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Micropollutants and biological effects as control indexes for the operation and design of shallow open-water unit ponds to polish domestic effluent

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ABSTRACT

Additional control indexes should be considered for the operation and design of post-treatment systems, as the wastewater treatment objectives are developing toward protecting the safety of ecological environments. In this study, two control indexes were selected and examined systematically in pilot-scale shallow open-water unit (SOWU) ponds for domestic effluent polishing: micropollutants and biotoxicities. The total risk quotient (RQ_{Total} ≤ 1) and effect-based trigger value (EBT) were set as the thresholds for known micropollutants and biological effects, respectively. The results showed that RQ_{Total} of micropollutants ($n = 46$) could be mitigated to an acceptable level and the luminescent bacteria toxicity was in compliance with the EBT after SOWU polishing in the warm season. The reduction of micropollutants and biotoxicities in the SOWUs both fit the *k–C** model well ($R^2 > 0.9$) in the warm and cold seasons. Finally, the *k–C** model integrated with the control indexes was developed to design the SOWU dimensions, and the results indicated that a pond area of 21.7–108.5 m^2 was required for every 1 m^3/d of effluent when micropollutants were set as the control index, while a pond area of 3.6–18.2 m^2 was required when luminescent bacteria toxicity was set as the control index.

1. Introduction

The wastewater discharged from domestic wastewater treatment plants (WWTPs) still contains abundant dissolved effluent organic matter, such as recalcitrant natural organic matter, soluble microbial products, trace concentrations of synthetic organic compounds and transformation products (Hu et al., 2016; Michael-Kordatou et al., 2015). These heterogeneous mixtures represent a key point source of environmental pollution and may induce adverse effects on aquatic organisms and human health (Coors et al., 2018; Petrie et al., 2015; Schwarzenbach et al., 2006). The treatment objectives of domestic wastewater, however, are generally focused on traditional pollution parameters, such as nutrients and organic loads. Domestic effluents that meet relevant regulatory standards for discharge or reuse, may not be able to satisfy the increasing safety needs related to aquatic ecosystems (Pedrazzani et al., 2019; Valitalo et al., 2017). As wastewater treatment objectives develop toward protecting the safety of ecological environments, additional control indexes such as micropollutants or biological effects should be considered for treatment system operation, especially when the system is employed as post-treatment for improved effluent quality.

In recent years, there has been increased awareness that monitoring hazardous micropollutants and screening the biological effects of chemical mixtures are important in evaluating water quality and the effectiveness of wastewater treatment (Barbosa et al., 2016; Escher et al., 2018). Some regulations on priority micropollutants have been published in the European Union (European Commission Implementation Decision 2015/495/EC, 2015; European Commission Implementation Decision 2018/840, 2018) and Australia (NRMMC & EPHC & NHMRC, 2008). Switzerland proposed that the removal of pharmaceuticals (e.g., carbamazepine, clarithromycin and citalopram) should be higher than 80% (from influent to effluent in WWTPs). In the US, California requires that the removal of 1,4-dioxane should be higher than 69% for the reclaimed water used to augment drinking water source (Eggen et al., 2014; Wang et al., 2020a). Standard bioassays with distinct endpoints have also been suggested for water quality assessment, such as xenobiotic metabolism, estrogenic effects, bacterial cytotoxicity, and genotoxicity (Jia et al., 2015; Xu et al., 2020).

However, detection of the individual micropollutants or biotoxicities does not necessarily mean that the ecological risk of domestic effluents is unacceptable. Studies have recommended several thresholds in this regard. For micropollutants, the risk quotient (RQ) provides a simple and

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pragmatic approach for environmental risk assessment (Diaz-Garduno et al., 2017; Ma et al., 2016; Papageorgiou et al., 2019). Common criteria for interpreting the RQ of micropollutants are used to establish different risk levels; the risk is deemed "acceptable" when RQ ≤ 1, and "unacceptable" when RQ > 1. Regarding the biological effects of chemical mixtures, effect-based trigger values (EBTs) have been recently derived to define the thresholds that differentiate acceptable biological toxicity (bioanalytical equivalent concentration, or BEQ) from unacceptable toxicity (Escher et al., 2018; Ma et al., 2019). Escher et al. (2018) obtained an EBT-baseline-BEQ of 1.26 mg/L for bioluminescence inhibition assay based on the existing list of environmental quality standards (EQS). Ma et al. (2019) reported an EBT of 6.04 mg/L BEQ_{phenol} for luminescent bacteria toxicity based on the hazardous concentration for 5% of aquatic organisms (HC5). In addition, EBT thresholds have been recently used to allocate wastewater effluents into four categories based on their measured toxicity (Alygizakis et al., 2019). Based on the exceedance of the EBT values, a different response plan for WWTP operators has been developed. For example, if the result of biotoxicity is 1-times $<$ EBT $<$ 3-times, WWTP operators should perform a quality check of the data and continue to monitor the effluents every three months, until one year has passed and the EBT < 1. These defined thresholds of micropollutants and biotoxicities will aid in the future design, operation, and management of wastewater treatment systems to ensure that the effluent is "acceptable".

Engineered natural treatment systems (ENSs), such as constructed wetlands and pond systems, appear to have great potential for the removal of micropollutants and reduction of biotoxicities. (Bear et al., 2017; He et al., 2018; Kumar and Asolekar, 2016). The shallow open water unit (SOWU) process is one of the most promising options. SOWU ponds comprise shallow engineered basins that stabilize and treat wastewater via natural processes driven by sunlight and photosynthetic microbial biomats (Bear et al., 2017; Jasper and Sedlak, 2013). As an ENSs, a SOWU pond can create a self-contained system or engage with other wastewater treatment facilities. This system is characterized as cost-effective and eco-friendly. especially in economically constrained countries and regions (Brandt et al., 2013; Kumar and Asolekar, 2016). In general, when ENSs are constructed for wastewater treatment, biochemical oxygen demand (BOD), chemical oxygen demand (COD), and total nitrogen (TN) are the typical control indexes for system operation and design (Ho et al., 2017). New control indexes such as micropollutants and biological effects should be considered for the protection of ecological or human health, especially when ENSs are employed as post- treatment to improve effluent quality. However, few studies have been devoted to exploring the operation and design of treatment systems with the objective of ecological safety. Jasper and Sedlak (2013) tried to set a 90% reduction of certain micropollutants (e.g., carbamazepine and sulfamethoxazole) as the treatment objective of open-water unit process treatment wetlands, and the area necessary for micropollutant photolysis was estimated. Nivala et al. (2019) reported first-order removal rate coefficients for individual micropollutants and discussed their use in conventional and intensified subsurface flow treatment wetlands. With the assistance of innovative analytical techniques, there is a pressing need to determine the applicability of additional control indexes in the operation and design of wastewater treatment facilities. Moreover, the ecological risk of wastewater should be considered simultaneously.

In this study, shallow open-water unit (SOWU) ponds were constructed for domestic effluent polishing and the dynamics of micropollutant removal and biological effect (luminescent bacteria toxicity and genotoxicity) reduction were examined systematically in both the warm and cold seasons. The purpose of this study was to explore the feasibility of new control indexes for the operation and design of post-treatment units. To ensure that the safety of the domestic effluent was "acceptable" after SOWU polishing, we set the micropollutants or biotoxicity as the new control indexes. The total risk quotient ($RQ_{Total} \leq 1$) and effect-based trigger value (EBT) were selected as the thresholds for known micropollutants and unknown chemical mixtures, respectively. The first-order model integrated with the control indexes was developed to determine the pond system dimensions.

2. Material and methods

2.1. Post-treatment unit

Two identical SOWU ponds for domestic effluent polishing were constructed in an open-air space close to the local WWTP. The SOWU pond comprised a cascade containing four shallow rectangular channels, whose dimensions were 2.4 m in length and 0.45 m in width. The treatability of individual micropollutants in the SOWU was investigated in our previous study (Wang et al., 2020b).

In this study, post-treatment experiments were performed in both the warm and cold seasons, and conducted selectively on sunny days. There was no precipitation during the experiments. Simplified experiments were performed in order to explore the dynamics of residual micropollutant removal and biotoxicity reduction in the SOWU. Specifically, the depth of domestic effluent in the SOWU was set at 0.45 m with working volumes of 1944 L. The system was operated in a batch-loaded model and carried out over fourteen consecutive days after the effluent was pumped into the SOWU ponds. The pond water in the last channel was transferred into the first channel to maintain an automatic recirculation in the system, which could promote the mixing of pond liquid and the penetration of natural sunlight. The schematic system diagram of the SOWU system is shown in Fig. 1, and the pictures of the pond system can be found in Fig. S1.

The average water temperature was 23.5 °C in the warm season (from June to July, 2018), and the natural sunlight intensity was observed to be 32,800–105,750 lux as recorded with a Lux meter. The average water temperature was 4.3 °C in the cold season (from November to December, 2018) with sunlight intensity ranging from 2260 to 65,500 lux. The real domestic effluents used in this study were collected from the local WWTP (lat. 34°14′N, 109°04′E), where an anaerobic-anoxic-oxic unit followed by a membrane bioreactor were employed to treat municipal domestic sewage (Ma et al., 2016). The properties of the domestic effluent are shown in Table S1.

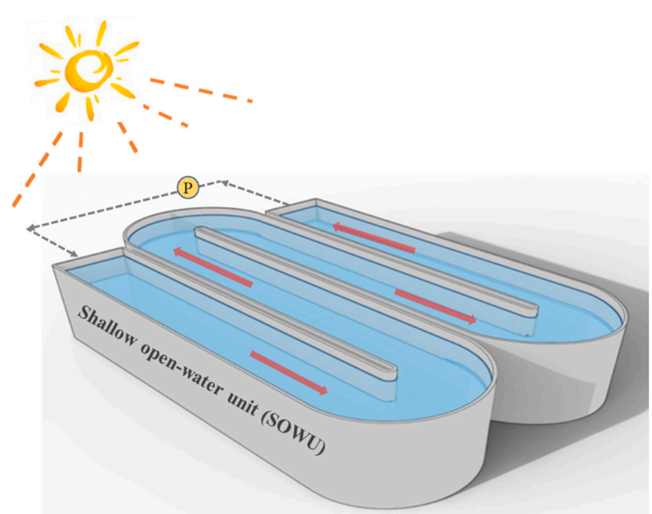

Fig. 1. Schematic system diagram of the shallow open-water unit (SOWU) pond. The red arrow represents the recirculation flow and the 'P' means 'pump'. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2.2. Sampling and sample preparation

Water sampling began immediately following the polishing treatment (day 0) and proceeded at approximately the same time (10:00–11:00 am) on days 2, 4, 6, 10, and 14. At each sampling event, approximately 5 L of pond water were collected in amber glass bottles. The water samples acquired from the SOWU were taken to the nearby laboratory immediately, and then separately filtered through a 0.7 µm glass microfiber filter (Φ 150 mm; Whatman). About 2 L of the filtered samples were subjected to micropollutant analysis and 1 L was used for bioassays. The sample preparation procedures for chemical analysis and bioassays are described in detail in Section S1.

2.3. Micropollutants and analytical determinations

A total of 46 micropollutants were selected and monitored during the SOWU polishing treatment processes (Table 1). Target analyses of the micropollutants in the samples were performed using UPLC-MS/MS (ACQUITY UPLC - Xevo TQ MS, Waters, USA) and GC/MS (TSQ Quantum XLS, Thermo, USA). The instrumental analysis parameters for the targeted micropollutants are shown in Tables S3 and S4. To ensure the accuracy of the method, quality assurance and quality control elements consisted of laboratory and field blanks, duplicates, and recovery indicators for each set of samples. The recovery of all 46 chemicals with individual concentrations of 5 ng/L and 50 ng/L were 62–130% and 58–129%, respectively, as shown in Table S2. The method limit of quantification (LOQ) was set at the laboratory LOQ which was 10 times of S/N, and the LOQs of the target chemicals are shown in Table S2.

2.4. Bioassays

Two bioassays were selected to evaluate the adverse effects of complex chemical mixtures (Table 2). The non-special toxicity was evaluated by bioluminescence inhibition assay using *Aliivibrio fischeri*, which is suitable for the toxic equivalency evaluation of complex environmental samples and has been shown to correlate well with in vivo

Table 1
Targeted micropollutants in this study, and their physicochemical descriptors, aquatic toxicity from the ECOSARv2.0 database, and the limits of concentration according to regulations. Australian Guidelines for Water Recycling (AGWR) (NRMMC & EPHC & NHMRC, 2008).

Chemical	CAS number	Log Kow	Solubility (mg/L)	Decision (EU) 2018/840 (ng/L)	AGWR guideline value (µg/L)	Aquatic toxicity (mg/L)		
						Fish 96 h-LC50	*Daphnia* 48 h-LC50	Green Algae 96 h-EC50
17a-Ethinylestradiol	57–63–6	4.12	11.3			1.42	1.60	0.14
17-alpha-Estradiol	57–91–0	3.94	3.9	0.035		1.71	1.78	0.16
17-beta-Estradiol	50–28–2	3.94	3.9	0.4		1.71	1.76	0.16
2,4,6-Trichlorophenol	32,296	3.45	800.0		20	2.72	2.27	0.25
2-Benzoyl-5-methoxy-1-phenol-4-sulfonic acid (BP4)	4065–45–6	0.37	250,000.0			5580.0	1160.0	462.0
2-Ethylhexyl 4-dimethylaminobenzoat (OD-PABA)	21,245–02–3	5.77	0.20			0.24	0.33	0.08
4-Aminobenzoic acid (PABA)	150–13–0	0.96	6110.0			709.0	26.3	82.3
Acetamiprid	135,410–20–7	2.55	4200.0	8.3		18.70	2.38	1.73
Ametryn	834–12–8	3.32	209.0			8.19	8.17	0.06
Atrazine	1912–24–9	2.82	34.7		40	20.2	15.7	0.11
Avobenzone (BM-DBM)	70,356–09–1	4.51	2.2			0.64	0.71	0.26
Azoxystrobin	131,860–33–8	1.58	6.0			95.5	208.0	94.5
Benzophenone −1 (BP1)	131–56–6	2.96	235.6			3.06	16.3	2.12
Bisphenol A	29,348	3.64	120.0			1.28	5.24	1.33
Carbamazepine	298–46–4	2.25	112.0		100	40.9	14.1	0.26
Carbendazim	10,605–21–7	1.55	29.0		100	56.4	48.7	0.35
Clarithromycin	81,103–11–9	3.18	1.7	19	250	24.2	3.31	2.08
Cyanazine	21,725–46–2	2.51	170.0			41.0	27.1	0.17
Difenoconazole	119,446–68–3	5.20	15.0			0.31	0.75	0.26
Dimethomorph	110,488–70–5	2.36	22.9			6.47	17.7	0.38
Diphenhydramine Hydrochloride	147–24–0	1.59	251.8			561.0	307.0	195.0
Dipterex	52–68–6	0.42	120,000.0			20.0	0.04	384,000.0
Erythromycin	114–07–8	2.48	4.2	19	17.5	68.4	8.62	6.37
Estriol	50–27–1	2.81	500.0			10.9	6.80	0.99
Estrone	53–16–7	3.43	30.0	0.4		3.82	3.16	0.36
Fluoxetine hydrochloride	56,296–78–7	4.65	60.3			1.08	0.18	0.08
Ibuprofen	15,687–27–1	3.79	21.0		400	41.6	27.8	41.1
Imidacloprid	138,261–41–3	0.56	610.0	8.3		437.0	44.0	50.7
Ketoprofen	22,071–15–4	3.00	51.0		3.5	264.0	164.0	179.0
Mefenamic acid	61–68–7	5.28	20.0			2.25	1.73	4.51
Naproxen	22,204–53–1	3.10	15.9		220	193.0	122.0	138.0
Octyl 4-methoxycinnamat (EHMC)	5466–77–3	5.80	0.15			0.23	0.32	0.08
Oxybenzone (BP3)	131–57–7	3.52	192.6			2.78	2.40	0.26
p-Cresol	106–44–5	2.06	21,500.0		600	13.4	5.96	1.18
Phenol	108–95–2	1.51	82,800.0		150	27.7	9.64	2.40
Prochloraz	67,747–09–5	4.13	34.0			0.16	1.29	0.19
Prometryne	7287–19–6	3.73	33.0			3.90	4.81	0.04
Roxithromycin	80,214–83–1	2.75	0.19		150	51.6	6.72	4.66
Simazine	122–34–9	2.40	6.2			42.1	26.40	0.17
Sulfamethoxazole	723–46–6	0.48	610.0		35	267.0	6.43	21.8
Terbuthylazine	5915–41–3	3.27	8.5			9.01	8.79	0.06
Thiamethoxam	153719–23–4	0.80	2861.8	8.3		346.0	35.8	39.0
Triadimefon	43121–43–3	2.94	71.5			12.7	12.3	2.45
Triallate	2303–17–5	4.57	4.0			1.74	0.45	0.13
Trimethoprim	738–70–5	0.73	400.0		70	212.0	6.4	20.7
Triphenylphosphine oxide	791–28–6	2.87	21.7			92.8	1.97	0.08

Table 2
Bioassays and the effect-based trigger values (EBTs) used in the present study.

Mode of action	Bioassay	Species	Reference compound	EBT
Non-specific cytotoxicity	Bioluminescence inhibition assay	*Aliivibrio fischeri*	Phenol	6.04 mg/L BEQ_{phenol} (Ma et al., 2019)
Reactive genotoxicity	umuC test without S9	*Salmonella typhimurium* TA1535/pSK1002	4-Nitroquinoline-N-oxide (4-NQO)	0.64 μg/L $BEQ_{4\text{-}NQO}$ (Xu et al., 2014)

Daphnia magna toxicity assays (Dewhurst et al., 2002). The umuC test without metabolic activation was selected to evaluate the reactive genotoxicity of the chemical mixtures. It has been demonstrated that the bioluminescence inhibition effect and umuC assay for genotoxicity were mostly highlighted in bioassay batteries for wastewater effluents (Jia et al., 2015; Reungoat et al., 2010). Bioluminescence inhibition assay using *Aliivibrio fischeri* and genotoxicity assay using the umuC test were performed as described in Section S2.

The effective concentration (EC_{50}) and induction ratio ($IR_{1.5}$) were used to quantify the luminescent bacteria toxicity and genotoxicity, respectively. The biological effect of chemical mixtures was standardized to BEQ, which was calculated through the EC_{50} or $IR_{1.5}$ of the reference compound divided by the EC_{50} or $IR_{1.5}$ of the water sample (Eq. (1)). BEQ represented the concentrations of a reference compound that would elicit the same effect as the chemical mixtures. Detailed information about the two bioassays was described in our previous studies (Ma et al., 2016; Zhang et al., 2017). The BEQ was calculated as follows:

$$BEQ = \frac{EC_{50}\ \ or\ \ IR_{1.5}\ \ of\ \ reference\ \ compound}{EC_{50}\ \ or\ \ IR_{1.5}\ \ of\ \ water\ \ sample} \quad (1)$$

2.5. Model-based approach

In the present study, the first-order k–C^* model (Kadlec and Wallace, 2009) was applied to describe the reduction of biological effects in SOWU, as well as the removal of micropollutants. The k–C^* model is given by Eq. (2):

$$\frac{C_t - C^*}{C_0 - C^*} = e^{-k_v t} \quad (2)$$

where C_t is the biological effect of the pond water at day t (d); C^* is the irreducible background value; C_0 represents the biological effect of the pond water at day 0; k_v is first-order volumetric rate constant (d^{-1}); and t is the sampling time (days 0, 2, 4, 6, 10, and 14), namely, the retention time of domestic effluent in the SOWU. For biotoxicity, C_t, C_0, and C^* were standardized to BEQ (mg/L or μg/L). Regarding micropollutants, C_t (ng/L) represents the total concentration of all detected micropollutants in the pond water at day t (d).

The k–C^* model has been used to describe the performance of batch-loaded systems for pollutant removal (such as BOD, COD, and micropollutants) in various ENSs (Kadlec, 2003; Nivala et al., 2019; Park and Roesner, 2012). The characteristics of wetlands, detention basins, and retention ponds are similar. As an illustrative case, the SOWU process

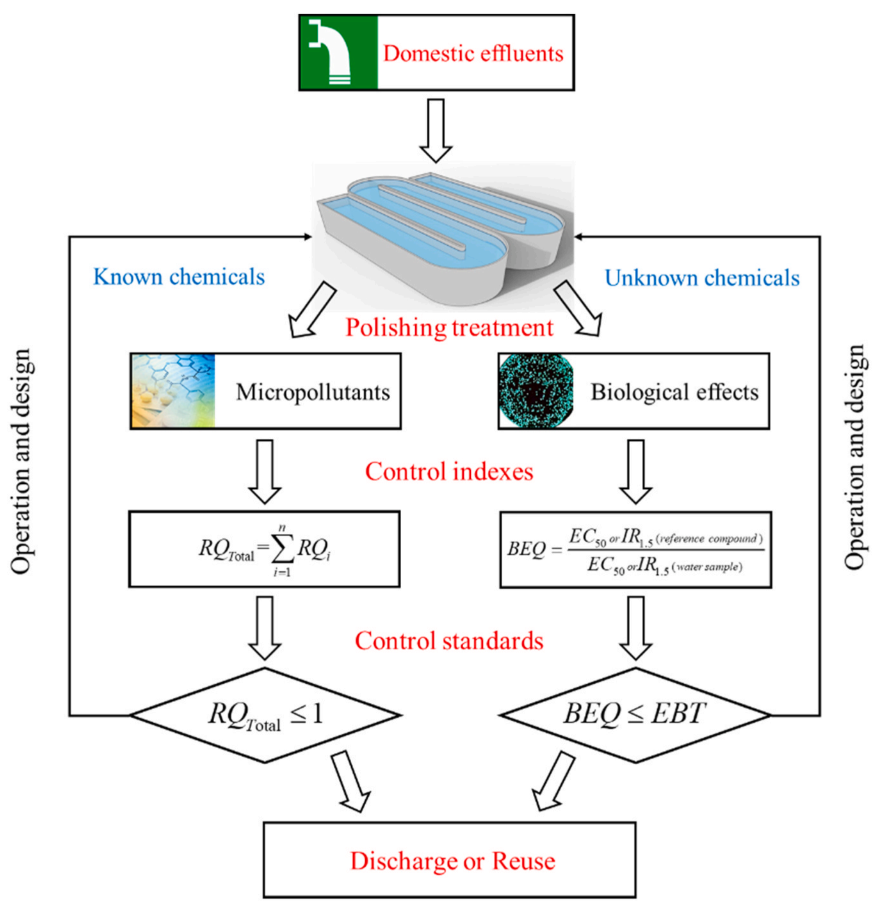

Fig. 2. Schematic of design strategies with new control indexes for the shallow open-water unit (SOWU) pond in this study.

was operated in batch-loaded model with well-mixed environments. The present study adopted this method to simulate SOWU performance.

2.6. Design strategies with new control indexes

The design strategies with new control indexes for SOWU pond is shown in Fig. 2.

For known chemicals, the evaluation of the potential ecological risks of residual micropollutants in the water sample was processed using RQ. The threshold for the concentration of individual micropollutants was defined as follows: the risk was deemed "acceptable" when RQ ≤ 1, and "unacceptable" when RQ > 1. The RQ of individual micropollutants (i) was calculated using the ratio (Eq. (3)) between the measured environmental concentration (MEC) and the predicted no-effect concentration (PNEC). The PNEC of each chemical was estimated using the ratio (Eq. (4)) between its acute toxicity L(E)C50 value (Table 1) and an assessment factor (AF) (usually 1000) (European Commission, 2003). In an attempt to improve the integration of the ERA regarding all the detected micropollutants in the water samples, RQ_{total} (Eq. (3)) was calculated to determinate the potential risk of the whole water samples, based on that chemical typically present in wastewater act concentration-additive effects.

$$RQ_{Total} = \sum_{i=1}^{n} RQ_i = \sum_{i=1}^{n} \frac{MEC_i}{PNEC_i} \quad (3)$$

$$PNEC = \frac{E(L)C_{50}}{AF} \quad (4)$$

For unknown chemical mixtures, the threshold for the biotoxicity was defined as follows: the risk was deemed "acceptable" when BEQ ≤ EBT, and "unacceptable" when BEQ > EBT. The value of EBT was primarily derived from the existing EQS or from the HC5 based on species sensitivity distributions. The assessment results were consistent when using both EQS-EBT and HC5-EBT (Ma et al., 2019). Commonly-agreed EBTs were collected and used in this study. These EBTs are shown in Table 2.

3. Results and discussion

3.1. Removal of micropollutants

3.1.1. Seasonality of removal efficiencies

Twenty-nine organic micropollutants were detected in the warm season and the concentration ranged from undetected to 226 ng/L in the studied effluent, while 38 micropollutants were detected in the cold season and the concentration ranged from undetected to 540 ng/L (Table S5). These findings were in line with the previously reported concentration ranges (Luo et al., 2014; Tran et al., 2018). Fig. 3 summarizes the overall removal of the residual micropollutants during the SOWU polishing treatment processes.

After SOWU treatment, the total concentration of residual micropollutants decreased (from 914 to 276 ng/L) continuously in the warm season, as well as in the cold season (from 2608 to 1912 ng/L). In contrast to the cold season, the warm micropollutants exhibited lower overall concentrations (day 0: 914 ng/L vs 2608 ng/L) but much higher removal efficiencies (day 14: 69.8% vs 26.7%) in the SOWU. Regarding the detected EU watch list chemicals, the concentrations of acetamiprid, erythromycin, imidacloprid, and thiamethoxam in the warm season all exceeded the prescribed values (Table S5). Importantly, these priority hazardous substances could be effectively eliminated by SOWUs, except for acetamiprid. Although 14 AGWR list chemicals were detected in the initial domestic effluent (Table S5), the concentrations were all lower than the guideline values in both the warm and cold seasons, which indicated that there were no potential health risks. Matamoros and Salvado investigated a polishing pond (1 m in depth) that was utilized as the polishing step for secondary effluent and found that it was capable of removing up to 51% of 27 micropollutants (Matamoros and Salvado, 2012), which was in accordance with the results of the present study. Studies have also shown that carbamazepine was removable in the shallow polishing pond to a significant extent, although it is fairly difficult to degrade in many other treatment units (Matamoros et al., 2008). The SOWU ponds employed as post-treatment could provide a good alternative for the attenuation of residual micropollutants.

3.1.2. Risk quotient of micropollutants

Three different trophic levels including algae, *Daphnia*, and fish were considered to investigate the adverse impact of individual micropollutants on the aquatic environment (Table 1). Fig. 4 shows the RQ_{Total} of the detected micropollutants in the studied effluent and their significant individual contributions.

BP3 and EHMC were the dominant chemicals that posed an acute risk to fish. In the warm season, the RQ values of BP3 and EHMC were 0.023 and 0.3, respectively, while the RQ of BP3 was 0.17 in the cold season (Fig. 4a and b). The RQ_{Total} was lower than 1 and represented an "acceptable" risk of the studied effluent in both the warm and cold seasons. Concerning the risk in *Daphnia*, BP3 and EHMC were also the

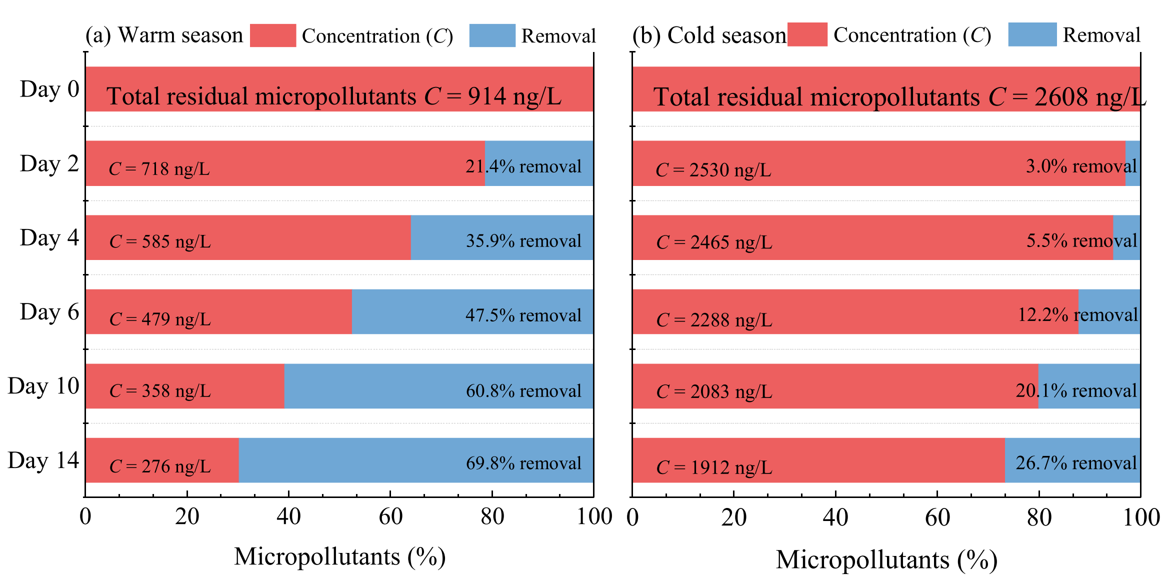

Fig. 3. Removal of micropollutants in shallow open-water unit (SOWU) during (a) warm and (b) cold seasons for domestic effluent polishing.

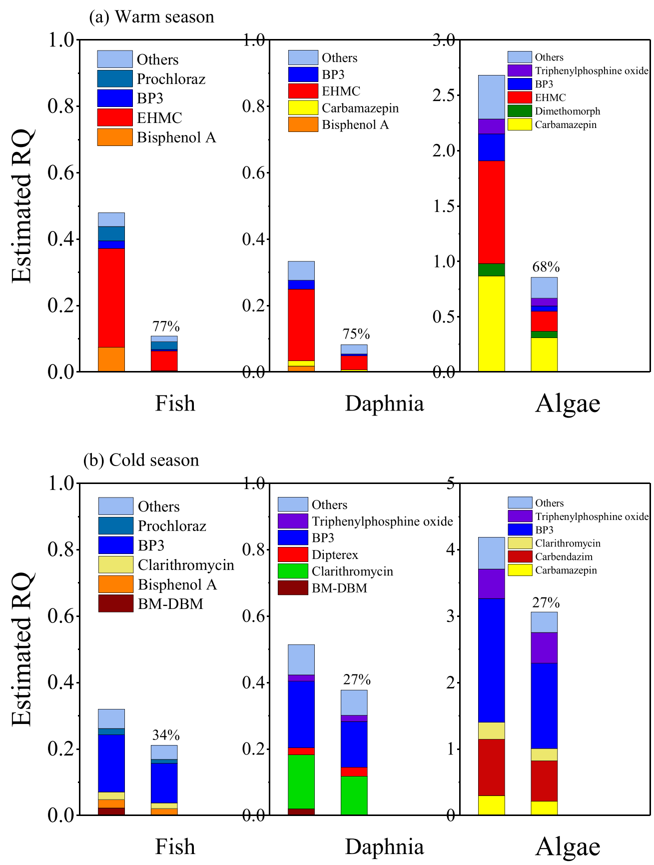

Fig. 4. Estimated RQ of residual micropollutants before and after shallow open-water unit (SOWU) polishing treatment (day 0 vs day 14) in the (a) warm and (b) cold seasons. Significant individual contributions for RQ_{Total} and total percentage depletion are shown.

most harmful substances and accounted for a major proportion of the RQ_{Total}. In the warm season, the RQ of EHMC was 0.22 which accounted for 65% of RQ_{Total} (0.33), while the RQ of BP3 was 0.2 which accounted for 39% of RQ_{Total} (0.51) in the cold season. It should be noted that EHMC is also an EU list compound (Decision 2015/495). It is an emerging organic UV filter with a relatively high LogKow value (5.8) and has been proven to induce endocrine-disrupting activity and coral bleaching effects (He et al., 2019). Regarding the risk in algae, the studied effluent exhibited high RQ_{Total} values in both the warm (2.7) and cold (4.2) seasons. The "unacceptable" risk of the effluent was mainly attributed to the presence of BP3 (RQ = 0.24), EHMC (RQ = 0.93), and carbamazepine (RQ = 0.87) in the warm season, and BP3 (RQ = 1.9), carbendazim (RQ = 0.85), and triphenylphosphine oxide (RQ = 0.45) in the cold season. As expected, the RQ_{Total} decreased with a decay percentage of 68% in the warm season ($RQ_{Total} \leq 1$) following SOWU polishing treatment (Fig. 4a), but the RQ_{Total} was still higher than 1 after 14 full days in the cold season (Fig. 4b). These results were in keeping with the fact that the micropollutant concentrations were at high levels and had a poor removal rate in the cold season as mentioned in Section 3.1.1. Moreover, the results indicated that residual micropollutants provoke higher or lower effects depending on the target organisms, thus confirming an integrative risk assessment considering the most conservative effect level should be used when predictions are made from multiple classes (Diaz-Garduno et al., 2017).

Overall, when the SOWU ponds were constructed as polishing step for domestic effluent, the potential ecological risks of residual micropollutants could be mitigated to an acceptable level ($RQ_{Total} \leq 1$) in warm season conditions. The tropical environment, with adequate light and appropriate temperatures, may be more conducive to improving SOWU performance (Ho et al., 2017).

3.2. Reduction of biotoxicity

The results of in vitro bioassays for monitoring the biological effects of organic chemical mixtures are shown in Fig. 5. Significant luminescent bacteria toxicity was observed for the studied effluent in both the warm (BEQ_{phenol}, 14.42 mg/L) and cold seasons (BEQ_{phenol}, 14.02 mg/L). The luminescent bacteria toxicity of the effluent was obviously in excess of the proposed EBT values (BEQ_{phenol}, 6.04 mg/L), which suggested that the domestic effluent still had potential acute toxicity. After the polishing treatment by SOWU ponds, the pond water was quickly in compliance with the EBT values in the warm season (Fig. 5a), whereas the SOWU was incapable of mitigating the luminescent bacteria toxicity in the cold season (Fig. 5b). Specifically, the luminescent bacteria toxicity decreased from 14.42 to 5.50 mg/L (warm season) after two days in the SOWU, but it remained at 9.11 mg/L in the cold season even after 14 days. Overall, the SOWU ponds showed high performance in the reduction of luminescent bacteria toxicity in warm conditions, and the adverse biological effect was "acceptable" after the polishing treatment.

Regarding the genotoxicity, the studied effluent showed a lower $BEQ_{4\text{-}NQO}$ value of 0.21 μg/L in the warm season but a much higher $BEQ_{4\text{-}NQO}$ of 2.24 μg /L in the cold season. The reported $BEQ_{4\text{-}NQO}$ of the wastewater effluents ranged from 0.1 to 4 μg/L, which was in keeping with the present study (Jia et al., 2015; Ma et al., 2019). In the cold season, the initial genotoxicity declined gradually to 0.5 μg/L (≤0.64 μg/L) on day 10 with 77.8% removal efficiency (Fig. 5d). The results indicated that SOWU ponds showed excellent performance for genotoxicity reduction despite of the cold season conditions. This may be related to the fact that aromatic groups (e.g., chromophores and fluorophores) in effluent organic matter have been found to show an inherent correlation with genotoxicity (Chen et al., 2017), as was also found in this study (Fig. S2).

For the luminescent bacteria toxicity, all chemical mixtures present in the water samples contributed to the adverse biological effects, while the umuC test (genotoxicity) used in this study are closely related to direct-acting mutagens. The initial genotoxicity was 10 times lower for the warm season compared with that of the cold season, which might be ascribed to the higher total concentration of residual micropollutants in the cold (2608 ng/L) compared with the warm season (914 ng/L). It has been indicated that the detected micropollutants could only explain less than 1% of measured luminescent bacteria toxicity (Tang et al., 2014). Therefore, the "toxic unknowns" might be responsible for the luminescent bacteria toxicity, such as macromolecular dissolved organic matters.

3.3. Model-based approach

3.3.1. Integration of micropollutants into the k–C* model

The reduction of residual micropollutants as a function of time in SOWU is shown in Fig. 6a. The results demonstrated that the *k*–*C** model represented micropollutant (total concentrations) times series well in both the warm ($R^2 = 0.999$) and cold ($R^2 = 0.987$) seasons, and the obtained parameters are listed in Table 3.

During the warm experimental stage, the apparent rate coefficient k_v was 0.155 d^{-1} and the fitted artificially introduced C^* value was 199 ng/L. The negligible attenuation of micropollutants in the cold season yielded a k_v of only $2.1 \times 10^{-4}\ d^{-1}$. Micropollutants are unable to be fully phototransformed or biotransformed in ENSs (Gonzalez-Gil et al., 2018; Jasper and Sedlak, 2013), which results in a non-zero lower limit. In this study, the irreducible background of concentration C^* could be ascribed to the recalcitrant fractions in the residual micropollutants such as azoxystrobin, carbamazepine, carbendazim, and triphenylphosphine oxide (Table S5). Although each micropollutant is removed by a different mechanism and the *k* is compound-dependent (Nivala et al., 2019), the results showed that when different

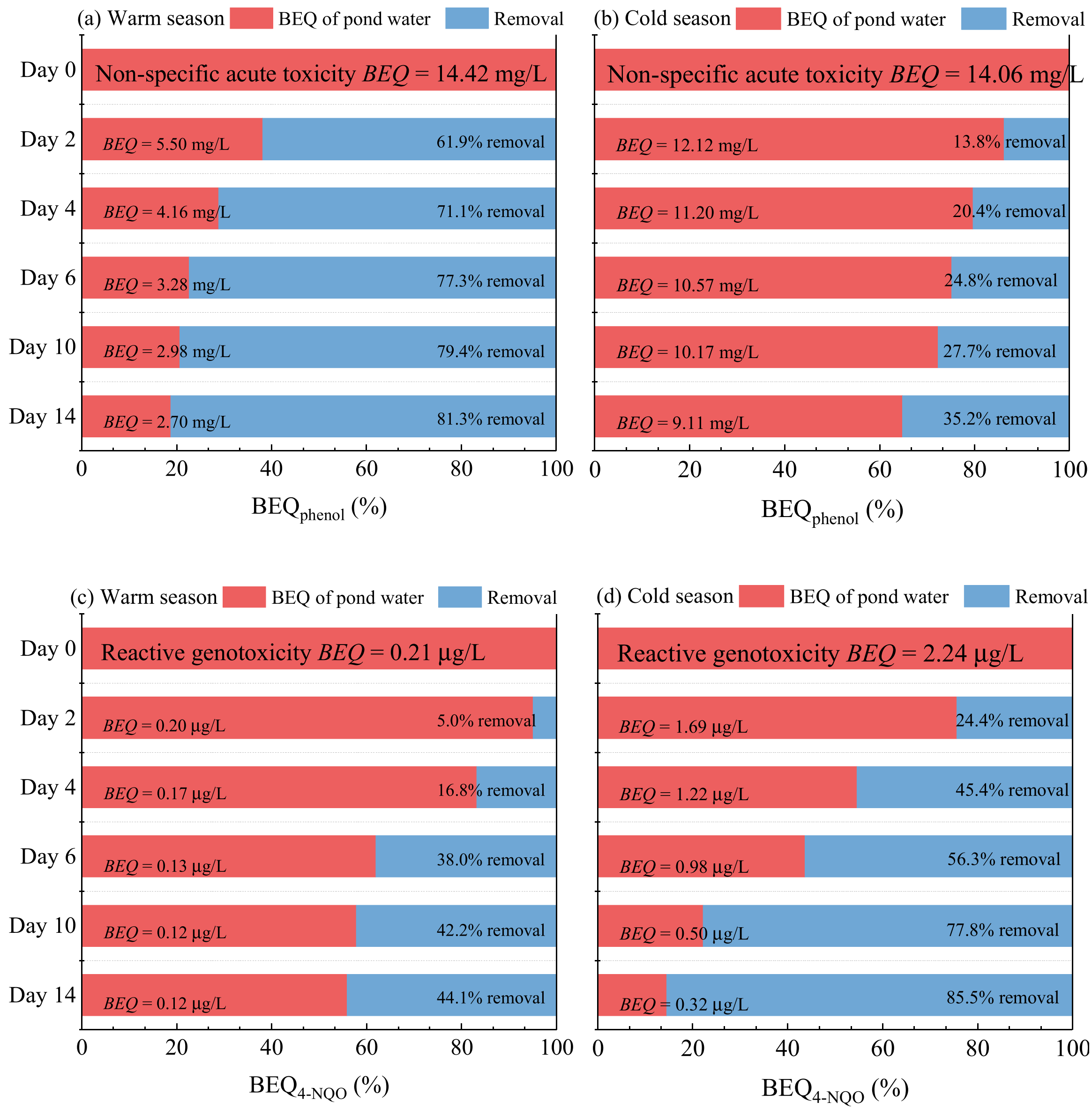

Fig. 5. Reduction of luminescent bacteria toxicity and genotoxicity in shallow open-water unit (SOWU). The variation of luminescent bacteria toxicity is shown in bioanalytical equivalent concentration (BEQ) values and the relevant removal (%) is shown in the (a) warm and (b) cold seasons, and as well as the genotoxicity in the (c) warm and (d) cold seasons. The limits of detection were <1.3 mg/L BEQ_{phenol} for the luminescent bacteria toxicity test and <0.10 μg/L $BEQ_{4\text{-}NQO}$ for the umuC test.

micropollutants were taken as a whole, their attenuation still followed the *k–C** model. We know that the global organic micropollutants are just a small portion of the total dissolved organic carbon in the wastewater. The apparent rate coefficient k_v of micropollutants estimated in the present study was lower than the reported COD ($k_v = 0.366$ d^{-1}) of unplanted wetlands (Stein et al., 2006), or the BOD_5 ($k_v = 1.18$ d^{-1}) of treatment wetland (Kadlec, 2003). The main reason may be the fact that organic micropollutants present in wastewater are generally more refractory than the total organic contents.

To determine when the domestic effluent was acceptable after SOWU polishing, the variation of RQ_{Total} was also fitted by the *k–C** model. In consideration of ecological safety, the lowest L(E)C50 values for the three representative species (fish, *Daphnia magna* and algae) were used for RQ_{Total} estimation (Table 1). As expected, the *k–C** approach applied to the RQ_{Total} data very well (Fig. 6b). The risk was deemed "acceptable" when $RQ_{Total} \leq 1$, thus the retention time (*t*) of pond water in SOWU could be obtained from the *k–C** equation. The derivation of *t* is included in Section S3.

3.3.2. Integration of biological effects into the k–C* model

The reduction of biotoxicities as a function of time in SOWU is shown in Fig. 6c and d. This is the first known time that the *k–C** approach has been applied to biological effects data from such an ENS. The biotoxicity reduction of pond water in the SOWU, including luminescent bacteria toxicity and genotoxicity, was fitted well by the *k–C** model ($R^2 > 0.9$) in both the warm and cold seasons (Table 3). For the luminescent bacteria toxicity, the apparent rate coefficient k_v was 0.715 d^{-1} with a C^* of 3.02 mg/L BEQ_{phenol} in the warm season, while the k_v was 0.218 d^{-1} with a C^* of 9.20 mg/L BEQ_{phenol} in the cold season. Regarding the genotoxicity, a k_v value of 0.116 d^{-1} in the warm season and a k_v value of 0.147 d^{-1} in the cold season were found.

Bioassays have been applied for decades in water quality monitoring and have been used to reflect the adverse biological effects of enriched organic mixtures. For the non-specific toxicity, all chemical mixtures present in the water samples contribute to the adverse biological effects (Tang et al., 2014). In this study, the obtained BEQ was a reasonable equivalent to the amount of organic matter in the studied effluent, which

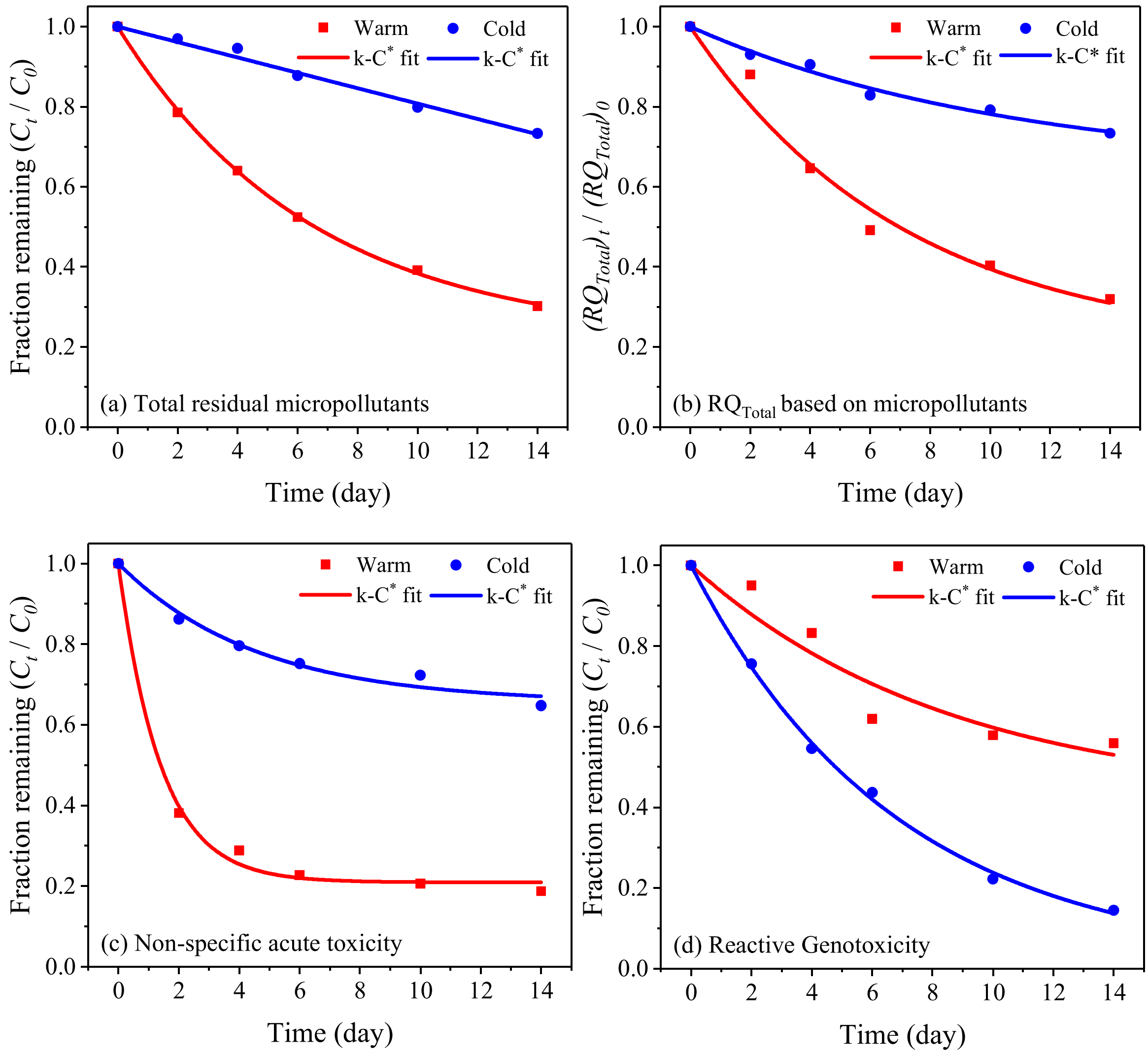

Fig. 6. Variations of target parameters during the shallow open-water unit (SOWU) polishing treatment processes. Data points are from the actual experiments in the warm and cold seasons. (a) Total residual micropollutants. (b) RQ_{Total} based on micropollutants. (c) Non-specific acute toxicity (luminescent bacteria toxicity). (d) Reactive genotoxicity. Lines are *k–C** model curves generated using Origin 2017 software.

Table 3
*k–C** model fit parameters, irreducible background value *C**, and first-order volumetric rate constant k_v during the shallow open-water unit (SOWU) polishing treatment processes.

Parameter	Warm season			Cold season		
	*C**	k_v (1/d)	R^2	*C**	k_v (1/d)	R^2
Micropollutants (ng/L)	199	0.155	0.999	—	2.11E-04	0.987
RQ_{Total}	0.527	0.140	0.976	2.7	0.092	0.984
Luminescent bacteria toxicity (mg/L BEQ_{phenol})	3.02	0.715	0.996	9.20	0.218	0.978
Reactive genotoxicity (μg/L $BEQ_{4\text{-}NQO}$)	0.087	0.116	0.915	0.027	0.147	0.998

"—": *C** of *k–C** model for micropollutants for the cold season was not applicable.

could induce adverse biological effects. Comparatively, conventional indicator of BOD is defined as the amount of dissolved oxygen demanded and equivalent to the amount of organic matter that can be biodegraded by the aerobic biological organisms in wastewater. The model-based approach indicated that the BEQ components had similar properties to the BOD components of the organic mixtures, which can be degraded or removed at different rates under natural environmental conditions. Based on the reduction rate of biotoxicity, BEQ might be used as an indicator in the operation and design of ENSs.

The adverse biological effects were deemed "acceptable" when BEQ ≤ EBT (BEQ_{phenol}, 6.04 mg/L) for luminescent bacteria toxicity, and BEQ ≤ EBT ($BEQ_{4\text{-}NQO}$, 0.64 μg/L) for genotoxicity. To determine when the domestic effluents were acceptable after SOWU polishing, the time (*t*) could be derived from the *k–C** equation. Details of the calculation are shown in Section S3.

3.4. Innovative design strategies

In the present study, the simplified SOWU experiments were conducted to polish domestic effluent before being discharged into the receiving water bodies or reused. Alternatively, we tried to take the micropollutants or biotoxicity as the new control indexes to design the SOWU pond from the perspective of aquatic ecological safety. As an illustrative case, we selected the SOWUs with high performance in warm environmental conditions, targeting the total residual micropollutants and the non-specific toxicity (luminescent bacteria toxicity). The control standards of water quality required that the RQ_{Total} of the global micropollutants was less than 1, or the BEQ of chemical mixtures was less than the corresponding EBT (BEQ_{phenol}, 6.04 mg/L), which could ensure that the domestic effluent was "acceptable" after SOWU polishing.

When the new control index was combined with the *k*–*C** model, the SOWU pond dimensions could be deduced from Eqs. (5) and (6):

$$A^{1}_{RQTotal}(m^2) = \frac{1.52}{Z \times 0.140} \quad (5)$$

$$A^{6.04}_{EBT}(\mathrm{m}^2) = \frac{1.3}{Z \times 0.715} \quad (6)$$

where $A^{1}_{RQTotal}$ and $A^{6.04}_{EBT}$ are the surface area of SOWU based on different indexes (m^2), and Z is the depth of the pond water (m). Details about the derivation of the two Eqs. (5) and (6) are shown in Section S3.

The SOWU dimensions expressed as the relationship between *A* and *Z* are shown in Fig. 7. The recommended depth of the pond water was less than 50 cm because depths greater than 50 cm result in slow photochemical reactions and are conducive to the growth of floating aquatic plants (Jasper and Sedlak, 2013; Maraccini et al., 2016). The design of the SOWU ponds based on the new control indexes was achieved successfully. The results were shown in Table 4.

When the residual micropollutants were set as the new control index, a surface area of 21.7 m^2 (water depth of 0.5 m) was required for the SOWU pond to polish 1 m^3/d of domestic effluent, which could ensure that the domestic effluent was "acceptable" (RQTotal $\leq$ 1). If the water depth was set at 0.1 m, a 108.5 m^2 surface area was required for every 1 m^3/d domestic effluent (Table 4). However, as wastewater is a "cocktail" of chemicals containing a vast number of natural or synthetic contaminants (Jia et al., 2015), the concentration addition model for estimating the RQ_{Total} was not valid for chemicals that had antagonistic or synergistic effects. The estimated RQ_{Total} based on the detected micropollutants probably underestimated or overestimated the potential ecological risk of whole effluents. Hence, setting micropollutant removal, namely RQ_{Total}, as the control index in real wastewater may not be applicable, though it is preferable as a fast and easy first line tool for hazardous micropollutant risk screening (Diaz-Garduno et al., 2017; Papageorgiou et al., 2019).

When the non-specific toxicity was set as the new control index, a surface area of 3.6 m^2 (water depth of 0.5 m) was required for the SOWU pond to polish 1 m^3/d of domestic effluent, which could ensure that the effluent was "acceptable" (BEQ $\leq$ EBT). If the water depth was set at 0.1 m, a surface area of 18.2 m^2 was required for every 1 m^3/d domestic

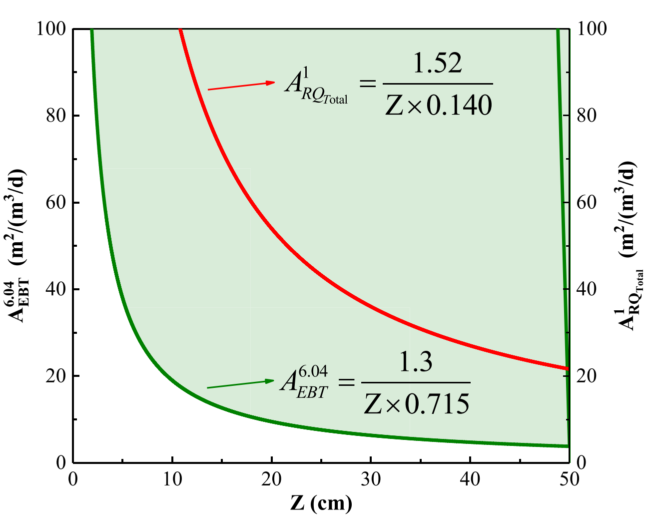

Fig. 7. Estimation of the shallow open-water unit (SOWU) pond dimensions necessary for luminescent bacteria toxicity reduction and micropollutant removal.

effluent. Comparatively, when the pond systems were constructed for removing conventional pollutants, the required surface area (on average) for BOD_5 removal was 16 m^2 (1 m^3/d wastewater) (Table 4). The results showed that the required land areas were comparable to the traditional control index of BOD_5, while the SOWU pond was constructed for domestic effluent polishing and the luminescent bacteria toxicity was set as the control index. This provides a simple basis for the feasibility of using new control indexes of biological effects to operate and design post-treatment units. From an application point of view, the adverse biological effects or micropollutants combined with the model-based approach provided a successful paradigm for the design and management of wastewater treatment systems. In the actual application process, the *k*–*C** models of micropollutant and biotoxicity obtained in the present study cannot be used simply. These two parameters (*k* and *C**) are affected by many internal and external factors such as pond configurations, effluent compositions, and weather conditions (e.g., temperature and sunlight) (Ali et al., 2018; Ho et al., 2017), and thus calibration of the parameters is required.

3.5. Environmental implications

With the assistance of advanced instrumental analysis and bioassays, an increasing number of organic micropollutants and the adverse effects from domestic effluent have been revealed. To ensure the safety of aquatic ecosystems, both the residual micropollutants and biotoxicities detected in domestic effluents are cause for concern and need to be better mitigated before wastewater is discharged or reused. However, most wastewater treatment systems are designed and operated with the focus on traditional control indexes, such as TN, TP, COD, and BOD. Researchers and engineers have primarily focused on whether treated wastewater meets the discharge requirements and how to optimize the operation of treatment systems. As the domestic effluents have been in compliance with the conventional regulatory standards for discharge or reuse, additional control standards should be considered to ensure the safety of ecological environments.

The feasibility of new control indexes involving micropollutants and biotoxicities and the relevant design strategies are still unknown. With the ability to attenuate micropollutants and improve the safety of ecological environments, the use of SOWUs as the post-treatment for domestic effluent polishing is a promising nature-based solution. In addition, the excellent photoreactivity of SOWUs was identified in our pervious study (Wang et al., 2020b). In this work, we set the micropollutants or biotoxicities as the new control indexes, and explored their applicability in the design of SOWUs. SOWUs need adequate surface area for sunlight exposure to achieve its functioning of wastewater purification. The results of this study show that the reduction of micropollutants and biotoxicities in SOWU both fit the *k*–*C** model very well in both the warm and cold seasons. Therefore, to ensure that the effluent is "acceptable" after SOWU polishing, sufficient exposure to sunlight is necessary for the attenuation of residual micropollutants and the reduction of adverse biological effects. Combined with the threshold, namely the control standards, the design of such ENSs could be derived from the new control indexes. The results of this study could aid in the management and development of wastewater treatment facilities. In the future, detailed and specific issues regarding the effects of the long-term operation of SOWUs should be investigated, while the ENS was designed with new control indexes. Moreover, critical specific biological effects such as estrogenic effects or the photosynthetic inhibition effect should also be considered in order to comprehensively guarantee ecosystem safety.

4. Conclusion

This study investigated the domestic effluent polishing method through SOWU ponds in both the warm and cold seasons. During the SOWU polishing treatment processes, the studied effluent exhibited

Table 4
The parameters of the shallow open-water unit (SOWU) pond dimensions based on the new control indexes.

Control indexes	Initial properties	Control standards	Estimation of pond system area		
			Water depth (m)	Required surface area (m^2)	HRT (day)
Micropollutant	914.00 ng/L	$RQ_{total} \leq 1$	0.1–0.5	21.7–108.5	10.9
Biotoxicity (Luminescent bacteria toxicity)	14.42 mg/L BEQ_{phenol}	EBT = 6.04 mg/L BEQ_{phenol}	0.1–0.5	3.6–18.2	1.9
*BOD_5	360.00 mg/L	25.00 mg/L	1.5	4.7–35.1	7–53

*BOD_5: The area data for BOD_5 was obtained from Ho et al. (2017).

overall lower concentrations (day 0: 914 ng/L vs 2608 ng/L) of a total of 46 micropollutants, but much higher removal efficiencies (day 14: 69.8% vs 26.7%) in the warm season compared with the cold season. The SOWUs also showed a remarkable reduction of luminescent bacteria toxicity in the warm season (81.3%), and substantial genotoxicity reduction in the cold season (85.5%). To ensure that the domestic effluent was "acceptable" after SOWU polishing, we tried to take the micropollutants or biotoxicities as the new control indexes to operate and design such an engineered natural treatment system. For every 1 m^3/d domestic effluents, a surface area of 21.7–108.5 m^2 was required when micropollutant removal ($RQ_{Total} \leq 1$) was set as the objective; a pond area of 3.6–18.2 m^2 was required when the luminescent bacteria toxicity reduction ($BEQ_{phenol} \leq$ EBT) was demanded. However, the RQ_{Total} was estimated based on the numbered micropollutants which probably underestimated or overestimated the potential risk of real wastewater. Thus, there were inevitably some limitations in the application of new control index of micropollutants. As expected, the adverse biological effects combined with the model-based approach provided an alternative paradigm for the design and management of wastewater treatment systems. The new control index can guarantee the safety of ecological environments, and SOWU ponds are designed to occupy a reasonable area.

CRediT authorship contribution statement

Yongkun K. Wang: Investigation, Methodology, Writing - Original draft preparation, Formal analysis. **Xiaochang C. Wang:** Conceptualization, Writing - Review & Editing, Supervision. **Xiaoyan Y. Ma**: Conceptualization, Writing - Review & Editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2021.126306.

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