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Environmental impact

The occurrence of emerging and priority pollutants in aquatic systems has been receiving widespread concern. Reverse osmosis concentrate (ROC) is an imperative popular topic in the field of wastewater treatment and reclamation. As for the determination and occurrence investigation of emerging and priority pollutants in ROC, it has been insufficiently described in the latest decade. In this paper, a method based on liquid-liquid extraction followed by gas chromatography-mass spectrometry is described to investigate the occurrence and concentrations of emerging and priority pollutants in the municipal ROC. The work contributes to the understanding of the types of emerging and priority pollutants that frequently appeared and the concentrations of these pollutants in the municipal ROC.

1   **Occurrence of emerging and priority pollutants in municipal reverse osmosis**

2   **concentrates**

3

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5

6   **ABSTRACT**

7   This paper aimed to investigate the occurrence and concentrations of emerging

8   and priority pollutants in the municipal reverse osmosis concentrate (ROC) using

9   liquid-liquid extraction (LLE) followed by gas chromatography-mass spectrometry.

10   The results indicated that there were varieties of pollutants, including chlorinated

11   organic compounds, polycyclic aromatic hydrocarbons (PAHs), phthalate esters

12   (PAEs), pharmaceutical and personal care products (PPCPs), herbicides and flame

13   retardants, in the ROC. Most of the pollutants were quantified, and the performance of

14   the analytical method was explored. For most of the target compounds, the mean

15   recoveries at two concentration levels (0.17 μg L^{-1} and 1.67 μg L^{-1}) ranged from 70%

16   to 130% and the relative standard deviation (RSD) values were less than 20%,

17   indicating excellent accuracy and precision. Typical concentrations of most pollutants

18   were as low as tens or hundreds of ng L^{-1}, whereas others were as high as several μg

19   L^{-1} (such as 2-Chloroethyl ether 1.42 μg L^{-1}, caffeine 3.73 μg L^{-1}, benzyl butyl

20   phthalate 4.90 μg L^{-1}).

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25   **1. Introduction**

26   Wastewater reuse has aroused widespread concern, to protect the limited

27   freshwater resources and to prevent the aquatic environment from being harmed by

28   the contaminants in wastewater. The dual membrane process, a combination of

29   microfiltration (MF) or ultrafiltration (UF) followed by reverse osmosis (RO), has

30   been applied in this field, to a certain extent, and proved to be a good solution to the

31   shortage of freshwater resources and wastewater pollution.

32   Despite supplying 60~70% of high-quality permeate for the users, the RO

33   process generates approximately 30~40% of the feeding as reverse osmosis

34   concentrate (ROC), depending on the recovery. The ROC from wastewater treatment

35   plants (WWTPs) usually presents a higher load of organic pollutants (DOC 19.2~57.2

36   mg L^{-1}, COD 60~184 mg L^{-1}) [1]. Among them, there may be varieties of emerging and

37   priority pollutants of concern in recent years [2-9]. The US EPA (United States

38   Environmental Protection Agency) defines emerging pollutants as new chemicals

39   without regulatory status and which the impact on the environment and human health

40   are poorly understood [7], such as pharmaceutical residues, personal care products and

41   suspected endocrine disrupting compounds. Priority pollutants refer to the organic

42   pollutants that are in the list of priority substances published by US EPA or EU WFD

43   (EURO Water Framework Directive).

44   Large quantities of chemicals belonging to emerging and priority pollutants are

45   used in our daily life and in the industrial and agricultural fields. These pollutants

46   enter the wastewater and then transfer to WWTPs; hence, the emerging and priority

47   pollutants may be present in the secondary effluents of WWTPs [10-14]. In a municipal

48   wastewater reclamation plant using a dual membrane process, due to the strong

49   rejection of organic compounds for RO, there may be a several-times higher

50   concentration of emerging and priority pollutants in the ROC than that in the effluents

51   of the WWTPs.

52   Although the emerging and priority pollutants should not be expected to exhibit

53   an acute toxicity at low concentration (typically a few $\mu g \ L^{-1}$ or even $ng \ L^{-1}$), they

54   have potential effects on the receiving environments, such as bioaccumulation or

55   synergetic toxicity. For example, 2-Chloroethyl ether has been classified as a probable

56   human carcinogen by the US EPA, with a 10^{-6} cancer risk at a water concentration of

57   0.03 $\mu g \ L^{-1}$; consequently, the US EPA region III has established a risk-based

58   concentration for 2-Chloroethyl ether of only $9.6 \times 10^{-3} \ \mu g \ L^{-1}$ in tap water [15]. As a

59   result, there is an increasing concern regarding the emerging and priority pollutants.

60   Currently, concerns regarding the ROC are focused on the removal of organics

61   indicated by BOD_5 and COD to meet the wastewater discharge standards. The

62   removal methods included electrodialysis [16, 17], lime softening or ion exchange (MIEX)

63   [18], coagulation or flocculation [18-21], activated carbon adsorption [19, 22-24] and advanced

64   oxidation processes (ozonation, Fenton process, photocatalysis or photooxidation,

65   sonolysis and electrochemical oxidation [1, 25-30]). For the investigation of organics in

66   ROC, such as overall organic constituents, occurrence and determination of emerging

67   and priority pollutants, however, there were few documents reported in the latest

68   decade [31]. Hence, it was deserved more attention and would be beneficial to the

69   development of ROC treatment methods. Thus organic constituents in ROC,

70   especially for emerging and priority pollutants, have become an imperative topic need

71   to investigate.

72   This study includes three sections: first, the investigation of the occurrence of the

73   emerging and priority pollutants in the municipal ROC using liquid-liquid extraction

74   (LLE) followed by gas chromatography-mass spectrometry (GC-MS); second, the

75   determination of the concentrations of the pollutants depending on the result of the

76   previous section and the frequency of occurrence for emerging and priority pollutants

77   in aquatic systems; third, a discussion of the sources of the targeted emerging and

78   priority pollutants.

79   **2. Experimental**

80   **2.1. Chemicals and reagents**

81   The organic pollutants investigated in this work are listed in Table 1. Dimethyl

82   phthalate,   diethyl   phthalate,   1,4-dichlorobenzene,   1,2-dichlorobenzene,

83   1,3,5-trichlorobenzene, 1,2,4-trichlorobenzene, 1,2,3-trichlorobenzene, naphthalene,

84   anthracene and fluorene, all were A.R. grade and purchased from Guangfu Corp.,

85   China. 2-Chloroethyl ether, dibutyl phthalate and 1,3-dichlorobenzene, were also

86   A.R. grade and synthesised by Sinopharm Chemical Reagent Corp., China.

87   Acenaphthene, phenanthrene, caffeine and benzyl butyl phthalate, all were of purity

88 over 97% and supplied by Aladdin Chemistry Co., LTD, China. Simazine (purity >

89 96%) was obtained from Alfa-Aesar (Tianjin) Chemistry Co., LTD, China. Atrazine

90 (purity>97%) was obtained from TCI Shanghai Chemical Industry Co., LTD, China.

91 Sodium chloride, anhydrous sodium sulphate and sodium hydroxide were G.R. grade

92 and obtained from Guangfu Corp., China. Sodium chloride was dried before use at

93 350 °C and anhydrous sodium sulphate at 400 °C for 6 h using a muffle furnace.

94 Naphthalene-d_8 and p-terphenyl-d_{14} was obtained from Dr. Ehrenstorfer (Augsburg,

95 Germany) and were used as an internal standard and a surrogate standard compound,

96 respectively. Acetone (Absolv) was supplied by TEDIA Inc., Limited, USA.

97 Dichloromethane (Anapremium) was purchased from Anaqua Chemicals Supply Inc.,

98 Limited, USA. Ultrapure water was prepared using a MilliQ system made in the USA.

99   Individual stock standard solution of the target compounds was prepared in

100 acetone at a concentration of approximately 2000 μg mL^{-1} (except that of simazine

101 and p-terphenyl-d_{14}, whose concentrations were each 1000 μg mL^{-1}) and stored in a

102 freezer at 4 °C. The working solutions were prepared by mixing known volumes of

103 individual stock solution and appropriately diluted to different concentrations using

104 acetone for sample fortification and using dichloromethane for the calibration curve.

105 Naphthalene-d_8, used as an internal standard, was prepared in acetone at a

106 concentration of 100 μg mL^{-1} and was diluted to 10 μg mL^{-1} with dichloromethane for

107 calibration and sample preparation. P-terphenyl-d_{14}, used as a surrogate, was prepared

108 by appropriately diluting the stock standard solution with acetone to 0.5 μg mL^{-1}.

5

109   All glassware was cleaned sequentially with surfactant, chromic acid solution,

110   distilled water, ultrapure water and acetone.

111   Table 1 Compound studied, retention time and target ions for SIM mode for each compound

Compound (abbreviation)	CAS number	Retention time (min)	Target ions for SIM mode (m/z)[a]	Compound (abbreviation)	CAS number	Retention time (min)	Target ions for SIM mode (m/z)[a]
2-Chloroethyl ether (BCEE)	111-44-4	9.066	93,63,95	Fluorene (Flu)	86-73-7	17.808	165,166
1,3-Dichlorobenzene (1,3-DCB)	541-73-1	9.399	146,148,111	Diethyl phthalate (DEP)	84-66-2	17.826	149,177,150
1,4-Dichlorobenzene (1,4-DCB)	106-46-7	9.514	146,148,111	Simazine (Sim)	122-34-9	19.519	201,173,186
1,2-Dichlorobenzene (1,2-DCB)	95-50-1	9.920	146,148,111	Atrazine (Atr)	1912-24-9	19.624	200,215,173
1,3,5-Trichlorobenzene (1,3,5-TCB)	108-70-3	11.562	180,182,145	Phenanthrene (Phe)	85-01-8	20.070	178,179
1,2,4-Trichlorobenzene (1,2,4-TCB)	120-82-1	12.283	180,182,145	Anthracene (Ant)	120-12-7	20.184	178,179,176
Naphthalene-d$_8$ (Nap-d$_8$)[b]	1146-65-2	12.352	136,68	Caffeine (Caf)	58-08-2	20.695	194,109,193
Naphthalene (Nap)	91-20-3	12.393	128,129,127	Dibutyl phthalate (DBP)	84-74-2	21.764	149,104,150
1,2,3-Trichlorobenzene (1,2,3-TCB)	87-61-6	12.834	180,182,145	p-Terphenyl-d$_{14}$ (p-Ter-d$_{14}$)[c]	1718-51-0	23.967	244,122,212
Dimethyl phthalate (DMP)	131-11-3	16.115	163,194,164	Benzyl butyl phthalate (BBP)	85-68-7	25.323	149,91,206
Acenaphthene (Ace)	83-32-9	16.604	153,154				

112   Note: a -- The first ion was used as quantifier, and the second and third ions were used as qualifiers;
113   b -- Internal standard compound;
114   c -- Surrogate standard compound;

115   **2.2. Samples**

116   The ROC used in this study was produced from the MF/RO system following the

117   biologically secondary treatment in a municipal WWTP located in Tianjin, China. The

118   recovery of the RO system was 75%, and the treatment capacity was 10,000 m^3 d^{-1}.

119   The ROC sample was collected using a 5 L amber glass sampling bottle capped with a

120   ground glass stopper. Before sampling, the bottle was rinsed with the same water

121   sample three times. Four batches of samples collected in November 2011, May 2012,

122   August 2012 and March 2013, were defined as sample 1, sample 2, sample 3 and

123   sample 4, respectively. The samples were stored at 4 °C in a refrigerator until the

124   analysis was performed, which was performed within seven days.

125   **2.3. Sample pre-treatment procedure**

126   The ROC (300 mL) was spiked with 1 mL of surrogate solution (0.5 μg mL^{-1})

127   and 0.8 g NaCl. After adjusting the pH to approximately 6.0 with H_2SO_4 (1:3 v/v), the

128   mixture was transferred to a 1-L separatory funnel with a polytetrafluoroethylene

129   stopcock. A three-step LLE was undertaken. In each step, the mixture was diluted by

130   15 mL of dichloromethane and vigorously shaken for 5 minutes, and then the organic

131   layer was separated from the water phase after placing for 10 minutes. The organic

132   phases collected in the LLE were mixed and the trace water was removed by adding

133   anhydrous sodium sulphate. After separating the sodium sulphate, the extract was then

134   carefully evaporated to less than 1 mL using a vacuum rotary evaporator equipped

135   with a heating bath operating at 45 °C and an operating rotation speed at 80 rpm.

136   Finally, the residue was mixed with 0.05 mL of naphthalene-d$_8$ solution (10 μg mL^{-1}),

137   re-dissolved to 1 mL with dichloromethane and stored at 4 °C until analysis.

138   **2.4. GC-MS system and operating conditions**

139   The identification and quantification of organics was performed using a GC-MS

140   instrument (Agilent Technologies) that consists of an Agilent 6890N gas

141   chromatograph and an Agilent 5975 Mass Selective Detector.

142   Electron ionisation was performed at 70 eV. Helium was used as the carrier gas

143   at a constant flow condition of 1.0 mL min^{-1} in the Agilent 6890N GC system. The

144   analytes were separated on a HP-5MS (30 m × 0.25 mm, 0.25 μm, Agilent

145   Technologies) column. The injector operating conditions were as follows: injection

146   mode splitless; injection volume 1 μL; injector temperature 280 °C; the ion source and

147   quadrupole analyser temperatures were maintained at 230 and 150 °C, respectively.

148   The oven temperature program for scan mode was as follows: start at 40 °C for 3 min,

149   increase to 250 °C at 5 °C min^{-1}, hold at 250 °C for 5 min, increase to 300 °C at 10 °C

150   min^{-1}, hold at 300 °C for 10 min, with the solvent cut time of 3 min. The oven

151   temperature program for the selected ion monitoring (SIM) mode was as follows: start

152   at 40 °C for 3 min, increase to 280 °C at 10 °C min^{-1}, hold at 280 °C for 3 min, with

153   the solvent cut time of 7 min. The target ions for the SIM mode are listed in Table 1.

154   Twenty percent of each batch of samples was measured repeatedly. The method

155   blank was analysed with each batch of samples to check and correct for possible

156   contamination and interference. Dibutyl phthalate and 1,4-dichlorobenzene were

157   detected in the method blank. Phthalates, in particular di (2-ethylhexyl) phthalate and

158   dibutyl phthalate, often cause "blank" problems when analysed at low concentrations

159   [32]. As a result, the concentrations of dibutyl phthalate and 1,4-dichlorobenzene were

160   calculated using blank subtraction.

161   **2.5. Validation of the method**

162   The validation studies were performed by evaluating the parameters of the

163   linearity of the calibration curves, the recovery (%), the relative standard deviation

164   (RSD, %), the limit of detection (LOD) and the limit of quantification (LOQ).

165   The calibration curves were obtained by analysing the reference standard

166   solutions at six concentration levels (ca. 10, 50, 100, 500, 1000 and 5000 μg L^{-1})

167   which corresponded to 0.03 μg L^{-1} ~ 16.67 μg L^{-1} in the water samples (the

168   concentration factor applied in the sample pre-treatment was 300:1).

169   The recovery experiments were performed by analysing ultrapure water (n = 6)

170   spiked at two concentration levels (ca. 0.17 μg L^{-1} and ca. 1.67 μg L^{-1}). In the spiked

171   procedure, 1 mL of the working solution containing the 20 target compounds (the

172   concentration of each compound was 50 μg L^{-1} or 500 μg L^{-1}) was added into 300 mL

173   ultrapure water. Afterwards the ultrapure water was pre-treated by the procedure

174   addressed in section 2.3 (without adding the 1 mL surrogate solution).

175   The relative standard deviation (RSD) was obtained from the recovery

176   experiments (n = 6) at each fortification level.

177   Except for dibutyl phthalate and 1,4-dichlorobenzene, the limit of detection

178   (LOD) and limit of quantification (LOQ) of the instrument were calculated at a

179   signal-to-noise ratio of 3 and 10, respectively.

180   Because of the blank contribution, for dibutyl phthalate and 1,4-dichlorobenzene,

181   the LOD was calculated using the arithmetic mean of the blank concentration plus

182   three times the standard deviation (n = 6), and for the LOQ, ten times the standard

183   deviation was used.

9

184 **3. Results and discussion**

185 **3.1. Method performance**

186   The chromatogram of the mixed standard solution at ca. 1000 μg L^{-1} in SIM

187 mode is shown in Fig. 1. Under the specified GC-MS analysis conditions, good

188 separation for the target compounds was achieved, except for fluorene and DEP,

189 which had extremely similar retention times.

190   The validation of the procedure was performed in terms of the linearity of the

191 calibration curve, the recovery, the RSD, the LOD and the LOQ. The results for each

192 compound are described in Table 2.

193   In Table 2, the correlation coefficients of the calibration curves for the target

194 compounds were all higher than 0.99, exhibiting excellent linearity. The recoveries

195 were satisfactory, with average values between 70% and 130% for most compounds at

196 the two concentrations (ca. 0.17 and ca. 1.67 μg L^{-1}), except simazine (45.4%), DBP

197 (186.1%) at ca. 0.17 μg L^{-1} and anthracene (62.7%), caffeine (54.6%), DBP (169.2%)

198 at ca. 1.67 μg L^{-1}. RSD values were less than 20% for majority of the compounds

199 except for 1,4-dichlorobenzene (98.2% at a concentration of 0.17 μg L^{-1}) and DBP

200 (59.2% at a concentration of 0.20 μg L^{-1} and 55.9% at a concentration of 2.00 μg L^{-1}).

201   To check the matrix effect, recovery experiments were performed by analysing

202 the samples (n = 8) from the four batches of ROC spiked at two concentration levels

203 (ca. 0.17 μg L^{-1} and ca. 1.67 μg L^{-1}). The average recovery and RSD values were

204 reported in Table 2. The average recoveries ranged from 70% to 130%, and the RSD

205 values were less than 20% for majority of the compounds, which is consistent with the

206 results obtained previously from the ultrapure water.

207

208 Table 2 Relevant validation data for the analysis method

209 (Numbers in parentheses are the corresponding values for ROC samples)

Compound	Conc. range tested (µg L⁻¹)	Regression (correlation coefficient) (r)	LOD (µg L⁻¹)	LOQ (µg L⁻¹)	Conc. (µg L⁻¹)	Recovery (%)	RSD (%)	Conc. (µg L⁻¹)	Recovery (%)	RSD (%)
BCEE	11.25~5625	0.9999	0.07	0.23	0.19	71.1	15.8	1.87	80.9	9.3
						(108.4)	(18.8)		(86.9)	(8.6)
1,3-DCB	10.00~5000	0.9999	0.09	0.30	0.17	83.3	9.8	1.67	76.7	9.7
						(78.0)	(17.3)		(68.6)	(11.7)
1,4-DCB	10.20~5100	0.9996	0.65	1.45	0.17	75.2	98.2	1.70	84.3	9.6
						(115.3)	(47.7)		(62.5)	(11.5)
1,2-DCB	11.25~5625	0.9999	0.03	0.10	0.19	80.0	12.2	1.87	77.0	10.1
						(79.0)	(12.8)		(72.5)	(12.7)
1,3,5-TCB	10.15~5075	0.9998	0.09	0.30	0.17	87.4	10.4	1.69	78.5	10.0
						(73.1)	(17.5)		(83.4)	(6.1)
1,2,4-TCB	11.25~5625	0.9999	0.04	0.13	0.19	87.4	10.3	1.87	78.8	9.5
						(90.9)	(4.5)		(84.8)	(6.3)
Nap	10.10~5050	0.9999	0.04	0.13	0.17	99.3	14.9	1.68	104.6	14.2
						(64.1)	(20.3)		(85.6)	(6.5)
1,2,3-TCB	10.25~5125	0.9999	0.03	0.10	0.17	86.5	10.4	1.71	79.7	9.6
						(90.8)	(10.3)		(85.1)	(6.8)
DMP	11.50~5750	0.9998	0.04	0.13	0.19	78.0	17.0	1.91	86.1	15.5
						(83.9)	(13.4)		(93.4)	(7.2)
Ace	10.15~5075	0.9999	0.03	0.10	0.17	103.4	10.6	1.69	85.7	9.4
						(96.0)	(11.1)		(91.1)	(7.3)
Flu	10.30~5150	0.9999	0.11	0.36	0.17	83.5	10.4	1.71	86.1	10.6
						(96.5)	(6.1)		(92.6)	(7.9)
DEP	10.00~5000	0.9998	0.09	0.30	0.17	95.0	13.2	1.67	88.0	17.4
						(105.6)	(13.0)		(97.8)	(8.1)
Sim	10.20~5100	0.9968	1.96	6.54	0.17	45.4	15.6	1.70	103.3	11.9
						(49.0)	(28.3)		(61.3)	(16.1)
Atr	10.00~5000	0.9996	0.37	1.22	0.17	106.7	7.6	1.67	79.0	19.5
						(110.0)	(12.9)		(107.6)	(14.8)
Phe	10.25~5125	0.9998	0.10	0.33	0.17	79.4	13.9	1.71	84.6	13.1
						(104.0)	(8.6)		(94.9)	(10.8)
Ant	10.05~5025	0.9999	0.08	0.27	0.17	105.2	14.7	1.67	62.7	18.2
						(94.8)	(18.8)		(87.6)	(13.2)
Caf	10.25~5125	0.9981	0.12	0.40	0.17	84.3	19.3	1.71	54.6	16.8
						(117.1)	(23.6)		(77.0)	(14.3)
DBP	12.00~6000	0.9992	0.97	2.94	0.20	186.1	59.2	2.00	169.2	55.9
						(140.2)	(36.5)		(83.4)	(42.7)

11

p-Ter-d$_{14}$	10.00~5000	0.9999	\	\	0.17	88.7	10.2	1.67	86.0	13.2
						(113.2)	(10.2)		(100.9)	(12.3)
BBP	11.25~5625	0.9986	0.18	0.60	0.19	80.0	18.6	1.87	84.2	11.9
						(90.1)	(20.7)		(117.2)	(11.0)

210 Note: The value underlined denotes an unsatisfactory result.

211   Conc. is the abbreviation of concentration

212   All of the above results indicated that the method exhibited a high degree of

213 precision and accuracy for the analysis of the majority of the target compounds in the

214 ROC samples.

215 **3.2. Occurrence of the emerging and priority pollutants in the ROC**

216   In this section, for each batch of ROC sample, the pre-treatment procedure for

217 GC-MS determination were done twice, and the concentrations of pollutants were

218 reported as the average values.

219   For each ROC sample, the LLE procedure was repeated until 900 mL of ROC

220 was extracted, and then the mixed organic phase was evaporated to less than 1 mL.

221 After the internal standard was added, the residue was re-dissolved to 1 mL. The

222 concentration factor was 900:1. After pre-treatment, the water samples were analysed

223 using a GC-MS in scan mode for identification purposes. The compounds detected

224 from the water samples were tentatively identified under the guidance in Section

225 11.6.2 of US EPA method 8270D with database NIST05a. The main emerging and

226 priority pollutants detected are listed in Table 3 by category. For final identification

227 and confirmation purposes, the three characteristic ions and their relative abundances

228 plus their retention times were compared between the water samples and compounds

229 listed in Table 1. The quantification of the target emerging and priority pollutants in

230 the ROC samples were performed using SIM mode, and the results are described in

231   Table 4. 1,3-Dichlorobenzene, 1,2,4-trichlorobenzene and 1,2,3-trichlorobenzene were

232   not detected in all of the four batches of samples.

233

234   Table 3 Main emerging and priority pollutants detected in the ROC

Origins	Sample 1	Sample 2	Sample 3	Sample 4
Chlorinated compounds	Dibromochloromethane (124-48-1)	Bromoform	Dibromochloromethane	1,1,2-Trichloroethane (79-00-5)
	Bromoform (75-25-2)	1,1,2,2-Tetrachloroethane	Bromoform	1,1,2,2-Tetrachloroethane
	1,1,2,2-Tetrachloroethane (79-34-5)	2-Chlorotoluene (95-49-8)	1,4-Dichlorobenzene	1,4-Dichlorobenzene
	Bromodichloromethane (75-27-4)	2-Chloroethyl ether		1,2-Dichlorobenzene (95-50-1)
		1,4-Dichlorobenzene		2,4,6-Trichlorophenol (88-06-2)
				4-Chloro-3,5-dimethylphenol (88-04-0)
				Benzene,1,2,4,5-tetrachloro-3-methoxy- (6936-40-9)
				Phenol,2,3,5,6-tetrachloro-4-methoxy- (484-67-3)
PAHs	Phenanthrene	Naphthalene		
PAEs	Dimethyl phthalate	Dimethyl phthalate	Dibutyl phthalate	
	Diethyl phthalate	Dibutyl phthalate		
	Dibutyl phthalate			
PPCPs	Borneol (507-70-0)	Dimetridazole	Dimetridazole	2,6-Di-tert-butyl-4-methylphenol
	Dimetridazole (551-92-8)	2,6-Di-tert-butyl-4-methylphenol (128-37-0)	2,6-Di-tert-butyl-4-methylphenol	Caffeine
	(+)-Cedrol (77-53-2)	Metronidazole (443-48-1)	Metronidazole	Aminopyrine
		Caffeine	Caffeine	Phenobarbital (50-06-6)
		Aminopyrine (58-15-1)		Irgasan (3380-34-5)
		Nifedipine (21829-25-4)		

13

Herbicides	Atrazine	Atrazine	Atrazine
Flame retardants	Tributyl phosphate (126-73-8)	Triethyl phosphate (78-40-0)	Triethyl phosphate	Triethyl phosphate
	Tri(2-chloroethyl) phosphate (115-96-8)	Tri(2-chloroethyl) phosphate	Tri(2-chloroethyl) phosphate	Tri(2-chloroethyl) phosphate
	Tri(2-chloroisopropyl) phosphate (13674-84-5)	Tri(2-chloroisopropyl) phosphate	Tri(2-chloroisopropyl) phosphate	
Other classes	N-Methylacetamide (79-16-3)	N-Methylacetamide	N-Methylacetamide	N-Methylacetamide
	2,4-Di-tert-butylphenol (96-76-4)	Benzaldehyde (100-52-7)	Tetramethylbutanedinitrile (3333-52-6)	Tetramethylbutanedinitrile
		Isoquinoline (119-65-3)		Isoquinoline

235   Note: the number in parenthesis is the CAS number.

236

237   Table 4 Concentrations of the target emerging and priority pollutants ($\mu g\ L^{-1}$)

Compounds	Sample 1	Sample 2	Sample 3	Sample 4	WWTP effluent reported
2-Chloroethyl ether	0.23	1.42	0.07	0.20	\
1,4-Dichlorobenzene	0.53	0.78	0.37	0.77	\
1,2-Dichlorobenzene	0.03	n.d	n.d	0.27	\
1,3,5-Trichlorobenzene	0.04	n.d	n.d	0.03	0.13~0.18 [33]
Naphthalene	0.07	0.16	0.04	0.13	\
Dimethyl phthalate	0.04	0.08	0.04	0.07	0.09 [14]
Acenaphthene	0.06	0.03	n.d	0.03	0.005~0.011 [34]
Fluorene	0.08	0.03	0.04	0.03	0.031 [12]
Diethyl phthalate	0.07	n.d	0.07	0.20	0.15 [14]
Simazine	n.d	n.d	0.04	n.d	0.02~0.2 [35]
Atrazine	0.17	0.48	0.13	0.40	0.01~0.09 [35]
Phenanthrene	0.04	0.23	0.04	0.03	0.04~0.16 [33]
Anthracene	n.d	0.19	n.d	n.d	0.03 [34]
Caffeine	0.10	1.00	0.10	3.73	0.086~0.692 [34]
Dibutyl phthalate	0.30	0.76	0.47	0.53	0.34 [14]
Benzyl butyl phthalate	n.d	0.80	n.d	4.90	0.31 [14]

238   Note: n.d = not detected.

239   **3.3. Source of the emerging and priority pollutants**

240   Tables 3 and 4 indicated that there were many emerging and priority pollutants in

241   the municipal ROC. The possible sources of the pollutants are detailed as follows:

14

242   First, one obvious source was the secondary effluents of the WWTPs, which may

243   contained a variety of emerging and priority pollutants as shown in Table 4. The RO

244   membrane has a strong ability to retain organic compounds; thus, most of the

245   emerging and priority pollutants are retained in the ROC. However, what types of

246   emerging and priority pollutants frequently appeared and at what concentrations in the

247   municipal ROC has only been reported in a few papers [36, 37].

248   Test results indicated that many emerging and priority pollutants belonging to

249   PAHs, PAEs, PPCPs, herbicides, flame retardants, etc. appeared in the ROC.

250   Regarding the PAHs, naphthalene, acenaphthene, fluorene, phenanthrene and

251   anthracene were detected at a relatively low concentrations of 0.03~0.23 μg L^{-1}. Four

252   PAEs (DMP, DEP, DBP and BBP) were detected. DMP and DEP were at a relatively

253   low concentration of 0.04~0.20 μg L^{-1}, but BBP was at a concentration as high as 4.90

254   μg L^{-1} in sample 4. For herbicides, simazine was detected only in sample 3 at 0.04 μg

255   L^{-1} and atrazine was detected in all of the four samples at a concentration of 0.13~0.48

256   μg L^{-1}. The compounds of the PPCPs and the flame retardants detected in this work

257   are widely used in the daily life. For example, aminopyrine, irgasan and phenobarbital

258   are familiar pharmaceuticals, 2,6-Di-tert-butyl-4-methylphenol is used as the

259   antioxidant in the cosmetics industry, dimetridazole and metronidazole are common

260   nitroimidazole antibiotics. These compounds probably existed in the effluents of

261   WWTPs and hence were transferred to the municipal ROC at relatively high

262   concentrations; for example, the concentration of caffeine was as high as 3.73 μg L^{-1}

263   in sample 4.

264   Second, another source that is easy to ignore was the disinfection of the

265 MF/UF-RO system. Because biofouling is a major problem that RO process must

266 address, reducing the concentration of microorganisms in the feed stream of a RO unit

267 by disinfection is an effective way to control biofouling [38]. Thus, the samples would

268 be accompanied with the formation of some of the carcinogenic emerging and priority

269 pollutants known as disinfection by-products (DBPs).

270   In our study, many chlorinated compounds, including dibromochloromethane,

271 bromodichloromethane,   1,1,2,2-tetrachloroethane,   1,1,2-trichloroethane,

272 4-Chloro-3,5-dimethylphenol and 2-Chloroethyl ether, were detected. Some were

273 frequently detected at high concentrations, such as 2-Chloroethyl ether, in the four

274 samples, with concentrations in the range of 0.07~1.42 μg L^{-1}. These compounds were

275 probably generated in the chlorination disinfection for the feeding of the RO unit.

276 Hence, more attention should be paid to the ROC than the secondary effluents of

277 WWTPs because some carcinogenic pollutants were probably yielded with high

278 concentration in the disinfection for the RO feed.

279 **4. Conclusions**

280   In this work, a method for analysing the trace levels of emerging and priority

281 compounds using LLE followed by GC-MS was described. The parameters, including

282 the linearity of the calibration curves, recovery and RSD, indicated that the method

283 exhibited good performance in analysing the target compounds.

284   By examining the ROC from a municipal wastewater reclamation plant, the

285 results indicated that there were a variety of emerging and priority pollutants,

286   including chlorinated compounds, PAEs, PAHs, PPCPs, herbicides and flame

287   retardants, in the ROC. Some pollutants were at low concentrations (typically tens or

288   hundreds of ng L^{-1}), whereas others were at particularly high concentrations (such as

289   2-Chloroethyl ether at 1.42 μg L^{-1}, caffeine at 3.73 μg L^{-1} and benzyl butyl phthalate

290   at 4.90 μg L^{-1}).

291   More attention should be paid to the ROC because some of the emerging and

292   priority compounds would probably be transferred from the secondary effluents of the

293   WWTPs or formed in the disinfection of the MF/UF-RO system.

294   **Acknowledgements**

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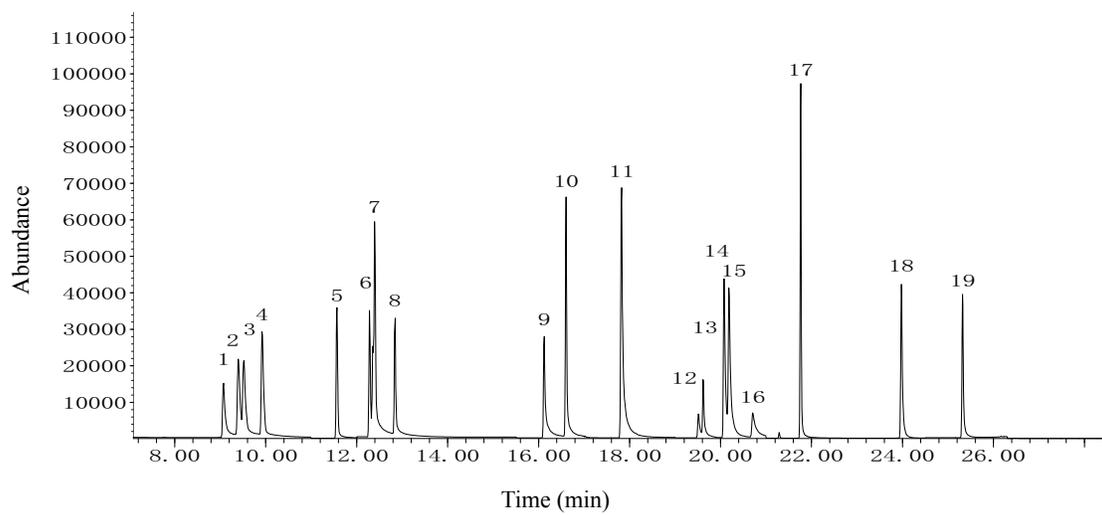351   38. N. Prihasto, Q. F. Liu and S. H. Kim, *Desalination*, 2009, **249**, 308-316.
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Fig. 1. Chromatogram of the mixed standard solution at 1000 µg L^{-1} in SIM mode.

1 BCEE; 2 1,3-DCB; 3 1,4-DCB; 4 1,2-DCB; 5 1,3,5-TCB; 6 1,2,4-TCB; 7 Nap-d$_8$ and Nap; 8 1,2,3-TCB; 9 DMP;
10 Ace; 11 Flu and DEP; 12 Sim; 13 Atr; 14 Phe; 15 Ant; 16 Caf; 17 DBP; 18 p-Ter-d$_{14}$; 19 BBP.