicals amendable by LC-MS. The target screening in this study assessed the occurrence of 291 chemicals including pharmaceuticals (88 compounds), pharmaceutical-metabolites (27 compounds), illicit drugs and metabolites (14 compounds), pesticides (79 compounds), pesticide-metabolites (51 compounds), biocides and metabolites (11 compounds), artificial sweeteners (6 compounds), personal care products (3 compounds), corrosion inhibitor and metabolites (5 compounds), industrial chemicals (5 compounds) and miscellaneous (2 compounds). Chemicals were selected based on 1) prior knowledge of their occurrence in wastewater inflow and outflow; 2) existing studies of recycled water and surface waters from previous surveys and literature.[4,5,10,11] A snapshot of the chemicals and their transformation products and metabolites assessed in the target screening analysis is given in Figure 1 and the full list of the chemicals is reported in Table S1 available in the Supporting Information. Eighty five percent (248 of 291) of the target compounds were analysed in the Perth AWRP for the first time in this study. The contribution of detected chemicals to the residual dissolved organic carbon (DOC) measured in UV treated water was also assessed. For a screening health risk assessment, risk quotients (RQ) were calculated by comparing median and maximum concentrations of chemicals measured in UV treated water with the corresponding health values.

2. Experimental

2.1 Sampling

Samples were collected on four days (16/01/12 to 19/01/12), from an AWRP in Perth, Western Australia. Details of the AWRP have been previously published,[11-13] but briefly, the AWRP receives secondary wastewater (WW) from Beenyup WWTP and produces high purity recycled water that is then injected into a deep drinking water aquifer. Beenyup WWTP receives predominantly urban residential wastewater, and the raw WW is screened to remove large material, before grit removal and primary sedimentation. The primary treated WW then undergoes conventional activated sludge treatment with biological nutrient removal before clarification. Most secondary WW from Beenyup WWTP is discharged into the Indian Ocean, while a small portion (7 ML/d) is fed into the AWRP. Treatment at the AWRP consists of chloramination to minimise biofouling on membranes, ultrafiltration, reverse osmosis, and UV disinfection. A caustic dosing between the UV reactors is also present to adjust the pH to neutral conditions before the product water is degassed, stored and reinjected into the groundwater. After UF/RO/UV treatment, about 4.5 ML/d are reinjected into the groundwater aquifer, while the RO reject (about 2.5 ML/d) is sent back to the head of the WWTP. A schematic of the treatment train at Beenyup WWTP-AWRP including sampling points is shown in Figure 2.

Grab samples were collected directly after RO and UV treatment (i.e. after caustic dosing, see Figure 2) in 2 L amber glass bottles, previously annealed at 550 °C overnight to ensure thermal degradation of and residual organic material. Bottles were also rinsed with the sample prior to sample collection. Sample were chilled with ice packs during transport to the CWQRC laboratory, and then stored at 4 ºC until extraction. Prior to processing though solid-phase extraction (SPE), all samples were re-equilibrated to room temperature and then filtered through 0.45 µm Microfiberglass Duo-Fine® Filter cartridges (PALL Life Sciences, East Hills, USA) pre-conditioned with 10 L of ultrapure water. To avoid cross contamination, a single filter cartridge was dedicated to each type of water processed. Quality control samples consisted of post RO water and laboratory ultrapure water, fortified with different concentrations of standards and surrogate standards. Laboratory blanks were also processed along with the batch of samples and analysed for quality control purpose.

2.2 Sample extraction

Because of the low concentrations expected in the post RO and post UV water samples, solid-phase extraction (SPE) as described by Kern *et al*.[14] was used to concentrate the analytes from the samples. Briefly, the pH of each sample (2 L) was adjusted to 6.5−6.7 by adding 1 mL of ammonium acetate buffer (1 mol/L) and formic acid or ammonia solutions as required. For accurate quantification using LC-MS analysis, 100 ng of a surrogate standard mix containing 113 isotopically labelled substances were spiked to each sample. The layered 'mixed bed' cartridges for SPE consisted of 200 mg of OASIS HLB material (30 micro-M; Waters AG, USA) and mixed phase (350 mg in all: 100 mg Strata-X-AW (Phenomenex, USA), 100 mg Strata-X-CW (Phenomenex, USA), 150 mg Isolute ENV+ (Separtis GmbH, Germany). An automated Aspec XLi extractor (Gilson, USA) was used for conditioning and elution of the cartridges. For conditioning, 5 mL of methanol and 10 mL of ultrapure water were dispensed at 2 mL/min. After conditioning, samples were loaded onto the SPE cartridges using two 8-channel off-line peristaltic pumps (Gilson) at a flow rate of 5 mL/min. Prior to elution, cartridges were completely dried using a vacuum manifold. The elution of the analytes from the SPE stationary phase was achieved by applying a basic solution (8 mL of ethylacetate/methanol containing 0.5% ammonia hydroxide (v/v)), followed by an acidic solution (4 mL of ethylacetate/methanol containing 1.7% formic acid (v/v)) dispensed at 2 mL/min. The eluates were concentrated to about 100 µL using a dry block heater (30°C) fitted with nitrogen blowdown (Ratek 30D, Australia), before being rediluted to 1 mL using ultra pure water. Finally, the extracts were filtered directly into a 2 mL brown glass vial using a syringe fitted with a 0.45 µm regenerated cellulose membrane filter (Infochroma AG, Switzerland). Samples extracts chilled with ice packs were shipped using an international express delivery service to EAWAG laboratories in Dübendorf (Switzerland) for analysis.

2.3 Chromatographic separation

For the reversed phase chromatographic separation, an aliquot of the extract (20 µL) was injected onto a XBridge C18 column (Waters USA, 2.1 x 50 mm, 3.5 µm particle diameter) using a guard column (2.1 x 10 mm) of the same stationary phase. The eluent consisted of nanopure water (eluent A) and methanol (eluent B), both

containing 0.1% (v/v) formic acid. The LC gradient used for the separation was as follows: 0 – 4 min, eluent B was increased from 10 - 50%; 4 – 17 min, eluent B was increased from 50 – 95%, then continued at 95% for 8 minutes. Prior to the next injection, the column was re-equilibrated with 90% eluent A and 10 % eluent B for 5 min. The eluent flow rate was 0.2 mL/min at a temperature of 30 °C.

2.4 Detection and quantification using high resolution mass spectrometry (HRMS)

Analytes were detected using a high resolution mass spectrometer (Q Exactive; Thermo Fisher Scientific Corporation, USA). Ionisation of analytes was achieved using electrospray ionisation (ESI) operated in both positive (+eV) and negative (-eV) modes. The ESI and HRMS settings are reported in Table S2, available in the Supporting Information. A screening analysis was conducted where the selected target analytes were recorded using Q Exactive mass spectrometer full-scan spectra from 100-1000 m/z with a mass resolution (R) of 140,000 (@ 200 m/z) in positive and negative ionisation mode. For confirmation, all target analytes were fragmented in the HCD collision cell (high energy collision dissociation) using a data-dependent MS2 fragmentation approach. The top 5 MS2 spectra were measured in the Orbitrap mass analyser with a resolution of 17,500, normalized collision energies ranged from 20-100%.

2.5 Data processing and quantification

A target screening was conducted on the Q Exactive raw data files using the software package enviMass 1.2 [15]. Peak lists for each sample were generated from raw data files using the freely available peak picking software Formulator (rev3, Thermo Fisher Scientific). Parameters for both the enviMass 1.2 and the Formulator software are listed in Table S3-S4 available in the Supporting Information. Peak lists were then loaded into the enviMass1.2 software for a qualitative target screening of 291 target substances. Positive detects were manually reprocessed and quantified using the Xcalibur 2.2 QuanBrowser Software (Thermo Fisher Scientific). Quantification was performed with seven extracted standard samples containing all spiked target compounds with concentrations of 1, 5, 10, 25, 50, 100 ng/L and a blind sample (extracted nanopure water with spiked internal standards mix).

For quality control, the relative SPE recoveries of the method were determined. One matrix sample constituted of post RO water was split in two equal portions. The first

portion was spiked with 100 ng/L of standard mix and labelled surrogates while the second portion was treated as a blank and spiked with the labelled surrogates only, Both samples were treated exactly as the other samples in the batch. Relative deviations of recoveries within ± 30% were accepted (See Table S5 available in the Supporting Information).

All detected substances were confirmed using the data-dependend MS2 spectra which were compared against single substance injection MS2 spectra acquired in house with varying collision energies.

3. Results and Discussion

3.1 Compounds detected in RO treated water

Table 1. Concentration range (min–max) and median concentration (ng/L) of detected target compounds in post RO and post UV water samples collected from Beenyup AWRP on four different days (16/01/12 – 19/01/12). The average UV removal with the relative standard deviation is also reported.

Chemicals	Post RO samples		Post UV samples		
	Concentration range min–max	Median	Concentration range min–max	Median	Average UV removal (±RSD)
4+5-Methyl-1H-benzotriazole	750–900	775	350–400	375	53±6
Benzotriazole	750–1300	800	375–550	412	51±5
Galaxalidone	15–52.5	29	5–30	14	37±48
Lamotrigin	5–5	5	2.5–5	2.5	N/A
Metolachlor	<1*–7.5	3.75	0.5**–5	2.5	N/A
Metformin	65–105	99	87.5–110	95	N/A
Propiconazole	5–8	7.5	2.5–7.5	6.25	N/A
Prosulfocarb	2.5**–5	5	<5*–5	5	N/A
Tramadol	0.5**–475***	0.5**	0.5**–100***	N/A	N/A
Acesulfame	25–35	26	<1*–2.5	N/A	95±2
Saccharin	<1*–2.5	2.5	<1*–5	5	N/A
Sucralose	2.5–10	10	2.5–10	8.75	N/A
Triethyl phosphate	200–200	200	100–100	100	50±N/A

*LOQ; ** tentatively quantified; N/A: not available; ***outlier

The concentrations of detected chemicals in RO treated water are reported in Table 1. Only 13 of the 291 chemicals targeted (i.e. ~4.5 %) were detected in RO water, although these chemicals were frequently detected in either 3 or 4 of the 4 sampling events. The chemicals detected included two corrosion inhibitors (4+5-Methyl-1H-benzotriazole and benzotriazole), three pesticides (metolachlor, propiconazol, prosulfocarb), three pharmaceuticals (lamotrigin, metformin, tramadol), 1 personal care product metabolite (galaxalidone), three artificial sweeteners (acesulfame, saccharin and sucralose) and 1 industrial chemical (triethyl phosphate). Most chemicals were detected at a concentration less than 50 ng/L. However, the corrosion inhibitors chemicals benzotriazole and 4+5-Methyl-1H-benzotriazole, the pharmaceutical metformin and the industrial chemical triethyl phosphate were detected at much higher concentrations, between 65 and 1300 ng/L.

Benzotriazole and its derivatives, including 4+5-Methyl-1H-benzotriazole are high volume production chemicals, with an estimated worldwide production of benzotriazoles in excess of 9000 tons/year.[16,17] They are commonly used in paints and polymers as UV absorbers, detergents, antifreeze, brake fluids and in aircraft de-icing fluids as corrosion inhibitors[18] and they are extensively found in WW and the environment.[19] They have been found to be acutely toxic to specific species,[20] but their chronic toxicity is not well studied. Benzotriazole and 4+5-Methyl-1H-benzotriazole were consistently detected in relatively high concentration ranges in RO treated water, and this is expected given the µg/L concentrations previously detected in Beenyup secondary treated WW,[12] the relatively low MW (<150 Da) and the high water solubility and mobility (log K_{ow} = 1.23 for benzotriazole and log K_{ow} = 1.89 for 4+5-Methyl-1H-benzotriazole, see Table S5 available in the Supporting Information). These results are also consistent with our previous findings, which showed benzotriazole and 4+5-Methyl-1H-benzotriazole concentrations in RO treated water averaging 974 (±28) ng/L and 416 (±34) ng/L, respectively.[12]

Galaxolidone, is a metabolite of galaxolide, a polycyclic musk widely used as a fragrance in personal care and consumer products including cosmetics, cleaning agents, detergents, air fresheners and perfumes.[21] Galaxolidone results from the degradation of the parent compound galaxolide during biological activated sludge.[22,23] Given their high log K_{ow} (5.9 and 5.3 respectively), both galaxolide and

galaxolidone can concentrate in blood, fat[24] and breast milk.[25] Synthetic musks can affect androgen and progesterone receptors and also stimulate estrogenic receptors in humans.[26] Polycyclic musks have been reported in water bodies and biota previously.[27] The median concentration of galaxolidone in RO treated water was 29 ng/L. However, galaxalidone was also detected in the CWQRC laboratory blanks at 10 ng/L (data not shown). This contamination could have resulted from an accidental exposure of the laboratory blank to the chemical at the time of sample collection or during the sample preparation process. Galaxolide and its metabolite galaxalidone will preferentially absorb onto plastic and glass (i.e. SPE equipment) and therefore are prone to cross-contamination. Despite this cross-contamination issue, it is still likely that low ng/L concentration of galaxolidone are present in RO treated water. The parent compound galaxolide was previously measured in wastewater and recycled samples from Beenyup WWTP and AWRP.[11] Even though galaxolidone is neutral, based on the scheme proposed by Bellona et al.[7] the physical-chemical properties of this chemical (MW > Molecular weight cut off (MWCO) of the membrane, approximately 150-200 Da, and log K_{ow} > 2), a moderate to high rejection is expected during RO treatment. Given the high volume of usage and high concentration of galaxolide in WW[11] and the high hydrophobicity of galaxolidone, it may have accumulated on the membranes and eventually achieved breakthrough from diffusion phenomena.[7]

The median concentration of the industrial chemical triethyl phosphate in RO treated water was 200 ng/L. Triethyl phosphate is a common flame retardant, a polymer resin modifier, a plasticizer (e.g. for unsaturated polyesters) and an intermediate in the manufacture of pesticides and other chemicals.[28-30] It is used as an industrial catalyst (in acetic anhydride synthesis) and as a solvent (e.g. cellulose acetate), a stabilizer for peroxides, and a strength agent for rubber and plastics including vinyl polymers and unsaturated polyesters.[28-30] Previously, we have detected a range of phosphate chemicals including triethyl phosphate, tris(chloropropyl) phosphate, tris(dichloropropyl) phosphate in wastewater samples from Beenyup WWTP. Furthermore, while all phosphate chemicals were below detection in samples collected post-RO treatment (LOD = 100 ng/L), they were all detected in the RO reject water.[11] Further research is needed to better understand the occurrence of triethyl phosphate in wastewater and assess the rejection of this class of chemicals

during UF/RO treatment. However, given the small molecular weight, the high pKa and the low log K_{ow} (see Table S5) a poor rejection is expected for this compound.[7]

Out of 79 pesticides, 51 pesticides metabolites, 9 biocides and 2 biocides metabolites targeted, only 2 pesticides (metolachlor and prosulfocarb) and 1 biocide (propiconazole) were detected at very low concentrations in RO treated water. Interestingly, the pesticide metolachlor was also detected in our previous work,[10] at similar concentrations, possibly indicating breakthrough during RO treatment. However, in this study metolachlor was detected in 100% of the samples tested (4 RO treated samples and 4 UV treated samples, see Table 1) compared to only 3% of the samples (1 sample out of 33 analysed) tested previously.[10] The high frequency in the detection observed for metolachlor in this work may be due to the much lower LOD (1 ng/L) achieved in this study compared to the LOD (60 ng/L) achieved in the previous study. Propiconazole, the biocide detected in this work, was not detected previously,[10] again possibly because the LOD (5 ng/L) achieved in this study was much lower than the LOD (100 ng/L achieved in the previous study. Prosulfocarb was not analysed previously and therefore a comparison is not possible. All three pesticides have MW that is greater than the MWCO of the RO membranes and also possess log $K_{ow} > 2$. In this scenario, good removal is expected, although membrane breakthrough could be caused by partitioning/diffusion within the membrane.[7]

Only 3 pharmaceuticals of the 88 pharmaceuticals and 27 pharmaceutical metabolites (27 compounds) tested were detected in RO treated water. Lamotrigine is an anticonvulsant drug used in the treatment of epilepsy and bipolar disorder.[31] It is also used off-label as an adjunct in treating depression. Tramadol is used similarly to codeine and it is a synthetic analgesic used to treat moderate to moderately-severe pain. The drug has a wide range of applications, including treatment of rheumatoid arthritis, restless legs syndrome and fibromyalgia.[32] Metformin is very commonly used for treatment of type 2 diabetes in obese and overweight people and it is listed as one (of only two) oral antidiabetics in the World Health Organization Model List of Essential Medicines.[33] All 3 pharmaceuticals are registered for use and commonly sold in Australia.[34] Concentration of lamotrigine and tramadol in RO treated water were below 5 ng/L, with the exception of tramadol, which was measured at 475 ng/L in one sample (19/01/2012). The reason for such high

concentration post RO treatment is not known. However, given that contamination from this compound (100 ng/L) was also seen in one laboratory blank, this single high detection level should be treated as an outlier. In contrast the median concentration of metformin over all RO treated water samples was 99 ng/L. Metformin, is commonly found in water bodies due to its high volume usage.[35] Moreover, given its relatively low molecular weight and high solubility (see Table S5), RO rejection is expected to be relatively poor. All 3 pharmaceuticals have been previously tested in Beenyup WWTP and Beenyup AWRP but were not detected in RO treated water possibly due to higher LOD.[11]

The 3 artificial sweeteners detected in RO treated water were acesulfame, sucralose and saccharin. While the presence of artificial sweeteners, a common constituent of low calorie food and beverages, in the aquatic environment has been reported in previous studies overseas,[36-43] little has been reported regarding their presence within Australian waters.[11] Recent studies have shown that artificial sweeteners are quite stable and persistent in the environment, and are excreted predominantly unchanged as waste from the body.[36,39,40] Sucralose in particular, is resistant towards biodegradation, and as a result is persistent in WWTP.[36,37,43] To the best of our knowledge, little has been reported regarding the behavior of artificial sweeteners during RO treatment. Acesulfame (MW = 162 Da) and saccharin (MW = 183 Da) both have molecular weights close to the MWCO of the RO membrane. Moreover both have high water solubility,[42,44,45] meaning they are unlikely to adsorb on membranes and therefore poor rejection is expected[7] (see Table S5). Furthermore, the presence of µg/L concentrations in secondary WW feed to Beenyup AWRP may also play an important role in the detection of these sweeteners post RO treatment, as high concentrations in secondary WW have been linked to detection in RO treated water, even when RO rejection is high.[10] Artificial sweeteners represent an ideal marker for wastewater contamination and the study of their behavior during RO treatment could significantly aid wastewater recycling and future management of groundwater replenishment.

3.2 Compounds detected in UV treated water

At Beenyup AWRP, the last treatment barrier is UV for pathogen inactivation. This barrier employs ITT Wedeco units (low pressure lamps, UV-C at 254nm, 4 UV units

in series, dose of up to 50mJ/cm^2 for each unit). Analysis of samples post-UV treatment showed that the concentration of some UV degradable compounds was reduced. Table 1 presents the concentration of chemicals detected in UV treated water as well the observed average removal after the UV treatment, calculated using the percentage difference in concentration between RO treated water and UV treated water for matched samples.

For both benzotriazole and 4+5-Methyl-1H-benzotriazole the UV treatment led to average removal of about 50% of the initial concentrations. This is in agreement with previous research showing benzotriazoles are prone to degradation by UV light (direct photolysis); benzotriazole and its derivatives are known UV absorbers,[46,47] so degradation and reactivity of this class of chemicals was expected to be significant. For galaxolidone, a moderate but highly variable removal was achieved (average UV removal = 37±48%). A significant and consistent reduction of the concentration of the artificial sweeteners acesulfame (average UV removal: 95±2%) was also observed. The kinetic and the mechanism of degradation of this compound has previously been described in full,[48] confirming the effectiveness of UV treatment to reduce the concentration of this compound in receiving waters. For triethyl phosphate the median UV removal was 50%. For the remaining compounds detected in RO treated water, it was not always clear whether UV treatment reduced concentrations in the final product water as most concentrations were low and near the LOQ of the compound or in some case, the concentration detected post UV was higher than the concentration detected post RO.

Tertiary treatments such as UV for virus inactivation, as well as advanced oxidation processes including use of strong oxidants such as ozone, H_2O_2 + UV and combination of them, usually result in the incomplete mineralisation of micropollutants, and the formation of mixtures of transformation by-products.[49-51] The chemical structures, but more importantly the toxicological properties, of the transformation by-products arising from incomplete oxidation of micropollutants remains unknown for a wide range of chemicals although research in this area has been rapidly developing in the last decade.[49-52] Nowadays, there is general consensus that whenever an oxidation process is applied to polish the final water,

transformation by-products should be also assessed through non-target analysis and included in the risk assessment where possible. Further research into the integrated use of target/non-target chemical screening and bioassays as a monitoring tool for water recycling is recommended.

3.3 Contribution of anthropogenic chemicals to the dissolved organic carbon

Previous research characterized RO water in Perth, Western Australia for 375 anthropogenic chemicals, with 108 chemicals detected on at least one occasion, and 30 chemicals detected in more than 25% of all samples.[5,10] However, assessment of the contribution of these detected chemicals to the DOC measured in RO treated water was only able to attribute 2.5 to 5% of the DOC to anthropogenic chemicals.[10] One of the objectives of this present work was to assess whether analysis of an extended list of polar organic chemicals could help to account for the remaining DOC. In this study, the RO treated water was analysed for 291 chemicals, of which 248 chemicals have not been analysed previously at Beenyup AWRP. Out of these 291 chemicals, only 13 compounds (~4.5%) were detected. The contribution of anthropogenic chemicals to the residual DOC in post UV treated water was estimated using the same methodology described in Linge et al., in which DOC contribution is calculated using the percentage carbon in each detected molecule.[10] Overall, the detection of these 13 compounds in the RO effluent could not account for the residual DOC in RO water, with the detected chemicals contributing between 0.6 µg/L (median value) to 1.3 µg/L (maximum value) of DOC. The DOC measured at Beenyup AWRP plant over the 4 days of sampling (16/01/12 - 19/01/12) averaged 58 µg/L and therefore, the total contribution of DOC from these anthropogenic chemicals remains very small (1.0 – 2.3%).

3.4 Screening Health Risk Assessment

A screening health risk assessment was conducted using the concept of the risk quotient (RQ), which is calculated as the ratio between the reported concentration of each chemical and the appropriate health values.[5,10] Median and maximum concentrations of chemicals detected in post UV treated water were used to generate median and maximum RQs (Table 2). A risk quotient below one implies no health impact is expected. Health values for benzotriazole, metolachlor and metformin were taken from the Australian Guidelines for Water Recycling,[53] while a

health value for propiconazole was taken from the Australian Drinking Water Guidelines.[54] The health value for tolyltriazoles (4+5-Methyl-1H-benzotriazole) is the value used for recycled water at Beenyup AWRP.[55] No Australian derived water guidelines exist for the other chemicals detected in this study and therefore other approaches were used to determine health values. For the metabolite galaxolidone, the AGWR guideline for the parent compound galaxolide (1750 µg/L) was used, with the addition of an extra safety factor of ten.[53] For triethyl phosphate, a health value of 1000 µg/L was used, as it belongs to the same class of phosphate flame retardants, including tri(dichlorisopropyl) phosphate, triphenyl phosphate; tris(2 chloroethyl)phosphate.[53] For the pharmaceuticals lamotrigine and tramadol, health values were calculated from the lowest daily therapeutic dose (LDTD)[56] using the approach outlined in the Australian Guidelines for Water Recycling:[53]

$$\text{Health value (µg/L)} = (\text{LDTD (mg/day)} \times P \times 10^3) / (SF \times V \text{ (L/day)}) \quad (1)$$

where P = proportion of LDTD estimated to come from drinking water (100%); 10^3 = unit conversion mg/L to µg/L; SF: safety factor (1000 for most pharmaceuticals); V = volume of water drunk (2 L/day). Health values for the artificial sweeteners, acesulfame, saccharine and sucralose,[44] and the pesticide prosulfocarb[57] were all derived from acceptable daily intake values (ADI, expressed as mg/kg body weight, assuming body weight = 70 kg) as outlined in the Australian Guidelines for Water Recycling.[53]

Table 2. Screening health risk assessment for UV treated water reporting median and maximum risk quotients (RQ_{med} and RQ_{max}).

Chemicals	Health Value (µg/L)	RQ_{med}	RQ_{max}	Reference
4+5-Methyl-1H-benzotriazole	20	0.019	0.020	[55]
Benzotriazole	20	0.021	0.028	[53]
Galaxolidone	175[a]	0.000008	0.00002	[53]
Lamotrigine	12.5[b]	0.0002	0.0004	[56]
Metolachlor	300	0.000008	0.00002	[53]
Metformin	250	0.0004	0.0004	[53]
Propiconazole	100	0.00006	0.000075	[54]

Prosulfocarb	0.175[c]	0.028	0.028	[57]
Tramadol	200[b]	N/A	0.0000125	[56]
Acesulfame	315[c]	N/A	0.0000079	[44]
Saccharin	133[c]	0.000037	0.000037	[44]
Sucralose	525[c]	0.000016	0.000019	[44]
Triethyl phosphate	1000[d]	0.0001	0.0001	[53]

[a]Galaxolidone, a metabolite of galaxolide, currently does not have a guideline value. The drinking water guideline for galaxolide (1750 µg/L) was used instead with an extra safety factor of ten. [b]Drinking water guideline calculated from the lowest daily therapeutic dose (LDTD). [c]Drinking water guideline calculated from the acceptable daily intake (ADI). [d]Drinking water guideline derived from similar phosphate flame retardants.

For all chemicals both RQ_{med} and RQ_{max} were between 2 and 6 orders of magnitude below 1 implying a high degree of safety associated with human consumption of recycled water.

4. Conclusions

The target screening conducted in RO and UV treated water samples from Beenyup AWRP has shown the presence of small (MW<200 Da), hydrophilic species such as corrosion inhibitors (i.e. benzotriazole and 4+5-Methyl-1H-benzotriazole), pharmaceuticals (i.e. metformin), artificial sweeteners (i.e. acesulfame and saccharin) and industrial chemicals (i.e. triethyl phosphate). These chemicals were consistently found in all samples and could potentially be used as treatment performance indicators in future studies. Very low concentrations (ng/L) of pesticides (metolachlor, propiconazole and prosulfocarb), along with other pharmaceuticals (lamotrigine and tramadol) were also detected. The break-through during RO treatment of some of these relatively large (MW >250 Da) and hydrophobic (log Kow > 2) chemicals could be due to diffusion/partitioning within the membrane. The UV treatment installed at Beenyup AWRP helped to reduced UV degradable compounds such as the corrosion inhibitors (>50% removal), the flame retardant triethyl phosphate (~50% removal) and the artificial sweetener acesulfame (~95% removal). Overall, the contribution of the detected anthropogenic chemicals to the DOC measured in post UV treated water was found to be minimal (1.0 – 2.3%). The target screening analysis also show that a number of anthropogenic chemicals (i.e. 278 out

of 291 compounds, >95.5%) such as pesticides, biocides, industrial chemicals, pharmaceuticals and metabolites were not detectable in RO and UV treated water. A screening heath risk assessment showed that RQ were generally 2 to 6 orders of magnitude below 1, implying a high degree of safety associated with human consumption of recycled water. Overall this chemical screening provides further evidence of the overall safety of the use of recycled wastewater treated by RO and UV as a potable water source, and it has confirmed that anthropogenic chemicals constitute a relatively small percentage of DOC in RO treated WW. However, the study also highlights the limitations of the traditional approach for assessing chemical safety, focused on end-product compliance testing for all potential chemicals. This approach is time consuming, expensive, and relies on the availability of appropriate health values for all chemicals tested. Given the time consuming nature of trace chemical analysis, further research into the use of bioassays as a monitoring tool for water recycling is recommended.[11,58-61] Bioanalytical tools can screen for a wide range of contaminants and transformation products, based on biological effect, rather than monitoring specific chemicals, and may provide an efficient high-throughput tool broad screen assessment of water quality or hazard identification, and risk characterisation.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found at in the online version.

Figure 1. Parents compounds, transformation products and metabolites assessed in the target screening analysis.

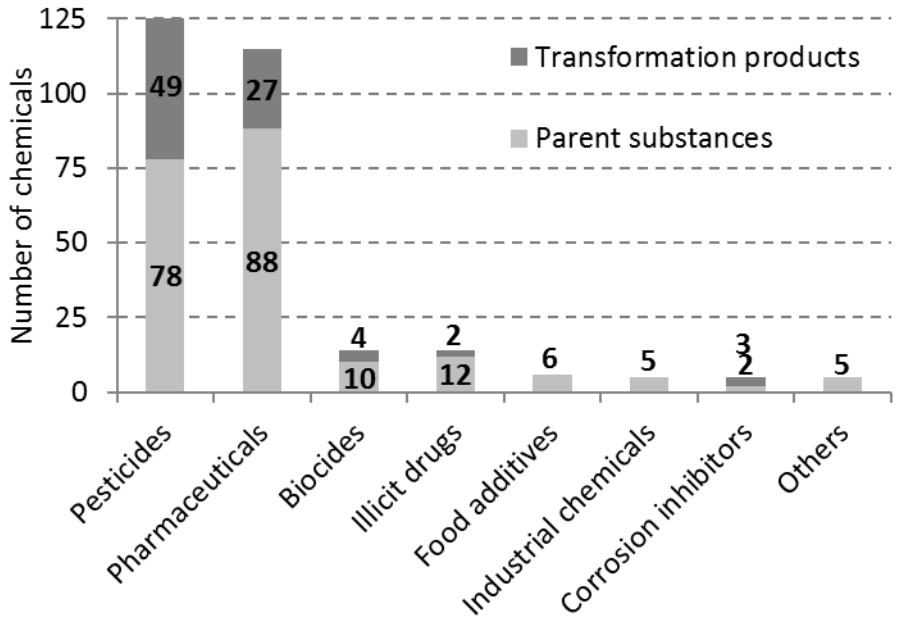
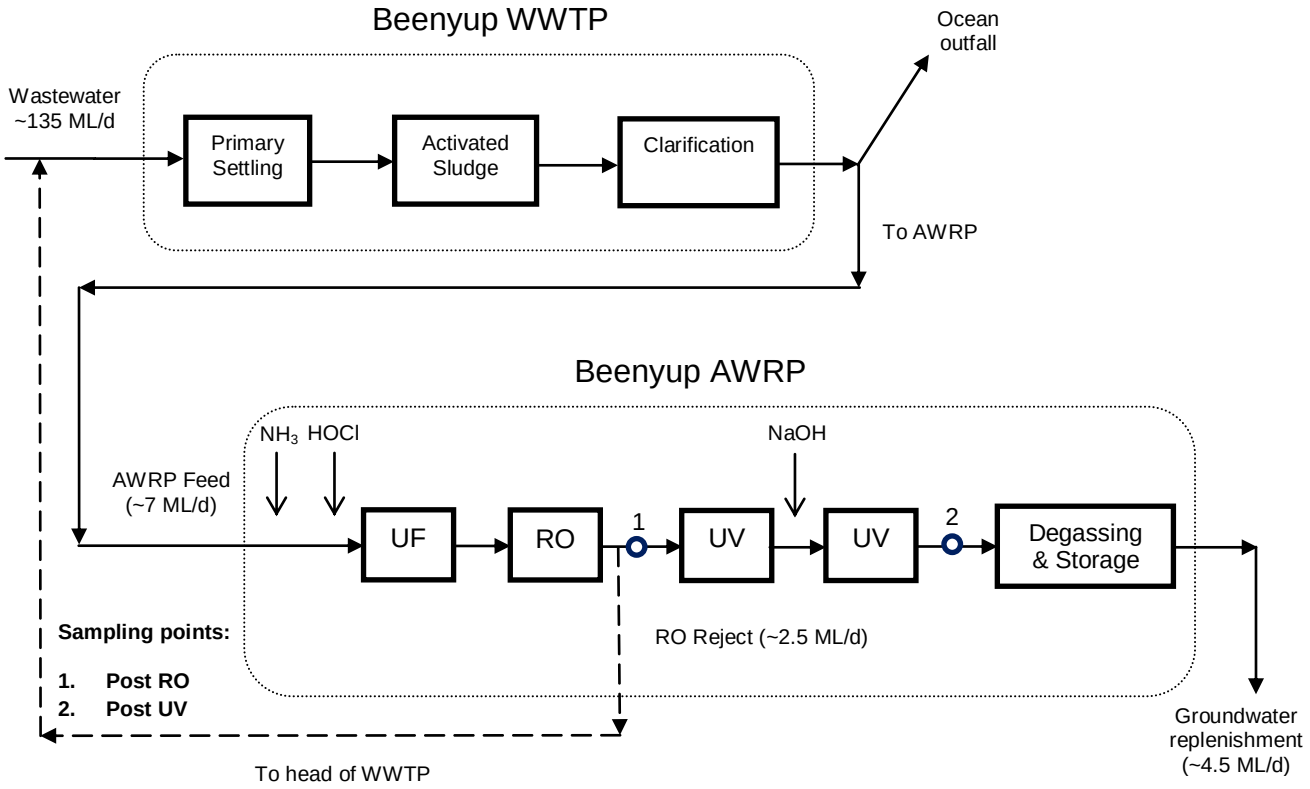


Figure 2. Schematic of Beenyup Wastewater Treatment Plant (WWTP) and Beenyup Advanced Water Recycling Plant (AWRP). Sampling points (i.e. 1-2) are also indicated. UF: ultrafiltration; RO: reverse osmosis; UV: UV disinfection; ML/d: mega litres per day.



Supporting Information

Target Screening of Chemicals of Concern in Recycled Water

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Table S1. Summary of the chemicals targeted in post RO and post UV treated water at Beenyup AWRP.

Chemical (labelled surrogate)	CAS-Nr.	Formula	Exact mass	Ionisation mode	LOQ	metabolite of/ sub-group
PESTICIDES						
2,4-D (2,4-D ^{13}C6)	94-75-7	C8H6Cl2O3	219.9689	-	5	herbicide
Acetochlor	34256-82-1	C14H20ClNO2	269.1177	+	100	herbicide
Alachlor (Alachlor-d13)	15972-60-8	C14H20ClNO2	269.1177	+	100	herbicide
Aldicarb (Aldicarb-d3)	116-06-3	C7H14O2N2S	190.0776	+	10	insecticide
Asulam	3337-71-1	C8H10N2O4S	230.0356	+	20	herbicide
Atraton	1610-17-9	C9H17N5O	211.1428	+	1	herbicide
Atrazine (Atrazine-d5)	1912-24-9	C8H14Cl1N5	215.0932	+	1	herbicide
Azoxystrobin	131860-33-8	C22H17N3O5	403.1163	+	1	fungicide
Bentazone (Bentazone-d6)	25057-89-0	C10H12N2O3S	240.0563	-	0.5	herbicide
Bromazil	314-40-9	C9H13BrN2O2	260.0155	+	3	herbicide
Bromoxynil	1689-84-5	C7H3Br2NO	276.8561	-	1	herbicide
Carbetamide	16118-49-3	C12H16N2O3	236.1155	-	1	herbicide
Chloridazon (Chloridazon-d5)	1698-60-8	C10H8Cl1N3O	221.035	+	2	herbicide
Chlortoluron (Chlorotoluron-d6)	15545-48-9	C10H13ClN2O	212.0711	+	0.5	herbicide
Clomazone	81777-89-1	C12H14ClNO2	239.0708	+	1	herbicide
Cymoxanil	57966-95-7	C7H10N4O3	198.0753	+	10	fungicide
Cyproconazole	94361-06-5	C15H18ClN3O	291.1133	+	10	fungicide
Cyprodinil	121552-61-2	C14H15N3	225.126	+	10	fungicide
Desmedipham	13684-56-5	C16H16N2O4	300.1105	+	20	herbicide
Diazinon (hydrolized)(Diazinon-d10)	333-41-5	C12H21N2O3PS	304.1005	+	n.q.	insecticide
Dicamba (Dicamba-d3)	1918-00-9	C8H6Cl2O3	219.9699	-	20	herbicide
Dichlorprop (Dichlorprop-d6)	120-36-5	C9H8O3Cl2	233.9845	-	5	herbicide
Diflufenican (Diflufenican-d3)	83164-33-4	C19H11F5N2O2	394.0735	+	70	herbicide
Dimethachlor	50563-36-5	C13H18ClNO2	255.1021	+	0.5	herbicide
Dimethenamid	87674-68-8	C12H18ClNO2S	275.0741	+	0.5	herbicide
Dinoseb	88-85-7	C10H12N2O5	240.0741	-	5	herbicide
Epoxyconazole	133855-98-8	C17H13ClFN3O	329.0726	+	10	fungicide
Ethofumesat	26225-79-6	C13H18O5S	286.0869	+	10	herbicide
Fenpropimorph	67306-03-0	C20H33NO	303.2557	+	1	fungicide
Fipronil	120068-37-3	C12H4Cl2F6N4O1S	435.9387	+	1	insecticide

Fluazifop (free acid)	69335-91-7	C15H12F3NO4	327.0724	-	1	herbicide
Fludioxonil	131341-86-1	C12H6F2N2O2	248.0392	-	0.5	fungicide
Flufenacet	142459-58-3	C14H13F4N3O2S	363.067	+	2.5	herbicide
Fluroxypyr (free acid)	69377-81-7	C7H5Cl2FN2O3	253.9667	-	5	herbicide
Flusilazole	85509-19-9	C16H15F2N3Si	315.0998	+	15	fungicide
Foramsulfuron	173159-57-4	C17H20N6O7S	452.1114	+	10	herbicide
Hexazinon	51235-04-2	C12H20N4O2	252.1581	+	0.5	herbicide
Imidacloprid	138261-41-3	C9H10ClN5O2	255.0523	+	3	insecticide
Ioxynil	1689-83-4	C7H3I2NO	370.8299	-	5	herbicide
Isoproturon (Isoproturon-d6)	34123-59-6	C12H18N2O	206.1414	+	0.5	herbicide
Kresoxim-methyl	143390-89-0	C18H19NO4	313.1309	+	2.5	fungicide
Linuron	330-55-2	C9H10Cl2N2O2	248.0114	+	2.5	herbicide
MCPA (MCPA-d6)	94-74-6	C9H9ClO3	200.0235	-	1	herbicide
MCPB	94-81-5	C11H13ClO3	228.0553	-	10	herbicide
Mecoprop (Mecoprop-d6)	93-65-2	C10H11ClO3	214.0391	-	1	herbicide
Mesotrione (Mesotrione-d3)	104206-82-8	C14H13NO7S	339.0407	-	25	herbicide
Metalaxyl	57837-19-1	C15H21NO4	279.1465	+	2.5	fungicide
Metamitron	41394-05-2	C10H10N4O	202.086	+	25	herbicide
Metazachlor	67129-08-2	C14H16ClN3O	277.0976	+	1	herbicide
Metolachlor (Metolachlor-d6)	51218-45-2	C15H22ClNO2	283.1334	+	0.5	herbicide
Metribuzin	21087-64-9	C8H14N4OS	214.0883	+	5	herbicide
Metsulfuron-methyl	74223-64-6	C14H15N5O6S	381.0738	+	3	herbicide
Monuron	150-68-5	C9H11ClN2O	198.0554	+	0.5	herbicide
Napropamid	15299-99-7	C17H21NO2	271.1567	+	0.5	herbicide
Nicosulfuron	111991-09-4	C15H18N6O6S	410.1003	+	5	herbicide
Orbencarb	34622-58-7	C12H16ClNOS	257.0647	+	10	herbicide
Pethoxamid	106700-29-2	C16H22ClNO2	295.1334	+	1	herbicide
Phenmedipham	13684-63-4	C16H16N2O4	300.1116	+	25	herbicide
Pirimicarb	23103-98-2	C11H18N4O2	238.143	+	1	insecticide
Prochloraz	67747-09-5	C15H16Cl3N3O2	375.0303	+	200	fungicide
Prometon	1610-18-0	C10H19N5O	225.1584	+	0.5	herbicide
Propachlor	1918-16-7	C11H14ClNO	211.0758	+	0.5	herbicide
Propaquizafop	111479-05-1	C22H22ClN3O5	443.1242	+	100	herbicide
Prosulfocarb (Surrogate: Propiconazole-d5)	52888-80-9	C14H21NOS	251.1349	+	5	herbicide
Pyraclostrobin	175013-18-0	C19H18ClN3O4	387.0986	+	7.5	fungicide

Pyrimethanil	53112-28-0	C12H13N3	199.1109	+	1	fungicide
Rimsulfuron	122931-48-0	C14H17N5O7S2	431.0564	+	25	herbicide
Simazine (Simazine-d5)	122-34-9	C7H12ClN5	201.0776	+	1	herbicide
Simeton	673-04-1	C8H15N5O	197.1271	+	0.25	herbicide
Spiroxamine	118134-30-8	C18H35N1O2	297.2668	+	2.5	fungicide
Sulcotrione (Sulcotrione-d3)	99105-77-8	C14H13Cl1O5S	328.0167	+	20	herbicide
Tebuconazole	107534-96-3	C16H22ClN3O	307.1446	+	15	fungicide
Tebutam (Tebutam-d4)	35256-85-0	C15H23NO	233.1774	+	2.5	herbicide
Terbumeton	33693-04-8	C10H19N5O	225.1584	+	0.5	herbicide
Terbutylazine (Terbutylazine-d5)	5915-41-3	C9H16ClN5	229.1089	+	2	herbicide
Thifensulfuron-methyl	79277-27-3	C12H13N5O6S2	387.0302	-	5	herbicide
Trinexapac-ethyl	95266-40-3	C13H16O5	252.0992	+	3	growth regulator
Tritosulfuron	142469-14-5	C13H9F6N5O4S	445.0279	+	5	herbicide
PESTICIDE METABOLITES						
2,4-dimethylphenylformamide	60397-77-5	C9H11NO	149.0835	+	20	Amitraz
2,6-Dichlorbenzamide	2008-58-4	C7H5Cl2NO	188.9743	+	3	Dichlobenil Thifensulfuron-methyl
2-Amino-4-methoxy-6-methyl-1,3,5 triazine	1668-54-8	C5H8N4O	140.0693	+	2.5	Metsulfuron-methyl
3,5,6-Trichloro-2-pyridinole	6515-38-4	C5H2Cl3NO	196.9202	-	1	Chlorpyrifos
3,5-dibromo-4-hydroxybenzoic acid	3337-62-0	C7H4Br2O3	293.8533	-	2	Bromoxynil
3-Phenoxybenzoic acid	3739-38-6	C13H10O3	214.0624	-	5	Permethrin
Acetochlor-ESA	187022-11-3	C14H21NO5S	315.1135	-	1	Acetochlor
Acetochlor-OXA	194992-44-4	C14H19NO4	265.132	-	1	Acetochlor
Alachlor-ESA	142363-53-9	C14H21NO5S	315.1135	-	1	Alachlor
Alachlor-OXA	171262-17-2	C14H19NO4	265.132	-	1	Alachlor
Atrazin-Desethyl (Atrazin-desethyl-15N3)	6190-65-4	C6H10ClN5	187.0619	+	2.5	Atrazine
Atrazin-Desisopropyl (Atrazine-desisopropyl-d5)	1007-28-9	C5H8ClN5	173.0463	+	5	Atrazine
Atrazine-2-Hydroxy (Atrazine-2-Hydroxy-d5)	2163-68-0	C8H15N5O	197.1271	+	1	Atrazine
Atrazine-desethyl-2-hydroxy	19988-24-0	C6H11N5O	169.0958	+	2	Prometon/Atrazine
Azoxystrobinic acid	N/A	C21H15N3O5	389.1012	+	3	Azoxystrobin
Bifenoic acid	53774-07-5	C13H7Cl2NO5	326.9707	-	1	Bifenox
Chloridazon-desphenyl (Chloridazon-desphenyl-^{15}N2)	6339-19-1	C4H4ClN3O	145.0047	+	200	Chloridazon
Chloridazon-methyl-desphenyl	17254-80-7	C5H6ClN3O	159.0199	+	0.5	Chloridazon
Dimethachlor-ESA	N/A	C13H19NO5S	301.0978	-	1	Dimethachlor

Dimethachlor-OXA	1086384-49-7	C13H17NO4	251.1158	-	5	Dimethachlor
Dimethenamide-ESA	205939-58-8	C12H19N1O5S2	321.0699	-	1	Dimethenamide
Dimethenamide-OXA	380412-59-9	C12H17NO4S	271.0873	-	1	Dimethenamide
N,N-Dimethylaminosulfanilid (DMSA)	4710-17-2	C8H12N2O2S	200.0614	+	1.5	Dichlofluanid
Fipronil-sulfide	120067-83-6	C12H4Cl2F6N4S	419.9438	-	1	Fipronil
Fipronil-sulfon	120068-36-2	C12H4Cl2F6N4O2S	451.9336	-	2.5	Fipronil
Flufenacet-ESA	201668-32-8	C11H14FNO4S	275.0622	-	1	Flufenacet
Flufenacet-OXA	201668-31-7	C11H12FNO3	225.0796	-	1	Flufenacet
Isoproturon-didemethyl	56046-17-4	C10H14N2O	178.1101	+	1	Isoproturon
Isoproturon-monodemethyl	34123-57-4	C11H16N2O	192.1257	+	1	Isoproturon
Mesotrione-MNBA	110964-79-9	C8H7NO6S	244.9989	-	75	Mesotrion
Metamitron-Desamino	36993-94-9	C10H9N3O	187.0746	+	1.5	Metamitron
Metazachlor-ESA	172960-62-2	C14H17N3O4S	323.0934	-	5	Metazachlor
Metazachlor-OXA	N/A	C14H15N3O3	273.1108	-	5	Metazachlor
Metolachlor-ESA	171118-09-5	C15H23NO5S	329.1291	-	1	Metolachlor
Metolachlor-Morpholinon	120375-14-6	C14H19NO2	233.141	+	1	Metolachlor
Metolachlor-OXA	152019-73-3	C15H21NO4	279.1465	-	1.5	Metolachlor
Metribuzin-Desamino	35045-02-4	C8H13N3OS	199.0774	+	0.5	Metribuzin
Metribuzin-Diketo	56507-37-0	C7H12N4O2	184.0966	+	25	Metribuzin
N-(2,4-dimethylphenyl)-N-methylformamidin	33089-74-6	C10H14N2	162.1152	+	5	Amitraz
N,N-dimethyl-N'-(4-methylphenyl)-sulfamid	66840-71-9	C9H14N2O2S	214.077	+	0.5	Tolyfluanid
Propachlor-ESA	123732-85-4	C11H15NO4S	257.0716	-	1	Propachlor
Propachlor-OXA	70628-36-3	C11H13N1O3	207.089	-	3	Propachlor
Propazine-2-hydroxy	7374-53-0	C9H17N5O	211.1428	+	5	Propazine
Pyrimidinole	2814-20-2	C8H12N2O	152.095	+	30	Diazinon
Simazine-2-hydroxy	2599-11-3	C7H13N5O	183.1115	+	1	Simazine
Sulcotrione-CMBA	53250-83-2	C8H7Cl1O4S	233.9748	-	20	Sulcotrione
Terbutylazine-2-hydroxy	66753-07-9	C9H17N5O	211.1428	+	5	Terbutylazine
Terbutylazine-desethyl	30125-63-4	C7H12Cl1N5	201.0776	+	0.5	Terbutylazine
Terbutylazine-desethyl-2-hydroxy	30125-63-4	C7H13N5O	183.1115	+	1	Terbutylazine
PHARMACEUTICALS						
4-Dimethylaminoantipyrine	58-15-1	C13H17N3O	231.1366	+	5	
Albuterol	18559-94-9	C13H21NO3	239.1521	+	2	
Amisulpride (Amisulpride-d5)	71675-85-9	C17H27N3O4S	369.1722	+	0.5	
Amitriptylin	50-48-6	C20H23N	277.183	+	2	

Atenolol (Atenolol-d7)	29122-68-7	C14H22N2O3	266.1625	+	1
Atomoxetine (Atomoxetine-d3)	83015-26-3	C17H21NO	255.1623	+	1
Atorvastatine	134523-03-8	C33H35FN2O5	558.253	+	50
Azithromycin (Azithromycin-d3)	83905-01-5	C38H72N2O12	748.508	+	2.5
Bezafibrate (Bezafibrate-d4)	41859-67-0	C19H20ClNO4	361.1075	+	2.5
Bicalutamide	90357-06-5	C18H14F4N2O4S	430.061	-	10
Bupropion	34911-55-2	C13H18ClNO	239.1077	+	1
Candesartan	139481-59-7	C24H20N6O3	440.1597	+	10
Carbamazepine (Carbamazepine-^{13}C, d2)	298-46-4	C15H12N2O	236.0944	+	1
Cetrizine	83881-52-1	C21H25ClN2O3	388.1554	+	15
Cilastatin	82009-34-5	C16H26N2O5S	358.1562	+	n.q.
Citalopram (Citalopram-d6)	59729-33-8	C20H21FN2O	324.1638	+	1
Clarithromycin (Clarithromycin-d3)	81103-11-9	C38H69NO13	747.4763	+	5
Clindamycin	18323-44-9	C18H33ClN2O5S	424.1798	+	5
Clopidogrel (Clopidogrel-d4)	144457-28-3	C15H14ClNO2S	307.0439	+	5
Clozapine (Clozapine-d8)	5786-21-0	C18H19ClN4	326.1298	+	10
Cyclophosphamide (Cyclophosphamide-d4)	50-18-0	C7H15Cl2N2O2P	260.0248	+	10
Cytarabine	147-94-4	C9H13N3O5	243.085	+	10
Dexamethasone	50-02-2	C22H29FO5	392.1999	+	5
Dextromethorphan	125-71-3	C18H25NO	271.1936	+	2.5
Diclofenac (Diclofenac-d4)	15307-86-5	C14H11Cl2NO2	295.0161	+	5
Dronedarone	141626-36-0	C31H44N2O5S	556.2971	+	n.q.
Ephedrine	299-42-3	C10H15NO	165.2345	+	2
Eprosartan (Eprosartan-d3)	133040-01-4	C23H24N2O4S	424.1457	+	5
Ethambutole	1070-11-7	C10H24N2O2	204.1838	+	n.q.
Exemestane	107868-30-4	C20H24O2	296.1771	+	1
Fenofibrate (Fenofibrate-d6)	49562-28-9	C20H21Cl1O4	360.1123	+	100
FK-506 (Tacrolimus)	104987-11-3	C44H69NO12	803.482	-	50
Fluconazole (Fluconazole-d4)	86386-73-4	C13H12F2N6O	306.1035	+	10
Fluoxetine (Fluoxetine-d5)	54910-89-3	C17H18F3NO	309.1335	+	2
Furosemide (Furosemide-d5)	54-31-9	C12H11ClN2O5S	330.0077	-	30
Gabapentin (Gabapentin-d4)	60142-96-3	C9H17NO2	171.1259	+	50
Gemcitabine (Gemcitabine-^{13}C, d2)	95058-81-4	C9H11F2N3O4	263.0718	+	50
Hydrochlorothiazide	58-93-5	C7H8ClN3O4S2	296.9645	-	10
Ibuprofen (Ibuprofen-d3)	15687-27-1	C13H18O2	206.1301	+	25

Ifosfamide	3778-73-2	C7H15Cl2N2O2P	260.0248	+	3
Indomethacin (Indomethacin-d4)	53-86-1	C19H16ClNO4	357.0768	+	10
Iobitridol	136949-58-1	C20H28I3N3O9	834.896	+	2000
Iohexol	66108-95-0	C19H26I3N3O9	820.8798	+	1000
Iopromide	73334-07-3	C18H24I3N3O8	790.8692	+	100
Ketamine	6740-88-1	C13H16ClNO	237.092	+	0.5
Ketoprofen	22071-15-4	C16H14O3	254.0937	+	25
Lamotrigine (Surrogate: Atrazine-desethyl-d5)	84057-84-1	C9H7Cl2N5	255.0079	+	1
Levamisole	14769-73-4	C11H12N2S	204.0721	+	2.5
Levetiracetam (Levetiracetam-d3)	102767-28-2	C8H14N2O2	170.1055	+	5
Lidocaine (Lidocaine-d10)	137-58-6	C14H22N2O	234.1732	+	1.5
Mefenamic acid (Mefenamic acid-d3)	61-68-7	C15H15NO2	241.1097	+	2.5
Metformin (Metformin-d6)	657-24-9	C4H11N5	129.1014	+	20
Methylprednisolone (Methylprednisolone-d4)	83-43-2	C22H30O5	374.2093	+	5
Metoclopramide	7232-21-5	C14H22ClN3O2	299.1401	+	1
Metoprolol (Metoprolol-d7)	37350-58-6	C15H25NO3	267.1829	+	1
Metronidazole	443-48-1	C6H9N3O3	171.0638	+	5
Moclobemide	71320-77-9	C13H17ClN2O2	268.0979	+	1
Mycophenolic acid	24280-93-1	C17H20O6	320.126	+	10
Naltrexon	16590-41-3	C20H23NO4	341.1627	+	1
Naproxen (Naproxen-d3)	22204-53-1	C14H14O3	230.0937	+	10
Oseltamivir	196618-13-0	C16H28N2O4	312.2044	+	2.5
Paracetamol (Paracetamol-d4)	103-90-2	C8H9NO2	151.0628	+	10
Phenazone (Phenazone-d3	60-80-0	C11H12N2O	188.0944	+	0.5
Pravastatin (Pravastatin-d3)	81093-37-0	C23H36O7	424.2461	-	20
Prednisolon	50-24-8	C21H28O5	360.1937	+	15
Primidone (Primidone-d5)	125-33-7	C12H14N2O2	218.105	+	5
Propranolol (Propranolol-d7)	525-66-6	C16H21NO2	259.1567	+	0.5
Ranitidine (Ranitidine-d6)	66357-35-5	C13H22N4O3S	314.1407	+	5
Ritonavir (Ritonavir-d6)	155213-67-5	C37H48N6O5S2	720.3128	+	10
Rosuvastatin	287714-41-4	C22H28FN3O6S	481.1683	+	5
Roxithromycin	80214-83-1	C41H76N2O15	836.524	+	5
Sitagliptin	486460-32-6	C16H15F6N5O	407.1181	+	10
Sotalol (Sotalol-d6)	3930-20-9	C12H20N2O3S	272.1189	+	5
Sulfadiazine (Sulfadiazine-d4)	68-35-9	C10H10N4O2S	250.0519	+	5

Sulfadimethoxine (Sulfadimethoxine-d4)	122-11-2	C12H14N4O4S	310.073	+	2.5	
Sulfamethazine (Sulfamethazine-^{13}C6)	57-68-1	C12H14N4O2S	278.0832	+	3	
Sulfamethoxazole (Sulfamethoxazole-d4)	723-46-6	C10H11N3O3S	253.0516	+	5	
Sulfapyridine (Sulfapyridine-d4)	144-83-2	C11H11N3O2S	249.0566	+	5	
Sulfathiazole (Sulfathiazole-d4)	72-14-0	C9H9N3O2S2	255.0131	+	5	
Telmisartan	144701-48-4	C33H30N4O2	514.2369	+	100	
Thiopental	76-75-5	C11H18N2O2S	242.1089	-	15	
Tramadol (Tramadol-d6)	27203-92-5	C16H25NO2	263.1885	+	1	
Trimethoprim (Trimethoprim-d9)	738-70-5	C14H18N4O3	290.1373	+	2	
Trimipramin	739-71-9	C20H26N2	294.2096	+	1	
Tylosin	1401-69-0	C46H77NO17	915.5186	+	50	
Valsartan (Valsartan-^{15}N, ^{13}C5)	137862-53-4	C24H29N5O3	435.227	+	5	
Venlafaxine (Venlafaxine-d6)	93413-69-5	C17H27NO2	277.2036	+	0.5	
Verapamil (Verapamil-d6)	152-11-4	C27H38N2O4	454.2826	+	2	
PHARMACEUTICAL METABOLITES						
2',3'-di-O-acetyl-5'-desoxy-5-fluorocytidine	161599-46-8	C13H16FN3O6	329.1023	+	10	Capecitabin
4-(Trifluoromethyl)phenol	402-45-9	C7H5F3O	162.0287	-	50	Fluoxetin
4-Acetamidoantipyrine	83-15-8	C13H15N3O2	245.117	+	1	Aminopyrine/Metamizol
4-Formylaminoantipyrine	1672-58-8	C12H13N3O2	231.1008	+	1.5	Aminopyrine/Metamizol
AMDOPH	519-65-3	C13H17N3O3	263.127	+	0.5	Aminopyrine
Atenolol-desisopropyl	81346-71-6	C11H16N2O3	224.1161	+	50	Atenolol
Atenololic acid (Atenolol acid–d5)	56392-14-4	C14H21N1O4	267.1465	+	1	Atenolol/Metoprolol
Carbamazepine-10,11-dihydro-10,11-dihydroxy	58955-93-4	C15H14N2O3	270.1004	+	5	Carbamazepine
Carbamazepine-10,11-epoxide (Carbamazepine 10, 11-Epoxide-^{13}C, d2)	36507-30-9	C15H12N2O2	252.0899	+	1	Carbamazepine
Clofibric acid (Clofibric acid-d4)	882-09-7	C10H11ClO3	214.0391	-	1	Clofibrate
D617	34245-14-2	C17H26N2O2	290.1994	+	0.5	Verapamil
Fenofibrinic acid	42017-89-0	C17H15ClO4	318.0653	+	2.5	Fenofibrate
Iminostilbene	256-96-2	C14H11N	193.0892	+		Carbamazepine
N,N-Didesvenlafaxine	93413-77-5	C15H23N1O2	249.1729	+	5	Venlafaxine
N,O-Didesvenlafaxine	135308-74-6	C15H23N1O2	249.1729	+	5	Venlafaxine
N4-Acetyl-Sulfadiazine	127-74-2	C12H12N4O3S	292.0625	+	5	Sulfadiazine
N4-Acetyl-Sulfadimethoxine	24341-30-8	C14H16N4O5S	352.0836	+	4	Sulfadimethoxine
N4-Acetyl-Sulfamethazine	100-90-3	C14H16N4O3S	320.0938	+	2.5	Sulfamethazine
N4-Acetyl-Sulfamethoxazole (N4-Acetyl-	21312-10-7	C12H13N3O4S	295.0621	+	3	Sulfamethoxazole

Sulfamethoxazole-d5)						
N4-Acetyl-Sulfathiazole (N4-Acetyl-Sulfathiazole-d4)	127-76-4	C11H11N3O3S2	297.0236	+	10	Sulfathiazole
N-Desvenlafaxine	149289-30-5	C16H25N1O2	263.1885	+	0.5	Venlafaxine
O-Desvenlafaxine	93413-62-8	C16H25N1O2	263.1885	+	1	Venlafaxine
Oseltamivir-carboxylate	187227-45-8	C14H24N2O4	284.1731	+	10	Oseltamivir
Ranitidine-N-oxide	738557-20-2	C13H22N4O4S	330.1362	+	2	Ranitidine
Ranitidine-S-oxide	73851-70-4	C13H22N4O4S	330.1362	+	20	Ranitidine
Ritalinic acid (Ritalinic acid-d10)	19395-41-6	C13H17NO2	219.1254	+	5	Methylphenidat
Valsartan acid (Valsartan acid-d4)	164265-78-5	C14H10N4O2	266.0804	+	5	Valsartan, Losartan, Candesartan, Irbesartan
BIOCIDES and METABOLITES						
2-Aminobenzimidazol	934-32-7	C7H7N3	133.0634	+	5	Carbendazim
2-n-Octyl-4-isothiazolin-3-on	26530-20-1	C11H19NOS	213.1182	+	1	
4,5-Dichloro-2-n-octyl-isothiazol-3(2H)-on	64359-81-5	C11H17Cl2NOS	281.0402	+	25	
Carbendazim (Carbendazim-d4)	10605-21-7	C9H9N3O2	191.0689	+	3	
Diuron (Diuron-d6)	330-54-1	C9H10Cl2N2O	232.0165	+	1	
Diuron-desdimethyl	2327-02-8	C7H6Cl2N2O	203.9852	+	5	Diuron
Diuron-desmonomethyl	3567-62-2	C8H8Cl2N2O	218.0008	+	5	Diuron
Irgarol (Irgarol-d9)	28159-98-0	C11H19N5S	253.1356	+	2	
Irgarol-descyclopropyl	N/A	C8H15N5S	213.1043	+	1	Irgarol
N,N-diethyl-3-methylbenzamid	134-62-3	C12H17NO	191.1305	+	1	
Prometryn	7287-19-6	C10H19N5S	241.1356	+	0.5	
Propiconazole (Propiconazole-d5)	60207-90-1	C15H17Cl2N3O2	341.0692	+	5	
Terbutryn (Terbutryn-d5)	886-50-0	C10H19N5S	241.1356	+	0.5	
Triclosan (Triclosan-d3)	3380-34-5	C12H7Cl3O2	287.9506	-	25	
ILLICIT DRUGS and METABOLITES						
1-(3-Chlorophenyl)-piperazine	6640-24-0	C10H13ClN2	196.0767	+	5	
1-(3-Trifluoromethylphenyl)-piperazine	15532-75-9	C11H13F3N2	230.1031	+	20	
1-Benzylpiperazine	2759-28-6	C11H16N2	176.1313	+	50	
Amphetamine	300-62-9	C9H13N	135.1048	+	3	
Benzoylecgonine	519-09-5	C16H19NO4	289.1314	+	2.5	Cocaine
Cocaine	50-36-2	C17H21NO4	303.1471	+	1	
Codeine (Codeine-^{13}C, d3)	76-57-3	C18H21NO3	299.1521	+	1	

Diazepam (Diazepam-d5)	439-14-5	C16H13ClN2O	284.0716	+	1	
2-Ethyliden-1,5-dimethyl-3,3-diphenylpyrrolidine	30223-73-5	C20H23N	277.183	+	5	Methadone
Mephedrone	1189805-46-6	C11H15NO	177.1154	+	5	
Methadone	76-99-3	C21H27NO	309.2093	+	0.5	
Methamphetamine	537-46-2	C10H15N	149.1204	+	1	
Morphine (Morphine-d3)	57-27-2	C17H19NO3	285.1359	+	2.5	
Oxazepam (Oxazepam-d5)	604-75-1	C15H11ClN2O2	286.048	+	2.5	
FOOD ADDITIVES (Artificial Sweeteners)						
Acesulfame (Acesulfame-d4)	55589-62-3	C4H5NO4S	162.9939	-	1	
Aspartame (Aspartame-d5)	22839-47-0	C14H18N2O5	294.121	+	70	
Cyclamate (Cyclamate-d11)	100-88-9	C6H13NO3S	179.0616	-	1.5	
Neotame (Neotane-d3)	165450-17-9	C20H30N2O5	378.2155	+	5	
Saccharine (Saccharine ^{13}C6)	81-07-2	C7H5NO3S	182.999	-	1	
Sucralose (Sucralose-d6)	56038-13-2	C12H19Cl3O8	396.0146	-	4	
INDUSTRIAL CHEMICALS						
1,2-Bis-(4,4'-dinitro-2,2'-disulfonic acid) -phenylethylenoxide	128-42-7	C14H10N2O10S2	429.9771	-	200	
2-Naphthalinsulfonic acid	120-18-3	C10H8O3S	208.0189	-	30	
4,4'-Diaminostilben-2,2'-disulfonic acid	81-11-8	C14H14N2O6S2	370.0288	-	20	
N-(4-Aminophenyl)-N-methyl-acetamide	119-63-1	C9H12N2O	164.0944	+	5	
N-Methylacetanilide	579-10-2	C9H11NO	149.0835	+	1	
CORROSION INHIBITORS						
1-Hydroxy-Benzotriazole	2592-95-2	C6H5N3O	135.0433	+	40	Benzotriazole
1-Methyl-Benzotriazole	13351-73-0	C7H7N3	133.0635	+	1	Benzotriazole
4 + 5-Methyl-Benzotriazole (5-Methyl-Benzotriazole-d6)	136-85-6	C7H7N3	133.0635	+	50	
4-Hydroxy-Benzotriazole	26725-51-9	C6H5N3O	135.0433	+	40	Benzotriazole
Benzotriazole (Benzotrazole-d4)	95-14-7	C6H5N3	119.0478	+	25	
OTHERS						
Benzophenone	131-57-7	C14H12O3	228.0781	+	10	Personal care product
Caffeine (Caffeine-d9)	58-08-2	C8H10N4O2	194.0798	+	50	Tracer
Climbazole	38083-17-9	C15H17ClN2O2	292.0979	+	50	Personal care product
Galaxolidon (Surrogate: Propiconazole-d5)	256393-37-0	C18H24O2	272.1771	+	10	Metabolite of Galaxolide
NN-Dimethyldicylamin N-oxide	2605-79-0	C12H27NO	201.2093	+	2	Disinfectant

In addition to the surrogate standards indicated in the table, the following surrogates were also used: N,N-diethyl-3-methylbenzamide-d7; octilinone-d17; propazine-d6; 2',2'-difluoro-2-deoxyuridine-$^{13}C,^{15}N2$; 5-fluorouracil-$^{15}N2$; bisphenol-A-d16; ciprofloxacin-d8; erythromycin-$^{13}C2$; irbesartan-d3; N,O-didesmethylvenlaflaxin-d3; N-desmethylvenlaflaxin-d3; nelfinavir-d3; norfloxacin-d5; O-desmethylvenlaflaxin-d6; oxcarbazepine-d4.

Table S2. Summary of ESI and HRMS parameters used for analysis of Beenyup AWRP samples.

Parameter	positive (+eV)	negative (-eV)
Source Voltage (kV)	4	3
Capillary Temp (°C)	350	350
Sheath Gas Flow (Arb)	40	40
Aux Gas Flow (Arb)	10	10
Sweep Gas Flow (Arb)	0	0
Gas Heater Temp	50	50
S-Lense-RF (V)	50	50
Quadrupole scan range (*m/z*)	100-1000	100-1000
FTMS Full AGC Target	5E5	5E5
FTMS MS2 AGC Target	5E5	5E5
Ion Trap and FT Micro Scans	1	1
Dynamic exclusion for MS2 (sec)	8	8
FTMS Full Max Ion Time (ms)	250	250
FTMS MSn Max Ion Time (ms)	250	250
MS2 Isolation window (*m/z*)	1	1

Arb: arbitrary units; ms: milli seconds

Table S3. Summary of the enviMass1.2 parameters adopted for quantitative screening of target substances.

EnviMass Parameter	Value
blank subtraction	
m/z tolerance	10 ppm
RT window	0.4 min
Safety factor	4
before recalibration	
m/z tolerance for internal standard	10 ppm
RT tolerance	1 min
after recalibration	
m/z tolerance for targets	4 ppm
RT tolerance	1 min
RT tolerance for isotopic/adduct peak	0.3 min
Isotopic abundance tolerance	50%
Intensity cut-off	5000

RT: retention time; m/z: mass-to-charge ration

Table S4. Summary of the Formulator parameters adopted for quantitative screening of target substances.

Formulator Parameter	Value
Average by scan	3
m/z tolerance	±5 ppm
RT tolerance	1 min
MassChromatogram S/N	0.85
Signal threshold S/N	10
RT window	0.5 - 20 min
Average by scan	3
m/z tolerance	± 5 ppm

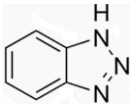
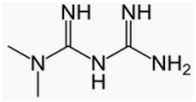
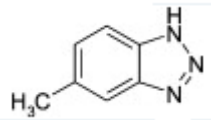
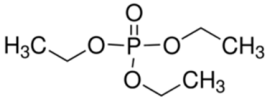
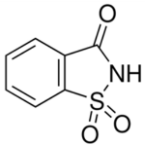
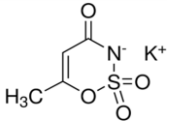
RT: retention time; S/N: signal-to-noise ratio; m/z: mass-to-charge ration

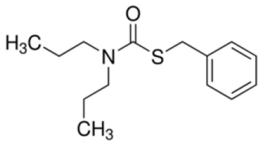
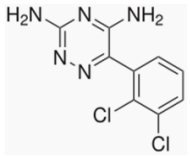
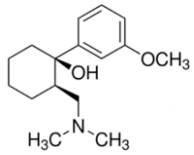
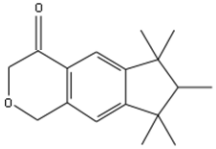
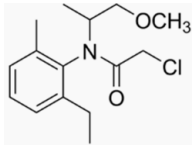
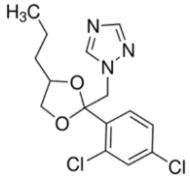
Table S5. Summary of the recovery percentages from a 100 ng spike. Recoveries are presented only for the 13 compounds which were subsequently detected in the post RO and post UV water samples.

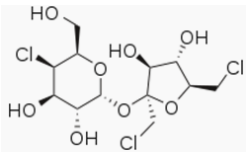
Chemical	RO water + 100 ng spike (ng in vial)	RO water Blank (ng in vial)	Relative recovery %	Ultrapure water blank
5-Methyl benzotriazole*	1700	1300	N/A	<LOD
Benzotriazole*	2200	1600	N/A	<LOD
Galaxolidone	170	40	130%	<LOD
Lamotrigine	100	5	95%	<LOD
Metholachor	125	30	95%	<LOD
Metformin	325	220	105%	<LOD
Propiconazol	115	30	85%	<LOD
Prosulfocarb	110	25	85%	<LOD
Tramadol	110	1	109%	<LOD
Acesulfam	170	55	115%	<LOD
Saccharin	115	14	101%	<LOD
Sucralose	110	15	95%	<LOD

**outside linearity range*

Table S6: Main physical-chemical properties of the chemicals that were detected in post RO and post UV water at Beenyup AWRP. Chemicals have been ordered by molecular weight.

Chemical	Molecular structure	Chemical type/ classification	Molecular weight (Da)	pKa	Log Kow	ChemSpider ID	Estimated RO rejection
Benzotriazole		Various household and industrial uses/ corrosion inhibitor	119	8.2	1.23	6950	Very poor[1-3]
Metformin		Pharmaceutical/ diabetes treatment	129	12.4	-1.43	3449	Very poor[1,2]
4 + 5 methyl benzotriazole		Various household and industrial uses/ corrosion inhibitor	133	8.7	1.89	109219	Very poor[1-3]
Triethyl phosphate		Flame retardant	182	19	0.80	6287	Very poor[1,2]
Saccharin		Food additive/ artificial sweetener	183	2.32	0.91	4959	Very poor[1,2]
Acesulfame-K		Food additive/ artificial sweetener	201	3.2	-1.33	55940	Very poor[1,2]

Chemical	Molecular structure	Chemical type/ classification	Molecular weight (Da)	pKa	Log Kow	ChemSpider ID	Estimated RO rejection
Prosulfocarb		Pesticide/ herbicide	251	…	4.65	55867	Good[1,2]
Lamotrigine		Pharmaceutical/ antiepileptic	255	5.7	-0.19	3741	Moderate to good[1,2]
Tramadol		Pharmaceutical/ analgesic	263	9.41	2.51	5322	Good[1,2]
Galaxolidone		Polycyclic musk fragrance/ personal care product	272	…	5.50	28290252	Good[2]
Metolachlor		Pesticide/ herbicide	283		3.00	4025	Moderate to good[1,2]
Propiconazole		Biocide/ fungicide	341	~1	3.88	39402	Moderate to good[1,2]

Chemical	Molecular structure	Chemical type/ classification	Molecular weight (Da)	pKa	Log Kow	ChemSpider ID	Estimated RO rejection
Sucralose		Food additive/ artificial sweetener	396	11.8	0.68	64561	Good[1,2]

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