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1 **Micropollutants removal and health risk reduction in a water**
2 **reclamation and ecological reuse system**

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15
16 **ABSTRACT**

17 As reclaimed water use is increasing, its safety attracts growing attention,
18 particularly with respect to the health risks associated with the wide range of
19 micropollutants found in the reclaimed water. In this study, sophisticated analysis was
20 conducted for water samples from a water reclamation and ecological reuse system
21 where domestic wastewater was treated using an anaerobic-anoxic-oxic unit followed

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22 by a membrane bioreactor (A²O-MBR), and the reclaimed water was used for
23 replenishing a landscape lake. A total of 58 organic micropollutants were detected in
24 the system, consisting of 13 polycyclic aromatic hydrocarbons (PAHs), 16 phenols, 3
25 pesticides, and 26 pharmaceuticals and personal care products (PPCPs). After
26 treatment by the A²O-MBR process, effective removal of pesticides and phenols was
27 achieved, while when the reclaimed water entered the landscape lake, PPCPs were
28 further removed. From the physicochemical properties of micropollutants, it could be
29 inferred that phenols and dichlorophos (the only pesticide with considerable
30 concentration in the influent) would have been mainly removed by biodegradation
31 and/or volatilization in the biological treatment process. Additionally, it is probable
32 that sludge adsorption also contributed to the removal of dichlorophos. For the
33 predominant PPCP removal in the landscape lake, various actions, such as adsorption,
34 biodegradation, photolysis, and ecologically mediated processes (via aquatic plants
35 and animals), would have played significant roles. However, according to their logK_{oc},
36 logK_{ow} and logD (pH=8) values, it could be concluded that adsorption by suspended
37 solids might be an important action. Although carcinogenic and non-carcinogenic
38 risks associated with all the detected micropollutants were at negligible levels, the
39 hazard quotients (HQs) of PPCPs accounted for 92.03%-97.23% of the HQ_{Total}. With
40 the significant removal of PPCPs through the ecological processes in the landscape
41 lake, the safety of reclaimed water use could be improved. Therefore, the introduction
42 of ecological unit into the water reclamation and reuse system could be an effective
43 measure for health risk reduction posed by micropollutants.

44

45 Keywords: micropollutants, ecological water reuse, health risk, removal efficiency,
46 pharmaceutical and personal care products (PPCPs)

47 **1. Introduction**

48 In 2015, 20.6% of treated wastewater from wastewater treatment plants (WWTP)
49 was used to yield reclaimed water in China, and the rate of reclaimed water use was
50 52.6% (4.45×10^9 m³) (China Urban Construction Statistics Yearbook, 2015). These
51 figures are increasing as a consequence of government policies (Chen et al., 2013;
52 Lyu et al., 2016). However, the safety of reclaimed water has attracted attention, even
53 after it has met the criteria for reuse. The presence of biological pollutants, such as
54 bacterial and viral pathogens, and emerging chemicals, such as endocrine disruptors,
55 pesticides, and pharmaceutical and personal care products (PPCPs), are safety
56 concerns in reclaimed water (Gavrilescu et al., 2015; Estévez et al., 2012; Courault et
57 al., 2017). Health risks caused by biological pollutants in reclaimed water are
58 eliminated through a disinfection process, and this is recognized as one of the most
59 effective strategies to remove bacterial and viral pathogens (Li et al., 2013). Emerging
60 chemicals pose an ecological and health risk, and are mainly removed by existing
61 treatment processes (Grandclément et al., 2017; Luo et al., 2014). However, there are
62 still persistent residual chemicals in the reclaimed water, which are characterized by
63 low concentrations (usually in the level of ng/L), high variety, and complicated
64 physicochemical properties (Li et al., 2015).

65 For those chemicals defined as micropollutants, studies have focused on their
66 biological effects (bioluminescence inhibition, photosynthesis inhibition, adverse
67 effects on aquatic organisms, endocrine disruption effects, genotoxicity, etc.) and their
68 ecological threats (Leusch et al., 2014; Backhaus and Karlsson, 2014). The neglect of

69 micropollutant influence on human health during reclaimed water reuse can be
70 ascribed to the difficulty in the detection of micropollutants, lack of toxicity data
71 regarding human health, and deficiencies in the assessment methods. Although some
72 studies have investigated the health risks caused by micropollutants, only one
73 category of micropollutants (e.g. polycyclic aromatic hydrocarbons (PAHs) or PPCPs)
74 or several detected micropollutants were involved (Man et al., 2013; Kumar and
75 Xagorarakis, 2010). Based on assessments of health risks, the World Health
76 Organization (WHO) concluded that appreciable adverse impacts on human health
77 arising from the consumption of the low concentrations of pharmaceuticals present in
78 drinking-water are very unlikely (WHO, 2011; WHO, 2012). The veracity of these
79 WHO findings has been further verified by additional research (de Jesus Gaffney et
80 al., 2015; Schwab et al., 2005). Furthermore, Chen et al. (2015) reported that there
81 were no potential carcinogenic or non-carcinogenic risks associated with the volatile
82 organic compounds in five rivers in China. However, there is little information
83 regarding the potential health risks caused by exposure to the wide range of
84 micropollutants detected during reclaimed water reuse processes.

85 The health risks of emerging micropollutants are closely associated with the
86 concentration of micropollutants in the water, hence it is imperative to investigate the
87 removal of micropollutants in the reclaimed water production system. It has been
88 shown that the removal efficiency of one category of chemicals was correlated with
89 their physicochemical properties, such as the degradation constant K_{biol} , octanol-water
90 partition coefficient K_{ow} , soil adsorption coefficient K_{oc} , and functional groups (Arola

91 et al., 2017; Grandclément et al., 2017). Therefore, it may be possible to improve the
92 removal of vital micropollutants in the reclaimed water treatment processes based on
93 their physicochemical property analysis and further reduce the potential health risk
94 posed by them.

95 The present study aimed to investigate the occurrence and removal of
96 micropollutants in a water reclamation and ecological reuse system where an
97 anaerobic-anoxic-oxic biological treatment followed with a membrane bioreactor
98 (A^2O -MBR) process were employed and the produced reclaimed water was used for
99 replenishing a landscape lake. The relationship between the removal and
100 physicochemical properties of micropollutants was explored to gain insight into the
101 action for micropollutants removal. The potential health risk from exposure to a wide
102 range of detected micropollutants in the system was then assessed, and vital
103 micropollutants were identified to help guarantee the safety of reclaimed water use.

104 **2. Materials and methods**

105 *2.1 Water reclamation and ecological reuse system and sample collection*

106 As Fig. 1 shown, this study was conducted on a water reclamation and ecological
107 reuse system where an A^2O -MBR system with a treatment capability of 2000 m³/day
108 was implemented to produce reclaimed water and then stored in an artificial landscape
109 lake (Ma et al., 2016). The stored reclaimed water was further used for landscaping,
110 toilet-flushing, road washing, gardening, and so on. The effluent quality of the A^2O -
111 MBR system achieved the requirements of the reclaimed water standard for aesthetic

112 environment uses and urban miscellaneous water consumption. Effluent of A²O–MBR
113 system was sent to replenish the landscape lake water (with a storage capacity of
114 about 5000 m³ and hydraulic retention time of 5 days) every day for beautifying the
115 environment and storing water for future reuse. In the landscape lake, fountain,
116 waterfall, and aquatic plants and animals forms an open and ecological storage
117 condition.

118

119

120 **Fig. 1** Outline of the water reclamation and ecological reuse system.

121

122 To investigate micropollutants in the system, water samples (2.5 L), including
123 the influent, A²O effluent, MBR effluent, and landscape lake water, were separately
124 collected using brown glass bottles and transferred to the laboratory immediately. To
125 avoid contamination, the bottles were soaked with a potassium dichromate -
126 concentrated sulfuric acid solution and rinsed with milli-Q water. Each sample was
127 filtered through a 0.7 µm glass microfiber filter (Φ 150 mm, WhatmanTM) and then
128 subjected to subsequent chemical analysis. Glass microfiber filters were heated to
129 450 °C for 2 h prior to use.

130 *2.2 Detected chemicals and instrumental analysis*

131 Based on micropollutant screening results, a total of 58 micropollutants were
132 selected and categorized into four groups, including 13 PAHs, 3 pesticides, 16 phenols,

133 and 26 PPCPs. PAHs, pesticides, and phenols were analyzed quantitatively using gas
134 chromatography-mass spectrometry (GC-MS) and PPCPs were detected using
135 ultra-performance liquid chromatography-series quadrupole mass spectra
136 (UPLC-MS/MS).

137 *2.2.1 GC-MS analysis*

138 Series-connected Supelclean™ LC-18 (500 mg, 6 mL) and Waters Oasis HLB
139 (500 mg, 6 mL) cartridges were used for the extraction of PAHs, pesticides, and
140 phenols in the water sample. The cartridges were individually preconditioned with 15
141 mL dichloromethane, 15 mL methanol, and 15 mL milli-Q water in succession. Then
142 the two cartridges were configured with a connector and a 1000 mL filtered water
143 sample was pumped through the cartridges. On completion, 10 mL milli-Q water was
144 added into the cartridges to remove impurities. Cartridges were separately eluted with
145 10 mL dichloromethane and the eluents were mixed and evaporated to 1 mL using
146 high-purity nitrogen. Additionally, derivatization was performed to reduce the polarity
147 of phenols prior to GC-MS analysis. The procedure of derivatization followed Zhong
148 et al. (2012). PAHs, pesticides, and phenols were analyzed on an Agilent 6890 GC
149 coupled to a 5975 MS (GC-MS), equipped with a DB-5MS (30 m × 0.25 mm × 0.25
150 m) capillary column. Detailed instrument conditions are described in Table S-1 in SI
151 1.

152 *2.2.2 UPLC-MS/MS analysis*

153 Before extraction, 12.5 mL of 20 g/L EDTA-2Na was added to 500 mL water

154 samples individually, and the pH was adjusted to 6–8. Samples were then extracted
155 using series-connected Waters WAX (200 mg, 6 mL) and Waters Oasis HLB (500 mg,
156 6 mL) cartridges. The cartridges were individually preconditioned with 15 mL of
157 methanol followed by 15 mL of milli-Q water. The elution process followed Sun et al.
158 (2015). Finally, 1 mL extracts were prepared for quantifying PPCPs in the water
159 samples using UPLC-MS/MS analysis. The UPLC-MS/MS was a UPLC coupled with
160 a Waters Micromass Quattro Premier XE tandem quadrupole mass spectrometer,
161 equipped with a reverse-phase BEH C18 column (100 m × 2.1 mm × 1.7 m). The
162 gradient conditions and instrument parameters for analyzing different categories of
163 PPCPs were listed in Table S-2 and Table S-3 in SI 1.

164 *2.2.3 Quality assurance and quality control*

165 Quality assurance and quality control elements consisted of laboratory and field
166 blanks, duplicates, and recovery indicators for each set of samples. The target
167 chemicals were not detected or found at negligible concentrations in the laboratory
168 and field blanks. Method quantification limits (MQLs) ranged from 0.008 to 2 ng/L.
169 For assessing the recovery of the method, ultrapure water injected with a mixture of
170 native compounds was analyzed. For guaranteeing the recoveries of chemicals in the
171 water samples, recovery indicators were added to each set of samples prior to
172 pretreatment. The recoveries of the indicators in water samples ranged from 54.32%
173 to 93.96%.

174 *2.3 Health risk assessment*

175 According to the “EPA’s Approach for Assessing the Risks Associated with Chronic
176 Exposure to Carcinogens”, the chemicals were divided into five categories: A: Human
177 Carcinogen; B: Probable human carcinogen (B1: indicates limited human evidence;
178 B2 indicates sufficient evidence in animals and inadequate or no evidence in humans);
179 C: Possible human carcinogen; D: Not classifiable as to human carcinogenicity; E:
180 Evidence of noncarcinogenicity for humans. Information regarding human cancer
181 hazards and risks of target micropollutants were from the US Environmental
182 Protection Authority Integrated Risk Information System database (US EPA IRIS
183 database) and the Office of Environmental Health Hazard Assessment (OEHHA)
184 chemical database. Because more than one conclusion may be reached for an
185 individual chemical, the highest category for the individual chemical was summarized
186 and applied, assuming a worst-case scenario in the present study. Categories of
187 detected chemicals were showed in Table 1 and Table S-4 in SI 1. The health risks
188 associated with the target micropollutants in the water reclamation and ecological
189 reuse system, including carcinogenic risks (CRs) and non-carcinogenic risks
190 (non-CRs), were assessed using the model proposed by the US EPA (Agency 1989).
191 Presumptively, people are exposed to micropollutants in reclaimed water mainly by
192 ingestion.

193 *2.3.1 Carcinogenic risk assessment*

194 Chemicals that were classified as B: Probable human carcinogen or higher (Table
195 1) were considered in the CR estimation; The CRs were estimated for the quantified

196 chemicals in the water samples following Equation (1) and (2) (US EPA, 2005). In the
 197 case of low-dose exposure, the CR was calculated by using Equation (1); if the CR
 198 exceeds 0.01, it should be recognized as high-dose exposure and calculated by using
 199 Equation (2).

$$CR = SF \times CDI, CR < 0.01 \quad (1)$$

$$CR = 1 - \exp(-SF \times CDI), CR \geq 0.01 \quad (2)$$

201 Where SF is the carcinogenic slope factor ($\text{kg} \cdot \text{day}/\text{mg}$), which was obtained from the
 202 US EPA IRIS database, CalEPA OEHHA chemical database, and the Risk Assessment
 203 Information System (RAIS), as Table 1 shown; CDI is chronic daily intake through
 204 ingestion ($\text{mg}/(\text{kg} \cdot \text{day})$), which is calculated following the Equation (3).

$$CDI = \frac{EF \times IR \times ED \times MEC}{AT \times BW} \quad (3)$$

206 Where EF is exposure frequency (305 days/year, school time); IR is the ingestion rate
 207 (0.1 L/day); MEC is the maximum measured environmental concentration of
 208 individual micropollutant found in the water sample (mg/L); ED is exposure duration
 209 (70 years); AT is average time (days); $AT = 70 \text{ years} \times 365 \text{ days/year} = 25550 \text{ days}$;
 210 and BW is the body weight of the exposed person (Adult = 60 kg). The setting of
 211 parameters, including EF, IR, ED, AT, and BW, were based on the practical situation
 212 and reference values of US EPA (US EPA, 2011).

213 The CR of the water sample posed by micropollutants, CR_{Total} , was calculated
 214 following the concept of additive action, where the combined effect of the
 215 micropollutants in the water sample is equal to the sum of their individual CR_i , as
 216 Equation (4) shown.

$$217 \quad CR_{\text{Total}} = \sum_1^n CR_i = CR_1 + CR_2 + \dots + CR_n \quad (4)$$

218 Where n is the number of the carcinogenic micropollutants.

219 Based on most regulatory programs and published research, a conservative
 220 cancer risk level (1×10^{-6}) was adopted, suggesting the maximum acceptable level
 221 (Chen et al. 2015; US EPA 2012; Kamal et al. 2014). A CR value below 10^{-6} indicates
 222 a negligible cancer risk, whereas a value between 10^{-6} and 10^{-4} suggests a potential
 223 cancer risk, and a value above 10^{-4} indicates high-potential risk (Kamal et al. 2014).

224 2.3.2. Non-carcinogenic risk (non-CR) assessment

225 Chemicals that were classified as category C or lower (Table S-4 in SI 1) were
 226 considered in the non-CR estimation; The non-CR of micropollutants in the water
 227 sample was quantified by estimating its hazard quotient (HQ), which is a ratio of its
 228 CDI value (calculated by using Equation 3) to acceptable daily intake (ADI) value or
 229 reference dose (RfD), according to Equation (5) (Kumar and Xagorarakis 2010, Chen
 230 et al. 2015, Li et al. 2016).

$$231 \quad HQ = \frac{CDI}{RfD \text{ or } ADI} \quad (5)$$

232 Where RfD is the reference dose (mg/(kg·day)) and ADI is the acceptable daily intake
 233 (mg/(kg·day)). In general, the RfD is an estimate of the daily exposure to the human
 234 population (including sensitive subgroups) that is not likely to result in an appreciable
 235 risk of deleterious effects during a lifetime. Furthermore, ADI is the value of the daily
 236 intake which does not result in any adverse health effects to the human population

237 from direct exposure (including sensitive subgroups) (Kumar and Xagorarakis 2010).
238 So, the RfD values were applied for the HQs estimate of PAHs, pesticides, phenols,
239 and ADI values were applied for the HQs estimate of PPCPs. The RfD or ADI of
240 target micropollutants for estimating hazard quotient (HQ) were obtained by using
241 four methods. The RfD or ADI values were obtained from various databases including
242 the US EPA IRIS database, RAIS, and Drug products database (DPD), etc.; if not
243 available, they could be obtained from published scientific papers; if not available, the
244 daily minimum treatment dose (MTD) which can be obtained from relevant website,
245 databases and references, were used to estimate the ADI; If not available, the RfD or
246 ADI were estimated by using no observed adverse effect level (NOAEL). The RfD or
247 ADI of the 58 target micropollutants and the methods for obtaining the relevant
248 toxicity data are shown in detail in Table S-4 of SI 1.

249 The HQ of the water sample posed by micropollutants, HQ_{Total} , was calculated
250 following the Equation (6).

$$251 \quad HQ_{Total} = \sum_1^n HQ_i = HQ_1 + HQ_2 + \dots + HQ_n \quad (6)$$

252 Where n is the number of micropollutants that could cause non-carcinogenic effects
253 on human health. It is widely accepted that if the HQ value is greater than 1, the
254 exposed population may undergo potential non-carcinogenic effects. If the HQ value
255 is greater than 0.2, further investigation is warranted to avoid the non-carcinogenic
256 effects on the exposed population. If the HQ value is less than 0.2, then no
257 appreciable concern to human health is assumed to exist (Schriks et al. 2010).

258 **3. Results and discussion**

259 *3.1 Occurrence of micropollutants in the system*

260 Instrumental analysis detected a total of 58 micropollutants in the water
261 reclamation and ecological reuse system with a total concentration (sum of the mean
262 concentration of detected micropollutants) ranging from 6753.41 ng/L in influent to
263 262.56 ng/L in landscape lake water, including 13 PAHs, 3 pesticides, 16 phenols, and
264 26 PPCPs (Fig. 2 and Table S-5 in SI 1). A total of 56 micropollutants were present in
265 influent, 48 in the A²O effluent, 51 in the MBR effluent, and 41 in the landscape lake
266 water (Table S-5 in SI 1). There were 39 micropollutants detected in all water samples.
267 As expected, the micropollutants detected in the system were mainly derived from the
268 WWTP influent. Of the targeted micropollutants, PAHs and phenols are ubiquitously
269 distributed in the environment and were universally detected in WWTP, reclaimed
270 water, and surface water (Zhong et al., 2012; Rabodonirina et al., 2015; Ozaki et al.,
271 2015; Kafilzadeh, 2015; Peng et al., 2008; Rubio-Clemente et al., 2014), while the
272 presence of pesticides and PPCPs in an aquatic environment depended on
273 circumstances and application events, and distinctly varied between different
274 countries and regions (Luo et al., 2014; Miège et al., 2009).

275 The mean concentration of individual micropollutants in the detected water
276 samples varied from ND (not detected) to 4360.3 ng L⁻¹ (4-Methylphenol in influent;
277 Table S-5 in SI 1). The magnitude of most quantified micropollutants in the system
278 was in the order of several ng/L or lower. Detected concentrations of micropollutants

279 in the influent of this study were generally lower than those commonly reported for
280 WWTP influent (Petrie et al., 2015; Qi et al., 2015; Qi et al., 2013; Bueno et al., 2012);
281 however, concentrations in reclaimed water (MBR effluent) and lake water were in
282 line with previously reported concentration ranges for reclaimed water and surface
283 water (Luo et al., 2014; Sun et al., 2015).

284 There were 13 PAHs detected at least once in the system. The total
285 concentrations of these PAHs in influent, A²O effluent, MBR effluent, and lake water
286 were 24.85 ng/L, 12.07 ng/L, 21.17 ng/L and 36 ng/L, respectively (Fig. 2), and they
287 account for 0.37%, 1.21%, 2.51%, and 13.71%, respectively, of the total concentration
288 of all detected micropollutants in the relevant water samples. The increase in the
289 proportion of PAHs among the target micropollutants along the water reclamation and
290 reuse processes was due to the significant decrease in the total concentrations of
291 phenols and PPCPs who were as the major pollutants in the water samples. The
292 concentration of most individual PAHs was below 1 ng/L on account of their
293 characters of lipophilicity and hydrophobicity. Of the 13 PAHs, phenanthrene,
294 fluorene, and fluoranthene were the primary pollutants in the water reclamation and
295 reuse system (Table S-5 in SI 1). Moreover, PAHs commonly accumulate in the
296 sludge, sediment, and biota; hence, PAHs with low concentrations in reclaimed water,
297 surface water, and drinking water do not generally receive much attention
298 (Rabodonirina et al., 2015).

299 For pesticides, only atrazine, chlorpyrifos, and dichlorphos were detected at least
300 once, with the total mean concentration ranging from 41.52 ng/L in influent to 2.56

301 ng/L in the landscape lake water. For the four sampling sites, pesticides only
302 composed between 0.61% and 0.98% of all detected micropollutants in the relevant
303 water samples. Dichlorophos (38.38 ng/L for influent and 4.02 ng/L for the MBR
304 effluent) was the primary pesticide in the WWTP for reclaimed water production. The
305 small quantities of pesticides in the water reclamation and reuse system was attributed
306 to the fact that schoolyard domestic wastewater was the only source of WWTP
307 influent.

308 The water reclamation and reuse system contained 16 phenols. Of the four
309 categories of micropollutants, phenols accounted for the majority of micropollutants
310 in influent (5007.2 ng/L, 74.14%) and landscape lake water (120.07 ng/L, 45.73%),
311 while they only comprised a small fraction of the detected micropollutants in A²O
312 (35.37 ng/L, 3.55%) and MBR effluent (90.53 ng/L, 10.72%) (Fig. 2). The
313 predominant phenols in influent were 4-methylphenol (4360.3 ng/L), phenol (323.47
314 ng/L), and 4-ethylphenol (170.86 ng/L); while 4-methylphenol (37.62 ng/L),
315 3-methylphenol (23.82 ng/L), and 2,4-dimethylphenol (13.94 ng/L) predominated in
316 landscape lake water (Table S-5 in SI 1). The vast majority of individual phenols in
317 the MBR effluent were below 10 ng/L, except for 4-chloro-3-methylphenol and
318 phenol (Table S-5 in SI 1).

319 A total of 24 PPCPs were detected in the reclaimed water production process,
320 while 15 were detected in the landscape lake water. No compounds that were found in
321 the landscape lake water were absent from the reclaimed water production process.
322 PPCPs contributed 24.87% of the total concentration of micropollutants in influent

323 and this increased to 85.85% following MBR treatment. However, PPCPs only
324 accounted for 39.54% of the total concentration of micropollutants in the landscape
325 lake water. The remarkable variation of PPCPs in this system is caused by the high
326 efficiency of phenol removal in influent during the A²O-MBR treatment process and a
327 significant decrease of PPCPs in the landscape lake. The dominant PPCPs in the
328 reclaimed water production process, with concentrations exceeding 100 ng/L, were
329 tetracycline, oxytetracycline, and ofloxacin. Ofloxacin (18.33 ng/L), oxytetracycline
330 (16.90 ng/L), and sulfamethoxazole (11.43 ng/L) were the main PPCPs in lake water
331 (Table S-5 in SI 1).

332

333

334 **Fig. 2** Concentrations of the four categories of target micropollutants in the water
335 reclamation and ecological reuse system.

336

337 ***3.2 The removal of micropollutants in the system***

338 ***3.2.1 The removal efficiency of individual micropollutants***

339 Individual micropollutants, were classified into four ranks based on the removal
340 efficiency at each stage of the treatment process. Micropollutants with removal
341 efficiencies in the range of 75%-100%, 50%-74%, 0%-49%, and below 0% were
342 given ranks of I, II, III, and IV, respectively. Fig. 3 displays the removal efficiency of
343 the 58 target micropollutants through the system. Removal efficiency was basically

344 consistent for most micropollutants in the A²O (19 “I”, 10 “II”, 11 “III”, 14 “IV”) and
345 MBR (17 “I”, 3 “II”, 20 “III”, 16 “IV”) effluent. Via the two processes, a single PAH,
346 single pesticide, most phenols, and a portion of the PPCPs were effectively removed
347 (rank “I”). Most PPCPs were removed with a low efficiency (rank “III”), or even
348 increased (rank “IV”) during the MBR treatment process. In the landscape lake, two
349 pesticides, a portion of the phenols, and most of the PPCPs were effectively removed
350 (19 “I”). A few chemicals were ranked “II” and “III” at the landscape lake; however,
351 the concentrations of all individual PAHs and most phenols were increased in the
352 landscape lake (rank “IV”).

353

354

355 **Fig. 3** The removal of micropollutants in the water reclamation and ecological reuse
356 system for (a) PAHs, pesticides and phenols; and (b) PPCPs. The removal efficiencies
357 of micropollutants after A²O and after MBR process were respectively calculated
358 based on the concentrations of raw wastewater. The removal efficiency of
359 micropollutants in the landscape lake was calculated based on MBR effluent. The
360 removal of micropollutants whose value was below 0% are not shown in this graph.
361 “*” referred to “not detected” in the corresponding process which indicated that the
362 micropollutant was totally removed in the previous treatment step.

363

364 *3.2.2 The removal efficiency of four categories of micropollutants*

365 Fig. 4 summarizes the overall removal of PAHs, pesticides, phenols, and PPCPs
366 during the water reclamation and reuse processes. In reclaimed water production
367 processes where the A²O-MBR treatment was employed, pesticides and phenols were
368 removed with high efficiency (>80%), while the efficiency of PPCPs removal was
369 moderate (56.85%). The total removal rate for PAHs during the A²O process, was
370 51.43% with a range of 13.33-100% for individual chemicals (except for
371 benzo(b)fluoranthene; Fig. 4 and Fig. 3(a)), which is consistent with previously
372 published studies (Tian et al., 2012). However, the total concentration of PAHs
373 increased during the MBR treatment process, resulting low overall PAH removal
374 (14.81%). In fact, the total concentration of PAHs was lower than that found in
375 WWTPs by published studies (Ozaki et al., 2015; Qiao et al., 2014); hence, PAH
376 concentrations in the MBR effluent were low despite their inefficient removal.

377 As shown in Fig. 4, PPCPs were effectively removed and pesticides were removed
378 with moderate efficiency when the reclaimed water was reused as landscape lake
379 water; however, the concentrations of PAHs and phenols increased. These increases
380 are attributed to nonpoint source pollution from the ambient environment of the
381 landscape lake, and to degradation products or by-products of natural or artificial
382 compounds within the lake (Ma et al., 2016). It was significantly different with
383 reclaimed water production processes. Generally, pesticides and phenols are removed
384 through biochemical treatment, and the ecological environment of the landscape lake
385 plays a dominant role in the removal of PPCPs.

386

387 **Fig. 4** Overall removal (%) of the four categories of micropollutants after A²O, after
388 MBR, and after being used for landscape lake water.

389

390 *3.2.3 Actions for removal of pesticides and phenols in biological treatment*

391 Micropollutants removal was closely related to their physicochemical properties;
392 including the K_{ow} , soil adsorption coefficient K_{oc} , octanol-air partition coefficient K_{oa} ,
393 and degradation constant K_{biol} . For pesticides, only dichlorphos was effectively
394 removed during the reclaimed water production process. The toxicity of pesticides
395 had a significant adverse impact on their degradation in the WWTP. Comparing the
396 toxicity of the three detected pesticides, the toxicity of dichlorphos on bacteria was
397 extremely low (for the *Vibrio fischeri* toxicity test, the EC_{50} values of atrazine,
398 chlorpyrifos, and dichlorphos were 168.72mg/L, 10.63 mg/L, and 4036.33 mg/L,
399 respectively), suggesting that biodegradation may have great contribution to its
400 removal in the A²O-MBR process. Furthermore, the $\log K_{oa}$ and $\log K_{oc}$ values of
401 dichlorphos were 6.06 (below 6.5) and 1.8194 (below 2.2), respectively, suggesting
402 that dichlorphos was defined as a volatile organic compound and was readily
403 adsorbed onto sludge. Therefore, volatilization and sludge adsorption may also
404 improve the removal efficiency of dichlorphos in this process. For phenols, the
405 dominant removal action was biodegradation due to the hydroxyl functional group,
406 followed by volatilization. Because the $\log K_{oa}$ of phenols was low, of which six
407 phenols (2-chlorophenol, 3-methylphenol, 4-methylphenol, 2-nitrophenol, O-cresol,

408 phenol) was below 6.5 (SI 2). Nevertheless, the biodegradability of phenols with
409 chlorine and nitrogen functional groups was weakened (except for
410 4-chloro-3,5-dimethylphenol, and 2,4,6-trichlorophenol) (Besha et al., 2017), which
411 resulted in a low removal efficiency after the A²O-MBR process (Fig. 3(a)).
412 Furthermore, the dominant action for removal of micropollutants was not in
413 accordance with the results of the EPI STPWIN prediction model, which suggested
414 that, for most pollutants, biodegradation played an important role, while sludge
415 adsorption and volatilization made a limited contribution to pollutant removal.

416 *3.2.4 Actions for removal of PPCPs in the landscape lake*

417 It is likely that a large proportion of PPCPs were removed by adsorption based
418 on their $\log K_{oc}$ values < 2.2 and $\log K_{ow} > 2.7$ (Fig. S-1 in SI 1), which resulted in high
419 efficiency during storage in the lake water and moderate efficiency during A²O-MBR
420 processes. Additionally, in Fig. 5, PPCPs with a $\log D$ (pH 8) > 3.0 except
421 sulfapyridine, could be efficiently removed in the system, while the removal
422 efficiency of PPCPs with $\log D$ (pH 8) ≤ 3.0 varied considerably. These results are
423 basically in accordance with the findings of Tadkaew (2011), who also stated that the
424 presence of electron withdrawing, or electron donating functional groups appeared to
425 be important factors governing PPCPs removal. So, the removal efficiency of
426 sulfapyridine and other PPCPs with $\log D$ (pH 8) ≤ 3.0 were mainly impacted by their
427 functional groups, even the operation condition (e.g. hydraulic retention time, sludge
428 retention time, redox conditions) (Lucas et al., 2016; Petrie et al., 2014). Generally,

429 Ketones (androstenedione, boldenone, diphenhydramine, metandienone) were well
430 removed (>90%) and sulfonamides (sulfadiazine, sulfapyridine, sulfamethoxazole)
431 were difficult to be removed (<20%).

432

433

434 **Fig. 5** The relationship between removal of PPCPs and logD (pH 8).

435

436 K_{biol} can be used to estimate the biodegradability of chemicals. It is defined that
437 the chemical whose K_{biol} is greater than 10 L/g_{SS}/d can be efficiently removed by
438 biological degradation (>90%), whose K_{biol} is in the range of 0.1 ~ 10 L/g_{SS}/d can be
439 partial removal by degradation (20 ~ 90%), whose K_{biol} is less than 0.1 L/g_{SS}/d is
440 difficult to be removed by degradation (<20%) (Joss et al. 2006). So, the high removal
441 efficiency (100%) of ibuprofen is due to its high biodegradability ($K_{\text{biol}} = 9\text{-}22$ L/g_{SS}/d)
442 (Arola et al. 2017). Furthermore, the low biodegradability of carbamazepine ($K_{\text{biol}} <$
443 0.01L/g_{SS}/d) and moderate biodegradability of trimethoprim ($K_{\text{biol}} = 0.05 \sim$
444 0.22L/g_{SS}/d) had a significant influence on their removal efficiency (11.50% and
445 79.24%, respectively), which is consistent with earlier studies (Arola et al., 2017).

446 Considering the intricate physicochemical parameters and functional groups, it
447 can be inferred that other actions may contribute to PPCPs removal; for example,
448 photolysis and the purification effect of aquatic plants and animals in landscape lake
449 water (Grandclément et al., 2017; Besha et al., 2017; Abellán et al., 2009; Długosz et
450 al., 2015). The overall influences of these physicochemical parameters on the removal

451 efficiency of PPCPs are complex, and understanding them requires the application of
452 quantitative structure activity relationships and extensive biochemical and/or
453 physicochemical interpretation. Further research needs to be undertaken in this
454 respect. Notwithstanding, it has been demonstrated that natural water bodies (e.g.
455 rivers, dams, and inland lakes) have the capacity to reduce pollutants through biotic
456 (microbial degradation, uptake by macrophytes, and consumption by organisms at
457 higher trophic levels) and abiotic (dilution, volatilization, adsorption of sediments,
458 oxidation, and photolysis) purification action (Taguchi and Nakata, 2009; Sun et al.,
459 2016; Kuppusamy et al., 2016; Hawker et al., 2011). Consequently, the target
460 pollutants that are effectively removed, and the corresponding actions for their
461 removal, are remarkably different in water bodies as compared to WWTPs.

462 ***3.3 Health risk assessment***

463 To the best of our knowledge, this is the first study to evaluate the health risks of
464 reclaimed water using so many micropollutants from a broad range of chemical
465 categories. To provide a worst-case scenario of exposure through reclaimed water
466 reuse, the maximum detected concentrations of micropollutants in the influent, A²O
467 effluent, MBR effluent, and lake water were used to estimate their carcinogenic and
468 non-carcinogenic risk. Table 1 details the detected carcinogens and their CRs and
469 shows that only eight carcinogens were detected in the water reclamation and
470 ecological reuse system. The CR_{Total} decreased from 3.69E-08 to 5.80E-09 along the
471 treatment process steps, and then further reduced to 4.66E-09 in the landscape lake

472 water. There was no potential carcinogenic risk caused by micropollutants in the
473 whole system ($CR_{Total} < 10^{-6}$). The landscape lake, as a semi-natural water body,
474 decreased the carcinogenic risk of the reclaimed water, although some micropollutants
475 were introduced. The CR reduction of the reclaimed water when storage in the lake
476 water occurred mainly because of the decreased risk from dichlorphos, which caused
477 a higher CR in the reclaimed water production process. Furthermore, flavonoids
478 compounds which were widely found in plants in the natural environment, could
479 against dichlorphos induced toxicity (Hou et al., 2014).

480

481

482 **Table 1** CRs of carcinogens in influent (IN), A²O effluent (AE), MBR effluent (ME),
483 lake water (LW), and their CR_{Total} .

484

485 For non-CRs, the HQ_{Total} of water samples from the water reclamation and reuse
486 system were all below 0.2 (Table 2), suggesting that there was no potential
487 non-carcinogenic risk caused by micropollutants. The variation of HQ_{Total} in the
488 system was similar to that of CR_{Total} . Table 2 lists the dominant chemicals which
489 governed the HQ_{Total} (Table S-6 in SI 1). Considering the HQ value, metandienone,
490 4-ethylphenol, tetracycline, androstenedione, and oxytetracycline were identified as
491 the primary non-CR factors in the system. The removal of tetracycline and
492 lamotrigine was the main reason for the reduction of non-CR in the lake water. In our
493 previous study, it was reported that chlorpyrifos, dichlorphos, 4-methylphenol,

494 acetaminophen, and tetracycline had great contribution to the ecological risk in this
495 system (Ma et al., 2016), which was different with the dominating chemicals driving
496 health risk.

497 It was determined that the reclaimed water before and after storage in the
498 landscape lake not present a potential health risk in this study, despite such many
499 micropollutants involved. However, additional risks may occur due to the presence of
500 undetected micropollutants through limitations in current instrumental analysis,
501 transformation production of the detected micropollutants, and the interaction of the
502 chemicals (Yang et al., 2017; Lienert et al., 2007; Tang et al., 2013). Furthermore, of
503 the four categories of target micropollutants, the HQs of PPCPs accounted for
504 92.03-97.23% of the HQ_{Total} in this system. Chen et al. (2015) also reported that 36
505 pharmaceuticals, especially antibiotics, imposed a significant ecological risk in China.
506 Many PPCPs, especially tetracycline and lamotrigine, could be degraded by
507 photolysis and aquatic plants (Li and Hu, 2016; Zhou et al., 2017; Li et al., 2017). As
508 compared to biochemical treatment in the WWTP, photolysis and ecologically
509 mediated occurred in the ecological environment compensates for the deficiency of
510 limited capacity for refractory organics removal. Hence, the introduction of an
511 ecological system during the water reuse process is likely to improve the safety of
512 reclaimed water.

513

514

515 **Table 2** HQs of dominating micropollutants (without carcinogens) in influent (IN),

516 A²O effluent (AE), MBR effluent (ME), lake water (LW), and their HQ_{Total} which
517 were calculated based on all target micropollutants (without carcinogens).

518

519 **4. Conclusion**

520 This study investigated the occurrence and removal efficiency of micropollutants
521 in a water reclamation and ecological reuse system. Actions for micropollutants
522 removal were discussed and the associated health risks from a range of detected
523 micropollutants were estimated. Four categories of micropollutants (PAHs, pesticides,
524 phenols, PPCPs) were detected and each showed different concentration levels and
525 removal characteristics. PAHs occurred with extremely low concentrations in the
526 whole process of treatment and reuse exposed little influence on health risk.
527 Dichlorophos, as the only pesticide with considerable concentration in the influent, was
528 effectively removed through the main action of biodegradation, volatilization and
529 sludge adsorption in the biological treatment, based on its toxicity, logK_{oa}, and logK_{oc}.
530 The efficiency of phenols removal by biological treatment was also very high, and
531 biodegradation and/or volatilization were inferred as the dominant actions for their
532 decay according to their functional group and logK_{oa}. In contrast to this, PPCPs were
533 moderately removed by biological treatment but significantly removed in the
534 landscape lake. Various ecological actions would have contributed to PPCPs removal
535 while adsorption might be an important action according to their logK_{oc}, logK_{ow}, and
536 logD (pH=8) values. As compared to biochemical treatment in the WWTP, the
537 photolysis and ecologically mediated occurred in the reuse process compensates for

538 the deficiency of limited capacity for refractory organics. All detected micropollutants
539 were taken into consideration for health risk assessment. Although no appreciable
540 carcinogenic and non-carcinogenic risks were presented, the hazard quotients (HQs)
541 of PPCPs accounted for more than 90% of the HQ_{Total} . With the effective removal of
542 PPCPs in the landscape lake, the safety of reclaimed water use could be much
543 improved. The results can be used to improve strategies for guaranteeing the safety of
544 reclaimed water reuse related to micropollutants.

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Table 1 CRs of carcinogens in influent (IN), A²O effluent (AE), MBR effluent (ME), lake water (LW), and their CR_{Total}.

Carcinogens	Category	SF (kg·day/mg)	Max concentration (ng/L)						CR	
			IN	AE	ME	LW	IN	AE		ME
Benz[a]anthracene	B2	1.2 ^a	0.8	0.57	0.68	1.19	1.34E-09	9.53E-10	1.14E-09	1.99E-09
Benzo (a) pyrene	B2	1 ^b	0.45	0.34	0.31	0.66	6.27E-10	4.74E-10	4.32E-10	9.19E-10
Benzo(b)fluoranthene	B2	1.2 ^a	0.28	1.22	0.29	0.49	4.68E-10	2.04E-09	4.85E-10	8.19E-10
Benzo (k)fluoranthene	B2	1.2 ^a	0.27	0.27	0.28	0.48	4.51E-10	4.51E-10	4.68E-10	8.02E-10
Chrysene	B2	0.12 ^a	0.6	0.72	0.96	0.77	1.00E-10	1.20E-10	1.60E-10	1.29E-10
Dichlorphos	B2	0.29 ^b	83.58	5.26	7.54	0	3.38E-08	3.05E-09	3.05E-09	0.00E+00
O-phenylphenol	≥B*	0.0019 ^c	33.49	2.8	27.07	1.52	8.86E-11	7.41E-12	7.16E-11	4.02E-12
2,4,6-Trichlorophenol	B2	0.011 ^b	3.54	0	0	0	5.42E-11	0.00E+00	0.00E+00	0.00E+00
CR_{Total}							3.69E-08	7.09E-09	5.80E-09	4.66E-09

Data from:

a OEHHA: The Office of Environmental Health Hazard Assessment (OEHHA) chemical database agented by the California Environmental Protection Agency

b US EPA: United States Environmental Protection Agency

c RAIS: The Risk Assessment Information System

*: No information could be found from US EPA. While, o-phenylphenol was classified into carcinogen based on the information from OEHHA

Table 2 HQs of dominating micropollutants (without carcinogens) in influent (IN), A²O effluent (AE), MBR effluent (ME), lake water (LW), and their HQ_{Total} which were calculated based on all target micropollutants (without carcinogens).

Micropollutants	RFD (mg/kg·d)	Max concentration (ng/L)				HQ			
		IN	AE	ME	LW	IN	AE	ME	LW
4-Ethylphenol	0.0009	219.04	1.1	1.55	2.21	3.39E-04	1.70E-06	2.40E-06	3.42E-06
Androstenedione	0.00033	43.2	0	0	0	1.87E-04	0.00E+00	0.00E+00	0.00E+00
Carbamazepine	0.0003	2.8	3.95	5.15	5.2	1.30E-05	1.83E-05	2.39E-05	2.41E-05
Diphenhydramine	0.0004	3.3	20.05	10.35	0	1.15E-05	6.98E-05	3.60E-05	0.00E+00
Lamotrigine	0.0003	6.8	37.85	31.5	17.7	3.16E-05	1.76E-04	1.46E-04	8.22E-05
Lincomycin	0.0022	46.7	20.2	11.45	0	2.96E-05	1.28E-05	7.25E-06	0.00E+00
Metandienone	0.000017	66.45	0	0	0	5.44E-03	0.00E+00	0.00E+00	0.00E+00
Norfloxacin	0.0114	99.6	74.8	102.8	15.7	1.22E-05	9.14E-06	1.26E-05	1.92E-06
Ofloxacin	0.0057	155.6	245	230.1	27.1	3.80E-05	5.99E-05	5.62E-05	6.62E-06
Oxytetracycline	0.003	218.4	154.5	137.8	18.95	1.01E-04	7.17E-05	6.40E-05	8.80E-06
Sulfamethoxazole	0.0057	36.85	63.3	39.85	15.25	9.00E-06	1.55E-05	9.74E-06	3.73E-06
Sulfapyridine	0.0033	24.15	37.8	24.15	6.05	1.02E-05	1.60E-05	1.02E-05	2.55E-06
Tetracycline	0.003	527.2	349.8	332.8	8.35	2.45E-04	1.62E-04	1.54E-04	3.88E-06
HQ_{Total}						6.61E-03	6.49E-04	5.66E-04	1.50E-04

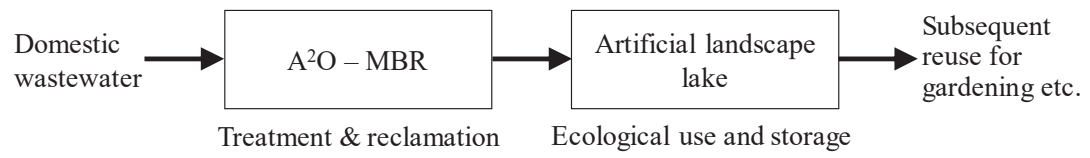


Fig. 1 Outline of the water reclamation and ecological reuse system.

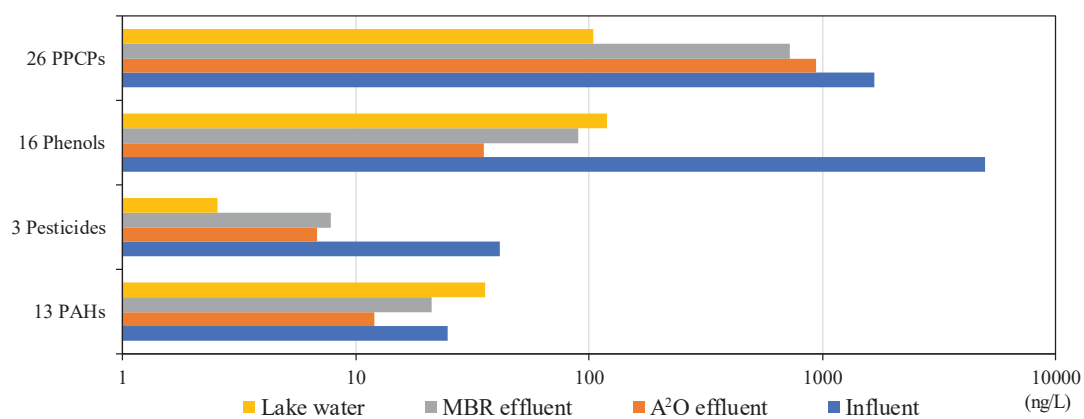


Fig. 2 Concentrations of the four categories of target micropollutants in the water reclamation and ecological reuse system.

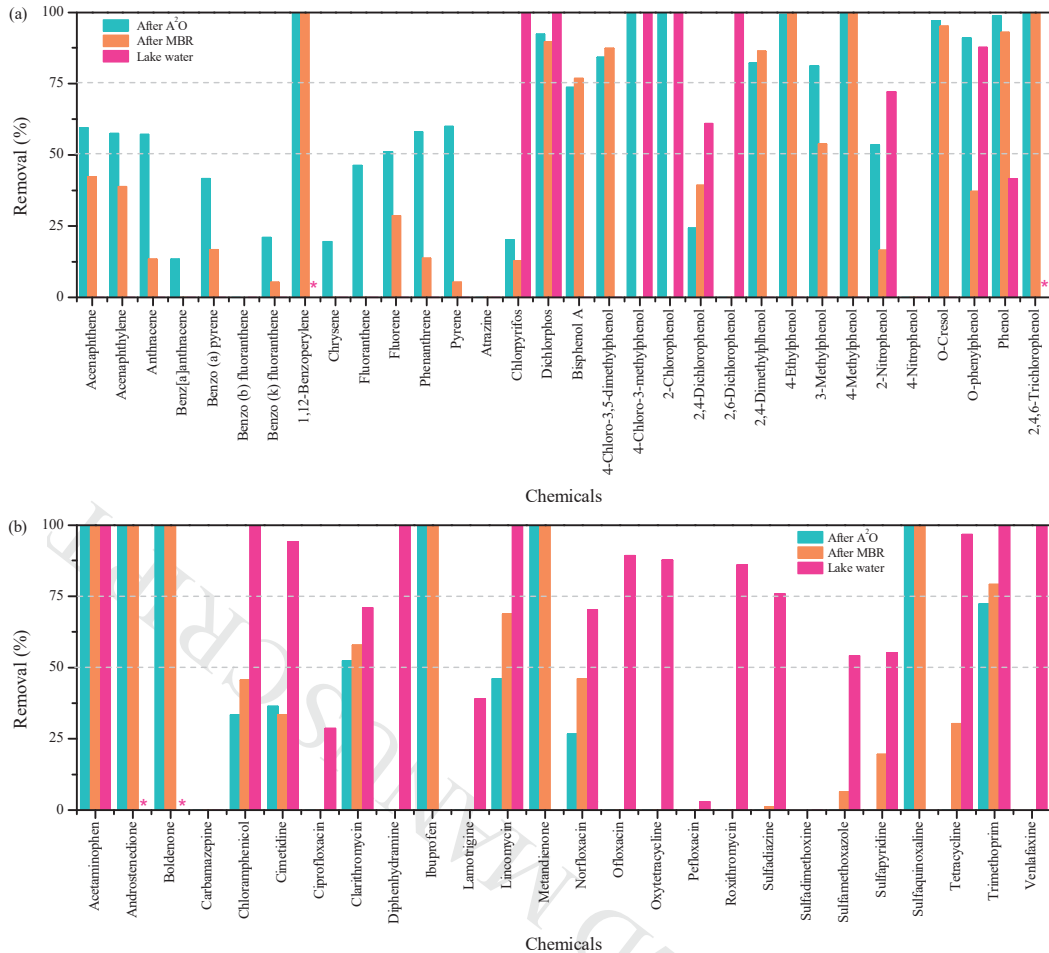


Fig. 3 The removal of micropollutants in the water reclamation and ecological reuse system for (a) PAHs, pesticides and phenols; and (b) PPCPs. The removal efficiencies of micropollutants after A²O and after MBR process were respectively calculated based on the concentrations of raw wastewater. The removal efficiency of micropollutants in the landscape lake was calculated based on MBR effluent. The removal of micropollutants whose value was below 0% are not shown in this graph. “*” referred to “not detected” in the corresponding process which indicated that the micropollutant was totally removed in the previous treatment step.

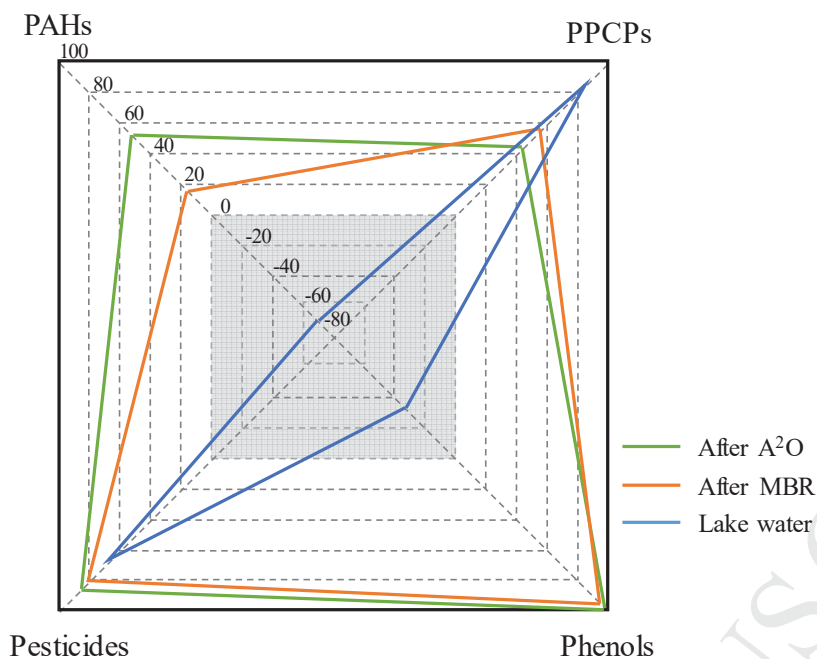


Fig. 4 Overall removal (%) of the four categories of micropollutants after A²O, after MBR, and after being used for landscape lake water.

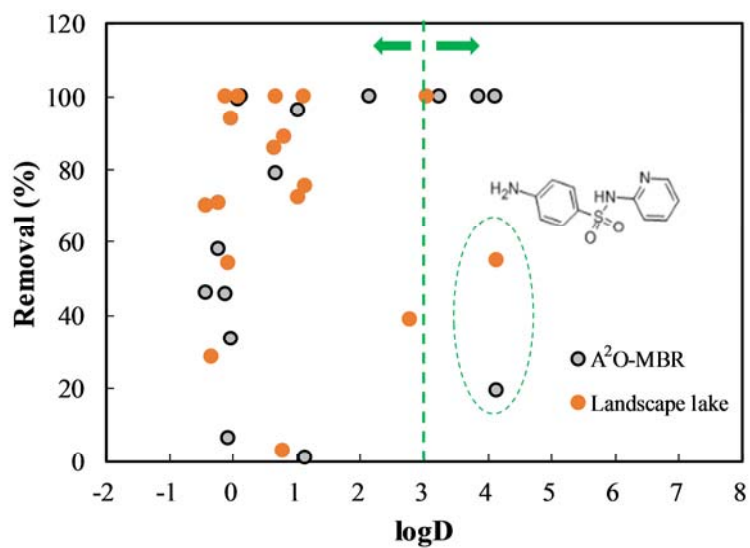


Fig. 5 The relationship between removal of PPCPs and logD (pH 8).