Screening level ecological risk assessment for phenols in surface water of the Taihu Lake

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ABSTRACT

A number of approaches have been proposed for screening level ecological risk assessment. In this paper, we first established a mass spectrum library including 50 phenols using retention time locking (RTL) technology and deconvolution reporting software (DRS). Distribution of phenols in surface water of the Taihu Lake was screened. Among the 22 identified phenols, 14 phenols were quantified. The concentrations of total phenols ranged 675.2–3346.1 ng L⁻¹. The distributions of ecological effect quotients (EEQs) of 14 phenols were characterized in terms of the exposure concentration distributions (ECDs) and species sensitivity distributions (SSDs). Those phenols with EEQs exceeding the threshold proposed by Water Environment Research Foundation of Alexandria were selected as priorities. As a result, 2-nitrophenol (2-NP), p-chloro-m-xylenol (PCMX) and pyrocatechol were determined as potential ecological risk stressors in surface water of the Taihu Lake. Results of the present study suggested that the proposed approach is feasible for the screening level ecological risk assessment.

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1. Introduction

In aquatic environment, phenols are a large group of organic contaminants because of their high solubility in water, strong reactivity, and poor biodegradation (Bielicka-Daszkiewicz et al., 2004). They are toxic, persistent and bioaccumulative in animal and vegetable organisms and may pose serious threat to public health (Davì and Gnudi, 1999). For example, some of phenols are capable of mimicking or disrupting the estrogenic activity which influences the development and maintenance of female sex characteristics (Korach, 1993; Terasaka et al., 2006). Furthermore, researches indicated that chlorophenols which may be formed in the procedures of chlorination treatment in water disinfection could give a nasty smell and taste even at a very low concentration (Davì and Gnudi, 1999).

Because of their adverse effects to aquatic environment, the pollution situations of phenols have been assessed by many researches. As reported by many researches, phenols exist in aquatic environment extensively (Davì and Gnudi, 1999; Bolz et al., 2001; Gao et al., 2008). However, most of the researches only focused on well recognized phenols. By contrast, many other types of phenols have been detected in surface water. For instance, phenol, cresols, 2-ethylphenol, 2-nitrophenol (2-NP) and 4-nitrophenol (4-NP) were found widely in the surface water of Berlin (Schmidt-Bäumler et al., 1999). Those phenols, which have not

been paid enough attention before, would pose a potential threat to aquatic life and human once they are introduced into the environment. Therefore, it is necessary to screen phenols in the environment and assess their full-scale ecological risk in order to improve risk control.

A risk assessment is based on numerous exposure and effect data and, therefore, it is more effective to focus on selected contaminants. The purpose of screening level ecological risk assessment is to find the priorities from hundreds of candidates. Many ranking and screening methods for chemicals have been developed in recent years, such as the studies of Swanson et al. (1997), Hansen et al. (1999) and Hughes et al. (2009). However, these complicated ranking and screening approaches were primarily designed for prioritizing chemical regulation purposes, but not for screening level ecological risk assessment. They could not provide enough information about the hazard of one pollutant to end-users and public water managers. For assessing ecological risk, exposure characterization is an important phase. One difficulty associated with screening purpose is how to characterize the occurrence of candidates in the environmental medium through simplified chemical analyses. In most of approaches, models with all kinds of simplified assumptions were used to simulate exposure level. Consequently, the simulated data can hardly agree with real exposure level. Therefore, effective methods for screening priority environment pollutants in defined regions are generally lacking. The recently developed techniques such as retention time locking (RTL) and spectral deconvolution can help to identify target compounds in a fast and accurate

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way even when they are buried under co-eluting matrix compounds (Wylie et al., 2004). So in this study, RTL and deconvolution reporting software (DRS) are developed to obtain exposure levels of phenols. The limitation of DRS is that it only qualifies and quantifies the compounds that are listed in the library. It ignores all the unlisted compounds in the raw spectra. But there is no special library of phenols available nowadays. In addition, the parameters of phenols, scattered in other libraries, are recorded based on un-derivative phenols. High responses could not be obtained on gas chromatography for un-derivative phenols, so false negative results were easily produced. To surmount these challenges, we establish a specialized library completely devoted to the derivatized phenols to screen phenols by RTL and DRS in this study.

Taihu Lake is the third largest freshwater lake in China (Qin et al., 2007). It provides the vital water resource for agriculture and industry to surrounding areas, and is also the potable water source of many cities and towns in Eastern China including Shanghai, Suzhou, and Wuxi (Kong et al., 1998). But with the development of industry and agriculture, an increasing amount of pollutants has been discharged into the lake directly and indirectly since the 1980s (Hu et al., 2006). The lake ecosystem has been deteriorated during the past decades.

The aims of this study are (i) to establish a mass spectrum library including 50 kinds of phenols using RTL technology and DRS; and (ii) to determine the concentration levels of phenols in surface water of the Taihu Lake, consequently, the ecological risks of the priority phenols were identified and their risks were characterized; (iii) to select the potential ecological risk stressors as priorities for further ecological risk assessment based on the risk quotients.

2. Materials and methods

2.1. Chemicals and materials

All the phenolic standards were purchased from Sigma–Aldrich (USA) and the detailed information of phenolic standard was listed in the Table 1. Stock solutions for each individual phenolic standard (1 mg L^{-1}) were prepared in *n*-hexane. All solvents [methanol, acetone, *n*-hexane, methyl-tert-butyl ether (MTBE) and dichloromethane (DCM)] were of pesticide residue grade and were purchased from Mallinckrodt Baker Inc. (USA). Ultrapure water generated by Milli-Q system (Millipore, USA) was used. Derivatization reagent N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) with 1% trimethylchlorosilane (TMCS) was purchased from Supelco (USA). The solid-phase extraction (SPE) cartridges used were C18 cartridge (500 mg) from Supelco (USA) and Oasis HLB cartridge (500 mg) from Waters (USA).

2.2. Approach for screening level ecological risk assessment

Exposure characterization, ecological effect characterization and risk characterization were the three phases of screening level ecological risk assessment. The approach for screening level ecological risk assessment is shown in Fig. 1.

Combined spectrum of samples analyzed by gas chromatography–mass spectrometry (GC–MS) with the library of phenols, a preliminary contaminants list including all the phenols which were identified in the samples was obtained using spectral deconvolution technology. Considering the frequencies of detection and environmental effects, some phenols in the preliminary contaminants list were quantified and their concentration levels were used

Table 1
The detailed information of 50 phenols.

Compound	Abbr.	CAS ID	M.F.	Purity (%)	Compound	Abbr.	CAS ID	M.F.	Purity (%)
2,4-dinitrophenol	2,4-DNP	51285	$\text{C}_6\text{H}_4\text{N}_2\text{O}_5$	100	4-nitrophenol	4-NP	100027	$\text{C}_6\text{H}_5\text{NO}_3$	100
Phenol	–	108952	$\text{C}_6\text{H}_5\text{Cl}_2\text{NO}_3$	100	2,3,5-trichlorophenol	2,3,5-TCP	933788	$\text{C}_6\text{H}_3\text{OCl}_3$	98.3
2-cresol	–	95487	$\text{C}_7\text{H}_8\text{O}$	100	2,4,5-trichlorophenol	2,4,5-TCP	95954	$\text{C}_6\text{H}_3\text{Cl}_3\text{O}$	99.7
3-cresol	–	108394	$\text{C}_7\text{H}_8\text{O}$	99.5	2,3,6-trichlorophenol	2,3,6-TCP	933755	$\text{C}_6\text{H}_3\text{OCl}_3$	99.6
4-cresol	–	106445	$\text{C}_7\text{H}_8\text{O}$	99	4-chlororesorcinol	–	95885	$\text{C}_6\text{H}_5\text{ClO}_2$	98
2-chlororphenol	2-CP	95578	$\text{C}_6\text{H}_5\text{ClO}$	100	4-chloro-2-nitrophenol	4-C-2-NP	89645	$\text{C}_6\text{H}_4\text{ClNO}_3$	98
2,4-xyleneol	–	105679	$\text{C}_8\text{H}_{10}\text{O}$	100	2-chlorohydroquinone	–	615678	$\text{C}_6\text{H}_5\text{ClO}_2$	99
4-chlorophenol	4-CP	106489	$\text{C}_6\text{H}_5\text{ClO}$	100	3,4,5-trichlorophenol	3,4,5-TCP	609198	$\text{C}_6\text{H}_3\text{OCl}_3$	100
2,6-xyleneol	–	576261	$\text{C}_8\text{H}_{10}\text{O}$	99.5	2-naphthol	–	135193	$\text{C}_{10}\text{H}_8\text{O}$	99
2-isopropylphenol	–	88697	$\text{C}_9\text{H}_{12}\text{O}$	99.5	2-Biphenylol	–	90437	$\text{C}_{12}\text{H}_{10}\text{O}$	97.7
2- <i>s</i> -butylphenol	–	89725	$\text{C}_{10}\text{H}_{14}\text{O}$	98	2-chloro-4-nitrophenol	2-C-4-NP	619089	CH_4ClNO_3	>97
Pyrocatechol	–	120809	$\text{C}_6\text{H}_6\text{O}_2$	100	2,3,5,6-tetrachlorophenol	2,3,5,6-TeCP	935955	$\text{C}_6\text{H}_2\text{Cl}_4\text{O}$	100
4-chloro-3-methylphenol	4-C-3-MP	59507	$\text{C}_7\text{H}_7\text{ClO}$	99.7	2,3,4,6-tetrachlorophenol	2,3,4,6-TeCP	58902	$\text{C}_6\text{H}_2\text{Cl}_4\text{O}$	99.5
2,5-dichlorophenol	2,5-DCP	583788	$\text{C}_6\text{H}_4\text{Cl}_2\text{O}$	99.2	2,3,4,5-tetrachlorophenol	2,3,4,5-TeCP	4901513	$\text{C}_6\text{H}_2\text{Cl}_4\text{O}$	99.9
2,6-dichlorophenol	2,6-DCP	87650	$\text{C}_6\text{H}_4\text{Cl}_2\text{O}$	100	2,4-dichloro-3-ethyl-6-nitrophenol	–	99817364	$\text{C}_8\text{H}_7\text{O}_3\text{NCl}_2$	100
2,3,6-Trimethylphenol	2,3,6-TMP	2416946	$\text{C}_9\text{H}_{12}\text{O}$	>95	Pentachlorophenol	PCP	87865	$\text{C}_6\text{HCl}_5\text{O}$	99.5
2,4-dichlorophenol	2,4-DCP	120832	$\text{C}_6\text{H}_4\text{Cl}_2\text{O}$	99.8	Ortho-benzyl-para-chlorophenol	–	120321	$\text{C}_{13}\text{H}_{11}\text{ClO}$	98
Resorcinol	–	108463	$\text{C}_6\text{H}_6\text{O}_2$	98	2-chloro-4-phenylphenol	–	92046	$\text{C}_{12}\text{H}_9\text{ClO}$	100
2,6-Diisopropylphenol	–	2078548	$\text{C}_{12}\text{H}_{18}\text{O}$	99	Tetrachlorohydroquinone	–	87876	$\text{C}_6\text{H}_2\text{Cl}_4\text{O}_2$	99
2-nitrophenol	2-NP	88755	$\text{C}_6\text{H}_5\text{NO}_3$	100	4,4'-Biphenyldiol	–	92886	$\text{C}_{12}\text{H}_{10}\text{O}_2$	100
Hydroquinone	–	123319	$\text{C}_6\text{H}_6\text{O}_2$	>99	Biphenol A	BPA	80057	$\text{C}_{15}\text{H}_{16}\text{O}_2$	99
p-chloro-m-xyleneol	PCMX	88040	$\text{C}_8\text{H}_9\text{ClO}$	99	Dichlorophene	–	97234	$\text{C}_{13}\text{H}_{10}\text{Cl}_2\text{O}_2$	100
3,5,6-trichloro-2-pyridinol	–	6515384	$\text{C}_5\text{H}_2\text{Cl}_3\text{NO}$	99.7	Hexanoestrol	–	84162	$\text{C}_{18}\text{H}_{22}\text{O}_2$	100
2,4,6-Trichlorophenol	2,4,6-TCP	88062	$\text{C}_6\text{H}_3\text{Cl}_3\text{O}$	98.9	Bithionol	–	97187	$\text{C}_{12}\text{H}_6\text{Cl}_4\text{O}_2\text{S}$	100
6-chlorothymol	–	89689	$\text{C}_{10}\text{H}_{13}\text{ClO}$	100	Hexachlorophene	–	70304	$\text{C}_{13}\text{H}_6\text{Cl}_6\text{O}_2$	99.6

Abbr.: abbreviation; M.F.: molecular formula; –: no abbreviation available.

Fig. 1. Approach for screening level risk assessment.

as exposure data. The preparation and analyses of samples and the library establishment of phenols were detailed in the following relevant sections.

No observed effect concentrations (NOECs) were collected as chronic toxicity data from ECOTOX database (US EPA, 2009). If the NOECs were not available, half of the lowest observed effect concentrations (LOECs) were used. If the LOECs were unavailable too, one thousandth of the median lethal concentration (LC₅₀) (Hansen et al., 1999) were used to substitute chronic toxicity data. In this study, Monte Carlo simulation (Crystal Ball) was used to obtain exposure concentration distribution (ECD) and species sensitivity distribution (SSD). Ecological effect quotient (EEQ) was calculated as a ratio of ECD to SSD, as in Eq. (1) which was used to characterize risk in this study.

$$EEQ = \frac{ECD}{SSD} \quad (1)$$

Using Monte Carlo simulation, distribution curves of EEQs and the probabilities of EEQs of phenols exceeding threshold was calculated. According to Water Environment Research Foundation of

Alexandria (WERF, 1996), although only chemicals of potential concerns (COPCs) with EEQs exceeding 1.0 present a clear risk potential, any COPCs with EEQ > 0.3 are subjected to more rigorous risk assessment, because chemical interactions and cumulative toxicity must also be considered. So the phenols with EEQs > 0.3 were selected as priority phenols.

2.3. Sampling and preparation

Fifty eight surface water samples (2 L) were collected covering the whole Taihu Lake with aid of a global positioning system (GPS; Fig. 2) in October, 2008 and April, 2009. All samples were filtered through Millipore glass microfiber filters (Millipore, USA) 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 μM hydrochloride buffer and enriched with SPE using C18 cartridge coupled with HLB cartridge. The cartridges were eluted with 10 mL DCM. All of the extracts were evaporated under a gentle stream of nitrogen. Derivatization was performed to reduce the polarity of phenols. The dry residues were derivatized by BSTFA with 1% TMCS, which were heated in a heating block at 60 °C for 2 h. The derivatives were cooled to room temperature and subjected to GC–MS analysis.

2.4. Procedures for building a library of phenols

Phenols, which were used extensively in China, with available toxic data, and easy for deriving, were chosen as target compounds. After derivatized by BSTFA with 1% TMCS, each standard compound was analyzed by GC–MS to obtain their mass spectrogram. A library of phenols is created as a *.tab file using Microsoft Excel in which compound name, retention time, target ion, quota ion and abundance ratio of ion of each target compound were recorded. A series of conversions were then carried out to build the library. Details for establishing a library can be found in Agilent Technical Overview (Weiner and Prest, 1999).

Fig. 2. Sampling sites and regionalisms. Region A–H represents Meiliang Bay, Zhushanhu, West coast of Taihu Lake, Center of Taihu Lake, Gonghu, East coast of Taihu Lake, Dongtaihu and South coast of Taihu Lake, respectively.

2.5. Analytical procedure

The samples were detected using an Agilent 6890 gas chromatograph equipped with Agilent MSD 5975 mass spectrometer. The capillary column of 30 m × 0.25 mm i.d. 0.25 μm HP-5 was used. Before analyzing samples, retention time would be locked by changing column pressure using standard samples. Then constant pressure model was used in the whole analysis process. Gas chromatography (GC) oven temperature was programmed from 40 °C to 300 °C via a ramp of 10 °C min⁻¹ and maintained at 40 °C for 2 min and at 300 °C for 15 min. Mass spectrum (MS) was operated in full-scan mode from *m/z*, 50–700 for qualitative analysis or selected ion monitoring (SIM) mode for quantitative analysis. The inlet and MS transfer line temperatures were maintained at 250 °C, and the ion source temperature was 300 °C. Sample injection (1 μL) was in splitless mode. The data of GC–MS were analyzed by the techniques of RTL and DRS (software provided by Agilent).

2.6. Toxicity data collection and selection

Different species may have very different responses to the same exposure. In order to supply appropriate protection for aquatic ecosystems of the Taihu Lake, a main base of aquaculture, the aquatic species existing widely in Taihu Lake or in freshwater of China or widely cultivated species were selected to construct SSD distribution. The information about the selected species has been listed in Table 2.

According to data selection standards described by Klimisch et al. (1997), the toxicity data were collected from the ECOTOX database (US EPA, 2009) following the principles of accuracy, relevance and reliability. The toxicity data will be collected only when they were characterized by a specific end point. In the case of multiple data on the same end point and species, the geometric mean was used.

2.7. Statistical analysis

The Monte Carlo technique was used to sample randomly values from distribution of exposure and toxicity (10,000 iterations) and to

generate a distribution expressing the probability of the quotients to be exceeded. Monte Carlo simulations were performed by using Crystal Ball (version 7.2). To characterize the ecological risk, data for exposure level and chemical toxicity were log-transformed in an effort to normalize the distributions. To select the most appropriate distribution for a given data, automatically goodness-of-fit statistics (embedded in Crystal Ball) were used. Preference is given to the log-normal test. A critical *p* value (statistical significance level) of 0.05 was used to determine goodness of fit."

3. Results and discussion

3.1. Building a library of phenols for DRS

In this study, a library of 50 phenols has been established. To our knowledge this is the first time to establish a library of 50 phenols for screening level ecological risk assessment. The related parameters of 50 phenols are listed in Table 3.

To assess the ecological risk, prediction environment concentration is important, but difficult to obtain. Even though GC–MS is most commonly used to separate and identify organic chemicals, it is difficult to get good separation for some phenols, such as 2,5-DCP and 2,6-DCP, 2,6-DCP and 2,3,6-TMP, 2,4,6-TCP and 2,3,5-TCP and so on. Generally, GC–MS conditions such as ion source temperature and GC oven temperature program were optimized to get good separation (Banerjee et al., 2008). The performance, however, is not satisfactory for a large number of target compounds. Simultaneously, matrix effect, a serious interference, could not be effectively eliminated or reduced by changing GC–MS conditions. Based on the retention time, quota ions and abundance ratios of ions, deconvolution technology could separate and identify chemicals accurately and fast, even when chemicals were buried by complex matrix. So RTL, spectral deconvolution and DRS were developed for screening target compounds in GC–MS analysis.

A library is necessary for deconvolution processes. The commercial mass spectral library (HCD, Agilent Co. USA) ready for deconvolution processes could not meet the requirement of screening because it only contains 20 phenols. Furthermore, the parameters in the currently available library are only limited to un-derivative

Table 2
The selected species.

Species	Genus	Family	Order	Class	Phylum
<i>Microcystis aeruginosa</i> ^a	<i>Microcystis</i>	Chroococcaceae	Chroococcales	Chroococcophyceae	Cyanohyta
<i>Scenedesmus subspicatus</i> ^a	<i>Scenedesmus</i>	Scenedesmaceae	Chlorococcales	Chlorophyceae	Chlorophyta
<i>Daphnia magna</i> ^a	<i>Daphnia</i>	Daphniidae	Cladocera	Branchiopoda	Arthropoda
<i>Ceriodaphnia dubia</i> ^b	<i>Ceriodaphnia</i>	Daphniidae	Cladocera	Branchiopoda	Arthropoda
<i>Artemia salina</i> ^a	<i>Artemia</i>	Aatemiidae	Anostraca	Branchiopoda	Arthropoda
<i>Crangon septemspinosa</i> ^a	<i>Crangon</i>	Crangonidae	Decapoda	Malacostraca	Arthropoda
<i>Moina macrocopa</i> ^a	<i>Moina</i>	Moinidae	Cladocera	Branchiopoda	Arthropoda
<i>Thermocyclops oblongatus</i> ^b	<i>Thermocyclops</i>	Cyclopoidae	Cyclopoida	Maxillopoda	Arthropoda
<i>Brycon cephalus</i> ^c	<i>Brycon</i>	Characidae	Characiformes	Actinopterygii	Chordata
<i>Oncorhynchus kisutch</i> ^c	<i>Oncorhynchus</i>	Salmonidae	Salmoniformes	Actinopterygii	Chordata
<i>Oncorhynchus mykiss</i> ^c	<i>Oncorhynchus</i>	Salmonidae	Salmoniformes	Actinopterygii	Chordata
<i>Oryzias latipes</i> ^a	<i>Oryzias</i>	Adrianichthyidae	Beloniformes	Actinopterygii	Chordata
<i>Chironomus plumosus</i> ^a	<i>Chironomus</i>	Chironomidae	Diptera	Insecta	Arthropoda
<i>Lepomis macrochirus</i> ^b	<i>Lepomis</i>	Centrarchidae	Perciformes	Actinopterygii	Chordata
<i>Carassius auratus</i> ^a	<i>Carassius</i>	Cyprinidae	Cypriniformes	Osteichthyes	Chordata
<i>Platichthys flesus</i> ^c	<i>Platichthys</i>	Pleuronectidae	Pleuronectiformes	Actinopterygii	Chordata
<i>Poecilia reticulata</i> ^b	<i>Poecilia</i>	Poeciliidae	Cyprinodontiformes	Actinopterygii	Chordata
<i>Cyprinus carpio</i> ^a	<i>Cyprinus</i>	Cyprinidae	Cypriniformes	Actinopterygii	Chordata
<i>Brachionus calyciflorus</i> ^a	<i>Brachionus</i>	Brachionidae	Plioma	Monogononta	Rotifera
<i>Tetrahymena pyriformis</i> ^a	<i>Tetrahymena</i>	Tetrahymenidae	Hymenostomatida	Oligohymenophorea	Ciliophora
<i>Macrobrachium rosenbergii</i> ^c	<i>Macrobrachium</i>	Palaemonidae	Decapoda	Malacostraca	Arthropoda

^a The species widely existed in Taihu Lake.

^b The species widely existed in freshwater of China.

^c An important freshwater products in Chinese aquaculture.

Table 3

The retention time, target ion, quota ion and abundance ratio of ion of each target phenolic compound.

Compound	R.T.	T.I.	q1	q1ratio	q2	q2ratio	q3	q3ratio
2,4-DNP	5.958	256	241	127.6	191	500	77	346.8
Phenol	7.809	166	166	100	151	390.9	77	49.5
2-cresol	9.100	180	165	183.5	149	25.6	91	141
3-cresol	9.277	180	165	272.9	149	14.8	91	53.1
4-cresol	9.434	180	165	273.6	149	15	91	43.3
2-CP	10.307	200	185	258.4	149	256.5	93	247.2
2,4-xyleneol	10.630	194	179	106.2	149	35.6	105	78.5
4-CP	10.733	200	185	266.1	149	10.2	93	30.3
2,6-xyleneol	10.760	194	179	100.7	149	42.8	105	99
2-isopropylphenol	10.825	208	193	297.6	151	41.4	77	46.8
2-s-butylphenol	11.904	222	193	499.3	149	31.6	77	74.5
Pyrocatechol	12.009	254	239	19.9	166	36.7	151	38.7
4-C-3-MP	12.096	214	199	188.7	149	11.3	77	24.6
2,5-DCP	12.401	234	219	333.6	183	17.1	93	287.4
2,6-DCP	12.463	234	219	258.1	183	121.3	93	96.8
2,3,6-TMP	12.467	208	193	113.3	119	88.2	77	30.1
2,4-DCP	12.693	234	219	297.9	183	72.3	93	240.1
Resorcinol	12.927	254	239	151.6	166	4.2	91	8.8
2,6-diisopropylphenol	13.159	250	235	261.6	177	6.1	91	16.4
2-NP	13.213	196	196	100	151	26.7	79	31.9
Hydroquinone	13.274	254	254	100	239	215.2	79	148
PCMX	13.314	228	213	164.5	93	25.5	77	29
3,5,6-trichloro-2-pyridinol	13.798	271	256	713.2	234	42.5	93	511.7
2,4,6-TCP	14.335	268	253	534.8	217	175.3	93	214.2
6-chlorothymol	14.452	256	45	214.3	183	10.5	77	24.1
4-NP	14.558	211	211	100	196	392.2	150	63.1
2,3,5-TCP	14.567	270	270	100	253	393.3	93	507.2
2,4,5-TCP	14.688	270	255	333	196	145.2	93	352.4
2,3,6-TCP	14.768	268	268	100	253	522.5	93	341.2
4-chlororesorcinol	14.851	288	288	100	273	85	93	37.4
4-C-2-NP	14.917	230	230	100	77	20.8	0	0
2-chlorohydroquinone	14.955	288	288	100	257	55.1	93	35.3
3,4,5-TCP	15.181	268	268	100	253	225.9	93	77.7
2-naphthol	15.324	216	201	129.5	185	12.4	127	21.8
2-biphenylol	15.768	242	227	145.5	211	196.2	77	12.7
2-C-4-NP	15.994	230	230	100	147	26.1	93	54.5
2,3,5,6-TeCP	16.62	304	304	100	289	549	93	337.3
2,3,4,6-TeCP	16.746	304	304	100	289	443.6	93	208.2
2,3,4,5-TeCP	17.058	304	304	100	289	418	93	455.4
2,4-dichloro-3-ethyl-6-nitrophenol	18.181	292	292	100	247	25.5	93	12.8
PCP	18.883	338	338	100	323	504.4	93	328
Ortho-benzyl-para-chlorophenol	19.337	290	290	100	275	94.2	181	14.9
2-chloro-4-phenylphenol	19.539	276	261	60	225	146.9	93	89
Tetrachlorohydroquinone	19.985	392	392	100	375	110	93	138.5
4,4'-biphenyldiol	21.725	330	330	100	315	13.2	150	7.4
BPA	22.250	357	357	100	372	11.2	0	0
Dichlorophene	23.207	412	412	100	377	82.9	0	0
Hexanoestrol	23.542	399	399	100	179	485.9	151	138.1
Bithionol	25.636	500	500	100	395	56.7	93	37.3
Hexachlorophene	27.47	550	550	100	515	226.3	208	532.2

R.T.: retention time; T.I.: target ion; q1: the first qualitative ion; q1 ratio: abundance of q1/abundance of target ion $\times 100$; q2: the second qualitative ion; q2 ratio: abundance of q2/abundance of target ion $\times 100$; q3: the third qualitative ion; q3 ratio: abundance of q3/abundance of target ion $\times 100$.

phenols. In GC, un-derivative phenols are prone to irreversible adsorption on active centers of the separation system, resulting in broad and tailed peaks, leading to relatively low efficiency of chromatographic columns separation. Therefore, derivatization is required to transform phenols to less polar compounds (Buchholz and Pawliszyn, 1994; Rodríguez et al., 2000; Kovács et al., 2008). So we established a library of phenols derivatized by BSTFA with 1% TMCS, and to our current knowledge that this is the first time to establish a library of derivatized phenols in the literature.

It is impractical to select all phenols as target compounds into the library. Based on following three criteria, phenols were selected as target compounds: (i) whether they are widely used (whether the production or requirement or import and export amount of one phenolic compound exceeds 1000 tons year⁻¹); (ii) whether the relevant toxicity data are available; (iii) whether the standard samples are available or not. Fifty phenols which satisfied all the three criteria were selected as target compounds.

These phenols include pharmaceutical intermediates (pyrocatechol and 2,6-DCP), industrial materials (2,4-DNP and phenol), and raw materials of pesticides (2-isopropylphenol and 2,6-diisopropylphenol), etc. In order to establish a more comprehensive library, the terms of application frequency, consumed amount, hazardous properties and commercial availability of phenols were considered. For these reasons, the established library is representative and could meet requirements for screening.

To build library of these 50 phenols, retention time of each target compound, target ions, quota ions and abundance ratios of ions are necessary. The full-scan has been done to get mass spectra of the silylated phenols after derivatized. From the mass spectra, the related parameters of establishing phenols library are obtained (Table 3). The TMS⁺ ion (*m/z*, 73) was obtained for all the compounds tested. After getting all the parameters, a library of phenols was established. To validate the reliability of the library, a mix standard including 16 phenols (2,4-DNP, phenol, 2-cresol, 3-cresol,

2-CP, 2,4-xyleneol, 4-C-3-MP, 2,6-DCP, 2,4-DCP, 2,5-DCP, 2,4,6-TCP, 2,4,5-TCP, 2,3,5,6-TeCP, 2,3,4,6-TeCP, 2,3,4,5-TeCP, PCP) was screened. The results showed that all the 16 phenols were identified accurately and the match ratios were greater than 90% except for 2,4,5-TCP (73%), implying that the library was reliable for screening phenols.

3.2. Identification and quantification of phenols in surface water of the Taihu Lake

Twenty two phenols (Table 4) were identified in the Taihu Lake using deconvolution technique. Among the 22 phenols, the frequencies of detection of phenol, 2-NP, 2,4-xyleneol, 2-cresol, 3-cresol, resorcinol, pyrocatechol and PCMX were more than 50%. The eight compounds were quantified by GC–MS. Simultaneously, 2-CP, 4-C-3-MP, 2,4-DCP and 2,4,6-TCP were quantified, because they have been classified as priority pollutants in the aquatic environment by US EPA (2005) and were detected in the Taihu Lake at least twice. And the frequency of detection of 2,4,6-TCP was greater than 50% in the West coast of the Taihu Lake. 2,4,5-TCP was detected three times. The World Health Organization (WHO, 1989) and IARC (Kalliokoski and Kauppinen, 1990) qualified 2,4,5-TCP as a possible carcinogenic compound. 2,5-DCP has been used as a biomarker of 1,4-dichlorobenzene (1,4-DCB) (Hill et al., 1995), and it may have a key function in 1,4-DCB induced genotoxicity (Tegethoff et al., 2000). 2,5-DCP was a potential risk pollutant because of its toxicity effect and high frequency of detection (>50%) in Zhushanhu. Therefore, 2,4,5-TCP and 2,5-DCP were quantified too.

Fourteen phenols including 2-NP, 2,4-xyleneol, 2-cresol, 3-cresol, resorcinol, pyrocatechol, PCMX, 2-CP, 4-C-3-MP, 2,4-DCP, 2,4,6-TCP, 2,5-DCP and 2,4,5-TCP were quantified by GC–MS analysis. The concentration ranges and means of 14 phenols are listed in Table 4. To assess the reliability of the preparation method, blank experiment, matrix spike experiment and parallel experiment had been conducted. No phenolic compound was detected from the blank samples. The relative standard deviation (RSD%) was lower than 13.6%. Biphenol A-d₁₆ was spiked to samples and

clean-up by SPE–GC–MS method. The recovery of Biphenol A-d₁₆ ranged from 48.7% to 139%.

3.3. Ecological risk assessment

Risk characterization is the final phase of ecological risk assessment. It is used to elucidate the relationships among stressors, effects, and ecological entities, and to reach conclusions regarding the occurrence of exposure and the likelihood of anticipated effects. The probability risk assessment technique has been used extensively, because its results were close to the realistic results (Brain et al., 2006). In probability assessment method, both uncertainty and the stochastic properties of exposure and effect can be fully considered. As recommended by Water Environment Research Foundation of Alexandria, a rigorous risk characterization might compare probability distribution of environmental exposure concentration (EEC) of the chemical with the probability distribution for ecological risk criterion (ERC) to estimate ecological effects (WERF, 1996).

NOECs or LOECs of phenol, 2,4-xyleneol, 2,4-DCP, 2,4,6-TCP and 2,4,5-TCP were collected as chronic toxicity data from ECOTOX database (US EPA, 2009). One thousandth of the median lethal concentration (LC₅₀) collected from ECOTOX database was used to substitute chronic toxicity data for other phenols (US EPA, 2009). The toxicity data and exposure concentrations for the 14 phenols and statistical values were summarized in Table 5, and the values have been log-transformed to make them fit log-normal distribution.

Using Monte Carlo simulation, the distributions curves of EEQs were calculated. The probabilities of EEQs of quantified phenols exceeding 0.3 are shown in Table 5. The EEQs of phenols except for 2-NP, PCMX and pyrocatechol were <0.3. Therefore, their risk could be neglected. The EEQs of 2-NP, PCMX and pyrocatechol were possible to exceed 0.3, and the probabilities were 15%, 15% and 10%, respectively. Therefore, 2-NP, PCMX and pyrocatechol were selected as priority phenols. According to European community regulations, the total concentration of phenols must be no higher than 500 ng L⁻¹ in domestic water and each phenolic compound must be lower than 100 ng L⁻¹ (Commission of the European Communities, 1980a, 1980b). As the source water of surrounding cities, the risk of total phenols should be brought to the immediate public attention.

The spatial distribution of risks is determined by examining the spatial distribution of EECs (WERF, 1996). The 2-NP was mainly distributed in Zhushanhu (Fig. 3A). The concentration of 2-NP in site 2 was 1547 ng L⁻¹, much higher than other sites. 2-NP is usually used as the raw material of pesticide, dye, medicine and anti-oxidant. Pharmaceutical factories may be the main source of 2-NP in Zhushanhu. Pyrocatechol was mainly distributed in Northwest coast of the Taihu Lake and Zhushanhu (Fig. 3B). The highest concentration of pyrocatechol (2169 ng L⁻¹) was found in site 5 in Zhushanhu. Pyrocatechol is used in rubber and synthetic material production and drug synthesis. It is also used in cosmetic, dye and insecticide production (Michałowicz and Duda, 2007). Many factories located around site 5, including leather plants, chemical plants, pharmaceutical industries, plasticizer plants, refineries and the plants producing raw materials of resin. All these factories were the potential sources of pyrocatechol. The high concentrations of PCMX were detected in the samples collected around residential areas (Fig. 3C). PCMX was the raw materials of disinfectant. The probable main source of PCMX was domestic sewage discharge.

From the analyses above, we conclude that the primary risk source of phenols is industrial effluents. Zhushanhu and West coast of the Taihu Lake are the high risk regions. Samples collected around sewage treatment plants in this study contain more phenols. This phenomenon has also been observed by Bolz et al.

Table 4
The qualitative and quantitative results of phenols (n = 58; ng L⁻¹).

Compound	Frequency of detection (%)	Concentration range	Mean
Phenol	98	n.d~205.6	75
pyrocatechol	93	309.9~2169	1039
3-cresol	90	n.d~65.4	5.7
2,4-xyleneol	73	n.d~49.3	11.8
PCMX	66	n.d~161.4	64.9
2-NP	58	n.d~1547	464.2
2-cresol	53	n.d~199.5	30.1
resorcinol	53	n.d~53.1	8.5
4-cresol	27	–	–
2,5-DCP	25	n.d~116.8	26.9
2,4,6-TCP	17	n.d~840.4	35.9
2-phenylphenol	14	–	–
2,6-xyleneol	10	–	–
2,6-DCP	10	–	–
4-C-2-NP	8	–	–
2-CP	8	n.d~166.1	6
2,4-DCP	5	n.d~143.1	19.6
2,6-diisopropylphenol	5	–	–
2,3,5-TCP	3	–	–
2,4,5-TCP	3	n.d~65.3	14.6
2-isopropylphenol	3	–	–
4-C-3-MP	2	n.d~35.9	0.6

n.d: not detected; –: not quantified.

Table 5
The ecological risk criterion (ERCs), environmental exposure concentration (EECs) and the probabilities of ecological effect quotients (EEQs) exceeding 0.3 of 14 phenols (ng/L).

	ERCs					EECs		The probabilities of EEQs exceeding 0.3
	Samples	Min.	Max.	Mean	SD	Mean	SD	
Phenol	59	4	9.25	7.16	1.2	1.75	0.39	0
2-NP	12	2.95	5.2	3.87	0.7	2.59	0.28	15%
2,4-xyleneol	22	5.12	6.87	6.29	0.41	1.22	0.22	0
2-cresol	63	3.7	5.26	4.4	0.36	1.47	0.3	0
3-cresol	8	3.95	4.75	4.3	0.31	1.07	0.29	0
Resorcinol	23	2.4	5.51	4.71	0.69	0.93	0.33	0
Pyrocatechol	7	3.54	4	3.85	0.21	2.93	0.29	10%
PCMX	7	2.23	3.43	2.83	0.48	1.75	0.24	15%
2-CP	38	3.24	4.35	3.99	0.24	0.99	0.37	0
4-C-3-MP	19	2.96	4.98	3.81	0.45	0.4	0.28	0
2,4-DCP	20	2	6.3	5.09	0.92	1.2	0.4	0
2,4,6-TCP	10	5.45	6.32	6.02	0.28	1.3	0.56	0
2,4,5-TCP	29	4.53	6	5.45	0.4	1.47	0.24	0
2,5-DCP	6	3.28	3.84	3.54	0.21	1.24	0.41	0

Samples: size of data set; Min.: minimum; Max.: maximum; SD: standard deviation. Min., max. and mean were in the nature logarithm values.

Fig. 3. Concentration distribution of priority phenols (ng L⁻¹527). (A) 2-NP; (B) pyrocatechol; (C) PCMX.

(2001), which showed that the effluents of sewage treatment plants cause the high concentrations of phenols in streams of Krösch and Krähenbach in German. So sewage treatment plants were another possible source of risk of phenols.

4. Conclusion

RTL and DRS were introduced into the screening level ecological risk assessment system first time. They make the risk assessment more easily and fast. A specialized library including 50 phenols for DRS has been first established to screen phenols. 22 phenols were identified in surface water of the Taihu Lake by the library of phenols. And 14 phenols were quantified because of high frequency of detection and serious threat to aquatic organisms. Zhushanhu and West coast of the Taihu Lake were the two regions with relatively higher risk of phenols. The main risk sources of phenols are industrial and sewage treatment plants effluents. The EEQs of 2-NP, PCMX and pyrocatechol probably exceed threshold, therefore these compounds were selected as priority phenols in the Taihu Lake.

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