



Phenol removal efficiencies of sewage treatment processes and ecological risks associated with phenols in effluents

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ABSTRACT

Phenols pose a risk to the environment and to human health. Phenols found in rivers mainly originate from sewage treatment plants (STPs). In this paper, analytical procedures, based on deconvolution technology and retention time locking technology, were investigated to simultaneously identify and determine the concentrations of fifty different phenols in sewage water and effluents. Seventeen different phenols were found in sewage and five – including two regulated phenols (phenol and 2,4,6-trichlorophenol) and three un-regulated phenols (2-chlorophenol, 2,5-dichlorophenol and 2,4-dichloro-3-ethyl-6-nitrophenol) – were identified in effluents of five STPs. A number of processes undertaken in five STPs were also investigated. These processes can be used to remove phenols at efficiency levels of between 88.95% and 99.97%. Among the processes tested, a combination of anaerobic/anoxic/oxic (A²/O), continuous microfiltration (CMF), ozone oxidation (O₃), and chlorination, appeared to be the best option for the removal of key phenols. Among the five phenols identified in effluents, 2,5-dichlorophenol (1.89 μg/L) and 2,4-dichloro-3-ethyl-6-nitrophenol (22.6 μg/L) pose the greatest ecological risk to receiving waters.

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1. Introduction

Chemical components in sewage effluent are among the critical factors that determine the quality of receiving waters and the potential of such waters for use and recycling of reclaimed water. The quality of municipal wastewater is normally evaluated in terms of conventional chemical parameters: nutrient levels, bulk organic matter (measured as COD/BOD and TOC) and suspended solids. These conventional chemical parameters are, however, no longer sufficient to reflect water quality. In recent years, increased attention has focused on micro-pollutants in sewage treatment plants (STPs), due to concerns relating to their potential negative impacts on the environment [1].

Phenols, regarded as a priority pollutant by USEPA, are used in both industry and agriculture. Effluent discharges from these sources may therefore contain a large number of phenols that ultimately form an important component of STP influents. Results from a number of different researchers have indicated that phenols are ubiquitous pollutants in STPs [2–6]. Owing to their adverse effects on human health and their toxicity, persistence and bioaccumulation in animals and plants [7], the occurrence of phenols

in STPs has become an issue of international concern. Nevertheless, sewage treatment systems are generally designed to eliminate solid particulate contaminants, nutrients, and biodegradable dissolved organic matter. In the case of phenols, treatment systems generally only focus on the removal of regulated phenols such as phenol, 2,4-dichlorophenol and pentachlorophenol. The occurrence of water-soluble un-regulated phenols in wastewater has not received sufficient attention. Nevertheless, many un-regulated phenols in effluents are potentially hazardous to aquatic environments. For example, Miller et al. [8] found that 32 phenolic additives – including 4-*t*-octylphenol and 4-chloro-3-methylphenol, identified in effluents by Körner et al. [3] and Lee and Peart [4] – display estrogenic activity. A study of the removal efficiencies of un-regulated phenols in various STPs in real-world conditions is therefore of considerable importance.

There are currently only a few studies on un-regulated phenols in effluents and these have mostly focused on a limited number of phenols – such as bisphenol A, nonylphenol, 2,4-dichlorophenol and pentachlorophenol – because of the well-known adverse effects of these compounds on aquatic organisms and humans. There are very few relevant reports on a large number of other potentially harmful phenols, such as cresols, 2-chlorophenol and 2-naphthol. In this study, we conducted a broad-spectrum analysis of municipal wastewaters to gain comprehensive understanding of the concentration ranges of 50 phenols in sewage influents and effluent in Tianjin, China, which is the third largest industrial center of China.

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Tianjin is located in northern China near Beijing and adjacent to the Bohai Sea. On average, industrial corporations in this region discharge 180 million tons of wastewater per annum [9]. Rivers in the Tianjin area are severely polluted with high loads of persistent organic pollutants [10], which pose a risk to aquatic environments and human health. There are however only a few studies on a limited number of phenols. Studies dealing with ecological risk assessment of broad-spectrum phenols in effluents of STPs are limited. It is therefore a matter of urgency to evaluate the removal efficiency of broad-spectrum phenols in order to ensure quality standards of STP effluents in the Tianjin region.

In this context, the objectives of the present study are as follows: (1) To identify and quantify the concentrations of a wide range of phenols in influents and effluents at STPs in Tianjin. (2) To determine phenols removal efficiencies in different treatment processes. (3) To assess potential hazards associated with phenols present in effluents.

2. Materials and methods

2.1. Chemicals and materials

Phenols that conform to required standards were purchased from Sigma–Aldrich Co. (USA). These are listed in Table 1. Stock solutions for each individual phenolic standard (1 mg/L) were prepared in n-hexane. N-hexane and dichloromethane (DCM) were of pesticide-residue grade and were purchased from Mallinckrodt Baker, Inc. (USA). Derivatization reagent N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) with 1% trimethylchlorosilane (TMCS) was purchased from Supelco Co. (USA). Two kinds of solid-phase extraction (SPE) cartridges were used. C18 cartridge (500 mg) was purchased from Supelco (USA) and Oasis HLB cartridge (500 mg) from Waters (USA).

2.2. Sampling and preparation

Influent and effluent samples for this study were collected from five STPs which located in the Tianjin region. Tianjin is the third largest industrial center of China. There are more than 15 STPs in urban area in Tianjin. The processes of these five STPs were most common in China. These processes included different wastewater treatment processes, advanced treatment processes, and disinfection processes. So the selected STPs could reflect the common level and types of treatment processes in China. The detailed information about five STPs is listed in Table S1 in supplementary information. A number of symbols were used to describe various influent and effluent waters as well as processes undertaken.

STP1A, STP2A, STP3A, STP4A, STP5A were influents and STP1D, STP2B, STP3B, STP4B, STP5C were the effluents of five STPs. The STP1 process encompasses anaerobic/anoxic/oxic (A²/O) + continuous microfiltration (CMF) + ozone oxidation (O₃) + chlorination (Cl₂). STP1B represents the effluent of the A²/O process, and STP1C represents the effluent of CMF. CMF is an advanced treatment process performed after secondary treatment in STP1. STP1D represents the final effluent water from the ozone oxidation-chlorination process, following the CMF process. The STP2 treatment is an anoxic/oxic (A/O) process. The STP3 process describes a conventional activated sludge process used to treat wastewater. STP4 represents the hydrolysis acidification followed by a biological filtration process and STP5 represents hydrolysis acidification + membrane bioreactor (MBR) + Cl₂. STP5B represents the effluent of MBR.

Samples were filtered through Millipore glass microfiber filters (APFF14250, pore size 0.7 μm) (Millipore, USA) and were immediately preserved in brown glass containers with 5% methanol at 4 °C, and processed with SPE within 2 days. Samples were spiked

with surrogate standard (Biphenol A-d₁₆), adjusted to pH < 2 with 6 μmol/L hydrochloride buffer, and enriched with SPE, using a C18 cartridge coupled with a HLB cartridge. The extraction was performed in tandem. All cartridges were eluted with 10 mL DCM. After that, extracts of the same sample were pooled and evaporated under a gentle stream of nitrogen. Derivatization was performed to reduce the polarity of phenols. The dry residues were derivatized by 100 μL BSTFA with 1% TMCS, which were heated in a heating block at 60 °C for 2 h [11]. The derivatives were cooled to room temperature prior to GC–MS analysis.

2.3. Analytical procedure

Detailed information relating to this sample analysis is listed in Table S2 in supplementary information. The analytical procedures could refer to previously published research [12]. The mass spectrum (MS) was operated in full-scan mode from *m/z* 50 to 700 for qualitative analysis and selected ion monitoring (SIM) mode for quantitative analysis. First of all, full-scan mode was used to identify phenols in samples. The full-scan spectra data file was sent to Automatic Mass Spectral Deconvolution and Identification System (AMDIS), which deconvolutes the spectra and searches the compounds using the deconvoluted full spectra. Then SIM mode was used to quantify the phenols identified in samples.

2.4. Quality assurance/quality control (QA/QC)

To assess the reliability of the preparation method, blank experiment, matrix spike experiment and parallel experiment had been conducted. No phenols were detected from the blank samples. While we sampled, 12 typical phenols were spiked to the samples to verify the recoveries of analytes. The 12 typical phenols (phenol, 2-cresol, 3-cresol, 4-cresol, 2-chlorophenols, 2,6-dichlorophenol, 2,4-dichlorophenol, 2-nitrophenol, 2,4,6-trichlorophenol, 2,4,5-trichlorophenol, 2,3,4,6-tetrachlorophenol and pentachlorophenol) were representative of the 50 phenolic compounds for polarity, substituent groups, substituent positions and substituent number. According to the experiment results, the matrix spike recoveries for 12 typical phenols ranged from 47.87% to 114.8% (Table S3 in supplementary information). Only the recovery for 4-cresol was lower than 60%. The RSD% values for all recovery experiments were lower than 13.6%. The instrument limits of quantification (LOQs) of 50 phenols ranged 0.7–87.7 pg (Table S4 in supplementary information). Applying the entire analytical method, phenols can be detected at the ng/L level in environmental samples independent of the origin of the sample and its matrix load.

2.5. Ecological risk assessment

The quotient method was used to characterize ecological risk. Ecological effect quotient (EEQ) was defined as a ratio of measured environmental concentration (MEC) and predicted no-effect concentration (PNEC), as Eq. (1). According to Water Environment Research Foundation of Alexandria, chemicals of potential concerns (COPCs) with EEQs exceeding 1.0 present a clear risk potential. Any COPCs with EEQ > 1 should be subjected to more rigorous risk assessment. So the phenols with EEQs > 1 were selected as priority phenols.

$$EEQ = \frac{MEC}{PNEC} \quad (1)$$

All phenols identified in effluents were quantified and their concentration levels were used as MECs.

The definition of the PNEC according to the European Union Technical Guidance Documents (EU-TGD) is: the concentration below which unacceptable effects on organisms will most likely

Table 1
Detailed information of 50 phenols.

Compound	CAS ID	Compound	CAS ID
2,4-Dinitrophenol	51285	4-Nitrophenol	100027
Phenol	108952	2,3,5-Trichlorophenol	933788
2-Cresol	95487	2,4,5-Trichlorophenol	95954
3-Cresol	108394	2,3,6-Trichlorophenol	933755
4-Cresol	106445	4-Chlororesorcinol	95885
2-Chlorophenol	95578	4-Chloro-2-nitrophenol	89645
2,4-Xylenol	105679	2-Chlorohydroquinone	615678
4-Chlorophenol	106489	3,4,5-Trichlorophenol	609198
2,6-Xylenol	576261	2-Naphthol	135193
2-Isopropylphenol	88697	2-Biphenylol	90437
2-sec-Butylphenol	89725	2-Chloro-4-nitrophenol	619089
Pyrocatechol	120809	2,3,5,6-Tetrachlorophenol	935955
4-Chloro-3-methylphenol	59507	2,3,4,6-Tetrachlorophenol	58902
2,5-Dichlorophenol	583788	2,3,4,5-Tetrachlorophenol	4901513
2,6-Dichlorophenol	87650	2,4-Dichloro-3-ethyl-6-nitrophenol	99817364
2,3,6-Trimethylphenol	2416946	Pentachlorophenol	87865
2,4-Dichlorophenol	120832	Ortho-benzyl-para-chlorophenol	120321
Resorcinol	108463	2-Chloro-4-phenylphenol	92046
2,6-Diisopropylphenol	2078548	Tetrachlorohydroquinone	87876
2-Nitrophenol	88755	4,4'-Biphenyldiol	92886
Hydroquinone	123319	Biphenol A	80057
p-Chloro-m-xylene	88040	Dichlorophene	97234
3,5,6-Trichloro-2-pyridinol	6515384	Hexanoestrol	84162
2,4,6-Trichlorophenol	88062	Bithionol	97187
6-Chlorothymol	89689	Hexachlorophene	70304

not occur [13]. There are two methods to derive its value. The first method uses assessment factors to establish the level of the PNEC from the lowest available median effective concentration (EC_{50}) or no observed effect concentration (NOEC) (using EC_{50} data and NOEC divided by a certain assessment factor). The second method uses a cut-off value (usually 5%) of a Species Sensitivity Distribution (SSD) based on chronic toxicity. If a large data set with chronic toxicity from long-term experiments for different taxonomic groups is available, these values can be used to draw a distribution. This distribution that describes the variability of hazard of a substance to organisms is called a SSD. The 5% point in the SSD which was identified as hazardous concentrations for 5% of species (HC_{5s}) were used as PNECs. Toxicity data were collected from the ECOTOX database [14] following the principles of accuracy, relevance and reliability. In order to supply appropriate protection, only the toxicity data of species that are widespread in Chinese freshwaters, or widely cultivated in Tianjin, were collected to construct SSD. The information about the selected species has been listed in Tables S5–S8 in supplementary information. When the toxicity data were not available in the ECOTOX database, the Chronic Value (Chv) – defined as the geometric mean of NOEC and the lowest observed effect concentration (LOEC) – were collected from the PBT Profiler [15]. Following the recommendations of OECD, ten was taken as the assessment factor (AF). Thus, a tenth of Chvs were used as PNEC [16,17].

The Monte Carlo technique was used to randomly sample values from distribution of toxicity (10,000 iterations) and to generate HC_5 . Monte Carlo simulations were performed by using Crystal Ball (Version 7.2). To select the most appropriate distribution for a given dataset, automatically generated goodness-of-fit statistics (embedded in Crystal Ball) were used. Preference was given to the log-normal test. A critical p value (statistical significance level) of 0.05 was chosen to determine goodness of fit.

3. Results and discussion

3.1. Identification of phenols in wastewater and effluents

Qualitative results of tests done on influents and final effluents of five STPs are listed in Table 2. All samples were analyzed by deconvolution report software (DRS); the match values were

more than 80% and retention time difference between the database values and observed values was less than 5 s.

Seventeen different phenols were identified in the influents of five STPs and the frequencies of detection (FD) of eleven identified phenols exceeded 60%. Among the phenols with high FD values, phenol and 2-chlorophenol (2-CP) were priority pollutants according to USEPA [18]; 3-cresol has been divided into possible carcinogen by the USEPA; 2,5-dichlorophenol (2,5-DCP) has been used as a biomarker for exposure to 1,4-dichlorobenzene (1,4-DCB) [19] and it may have a key function in 1,4-DCB-induced genotoxicity [20]; 2-biphenylol was listed as a carcinogen and developmental or reproductive toxin in the Toxic Release Inventory (TRI) of USEPA [21]; p-chloro-m-xylene (PCMX) is a major constituent of disinfectants and can cause skin allergies. Although the FD values of 2,4-dichlorophenol (2,4-DCP) and 2,4,6-trichlorophenol (2,4,6-TCP) were lower than 60%, they were classified as priority

Table 2
Results of qualitative analysis.

Influent		Effluent	
Compound	FD in influents (%)	Compound	FD in effluents (%)
2-Cresol	100	Phenol	100
3-Cresol	100	2,4,6-Trichlorophenol	80
4-Cresol	100	2-Chlorophenol	40
2-Chlorophenol	100	2,5-Dichlorophenol	20
2,5-Dichlorophenol	100	2,4-Dichloro-3-ethyl-6-nitrophenol	20
2-Naphthol	100		
2-sec-Butylphenol	80		
p-Chloro-m-xylene	80		
Phenol	60		
6-Chlorothymol	60		
2-Biphenylol	60		
4-Chlorophenol	40		
2,6-Dichlorophenol	40		
2,4,6-Trichlorophenol	40		
2,3,6-Trimethylphenol	40		
2,4-Dichlorophenol	20		
2,4-Dichloro-3-ethyl-6-nitrophenol	20		

FD: frequency of detection.

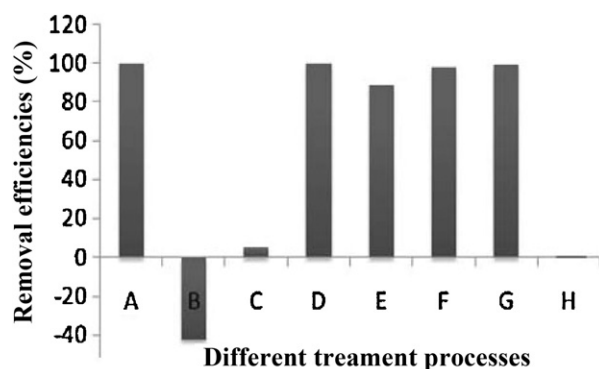


Fig. 1. Removal efficiencies of total phenols in different treatment processes. A–H represent the phenols removal efficiencies in different treatment processes. A represents the removal efficiency of anaerobic/anoxic/oxic (A^2/O) process; B represents the removal efficiency of continuous microfiltration (CMF) process; C represents the removal efficiency of ozone oxidation (O_3) + chlorination (Cl_2) process; D represents the removal efficiency of anoxic/oxic (A/O) process; E represents the removal efficiency of conventional activated sludge process; F represents the removal efficiency of hydrolysis acidification + biological filter process; G represents the removal efficiency of hydrolysis acidification + membrane bioreactor (MBR) process; H represents the removal efficiency of chlorination (Cl_2).

pollutants by USEPA [18]. An examination of these USEPA standards suggests that the occurrence of the phenols in various influents and effluents should be given more attention. It should be noted that, in contrast with the results from influents, only five different phenols were identified in effluents. There were two compounds – phenol and 2,4,6-TCP – in which the FD values of effluents were higher than those of influents. Literature reports indicate that phenol is an important degradation product of substituted phenols [22,23]. On the other hand, phenol, monochlorophenol, dichlorophenol or certain aromatic acids with hypochlorite, can be chlorinated to form 2,4,6-TCP during the disinfection of water [24,25]. According to literature reports, these observations suggest that some other phenols identified in influents could perhaps be transformed into phenol or 2,4,6-TCP by wastewater treatment processes, although other factors affecting the removal efficiency have not yet been identified. Further investigations need to be carried out to determine whether this transformation would cause serious environmental effects.

3.2. Removal efficiencies of phenols in five STPs

Table 3 lists the concentrations of the target chemicals in five STPs. These ranged from 0.05 to 22.6 $\mu\text{g/L}$. Fig. 1 describes the removal efficiency of total phenols in various treatment processes.

Ten phenols were identified in the influents of STP1, including phenol, 2-cresol, 3-cresol, 4-cresol, 2-CP, 2,5-DCP, 2-sec-butylphenol, PCMX, 2-naphthol, and 2-biphenylol at concentrations ranging from 0.34 to 404 $\mu\text{g/L}$. Only two phenols were identified in the effluents: phenol (0.05 $\mu\text{g/L}$) and 2-CP (0.14 $\mu\text{g/L}$). This indicates that the other eight phenols were removed, indicating that the treatment processes at STP1 were efficient. The removal efficiency of total phenols from STP1 was calculated as 99.97%. Quantitative results indicated that the removal efficiency of total phenols in A^2/O exceeded 99.98%. However, the concentrations of phenols increased after treatment by CMF (Fig. 1). The CMF process is expected to selectively retain particles with diameters $>0.2 \mu\text{m}$, while allowing smaller constituents – including water and most dissolved constituents – to freely pass through the membrane [26]. The negative effect of the CMF process may be due to the adsorption of phenols onto particles that accumulate on the membrane. This process is thus not suitable for removing phenols. Results summarized in Fig. 1 indicate that the $O_3 + Cl_2$ process

could remove a portion of the phenols, but the removal efficiency is not obvious. Furthermore, this process results in changes to the concentrations of 2-CP and phenol. A decrease in phenol was approximately equal to an increment in 2-CP. This may be due to the phenol being chloridized during chlorination [7].

STP2, STP3 and STP4 are the three STPs not coupled with advanced treatment processes. The treatment processes associated with these STPs are the A/O process (STP2), the conventional activated sludge process (STP3), and hydrolysis acidification–biological filtration process (STP4). The removal efficiencies of total phenols in STP2, STP3 and STP4 were calculated to be 99.95%, 88.95% and 98.04%, respectively (Fig. 1). A comparison of the three treatment processes indicates that A/O is the most efficient process, which results in the complete removal of nine different phenols, including 2-cresol, 3-cresol, 4-cresol, 2-chlorophenol, 2,5-dichlorophenol, 2-sec-butylphenol, p-chloro-m-xylene, 2-naphthol, and 6-chlorothymol. Nevertheless, the A/O process has a disadvantage in that phenol was introduced at the same time as the removal of other phenols. The conventional activated sludge process, used in STP3, was found to be the most inefficient process. Fifteen different phenols were identified in the influent of STP3 and three were identified in the effluent. Comparing the type and the concentrations of phenols identified in the influent and the effluent, we found that the conventional activated sludge process was completely unsuitable for removing 2,4-dichloro-3-ethyl-6-nitrophenol, although most other phenols are removed during this process. In addition, the other two phenols that were present in the effluent (phenol and 2,4,6-TCP) were not identified in the influent (STP3A). This result indicates that the conventional activated sludge process introduces phenol and 2,4,6-TCP as by-products, although most other phenols are removed in this process. Conventional activated sludge treatment is therefore not a suitable process for the removal of phenols. The hydrolysis acidification–biological filtration process, used in STP4, results in the production of most by-products, although its removal efficiency is better than that of the conventional activated sludge process. This process (hydrolysis acidification – biological filtration process) is therefore also not suitable for the removal of phenols.

The STP5 treatment process incorporates hydrolysis acidification + membrane bioreactor (MBR) + Cl_2 and its removal efficiency of total phenols was found to be 99.51%. The major difference in methods used in STP4 and STP5 relates to the treatment process used after hydrolysis acidification. MBR + Cl_2 is used in the STP5 and the biological filtration method is used in the STP4. The removal efficiency in STP5 was found to be slightly higher than that in STP4, but not at a significant level. It was found that even though the MBR method has been widely applied in wastewater treatment systems [27], this method was not more effective, in terms of total phenols removal, than the biological filtration method examined in this study. This may be because the MBR is not capable of removing low-molecular-weight cut-off organic matter [28] such as most of the phenols that enter the MBR process. In STP5, the concentration of 2,4,6-TCP in the final effluent water (STP5C) is greater than the concentration in the effluent water of the MBR (STP5B). In addition, the increment amount of 2,4,6-TCP is equal to the decrement of phenol. Chlorination is perhaps the reason for the observed increase in 2,4,6-TCP. Thus it appears that chlorination can transform some phenols into other phenols, but cannot remove phenols.

In comparing the removal efficiencies of total phenols, we found that A^2/O was the best treatment process for the removal of phenols from wastewater. Zhang et al. reported that A^2/O could remove 98% phenols [29]. This result confirmed our finding. Many researchers have also reported that A^2/O is a suitable treatment process for the removal of other matter, such as nitrogen and phosphorus [30,31]. In this study, the results indicated that advanced treatment processes were not more effective in terms of removal of phenols. This may

Table 3
Quantitative results of wastewater samples ($\mu\text{g/L}$).

	STP1				STP2		STP3		STP4		STP5		
	STP1A	STP1B	STP1C	STP1D	STP2A	STP2B	STP3A	STP3B	STP4A	STP4B	STP5A	STP5B	STP5C
Phenol	34.63	0.12	0.17	0.05	n.d.	0.27	n.d.	0.52	0.58	0.98	16.96	0.16	0.12
2-Cresol	16.45	n.d.	n.d.	n.d.	23.05	n.d.	16.15	n.d.	25.81	n.d.	4.4	n.d.	n.d.
3-Cresol	19	n.d.	n.d.	n.d.	30.99	n.d.	15.77	n.d.	19.11	n.d.	4.07	n.d.	n.d.
4-Cresol	18.23	n.d.	n.d.	n.d.	29.73	n.d.	15.13	n.d.	18.33	n.d.	3.9	n.d.	n.d.
2-Chlorophenol	32.77	0.02	0.03	0.14	101.43	n.d.	17.31	n.d.	24.48	0.12	10.59	n.d.	n.d.
4-Chlorophenol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.7	n.d.	13.17	n.d.	0	n.d.	n.d.
2,6-Dichlorophenol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	28.4	n.d.	n.d.	n.d.	0.98	n.d.	n.d.
2,4-Dichlorophenol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	30.66	n.d.	n.d.	n.d.	0	n.d.	n.d.
2,5-Dichlorophenol	30.15	n.d.	n.d.	n.d.	1.66	n.d.	41.82	n.d.	0.31	1.89	1.42	n.d.	n.d.
2,4,6-Trichlorophenol	n.d.	n.d.	n.d.	n.d.	0.36	0.07	n.d.	0.16	n.d.	0.25	0.57	0.06	0.1
2,3,6-Trimethylphenol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.3	n.d.	n.d.	n.d.	0.36	n.d.	n.d.
2-sec-Butylphenol	210.01	n.d.	n.d.	n.d.	348.04	n.d.	12.44	n.d.	55.77	n.d.	n.d.	n.d.	n.d.
p-Chloro-m-xylene	404.09	n.d.	n.d.	n.d.	16.22	n.d.	3.68	n.d.	7.29	n.d.	n.d.	n.d.	n.d.
2-Naphthol	0.34	n.d.	n.d.	n.d.	102.8	n.d.	4.14	n.d.	0.73	n.d.	0.61	n.d.	n.d.
6-Chlorothymol	n.d.	n.d.	n.d.	n.d.	0.19	n.d.	0.13	n.d.	n.d.	n.d.	1.11	n.d.	n.d.
2-Biphenylol	7.66	n.d.	n.d.	n.d.	n.d.	n.d.	0.18	n.d.	n.d.	n.d.	0.1	n.d.	n.d.
2,4-Dichloro-3-ethyl-6-nitrophenol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	22.18	22.63	n.d.	n.d.	0	n.d.	n.d.

n.d.: not detected.

be because secondary treatment had removed most phenols and only a small quantity of low-molecular-weight phenols entered the advanced treatment.

Three types of advanced treatment processes have been investigated in this study. From Fig. 1 we can conclude that the removal efficiency of O_3 was about 5%. Furthermore, many researchers have reported that the ozone oxidation process can be used to remove phenols effectively [32,33]. Comparing the advanced treatment processes investigated in this study, O_3 was found to be an effective advanced treatment process for the removal of phenols, particularly low-molecular-weight matter. In the case of STP1, the CMF process will introduce phenols into the processing system resulting in a decrease in removal efficiency. This can, however, be remedied in the ozone oxidation process. There is also a possibility that CMF could remove COD contained in particles with diameters $>0.2 \mu\text{m}$ [34]. The $\text{A}^2/\text{O} + \text{CMF} + \text{O}_3 + \text{Cl}_2$ process (used in STP1) is thus the best process for the removal of phenols from wastewater.

3.3. Potential hazard of phenols in effluents

Sewage treatment plants are a possible source of risk associated with phenols [12,35]. The quotient method was therefore used to characterize ecological risks and to assess the ecological risk of effluent discharge into receiving waters. Values for NOECs or LOECs of phenol and 2,4,6-TCP as chronic toxicity data were obtained from the ECOTOX database [14]. One thousandth of the median lethal concentration (LC_{50}) collected from the ECOTOX database was used to substitute chronic toxicity data for 2-CP and 2,5-DCP [14]. The toxicity data of the phenols identified in effluents have been supplied in supplementary information (Tables S5–S8 in supplementary information). And the SSDs of these phenols have been listed in supplementary information too (Figs. S1–S4 in supplementary information). The statistical values, summarized in Table 4, were log-transformed to make them fit log-normal distribution. Using Monte Carlo simulation, the distribution curves of toxicity data were calculated and $\text{HC}_{5\text{s}}$, used as PNECs, were listed in Table 4. Chv of 2,4-dichloro-3-ethyl-6-nitrophenol was collected from the PBT Profiler [15] and one-tenth of Chv was used as the PNEC (Table 4). The ecological risk quotients of effluent samples are listed in Table 5. Among the phenols identified in effluents, phenol and 2,4,6-TCP belong to regulated phenols. The concentrations of them met the discharge standard of pollutants for municipal wastewater treatment plants in China [36]. According to the discharge standards of China, their occurrence is safe. Their risk

quotients were also much lower than 1, so the ecological risks of phenol and 2,4,6-TCP could be neglected. However, the concentrations of 2,4,6-trichlorophenol in effluents from STP3 and STP4, have exceeded the human health criteria recommended by USEPA (1.4 $\mu\text{g/L}$ for the consumption of water and organism and 2.4 $\mu\text{g/L}$ for the consumption of organism only [37]). Its occurrence perhaps posed a risk to human. So we could not ignore the occurrence of 2,4,6-TCP in effluent. For the un-regulated phenols identified in effluents, 2-CP was a priority pollutant classed by USEPA [18]. USEPA [38] has reported that the odor threshold concentration of 2-chlorophenol is 0.1 $\mu\text{g/L}$. The concentrations of 2-CP in effluents were 0.14 $\mu\text{g/L}$ for STP1 and 0.12 $\mu\text{g/L}$ for STP4, both of which exceeded the threshold value. The ecological risk quotient of 2-CP (Table 5) was also much lower than 1, although it was more than the quotients of phenol and 2,4,6-TCP. The occurrences of 2-CP in such effluents would only be expected to cause sensory discomfort. The concentration of 2,5-DCP in the effluent of STP4 (1.89 $\mu\text{g/L}$) exceeds the odor threshold concentration (0.5 $\mu\text{g/L}$) proposed by the USEPA [38]. The ecological risk quotient of 2,5-DCP (Table 5) was greater than 1. The occurrence of 2,5-DCP in effluent of STP4 could cause other ecological risks besides sensory discomfort. 2,5-DCP has also been classified as a strongly toxic material by a PBT profiler, developed by the Environmental Science Center of the USEPA [15]. So special attention should be focused on the occurrence levels of 2,5-DCP. 2,4-Dichloro-3-ethyl-6-nitrophenol was only identified in STP3. The conventional activated sludge process applied by STP3 does not result in the complete removal of 2,4-dichloro-3-ethyl-6-nitrophenol. This compound is a benzene series intermediate and has been classified by the PBT profiler as having strong toxic potential and as a persistent material [15]. The ecological risk quotient of this substance (Table 5) was much greater than 1. Available information suggests that the occurrence of 2,4-dichloro-3-ethyl-6-nitrophenol could present a serious ecological risk. There is, however, little available data relating to the toxicity data of this compound. This means that the true ecological risk associated with this compound requires further evaluation.

To summarize the above discussion, the results indicate that concentrations of regulated phenols in the effluents of five STPs met the standard requirements and their ecological risks were not significant. Nevertheless, the occurrence of un-regulated phenols is a matter of concern as this could cause serious environmental damage. It is important that future investigations are focused on this topic.

Table 4
Statistical values of toxicity data and PNEC ($\mu\text{g/L}$).

	Toxicity data					PNEC
	Samples	Min.	Max.	Mean	SD	
Phenol ^a	54	1	6.25	4.16	1.2	2.15
2-CP ^a	38	0.24	1.35	0.99	0.24	0.59
2,4,6-TCP ^a	9	2.47	3.32	3.02	0.28	2.56
2,5-DCP ^a	6	0.25	0.84	0.54	0.21	0.20
2,4-Dichloro-3-ethyl-6-nitrophenol ^{b,c}						0.45

The value have been log-transformed except column 2 (samples); Min.: minimum; Max.: maximum; SD: standard deviation.

^a The data are collected from ECOTOX database.

^b The data are collected from PBT Profiler.

^c The PNEC was the tenth of Chv.

Table 5
Ecological risk quotient of effluents.

	STP1	STP2	STP3	STP4	STP5
Phenol	3.54×10^{-4}	1.91×10^{-3}	3.68×10^{-3}	6.94×10^{-3}	8.50×10^{-4}
2-CP	0.04	–	–	0.03	–
2,5-DCP	–	–	–	1.20	–
2,4,6-TCP	–	1.93×10^{-3}	4.41×10^{-3}	6.89×10^{-3}	2.75×10^{-3}
2,4-Dichloro-3-ethyl-6-nitrophenol	–	–	8.08	–	–

(–) the compound was not detected in that STP.

4. Conclusion

A method, which based on DRS and retention time locking (RTL) technology, was established to evaluate the removal efficiencies and the potential hazard of phenols in sewage water and effluents. RTL and DRS were two novelty technologies to detect environmental pollutants. They can help to identify target compounds in a fast and accurate way even when compounds are buried under co-eluting matrix compounds. In this study, RTL and DRS were applied to identify and quantify the fifty phenols in five different sewage treatment plants to evaluate phenols removal efficiencies from sewage treatment processes and ecological risks associated with effluents.

Seventeen phenols were identified in influents and only five phenols were identified in effluents, by means of consulting the library of phenols. Through the quantitative results, the initial removal efficiencies of STPs were estimated. A comparison of the removal efficiencies of total phenols associated with different treatment processes indicated that A²/O was the best treatment process for the removal of phenols from wastewater. Results of this study indicated that advanced treatment processes could not remove phenols effectively. Considering various factors, the A²/O + CMF + O₃ + Cl₂ process, used in the STP1, is the most suitable process for removal of phenols from wastewater.

Among the phenols identified in effluents, there are two regulated phenols (phenol and 2,4,6-trichlorophenol) and three kinds of un-regulated phenols (2-CP; 2,5-DCP and 2,4-dichloro-3-ethyl-6-nitrophenol). The un-regulated phenols in effluents may cause environmental effects and should be given more attention, although the concentrations of regulated phenols met the Chinese discharge standards for pollutants in municipal wastewater treatment plants.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2012.03.026.

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