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Removal of emerging drugs of addiction by wastewater treatment and water recycling processes and impacts on effluent-associated environmental risk

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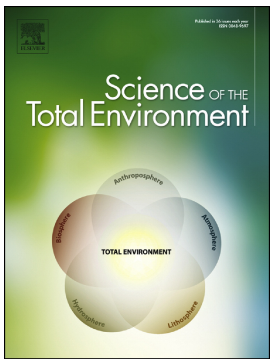
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Removal of emerging drugs of addiction by wastewater treatment and water recycling processes and impacts on effluent-associated environmental risk

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Abstract

Drugs of addiction, have been recognized as potential contaminants of concern to the environment. Effluent wastewater discharge is a major source of contamination to aquatic receiving environments. A year-long monitoring program was undertaken in Australia to characterise the fate of four emerging drugs of addiction: methamphetamine; MDMA; pharmaceutical opioids: codeine and morphine and a metabolite: benzoylecgonine in four wastewater treatment plants operating with different secondary treatment technologies: conventional activated sludge (CAS), membrane bioreactors (MBR), integrated fixed-film AS (IFAS) and sequencing batch reactors (SBR). The effect of subsequent tertiary treatment (coagulation/flocculation) on the removal efficiency was also assessed.

Drugs were detected in influent and effluent samples (mean concentration ranged 43–4,777 and 17–1,721 ng/L, respectively). Treated effluents had noticeably lower levels compared to raw influents. Removal efficiency of compounds depended on the secondary treatment employed, with IFAS and MBR

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performing the best with significant removal of compounds (≈90%) followed by CAS (54–96%) and lastly SBR (42–83%). Despite the low levels of drugs measured after the secondary treatment, near complete removal after tertiary treatment (≈99%) was recorded, which demonstrated the effectiveness of using coagulation/flocculation process as an effective step for enhancing the removal efficiency. The levels of drugs were at a low level in the effluents released into the environment and used for recycling and all posed a low environmental risk in urban water courses based on the risk assessment. The information given here provides new and useful information to the water industry and regulators on the efficiency of drug removal in a range of wastewater treatment configurations.

Keywords: activated sludge, tertiary treatment, drugs of addiction, removal efficiency

Highlights:

- Removal efficiency of drugs of addiction during wastewater treatment was evaluated
- IFAS process with chlorination was most efficient for removing targeted drugs
- Tertiary treatment by coagulation/flocculation can enhance drug removal efficiency
- Higher temperature (summer operations) showed enhanced drug removal
- Overall environmental risk from aquatic discharge of these drugs in effluent is low

1. Introduction

In the last 20 years (2007) the excretion of drugs of addiction into sewerage systems around the world has increased exponentially (Yadav et al., 2017). The majority of the administered drugs are expelled primarily via urine and faeces as a parent compound or their metabolites and, therefore, treated effluent wastewater discharge is considered to be the major source of contamination for receiving environments (Gaw et al., 2014). Furthermore, their presence has been reported in receiving water bodies, including surface water (rivers, oceans or lakes), groundwater and even drinking water sources (Bade et al., 2018;

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Castrignanò et al., 2018; Jurado et al., 2012; Riva et al., 2017; Wang et al., 2016). Hence, the assessment of the efficiency of various wastewater treatment practices is imperative in the successful management of these compounds. The extent of treatment achieved depends on numerous factors, including the technology used in WWTPs, their operating conditions (biomass concentrations and sludge age), environmental factors (pH, flow, temperature) or physicochemical properties of drugs such as molecular weight biodegradation/biotransformation, volatilization or organic carbon-water partition coefficient (K_{oc}) of compounds (Causanilles et al., 2017; Douziech et al., 2018; Yadav et al., 2017).

Drugs of addiction are classified as contaminants of emerging concern due to their increased presence in environmental systems, high biological activities and limited information on their likely effects on aquatic ecosystems (Baker and Kasprzyk-Hordern, 2013; Rosi-Marshall et al., 2015; Szymonik et al., 2017). Analysis of these drugs in raw influent is primarily associated with health perspectives and estimation of community-level consumption (Lai et al., 2011; Zuccato et al., 2005). Analysis of the drugs in treated effluent is equally important with respect to the environmental perspective and this of course will have a direct correlation with the removal efficiency of WWTPs. If drugs are not eliminated they will ultimately reach receiving waterways and there is evidence to suggest that some are potentially toxic to aquatic ecosystems. For example, Parolini et al. (2015) investigated the oxidative status of *Dreissena polymorpha* (zebra mussel) when exposed to a mixture of drugs of addiction and found a significant increase in the levels of carbonylated (oxidized) proteins that can pose a potential risk to the mussels because of loss of efficiency of defensive enzymes. Furthermore, the presence of cocaine was suggested to cause damage to cell DNA and reduces cell viability in mussels (Binelli et al., 2012; Parolini et al., 2017), so the discharge of treated effluent to coastal or estuarine environments could pose a potential environmental and economic risk in areas where shellfish are harvested or farmed.

Treatment technology incorporated at WWTPs will undoubtedly be important in the removal of drugs of addiction to minimize discharge into the receiving environment. However, there are limited studies

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highlighting the removal efficiency of these drugs by WWTPs adopting different treatment processes across the globe, and very limited data from Australia. Activated sludge reactor and trickling filter processes have been commonly used in WWTPs for many decades, while technologies like membrane bioreactors (MBRs) are an advanced treatment process that has only been adopted relatively recently in Australia. Generally, the drugs of addiction are hydrophilic (log K_{ow}<3) thus are less likely to adsorb to biomass or sludge, making treatment reactor hydraulic residence time an important parameter (Kim et al., 2016). A recent review (Yadav et al., 2017) of worldwide treatment technologies for drug removal reported that in general, the activated sludge system is more efficient than trickling filters for the removal of the majority of illicit drugs (meth/amphetamine, 3,4-methylenedioxymethamphetamine (MDMA), cocaine and its metabolites, opioids and cannabinoids). A few studies have reported almost complete removal of cocaine, benzoylecgonine (BE) and meth/amphetamine by the activated sludge treatment process, while much lower removals (<25%) by trickling filters (Bijlsma et al., 2012; Kasprzyk-Hordern et al., 2009; Postigo et al., 2010). However, there is limited information available on drug elimination by treatment processes like MBRs, sequencing batch reactors (SBR) and dissolved air flotation–filtration (DAFF) treatment.

Thus, the present study provides an assessment of the performance of several Australian WWTPs adopting different treatment technologies for removing selected drugs of addiction: cocaine (in the form of its major metabolite BE); methamphetamine (METH); MDMA; and the pharmaceutical opioids: codeine and morphine. Four full-scale WWTPs with various secondary treatment technologies (i.e. conventional activated sludge reactors MBR, SBR or IFAS) and tertiary treatments (i.e. DAFF or disinfectants like chlorination or UV) were investigated for their capacity to remove these compounds by assessing the relative concentration in treated effluent versus the raw influent sewage over the course of approximately one year. Since the treated wastewater effluent is discharged into the environment, the environmental risk associated with this practice was evaluated based on the measured concentrations in treated effluent, recycled water and urban lake water.

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2. Experimental

2.1 Study sites

In this study, four Australian WWTPs and one water recycling plant were selected, each with distinct secondary treatment process configurations (Table 1) and wastewater qualities (Table 2). The schematic diagrams of each WWTP are shown in supplementary material (Fig. SI.1). These WWTP facilities are fed by separate sewage and each serve different metropolitan catchments and range in size from approximately 100,000 to 1.1 million population equivalents based on 120 grams COD/person/day (PE_{COD120}). WWTP1 is the largest treatment plant and comprises conventional activated sludge (CAS) step feed process consisting of anoxic and aerobic zones followed by secondary sedimentation/clarification. The effluent is further treated through a series of large stabilisation lagoons (Short et al., 2010) before discharge to the adjacent coastal environment. Part of the lagoon effluent undergoes further additional tertiary treatment through a 120 ML/d DAFF plant, which comprises coagulation-flocculation, flotation, filtration followed by chlorination prior to water reuse in horticulture, public space irrigation and non-potable residential uses (Yap et al., 2012). WWTP2 uses an SBR process without primary sedimentation and treats high salinity wastewater (6–7 g/L total dissolved solids) (Thwaites et al., 2017) as distinct from the other WWTPs which treat freshwater sewage. The treated SBR effluent is disinfected using UV irradiation (dose 43 mJ/cm^2) prior to discharge. WWTP3 comprises two separate sub-plants which employ two different treatment processes: a) CAS: Modified Ludzack–Ettinger process with effluent chlorination (dose 9 mg/L) and b) 4-stage Bardenpho + MBR process followed by UV disinfection (dose 15 mJ/cm^2), enabling a side-by-side performance comparison. WWTP4 is unique among the selected plants in that is operates an integrated fixed-film activated sludge – Modified Ludzack–Ettinger process, that contains high surface area polypropylene media in aerobic zones (van den Akker et al., 2010). Prior to discharge, the effluent is chlorinated with an average dose of 8–10 mg/L.

In addition to the WWTP samples, a limited number (3) of grab water samples were collected at different

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times from a public lake. This lake receives a mixture of stormwater and recycled water (effluent from the DAFF plant at WWTP 1) and provides a representation of the selected contaminants in waterbodies within the built environment.

Table 1. Characteristics of selected wastewater treatment plants. Data provided by the managing water authority

Table 2. Water quality parameters of WWTPs. The concentrations (mg/L) are presented as mean ± SD values (n = 11) measured during the sampling period (April 2016 – Feb 2017). Data provided by the managing water authority.

2.2 Sample collection, preparation and analysis

24-hour flow dependent composite raw influent and treated effluent samples were collected from each WWTP for seven consecutive days at alternative months starting from April 2016 to February 2017. The influent wastewater to each WWTP was collected after screening while for WWTP2 the influent was collected at the inlet. The effluent wastewater was collected after secondary treatment and/or after tertiary treatment as shown in Fig. 1. Water samples were kept at −20°C until analysis (up to 48 h), with the target drugs shown to be stable under these conditions (Chen et al., 2012).

Fig. 1. Sampling locations (S) during the study for a) WWTP1 and b) WWTP2, WWTP3a, WWTP3b, WWTP4 (see Fig. SI.1 of the Supplementary information for detailed schematic diagram)

In this study, four emerging contaminants (METH, MDMA, codeine and morphine) as well as the cocaine metabolite BE were selected for examination of the WWTPs removal performance of these substances. This work follows an earlier study which characterized these compounds in the influent wastewater of these WWTPs (Yadav et al., 2018). According to the National Drug Strategy Household Survey (Australian Institute of Health and Welfare, 2017), these compounds or their precursors are commonly

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consumed in Australia. Further, Irvine et al. (2011) and Tscharke et al. (2016) reported high concentrations of these compounds present in influent waters from all WWTPs. All compounds were extracted using solid phase extraction (SPE) and analysed by liquid chromatography-tandem mass spectrometry (LC-MS/MS) methodology as reported earlier (Tscharke et al., 2016) with some modifications. Briefly, acidified and filtered influent (200 mL) and effluent (400 mL) samples were spiked with deuterated internal standards (200 µL) of each targeted drug and loaded onto UCT XRDAH SPE cartridges (500 mg/6mL) conditioned with methanol (6 mL) and acetate buffer (6 mL). The cartridges were washed consecutively with 6 mL methanol, acetate buffer and 2mL of 0.1M acetic acid. The elution of targeted compounds was attained with 96% dichloromethane: isopropanol (80:20) in 4% ammonia followed by evaporation under nitrogen. The final extract was determined by high-performance liquid chromatography (UFLC Shimadzu) coupled to a triple quadrupole mass spectrometer (Applied Biosystems API 3000). Chromatographic separation was achieved through a Phenomenex™ Luna PFP column (100 × 4.6 mm, 3µm) coupled to a guard column (4 × 2 mm, 5 µm). The analytes were analysed in a positive electrospray ionization mode via multiple reaction monitoring.

2.3 Calculations and statistical analysis

The occurrence of targeted compounds in different water sources was presented as concentration (ng/L) while mass loads in g/day (concentration × flow in L/day) was used for calculating removal efficiencies. The removal efficiencies were evaluated by assessing the relative effluent loads as compared to influent loads for each compound (based on below equation). Since only filtered samples were analysed in the study and not the sludge fraction, the removal efficiency here represents the percentage reduction for the dissolved aqueous phase component of the drugs in raw influent and treated effluent samples. If the target compounds have low sorption to the solids, then removal efficiency can be evaluated directly by comparing influent and effluent samples (van Nuijs et al., 2009). As the selected compounds here are all hydrophilic (log K_{ow} <3), estimating WWTP removal efficiency via water phase assessments only was

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considered reasonable.

$$Removal\ Efficiency\ (\%) = \frac{M_{In} - M_{Ef}}{M_{In}} \times 100 \quad (1)$$

(where M_{In} *and* M_{Ef} indicate mass loads (g/day) of compounds in influent and effluent, respectively).

Statistical analyses were conducted using Prism® 7.03 (GraphPad Software Inc., La Jolla, CA, USA). Analysis of variance (ANOVA) was performed to compare the difference between the drugs concentrations and removal efficiencies among the treatment plants. Outliers were identified from the datasets as those data lying beyond quartiles one and three at 1.5 times the interquartile range.

3. Results and discussion

Mean, maximum and minimum values of the targeted drugs in raw influent and treated effluent samples of the studied WWTPs, recycled water and lake water are presented in Table 3. All the compounds were detected in raw influent and treated effluent samples except for morphine which was below the limit of detection (LOD) in a few effluent samples. The mean drugs concentration in influent and effluent samples ranged from 43–4,777 ng/L and 17–1,721 ng/L, respectively. Codeine was the compound with the highest concentrations in influents and effluents across all WWTPs, followed by METH with the second highest concentrations. Treated effluent waters had distinctly lower concentrations of the measured drugs than raw influents. Statistical analyses revealed significant variations (two-way ANOVA, $F_{(4,\ 640)} = 44.95$, $p < 0.001$) in the concentrations of drugs discharged from the WWTPs. This variability in removal efficiency was considered to be due to differences in WWTP treatment process configuration and is discussed further in section 3.1.

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Table 3. Concentrations (ng/L) of targeted drugs in water samples collected from studied WWTPs and an urban lake representing a built environment water course (April 2016–February 2017)

3.1 Removal efficiency of WWTPs for measured drugs of addiction

The calculated drug removal efficiencies of the five WWTPs are presented in Fig. 2. Overall, the mean removal efficiencies estimated for the target compounds ranged from 25% to 99%, with the highest performance achieved by WWTP4 (IFAS secondary treatment process) and the lowest performance for WWTP2 (SBR process). However, from a wastewater treatment perspective, the treatment removal efficiency also depends strongly on the physical and chemical properties of the compounds (Petrovic et al., 2009).

3.1.1 Impact of secondary treatment and disinfection

Overall, a significant difference in removal efficiency was observed across all target drugs between WWTP3a (CAS plant with chlorination) and WWTP1 (CAS plant without chlorine disinfection) ($F_{(9, 358)}$ = 70.38, p<0.001). The removal efficiency was practically equivalent for both plants for METH and morphine, while BE removal was better in WWTP1 (p <0.001) (BE: 82 ± 11% by WWTP3a vs. 95 ± 4% by WWTP1; METH: 89 ± 4% vs. 89 ± 6%; MDMA: 68 ± 15% vs. 54 ± 18%; codeine: 96 ± 4% vs. 62 ± 23%; morphine: 97 ± 6% vs. 96 ± 3%). These data indicate that chlorination may not be effective in the removal of METH, morphine and BE, but may provide for enhanced removal of MDMA and codeine (p<0.001). The removal of drugs of addiction after chlorination disinfection in WWTPs is unknown; however, there are some laboratory-based studies on surface waters and drinking waters. For example, González-Mariño et al. (2012) studied the reaction of chlorine with cocaine in surface water samples and reported 50% degradation of cocaine within 24 hours after chlorination (dose 10 mg/L) while Huerta-Fontela et al. (2012) reported almost complete removal of amphetamine-type-stimulants after post-chlorination during drinking water treatment but also identified two new chlorinated transformation

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products. Several studies have been published demonstrating the reactivity of emerging contaminants, including antibiotics, pharmaceuticals or endocrine disruptors with chlorine-based disinfectants (Evgenidou et al., 2015; Huber et al., 2005; Noutsopoulos et al., 2015; Quintana et al., 2010). While chlorination may enhance the removal rates by conversion for specific drugs, it may also lead to the formation of by-products that could potentially be more toxic as compared to the parent drug and this should be considered in the context of overall WWTP removal performance for plants using chlorine disinfection.

Fig. 2. Box plots showing removal efficiency (%) of the targeted drugs from the aqueous phase across all WWTPs during the study duration (n=41 for all WWTPs while n=42 for WWTP4) (plots show absolute data range, interquartile range, mean, median and outliers).

Higher drug removal efficiencies (≈90%) were observed for WWTP4 using an IFAS treatment process as compared to WWTP3a utilizing CAS + Cl_2. IFAS + Cl_2 (WWTP4) removal efficiencies for targeted drugs were found to be higher compared to the CAS+Cl_2: WWTP3a (BE: 87 ± 7% by WWTP4 vs. 82 ± 11% by WWTP3a; METH: 96 ± 2% vs. 89 ± 4%; MDMA: 89 ± 7% vs. 68 ± 15%; codeine: 98 ± 2% vs. 96 ± 4%; morphine: 99 ± 1% vs. 97 ± 6%). Also, a significant difference (p <0.001) was found between both WWTPs removal rates despite both using chlorination disinfection (dose ≈9 mg/L) which could be related to the variance in the secondary treatment process. In general, the targeted drugs (except the cocaine transformation product BE) do undergo biological degradation (Bagnall et al., 2013; Evans et al., 2016; Lin et al., 2014). It is likely that the IFAS system of WWTP4 provides an environment with higher levels of more active microbial biomass for greater biodegradation of these drugs. For example, biomass concentrations (mixed liquor suspended solids; MLSS) in WWTP4 were almost double those of WWTP3a, while sludge age (SRT) was some three-fold shorter and operating dissolved oxygen levels several folds higher which ranged from 4.5–5.0 for aerated zones with IFAS compared to 2–2.0 without IFAS media. It should be noted that SRT in this case related to the suspended biomass fraction only and

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the average SRT of the overall system would be much higher due to the attached biomass on the IFAS media. These findings result in the conclusion that it is possible to enhance the degradation of compounds and improve the removal efficiency of WWTPs operated with high SRTs, as previously reported by (Clara et al., 2005; Gros et al., 2010). These conditions of higher microbial biomass in a more active state of growth and more rapid turnover would be expected to promote higher levels of drug removal for those compounds susceptible to microbial degradation and/or sorption as detailed above. Overall, the concentrations of all studied drugs were reduced by in IFAS + Cl_2 treatment WWTP4, with removals at this plant generally comparable to or better than all other WWTPs with the exception of WWTP3b (MBR+UV) (Fig. 2). These data indicate that although disinfection may appear to enhance drug removal efficiency by chemical conversion, secondary treatment technology configuration is another key factor that controls removal, as previously reported (Evgenidou et al., 2015; Kasprzyk-Hordern et al., 2009). Since the targeted drugs are hydrophilic (log K_{ow}<3), the aqueous volume is assumed to be the primary phase for elimination (Petrovic et al., 2009).

No significant difference in percentage drug removals was observed between WWTP3b (MBR+UV) and WWTP3a (CAS+Cl_2) except for MDMA removal which was better in WWTP3b (BE: 87± 9% by WWTP3b vs. 82 ± 11% by WWTP3a; METH: 93 ± 3% vs. 89 ± 4%; MDMA: 82 ± 9% vs. 68 ± 15%; codeine: 97 ± 3% vs. 96 ± 4%; morphine: 99 ± 1% vs. 97 ± 6%). Petrovic et al. (2009) provided an overview on emerging contaminants removal by conventional and advanced treatment processes, and reported that MBRs are more efficient in the elimination of micropollutants due to increased biomass concentration which intensifies the degradation process; although that study was concerned with pharmaceuticals and not drugs of addiction. Our findings, however, showed that MBRs perform similarly to CAS treatment for the removal of the targeted compounds, with the exception of MDMA which was removed slightly more during MBR+UV treatment. This outcome is not unexpected since there was no significant difference in operational conditions such as sludge age (SRT) or MLSS. Similar findings were reported by Clara et al. (2005) highlighting that when CAS and MBR were operated at similar SRT then

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no significant differences were observed in the treatment efficiency. This finding has important practical implications, since MBR+UV treatment processes are substantially more technologically advanced, operationally complex and costly than an equivalent CAS+Cl_2 process configuration. While MBR and CAS processes performed quite similarly overall for removal of the majority of target compounds, the MBR here was operated at a relatively low MLSS and SRT compared to what is common for MBRs elsewhere (i.e. MLSS of 10–12 g/L and SRT of 15–20 days), such that drug removals reported here may also be toward the low end of what could be expected for MBR systems with higher operating biomass concentrations and sludge ages.

The removal efficiency of target compounds was lowest at WWTP2 (SBR + UV) compared with all other WWTPs (BE: 42 ± 20%; METH: 76 ± 6%; MDMA: 42 ± 21%; codeine: 53 ± 27%; morphine: 83 ± 12%). The lowest removal by WWTP2 could be the difference in raw influent, as it receives high salinity influent wastewater (6–7 g/L total dissolved solids). This may affect drug removal based on chemical charge properties. In addition, UV transmittance was even lower in WWTP2 (56%) effluent, which may affect the efficiency of the UV oxidation/photolysis processes at this WWTP. Furthermore, biomass concentrations (MLSS) were lowest at WWTP2 of all surveyed plants and this probably further limited the biodegradation potential of these compounds (Table 1). It should be noted that WWTP2 is the only plant without primary sedimentation compared to other studied WWTPs which might have impact on the treatment process.

Ignoring WWTP technologies, the highest removal efficiencies were found for morphine (mean ± SD of 95 ± 9%) followed by METH (88 ± 8%) then codeine (82 ± 25%), BE (81 ± 20%) and lastly MDMA (69 ± 22%). Morphine is known to degrade very quickly in wastewater environments such as sewers (Thai et al., 2014) and others have reported similarly high removals for morphine (>85%) in WWTPs operating internationally with activated sludge processes (Devault et al., 2017; Subedi and Kannan, 2014). A negative removal for MDMA, BE and codeine was reported earlier that might be due to difficulties in pairing raw influent and treated effluent samples due to long hydraulic retention times, as well as

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potentially large temporal variability of these compounds in influents (Bijlsma et al., 2012; Terzic et al., 2010; Yadav et al., 2018). The negative removal of these compounds might also be due to deconjugation of glucuronides or transformation of conjugated metabolites into parent compounds during the treatment (Bijlsma et al., 2012; Boleda et al., 2009; Cosenza et al., 2018; Gilart et al., 2014; Rodayan et al., 2014; Terzic et al., 2010; Yadav et al., 2017).

3.1.2 Seasonal variation in WWTP drug removal efficiency

Variability in the average removal efficiency according to the season was analysed and is shown in Fig. 3. Despite the WWTP technologies, significantly better removal was observed during the summer season (December – February) compared to other seasons ($F_{(3, 965)} = 9.242$, $p < 0.001$), indicating that the target drugs were more amenable to removal during summer conditions. A significant difference was observed between the removal of compounds in summer (mean ± SD; 86 ± 19%) compared to winter (78 ± 29%) season ($t_{(4.46)} = 582$, $p < 0.001$); summer and winter wastewater temperatures ranged from 22–26°C and 17–21°C, respectively. For % removal efficiencies data, the largest performance differences between summer and all other seasons were seen in WWTP2. All of the studied WWTP reactors are outdoor and exposed to incident weather conditions including sunlight irradiation and water temperature in summer is typically ≈5°C warmer than in winter. This rise in temperature could enhance the biodegradation and volatilization process of the compounds and improve the removal efficiency of WWTPs. These results are consistent with findings from the study of Devault et al. (2017) who reported that the WWTPs with outside ponds were more efficient to remove cocaine, BE, morphine and THC-COOH (>85% removal) compared to the indoor pond WWTP (49–90%). In laboratory-based studies, illicit drugs were also found to be more stable at low temperature (Chen et al., 2012; McCall et al., 2016), again supporting higher removals during summer.

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Fig. 3. Seasonal removal performance of WWTPs for targeted compounds (a) average removal efficiency of WWTPs (see Eq. (1)) according to seasons (n=14 for summer and winter while n=7 for autumn and spring) and (b) relative removal efficiency for all targeted drugs

3.2 Drug levels in final WWTP effluents, recycled water and associated environmental risk

To evaluate the potential impact to receiving environments from drugs present in final WWTP treated effluent and recycled water, the levels of targeted drugs in WWTP1 are presented after CAS treatment, in the final recycled water after DAFF treatment and in an urban lake which receives some seasonal recycled water supply from WWTP1. Fig. 4 shows the drug concentrations at these different stages and their overall removal efficiencies relative to raw WWTP1 influent levels. In CAS treated effluent, the highest concentration was observed for codeine (mean ± SEM; 2,109 ± 230 ng/L) followed by METH (212 ± 17 ng/L). On the other hand, the compounds were mostly below LOD or at very low concentrations in DAFF effluent (recycled water), with a highest mean concentration of codeine at 25.5ng/L.

Morphine was not detected in the recycled water while MDMA was practically negligible (mean 0.4 ng/L). Only codeine and METH were detectable in the urban lake, but at very low levels ranging from 2.6–3.3 ng/L and <LOD–1.6 ng/L respectively. Govindarasu (2016) has reported the presence of METH (11 ng/L) in urban impacted water samples collected from regions of South Australia which was comparably higher than our levels.

Fig. 4. Studied drugs concentration in WWTP1 EF (effluent) and DAFF effluent along with the cumulative removal efficiency (RE) of WWTP1 and DAFF treatment plants relative to raw WWTP1 influent. Concentrations are presented as mean ± SEM and removal efficiency as a percent.

Despite the already very low drug concentrations after CAS treatment, samples collected after the tertiary DAFF treatment (coagulation/flocculation and flotation/filtration processes followed by chlorination)

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showed further removal in the final recycled water (BE: 99 ± 0.2% by WWTP1 + DAFF vs. 97 ± 0.3% WWTP1; METH: 100% vs. 93 ± 0.6%; MDMA: 100 ± 1% vs. 41 ± 1.9%; codeine: 99 ± 0.2% vs. 37 ± 7%; morphine: 100% vs. 95 ± 0.5%). As shown in Fig. 4, the effectiveness of tertiary DAFF treatment plus chlorination for enhanced drug removal is clearly demonstrated, in particular for MDMA and codeine which initially showed poor removal during secondary treatment (<40%) and near-complete removal following DAFF treatment. The higher removal of MDMA might be due to conversion during the chlorination as described in section 3.1. Others have reported a similarly poor removal rate for codeine (<50%) after activated sludge treatment (Kasprzyk-Hordern et al., 2009). Statistical analysis showed that MDMA ($t_{(0.05(2)16}$ = 16.28; $p<0.001$) and codeine ($t_{(0.05(2)16}$ = 4.612; p <0.001) removals following DAFF treatment were significantly higher than those achieved following secondary CAS treatment. Overall, tertiary DAFF treatment plus chlorination gave the best results, with near complete removal (≈99%) for all monitored compounds.

Fig. 5 presents an analysis of the environmental risk posed by each compound based on the risk quotient (RQ) values estimated for each compound in the final treated waters from WWTP1 (CAS effluent and DAFF effluent recycled water), in the simulated marine receiving environment following ocean outfall discharge and subsequent plume dilution, and in the urban lake environment. As shown, only codeine posed a high risk (RQ = 35) in the undiluted CAS effluent, but this risk level reduced to medium risk following simulated effluent discharge and dilution and also in the recycled water (RQ ≈ 0.5). It is important to highlight that the high risk for CAS effluent overestimates the likely risk level in receiving waters, since substantial dilution will occur post-discharge, as reflected in the RQ value for the diluted effluent (RQ = 0.35). Risk levels associated with codeine and METH in urban lake water were low and we were unable to calculate the RQ values for BE and MDMA in urban lake water and morphine in both urban lake and recycled water as they were not detected (assumed low risk). RQ levels for all drugs other than codeine were in the low-risk range, suggesting that these compounds are unlikely to pose any adverse impacts on aquatic receiving environments. However, such low concentrations of drugs may

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potentially become more toxic when considered in the context of multi-compound mixtures (Celiz et al., 2009) and such mixture effects should ideally be considered when assessing toxicity potentials. Also, while chlorine disinfection of secondary effluent prior to environmental discharge is commonplace in Australia, it is uncommon in many European countries and so the potential for increased risk levels associated with compounds which are susceptible to chlorine degradation should be considered.

Fig. 5. The estimated risk quotients (RQ) of measured drugs in WWTP1 CAS effluent and recycled water (DAFF effluent) and an urban lake. The PNEC values used for calculating RQs were obtained from (Grung et al., 2007; Verlicchi et al., 2012). The values above the red dotted line on y-axis pose a high risk, between red and black medium risk and below black low risk to the environment. The RQ values of BE, MDMA and morphine are not calculated for urban lake and morphine for recycled water as they were not detected.

#: RQs for the diluted effluent are for simulated discharge of WWTP1 secondary effluent to coastal waters which is subject to median near-field effluent outfall dilution of 1:100 (100-fold dilution) after Glamore et al. (2007)

Note: Values presented here for CAS effluent and recycled water are associated with the source and not the exposure and these sources are substantially diluted when discharged into receiving waters.

4. Conclusions

The removal efficiency of several drugs of addiction across a range of different wastewater treatment processes and process configurations was evaluated. Results revealed that activated sludge processes with effluent disinfection, such as IFAS with chlorination and MBR with UV, were the most efficient in eliminating the targeted compounds compared to other more conventional secondary treatment processes. Even though drugs of addiction were effectively removed to low levels (low ng/L) in secondary effluents, further and significant removal of all drugs (>97%) was still achieved after tertiary-level DAFF treatment plus chlorination. Therefore, additional tertiary treatments appear to be effective in achieving near-complete removal of these compounds in recycled waters destined for agricultural irrigation and other

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regulated municipal uses. An environmental risk assessment associated with the targeted drugs in wastewater treated effluents and recycled waters revealed that the majority of the compounds pose a low level of risk, with the exception of codeine which was rated at high to medium risk in undiluted effluents after secondary and tertiary treatment, respectively. In practice, however, these risks will be further diminished upon discharge due to dilution of effluent in receiving waters. Given that recycled waters are used undiluted for various purposes, including irrigation of parks and in horticultural applications, future work should be directed toward considering the potential environmental (soil) impacts and risks of these relatively higher risk reuse pathways.

Conflicts of interest

There are no conflicts to declare.

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Table 1. Characteristics of selected wastewater treatment plants. Data provided by the managing water authority

	WWTP1	WWTP2	WWTP3 (a)	WWTP3 (b)	WWTP4
Catchment size[a]	700,000	75,000	150,000		200,000
Population equivalent load[b]	1,150,000	100,000	120,000		230,000
Flow (ML/day)[c]	151–198	22–29	15–19	12–18	45–67
Water temperature (°C)[d]	18.6–23.9	18.7–23.8	17.1–23	17–23.1	17.2–25.8
Total dissolved solids (mg/L)[e]	1,281 ± 162	6,346 ± 219		901 ± 97	1,137 ± 186
Mixed liquor suspended solids (mg/L)	3,910	2,790	2,850	4,000	5,500
Sludge retention time (days)	16	14	16	13	5[f]
Hydraulic retention time (hours)	16	17	10	13	9–10
		Treatment Process			
Primary	Sedimentation	No Primary sedimentation	Sedimentation	Sedimentation	Sedimentation
Secondary	Conventional activated sludge – step feed process; Sedimentation	Sequencing batch reactor	Conventional activated sludge - Modified Ludzack-Ettinger process; Sedimentation	4-stage Bardenpho + Membrane Bioreactor; Sedimentation	Integrated fixed-film activated sludge: Modified Ludzack-Ettinger process Sedimentation
Disinfection	Polishing lagoons	UV (43 mJ/cm^2)	Chlorination (9 mg/L)[g]	UV (15 mJ/cm^2)	Chlorination (8–10 mg/L)[g]
Recycled water treatment	DAFF treatment; Chlorination[g]				

[a] Estimated catchment population from census data and information provided by the managing water authority
[b] Population equivalent organic load to WWTPs calculated based on 120 grams COD/person/day (PE_{COD120})
[c] Average daily sewage flow recorded during the sampling period (± 1 standard deviation)
[d] Effluent water temperature during the study period
[e] Average TDS ± SD recorded during the sampling period in influent wastewater
[f] Relates to the SRT of the suspended biomass fraction only; overall reactor SRT will be higher due to attached IFAS biomass
[g] Chlorine gas used for disinfection

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Table 2. Water quality parameters of WWTPs. The concentrations (mg/L) are presented as mean ± SD values (n = 11) measured during the sampling period (April 2016 – Feb 2017). Data provided by the managing water authority.

	WWTP1		WWTP2		WWTP3			WWTP4	
	Influent	Effluent	Influent	Effluent	Influent	Effluent		Influent	Effluent
						(a)	(b)		
pH	7.3 ± 0.1	7.2 ± 0.1	7.9 ± 0.1	7.2 ± 0.2	7.5 ± 0.2	6.9 ± 0.1	7.5 ± 0.1	7.6 ± 0.1	7.1 ± 0.5
BOD_5	341 ± 62	21 ± 16	138 ± 11	3.4 ± 1	258 ± 116	7.2 ± 4	2.1 ± 0.4	204 ± 35	11 ± 5
SS	398 ± 51	51 ± 43	182 ± 16	3.8 ± 2	451 ± 307	3.3 ± 0.7	1.0 ± 0.1	300 ± 62	6.2 ± 2
COD	849 ± 103	114 ± 15	520 ± 35	194 ± 17	923 ± 712	69 ± 12	65 ± 13	573 ± 80	79 ± 19
NH_4	39 ± 5	0.4 ± 0.2	30 ± 3	0.3 ± 0	42 ± 5	0.9 ± 0.3	0.2 ± 0	36 ± 3	1.0 ± 0.4
TKN	81 ± 7	5 ± 2.6	52 ± 6	1.8 ± 0	77 ± 19	2.3 ± 0.3	1.4 ± 0.2	62 ± 7	2.6 ± 0.4
NO_3+NO_2	0.1 ± 0.04	9.1 ± 1.3	0.5 ± 0.2	3.7 ± 0.9	0.1 ± 0.1	14.4 ± 4.3	3.9 ± 0.8	0.8 ± 0.8	7.5 ± 1.7
TP	11.2 ± 1.4	2.2 ± 1.9	5.9 ± 1	2 ± 0.5	11 ± 5	8.7 ± 1.4	3.7 ± 0.8	8.6 ± 1	5.0 ± 1

BOD: Biological oxygen demand; COD: Chemical oxygen demand; NH_4: Ammonia as nitrogen; NO_3+NO_2: Nitrate + Nitrite as nitrogen; SS: Suspended solids; TKN as nitrogen; TP: total phosphorus

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Table 3. Concentrations (ng/L) of targeted drugs in water samples collected from studied WWTPs and an urban lake representing a built environment water course (April 2016–February 2017)

		Benzoylecgonine		Methamphetamine		MDMA		Codeine		Morphine	
LOD	In	1.0		40		1.5		0.1		0.4	
	Eff	0.5		0.4		0.2		0.1		0.2	
LOQ	In	4.0		240		2.0		0.5		1.0	
	Eff	1.0		0.9		0.5		0.3		0.4	
Wastewater treatment plants											
		L–H	**M**	**L–H**	**M**	**L–H**	**M**	**L–H**	**M**	**L–H**	**M**
WWTP1	C_{in}	52–823	223	1,894–4,297	3,048	15–438	94	2,556–3,965	3,215	680–1,273	920
(CAS)	C_{eff}	1–83	17	142–934	330	8–147	42	120–3,940	1,721	3–529	88
WWTP2	C_{in}	51–462	154	1,562–3,388	2,448	7–133	43	1,845–3,059	2,447	334–776	590
(SBR+UV)	C_{eff}	40–334	117	209–922	622	6–72	28	381–3,368	1,302	18–259	104
WWTP3	C_{in}	13–364	124	2,296–5,064	3,638	14–197	62	3,348–6,510	4,777	1,082–2,487	1,746
a ($CAS+Cl_2$)	C_{eff}	4–109	34	233–1,672	675	8–89	35	1–3,114	488	<LOD–473	77
b(MBR+UV)		8–149	34	273–1,063	590	6–126	33	38–5,414	941	1–101	29
WWTP4	C_{in}	57–789	210	1,559–3,766	2,399	13–244	74	2,411–3,750	2,999	417–1,205	798
($IFAS+Cl_2$)	C_{eff}	20–191	82	150–1,302	387	2–103	24	2–2,706	307	<LOD –106	23
Recycled wastewater											
DAFF	In	11–14.5	12.5	37–78	55.2	3.8–14	7.5	116–173	147	<LOD–5.3	2.6
	Eff	3.7–8	5.2	4.5–6.2	5.3	<LOD–1	0.4	11–46.4	25.5	ND	ND
Receiving water body											
Urban lake		ND	ND	<LOD–1.6	1.0	ND	ND	2.6–3.3	3.0	ND	ND

C_{in} and C_{eff}: Concentration in influent (in) and effluent (eff) samples; L–H: Low–High data range; M: Mean concentration – averaged across all sampling months (n=41 for all WWTPs while n=42 for WWTP4); LOD: Limit of detection; LOQ: Limit of Quantification; ND: not detected

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Credit Author Statement

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Highlights:

- Removal efficiency of drugs of addiction during wastewater treatment was evaluated
- IFAS process with chlorination was most efficient for removing targeted drugs
- Tertiary treatment by coagulation/flocculation can enhance drug removal efficiency
- Higher temperature (summer operations) showed enhanced drug removal
- Overall environmental risk from aquatic discharge of these drugs in effluent is low

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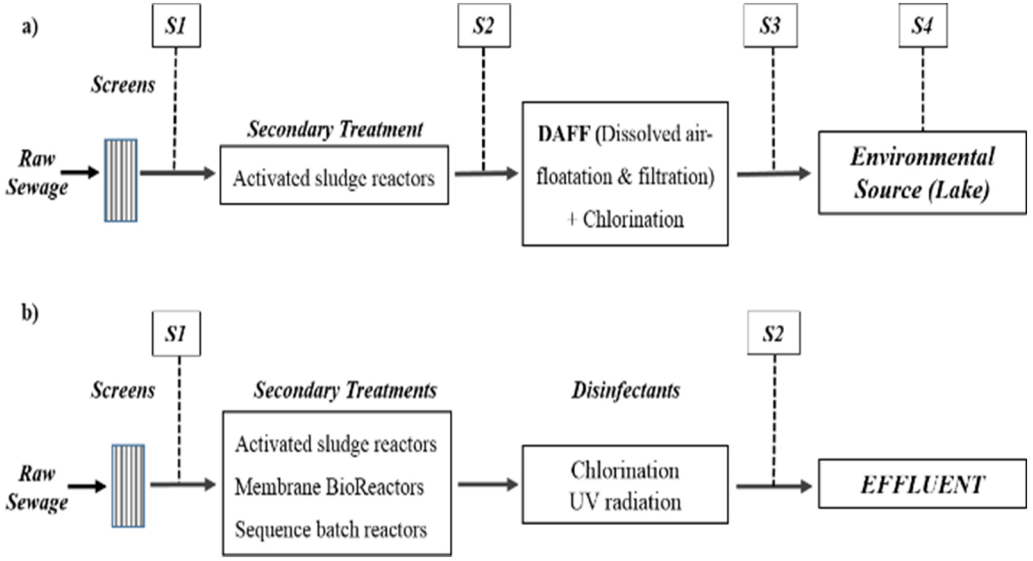

a)
S1
S2
S3
S4
Screens
Raw Sewage
Secondary Treatment
Activated sludge reactors
DAFF (Dissolved air-floatation & filtration) + Chlorination
Environmental Source (Lake)
b)
S1
S2
Screens
Raw Sewage
Secondary Treatments
Activated sludge reactors
Membrane BioReactors
Sequence batch reactors
Disinfectants
Chlorination
UV radiation
EFFLUENT

Figure 1

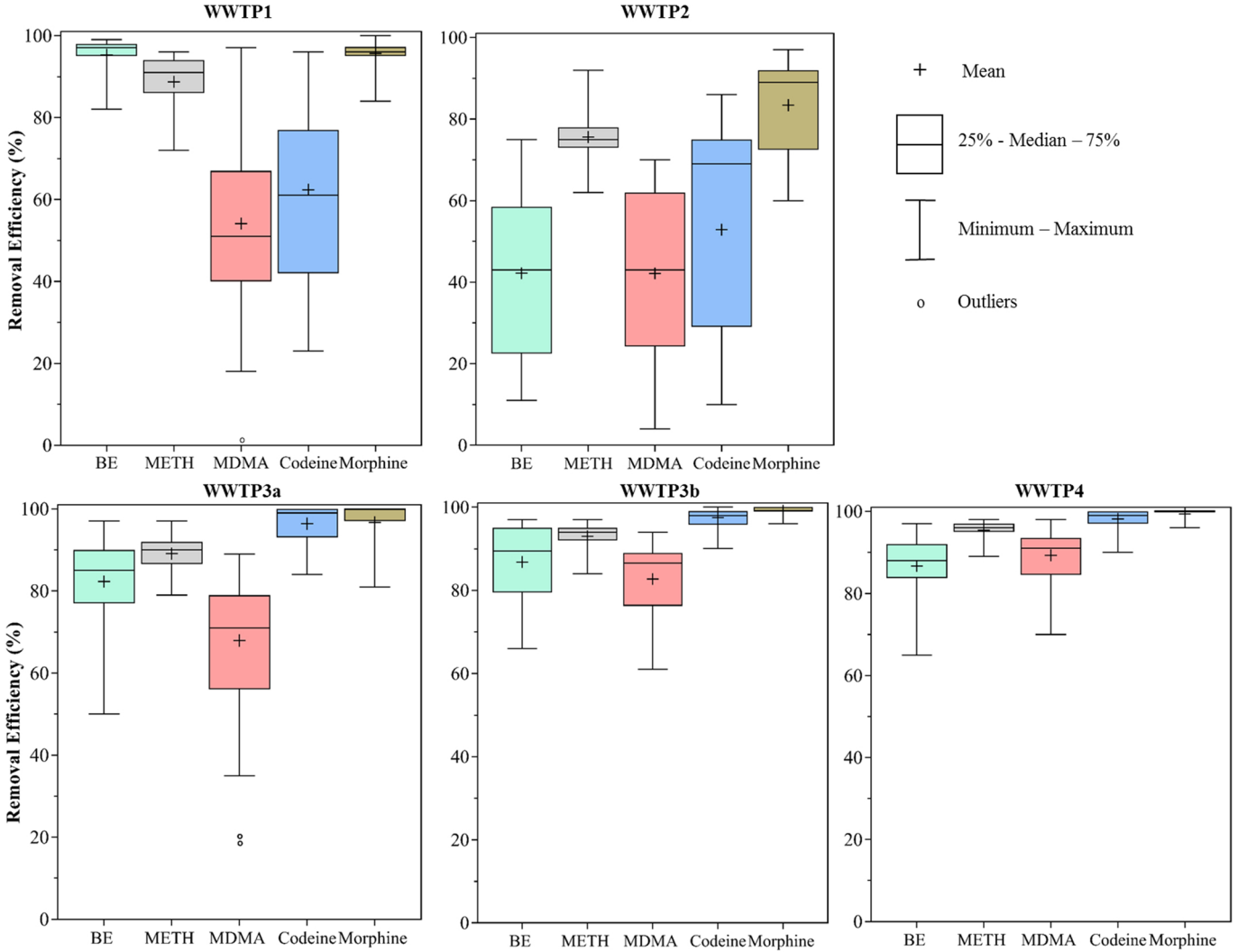

WWTP1
WWTP2
WWTP3a
WWTP3b
WWTP4
Removal Efficiency (%)
0
20
40
60
80
100
BE
METH
MDMA
Codeine
Morphine
Mean
25% - Median – 75%
Minimum – Maximum
Outliers

Figure 2

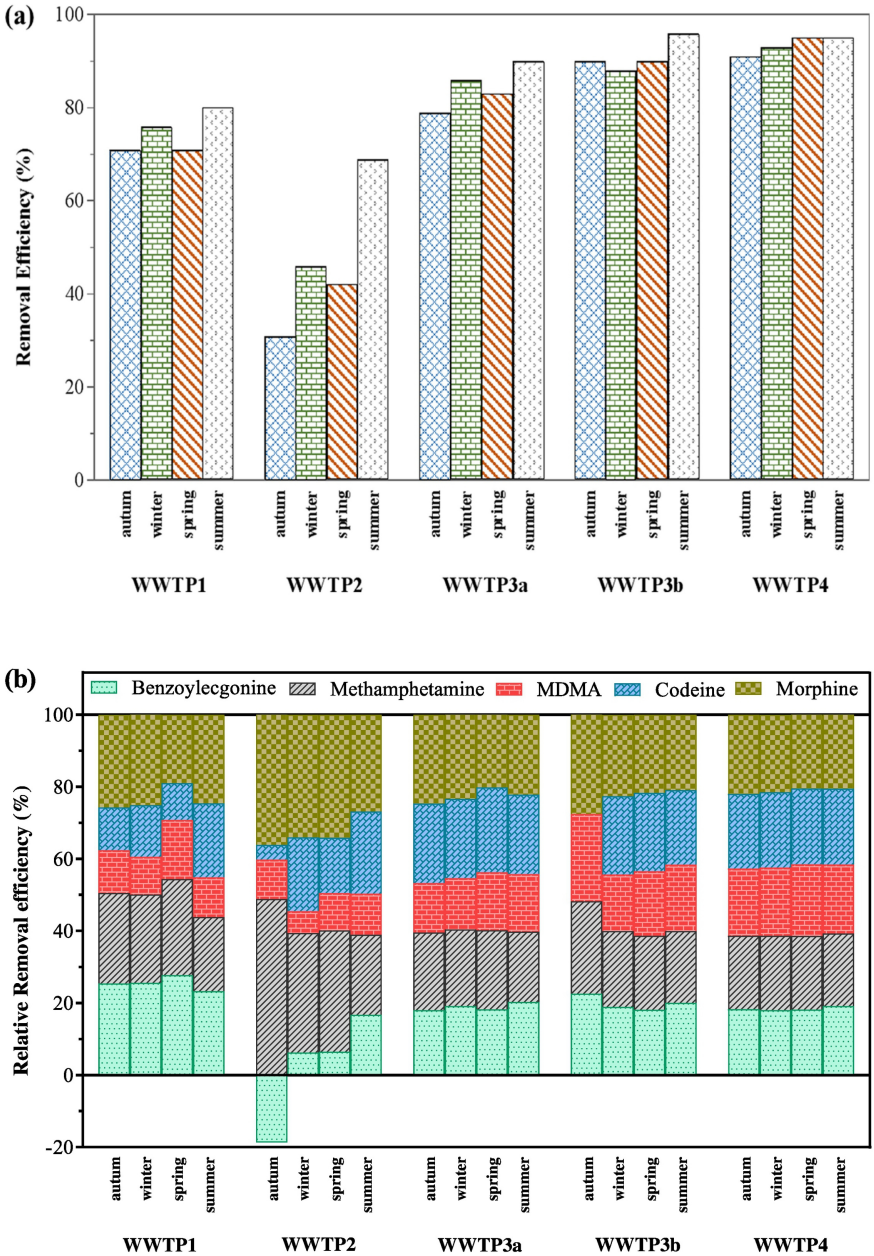

(a)
Removal Efficiency (%)
0
20
40
60
80
100
autum
winter
spring
summer
WWTP1
WWTP2
WWTP3a
WWTP3b
WWTP4
(b)
Benzoylecgonine
Methamphetamine
MDMA
Codeine
Morphine
Relative Removal efficiency (%)
-20
0
20
40
60
80
100

Figure 3

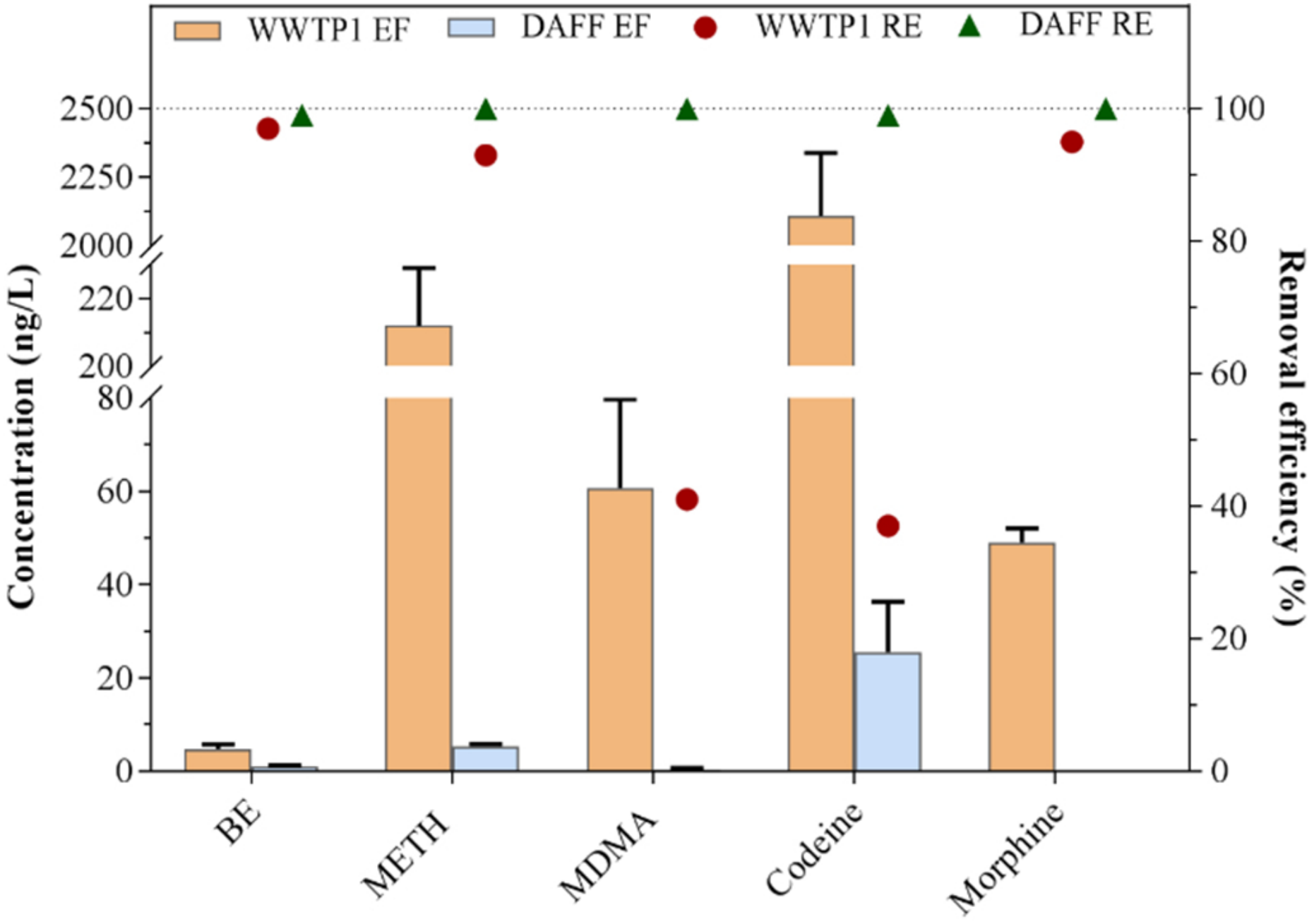

WWTP1 EF
DAFF EF
WWTP1 RE
DAFF RE
Concentration (ng/L)
Removal efficiency (%)
2500
2250
2000
220
200
80
60
40
20
0
100
80
60
40
20
0
BE
METH
MDMA
Codeine
Morphine

Figure 4

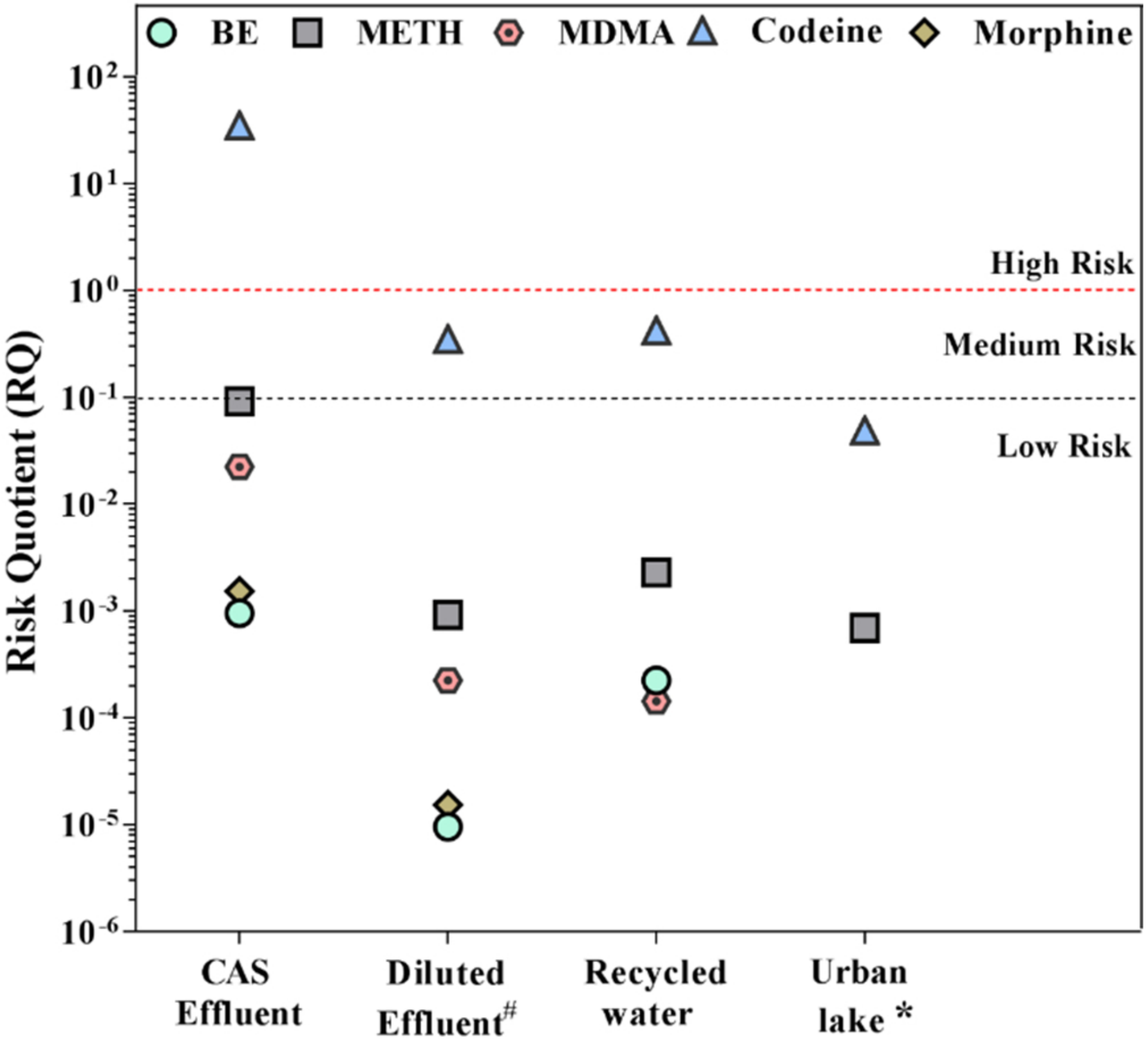

BE
METH
MDMA
Codeine
Morphine
Risk Quotient (RQ)
10^{2}
10^{1}
10^{0}
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
High Risk
Medium Risk
Low Risk
CAS Effluent
Diluted Effluent#
Recycled water
Urban lake *

Figure 5