Identification and ranking of the risky organic contaminants in the source water of the Danjiangkou reservoir

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Abstract The Danjiangkou reservoir was selected to provide the source water for the middle routes of the South to North Water Transfer Project, which has provoked many environmental concerns. To date, investigations of water contamination of the source water of the Danjiangkou reservoir with organic micro-pollutants have been limited. This study was conducted to identify and rank organic contaminants that pose risks in the Danjiangkou reservoir. To this end, the Chemical Hazard Evaluation and Management Strategies (CHEMS-1) approach was adapted to integrate the deconvolution technology of qualitative identifying contaminants for site-specific environmental matrices. The samples were screened for the presence of 1093 contaminants using deconvolution technologies and the hazard values of the identified contaminants were calculated using the adapted CHEMS-1 approach according to their hazardous properties and occurrence in source water. The results showed that 46 contaminants from 1093 targets were present in Danjiangkou water, 23 of which appeared at frequencies higher than 50%, and 15 of which were identified as priorities. Over half (53%) of the high-ranked contaminants were polycyclic aromatic hydrocarbons (PAHs), with chrysene ranked highest on the list. Health risk assessment of the top-ranked PAHs was conducted and revealed that cancer risks of PAHs detected in the source water of Danjiangkou to different populations ranged from 10^{-7} to 10^{-6} , indicating a low cancer risk to consumers. The results of this study indicated that the adapted CHEMS-1 approach was feasible for site-specific screening of organic contaminants to identify and rank potential priority pollutants.

Keywords identification and ranking, source water, deconvolution, risk assessment, Danjiangkou, South to

North Water Transfer Project

1 Introduction

Ensuring the safety of source water remains a major focus because of the direct and indirect threats to human health from water contaminants [1–3], although the quality of drinking water has improved worldwide in the past 30–40 years [4]. Recently however, the use and release of a vast number of chemicals into the environment have made the situation worse, and brought great challenges to water management and drinking water processing [2,5].

Conventionally, the quality of source water was regulated according to the standards established by different countries and organizations [6–8] to ensure the quality of tap water. However, water managers have expressed uncertainty as to whether some remaining unregulated contaminants should be included in the regulations. The approaches applied to identify and prioritize unregulated contaminants were summarized in our previous review [9]. As an example, the United States Environmental Protection Agency (USEPA) publishes a Contaminant Candidate List (CCL) every five years under the authorization of the Safe Drinking Water Act [10]. The third CCL list was published in 2009 and included 104 chemicals or chemical groups and 12 microbiological contaminants that were not included in the current drinking water regulations. Conversely, about 82000 chemicals were listed in the USEPA Toxic Substances Control Act inventory [11], and 95% of the most commonly used chemicals consist of organic substances. For site-specific source water, it is neither possible nor reasonable to conduct a full hazard assessment for all chemicals. Therefore, identification of the organic contaminants posing the highest human health and/or ecological risks in source water is of great importance.

The Danjiangkou reservoir is located in central China and has a drainage area of $9.52 \times 10^4 \text{ km}^2$ [12]. This reservoir was selected as the water source for the middle routes of the South to North Water Transfer Scheme, which is a multi-decade infrastructure project to better utilize China's water resources. The scheme provides water to many districts along the routes, including Beijing. This water diversion scheme has provoked many environmental concerns [13,14]. However, investigations of water contamination of the source water of Danjiangkou by organic micro-pollutants have been limited to date. Therefore, it is of great importance to identify organic contaminants that pose risks in the Danjiangkou reservoir for further evaluation and management.

The purpose of this study was to identify and rank organic contaminants in the source water of Danjiangkou that pose risks. To accomplish, the Chemical Hazard Evaluation and Management Strategies (CHEMS-1) approach [15,16] was adapted to integrate the deconvolution technology of qualitative identifying contaminants for site-specific environmental matrices. CHEMS-1 has been developed to provide a relative assessment of chemical risks to human health and the environment [16]. The method was selected because it is simple to use, sufficiently flexible to apply to other applications, and in line with our scenario analysis. The introduction of the identification method offered occurrence data for CHEMS-1, which used the release amount as an estimate of exposure for a particular contaminant. The adapted approach was validated and applied to identify and rank organic contaminants in the source water of Danjiangkou.

Although the main function of the Danjiangkou reservoir is to supply drinking water, ecological risk was included in the adapted approach considering the importance of ecological status to water safety and function. Finally, the health risk of the top-ranked contaminants was evaluated.

2 Materials and methods

2.1 Chemicals and materials

All solvents (methanol, acetone, dichloromethane (DCM), *n*-hexane) were of pesticide grade and supplied by Mallinckrodt Baker Inc. (USA). The ultra-pure water used in this study was generated by a Milli-Q system (Milli-Q Biocel, Millipore, USA). Solid phase extraction (SPE) was conducted using C18 cartridge (500 mg, 6 mL) from Supelco (USA) and Oasis hydrophilic-lipophilic balance (HLB) cartridge (500 mg, 6 mL) from Waters (USA).

2.2 Sample collection and pretreatment

Based on the water functional types and the objectives of this study, the environs of the Danjiangkou Dam were selected as the study area. The contamination status of the study area may reflect the worst-case scenario, due to the relatively more intense human activities in this zone. Five national monitoring cross-sections were selected: Xiaotai-pingyang (XTPY), Taizishan (TZS), Baqian (BQ), Caiwan

Fig. 1 Sampling sites of source water in Danjiangkou. Sampling sites: 1, XTPY; 2, TZS; 3, BQ; 4, CW; 5, LHK

(CW) and Langhekou (LHK) (Fig. 1). Sections XTPY and TZS are located in the Danjiang reach. CW and LHK are located in the Hanjiang reach. At each section, 2 L of water was collected in May 2011. A total of five samples at different sites were collected in the study area. All samples were filtered using Millipore glass microfiber filters (0.7 μm , Φ 142 mm, Millipore, USA) and immediately preserved in amber glass bottles with 5% methanol at 4°C. Phenanthrene-d10 was spiked into water samples prior to extraction as a surrogate standard during sample pretreatment. The samples were enriched by SPE with C18 coupled with HLB cartridges within 24 h. The cartridges were eluted by 10 mL of DCM. The extracts were concentrated under a gentle stream of nitrogen and analyzed by gas chromatography-mass selective detector (GC-MSD).

2.3 Instrumental analysis

The samples were analyzed using an Agilent 6890 GC connected to Agilent MSD 5975 mass selective detector (Agilent Technologies, USA) equipped with a DB-5 capillary column (30 m $\times$ 0.25 mm i.d. $\times$ 0.25 μm film thickness, J&W Sci., USA). Highly pure helium (99.9999%) was used as the carrier gas. In this study, two retention time locked (RTL) databases, Hazardous Contaminant Database (HCD) and Pesticide and Endocrine Disruptor Database, were used to screen the potential contaminants in the samples. For the HCD method, the constant pressure mode was used during the whole analysis process. The oven temperature was held at 40°C for 2 min, raised to 300°C at 10°C min⁻¹ and held for 15 min. The inlet and mass spectrometry (MS) transfer line temperatures were both set at 250°C, and the ion source temperature was 230°C. 1 μL of the sample was injected in splitless mode. For the Pesticide and Endocrine Disruptor Database method, GC-MSD conditions were the same as for HCD method with the exception of the oven temperature, which was held at 70°C for 2 min, raised to 150°C at 25°C min⁻¹, raised to 200°C at 3°C min⁻¹, raised to 280°C at 8°C min⁻¹ and held for 15 min. RTL, data acquisition and processing were performed by the Agilent MSD ChemStation Software (version E.0200.493, Agilent Technologies, USA).

Polycyclic aromatic hydrocarbons (PAHs) were determined using Agilent GC-MSD in the selected ion monitoring mode. A DB-5 capillary column (30 m $\times$ 0.25 mm i.d. $\times$ 0.25 μm film thickness, J&W Sci., USA) was equipped with helium as the carrier gas. The flow rate was maintained at 1 mL min⁻¹ during analysis. The injection temperature was set at 300°C. The chromatographic column was held at 50°C for 2 min, raised to 200°C at 20°C min⁻¹, held for 2 min, raised to 290°C at 3°C min⁻¹ and held for 15 min. 1 μL of sample was injected in splitless mode. Quantification of PAHs was conducted based on comparison of peak area with PAH standard.

2.4 Automatic screening and identification of chemicals

The samples were analyzed by GC-MSD using the RTL method detailed above. The scan data were analyzed using Deconvolution Reporting Software (DRS) to identify the contaminants in samples. There are 1655 contaminants in the two above-mentioned databases, with 562 contaminants in both databases, or 1093 individual contaminants. The database covers a wide range of contaminants, including pesticides and their metabolites, endocrine disruptors, important polychlorinated biphenyls, PAHs, some dyes (e.g., sudan red), organophosphorus fire retardants, etc [17]. The identification of contaminants was based on three characteristic ions located at the correct retention time and with the correct relative ion intensity. DRS is a marriage of three different GC-MSD software packages: 1) the Agilent GC-MSD ChemStation, 2) the National Institute of Standards and Technology (NIST) Mass Spectral Search Program with NIST 08 MS library, and 3) the Automated Mass Spectral Deconvolution and Identification System (AMDIS) software, also from NIST. Retention index data were employed to identify the contaminants in samples. The deconvolution parameters in AMDIS were fixed as follows: adjacent peak subtraction: one; resolution: medium; sensitivity: high; shape requirements: medium. More details on DRS settings can be found in Agilent's application notes and literature elsewhere [18–20].

2.5 Adapted CHEMS-1 method

2.5.1 Parameters and endpoints in the adapted CHEMS-1

In this study, an adapted version of CHEMS-1 was used to rank contaminants in water samples. CHEMS-1 was developed to assess safer substitutes for hazardous chemicals listed in Toxics Release Inventory data and annual pesticide usage data. Different exposure routes to different receptors were considered in CHEMS-1, while not all of the endpoints were used in the adapted version considering the matrix studied. In particular, release amount for a particular contaminant was substituted by detection frequency to characterize exposure potential in the real environment. The detection frequency of a particular contaminant refers to the ratio of the number of sites where the positive DRS results were obtained in the qualitative screening to the total number of sites. Table 1 lists the parameters and endpoints used in the adapted CHEMS-1.

2.5.2 Scoring method and algorithm

The scoring algorithm for hazard value (*HV*) was established as described in the previous studies [15,16]. In brief, a total hazard value (*HV_t*) for a contaminant was

Table 1 Parameters and endpoints used in the adapted algorithm

parameter	type of toxicity/criteria	endpoint
human health effects	acute	rodent oral LD50
	chronic	weight of evidence for carcinogenicity
	chronic	other specific effects, including cholinesterase inhibitor, developmental or reproductive toxin, endocrine disruptor
environmental effects	aquatic, acute	fish LC50
	aquatic, chronic	fish NOEL
exposure	persistence	hydrolysis half-life, $t_{1/2}$
	bioaccumulation	BCF
	environmental occurrence	frequency of detection

Notes: LD50, medium lethal dose; BCF, bioaccumulation factor; LC50, medium lethal concentration; NOEL, no-observed effect level

calculated as the production of exposure and effect scores:

$$HV_t = (HV_{Env} + HV_{Hum}) \times HV_{Exp}, \quad (1)$$

where HV_t , HV_{Env} , HV_{Hum} , and HV_{Exp} are hazard values for total hazard, environmental effects, human health effects, and exposure potentials, respectively.

HV_{Env} was the sum of hazard values for acute aquatic toxicity (HV_{FA}) and the chronic aquatic toxicity (HV_{FC}):

$$HV_{Env} = aHV_{FA} + bHV_{FC}, \quad (2)$$

where a and b are weighting factors.

HV_{Hum} was the sum of hazard values for acute oral toxicity (HV_{OR}), carcinogenicity (HV_{CAR}) and other specific chronic effects (HV_{NC}) to humans:

$$HV_{Hum} = cHV_{OR} + dHV_{CAR} + eHV_{NC}, \quad (3)$$

where c , d and e are weighting factors.

HV_{Exp} was the sum of the hazard values for persistence (HV_{HYD}) and bioaccumulation (HV_{BCF}):

$$HV_{Exp} = fHV_{HYD} + gHV_{BCF}, \quad (4)$$

where f and g are weighting factors.

For the adapted version, frequency-weighted hazard value (wHV_t) was calculated as follows:

$$wHV_t = (HV_{Env} + HV_{Hum}) \times HV_{Exp} \times Frequency, \quad (5)$$

All of the toxicity terms were equally weighted by assigning a hazard value to each, ranging on a scale from 0 to 5. The hazard value for very high or low toxicities was assigned as 5 or 0, respectively, according to the chosen cutoff values for the endpoints [16]. The scoring method was the same as that in CHEMS-1 except wHV_t . Refer to Davis et al. [15] and Swanson et al. [16] for more details on scoring toxicity terms and the calculation of hazard values.

2.5.3 Data selection

2.5.3.1 Human health effects

Experimental data were preferred, and they were obtained from the USEPA ECOTOXicology (ECOTOX, Release 4.0, USA) database and/or the Pesticide Action Network (PAN, version 10.0, USA) database for 14 days acute rodent oral LD50. The most sensitive test result was selected if more than one experimental data point was available. The Toxicity Estimation Software Tools (TEST, version 4.0, USA) was used to estimate LD50 values if experimental data were unavailable. If toxicity data (either experimental or modeled data) were unavailable, HV was set as 0.

International Agency for Research on Cancer (IARC) ratings were used for carcinogenicity rankings. If neither the IARC nor the EPA had grouped the chemical according to its carcinogenicity, the HV value was set as 0. As for other specific effects, cholinesterase inhibition effects, developmental or reproductive effects, and endocrine disruption effects were considered. Experimental data for these specific effects were obtained from the PAN database.

2.5.3.2 Environmental effects

Experimental fish LC50 data were preferred and obtained from the ECOTOX database. TEST was used to estimate the 96-h fathead minnow toxicity data if experimental data were unavailable. As described in Swanson et al. [16], the LC50 data were selected in the following order of preference: 1) *Pimephales promelas* (fathead minnow) in a 96-h flow-through test; 2) 96-h flow-through LC50 data for other freshwater fish (excluding trout); 3) a static 96-h fathead minnow test; 4) a static 96-h test for other freshwater fish (excluding trout); and 5) the 96-h fathead minnow result estimated using TEST.

As described in Swanson et al. [16], the fish NOEL data were estimated from fish LC50 and octanol-water partition coefficient (K_{ow}).

2.5.3.3 Persistence

Hydrolysis half-life ($t_{1/2}$) data were selected to characterize persistence of the contaminants. CHEMFATE (SRC Inc., USA) and BioDEG (SRC Inc., USA) databases were used to search for experimental hydrolysis half-life data. The most conservative value was selected if more than one experimental data were available. Persistent, Bioaccumulative, and Toxic (PBT) profiler data were selected in case of the absence of experimental data.

2.5.3.4 Bioaccumulation

Aquatic bioconcentration factor (BCF) data in CHEMFATE were retrieved as the source of experimental BCF data. The most conservative experimental value was selected if more than one data point for BCF was available. Estimation Program Interface Suite (EPI Suite, version 4.0, USA) from USEPA was used to estimate BCF values if there were no experimental data.

2.5.3.5 Detection frequency

The detection frequency for one particular contaminant was calculated as the ratio of the number of samples detected to the total. The detection frequency was used as the weighting factor in the adapted CHEMS-1 approach.

2.6 Quality assurance/quality control

For qualitative analysis, good recoveries were desired for a broad range of contaminants with varying properties. To validate, the recoveries of contaminants with different $\lg K_{ow}$ were calculated. For 54 contaminants with $\lg K_{ow}$ from 1.44 to 6.75, the recoveries were 60.2%–128.1%. Therefore, this method can satisfy the need for preliminary qualitative screening for a broad range of contaminants with varying properties. For PAH quantification, the contaminant-free ultra-pure water was spiked with PAHs in six duplicates. The recoveries of PAHs were 80.5%–110.6%, with relative standard deviations less than 15%. The method detection limit was 0.01–0.06 $\mu\text{g}\cdot\text{L}^{-1}$. Method blanks were run and no contaminants were found. The recoveries of the surrogate standard (phenanthrene-d10) were 77.1%±8.6%, with a range of 66.3%–89.0%.

2.7 Statistical analysis

Statistical analyses, including the multiple linear regression analysis, Kolmogorov–Smirnov test, statistical significance test, and Pearson correlation test, were performed

by using SPSS software package (version 13.0, SPSS Inc., Chicago, IL, USA). A critical p value (statistical significance level) of 0.05 was used to determine goodness of fit.

3 Results and discussion

3.1 Reliability of the adapted CHEMS-1 method

For a good-ranking algorithm, each individual term should make an equivalent contribution to the final results [16]. Multiple linear regression analysis was run for HV_t versus HV_{Env} , HV_{Hum} , and HV_{Exp} , respectively. To test whether particular terms dominated HV_t , the standardized regression coefficients were calculated. In statistics, the standardized regression coefficient is usually calculated to determine which independent variable has a greater effect on the dependent variable, reflecting the relative importance of each independent variable. The standardized regression coefficients of HV_{Env} , HV_{Hum} , and HV_{Exp} versus HV_t were 0.58, 0.42, and 0.39, respectively, indicating that parameters in the algorithm possess equivalent weights.

Moreover, correlations between each individual parameter value were examined. The correlations were not significant ($p > 0.05$) for most of the test pair parameter values. The strong correlation between fish LC50 and fish NOEL ($r = 0.999$) occurred because fish NOEL was estimated from fish LC50 using quantitative structure-activity relationships. The above analysis showed that the adapted CHEMS-1 approach was proper for ranking the contaminants with potential risks in the source water of the Danjiangkou reservoir.

3.2 Identification and ranking of the potential risky contaminants

3.2.1 Identification

All samples were analyzed using DRS. The AMDIS match values were higher than 60%, and the retention time differences between the expected and observed values were less than 10 s. Moreover, the identification was reverse-matched with the NIST 08 library using the extracted spectrum. The results showed that 46 contaminants in 17 chemical classes were identified in water samples of the Danjiangkou reservoir (Table 2), 23 of which were detected at frequencies higher than 50%. The following contaminants were detected in all the samples: acenaphthene, 2-methylnaphthalene, difenoxuron, benzophenone, naphthalene, terbutol, phenanthrene, fluoranthene, anthracene, biphenyl, *o*-phenylphenol, phenol, and fluorene. Additionally, the following contaminants were detected in almost all the samples: dibenzofuran, 9,10-anthraquinone, chrysene, pyrene, metribuzin, bromo-

propylate, chlorflurecol-methyl ester, *sec*-butylbenzene, triclosan, and diphenylamine. All detected contaminants are listed in Table 2.

3.2.2 Ranking results

The results shown in Table 2 were derived by applying the

Table 2 Ranking results for contaminants from the adapted CHEMS-1 algorithm

CAS No. ^{a)}	contaminant	chemical class	frequency/%	rank	
				weighted by frequency	not weighted by frequency
218-01-9	chrysene	PAH	80	1 (100) ^{b)}	2 (96)
91-20-3	naphthalene	PAH	100	2 (99)	6 (76)
1918-11-2	terbutol	carbamate	100	3 (92)	7 (70)
85-01-8	phenanthrene	PAH	100	4 (91)	8 (70)
206-44-0	fluoranthene	PAH	100	5 (86)	11 (66)
120-12-7	anthracene	PAH	100	6 (85)	12 (65)
83-32-9	acenaphthene	PAH	100	7 (75)	20 (57)
92-52-4	biphenyl	biphenyl	100	8 (70)	22 (53)
90-43-7	<i>o</i> -phenylphenol	phenol	100	9 (67)	23 (51)
129-00-0	pyrene	PAH	80	10 (66)	15 (63)
132-64-9	dibenzofuran	furan	80	11 (62)	18 (59)
3380-34-5	triclosan	chlorinated phenol	60	12 (60)	5 (77)
108-95-2	phenol	phenol	100	13 (52)	33 (40)
18181-80-1	bromopropylate	benzilate	60	14 (50)	16 (63)
91-57-6	2-methylnaphthalene	PAH	100	15 (48)	35 (37)
21087-64-9	metribuzin	triazine	80	16 (45)	29 (43)
56-55-3	benzo[a]anthracene	PAH	40	17 (43)	3 (82)
14214-32-5	difenoxuron	urea	100	18 (42)	38 (32)
119-61-9	benzophenone	ketone	100	19 (39)	40 (30)
84-65-1	9,10-anthraquinone	quinone	80	20 (38)	36 (37)
2536-31-4	chlorflurecol methyl ester	PAH, ester	60	21 (34)	28 (43)
135-98-8	<i>sec</i> -butylbenzene	substitute benzene	60	22 (32)	31 (41)
122-39-4	diphenylamine	amine, biphenyl	60	23 (32)	32 (41)
2463-84-5	dicapthon	organophosphorus	40	24 (31)	17 (59)
52-85-7	famphur	organophosphorus	40	25 (30)	19 (58)
50-32-8	benzo[a]pyrene	PAH	40	26 (29)	21 (56)
86-73-7	fluorene	PAH	100	27 (28)	41 (21)
205-99-2	benzo[b]fluoranthene	PAH	20	28 (26)	1 (100)
119-90-4	<i>o</i> -dianisidine	biphenyl	40	29 (22)	30 (43)
101-05-3	anilazine	triazine	20	30 (21)	4 (79)
1420-06-0	trifenmorph	morpholine	20	31 (18)	9 (70)
2597-03-7	phenthoate	organophosphorus	20	32 (18)	10 (67)
207-08-9	benzo[k]fluoranthene	PAH	20	33 (17)	13 (64)
92-67-1	4-aminobiphenyl	biphenyl	20	34 (17)	14 (63)
1912-24-9	atrazine	triazine	20	35 (13)	24 (51)
208-96-8	acenaphthylene	PAH	20	36 (13)	25 (48)
57-97-6	7,12-dimethylbenz[a]anthracene	PAH	20	37 (12)	26 (45)
541-73-1	1,3-dichlorobenzene	substitute benzene	20	38 (12)	27 (44)
105-67-9	2,4-dimethylphenol	phenol	20	39 (10)	34 (38)
626-43-7	3,5-dichloroaniline	amine	20	40 (9)	37 (34)

(Continued)

CAS No. ^{a)}	contaminant	chemical class	frequency/%	rank	
				weighted by frequency	not weighted by frequency
26259-45-0	secbumeton	triazine	20	41 (8)	39 (31)
134-62-3	<i>N,N</i> -diethyl- <i>m</i> -toluamide	benzamide	40	42 (7)	43 (14)
58-08-2	caffeine	botanical	40	43 (6)	46 (11)
78-59-1	isophorone	ketone	20	44 (4)	42 (17)
78-40-0	triethyl phosphate	organophosphorus	20	45 (3)	44 (13)
98-86-2	acetophenone	ketone	20	46 (3)	45 (12)

Notes: a) CAS No, chemical abstract service registration number; b) Number in parentheses is the total hazard value for one particular chemical, normalized to a 0–100 scale

adapted CHEMS-1 algorithm to the contaminants identified in water samples of the Danjiangkou reservoir. Both the HV_t and wHV_t values were calculated according to Eqs. (1)–(5) and normalized to a 0–100 scale.

A Kolmogorov-Smirnov test of the HV_t scores revealed a Gaussian distribution with a mean of 50.7 and a standard deviation of 21.5. The same distribution was found for wHV_t scores with a mean of 38.4 and a standard deviation of 28.6. These findings indicated that the adapted CHEMS-1 algorithm performed well at differentiating contaminants according to their environmental exposure and harmfulness to human health and the environment [21].

The ranking of contaminants based on the frequency-weighted and unweighted results are presented in Table 2. The top 15 ranked contaminants from the unweighted results were mainly from seven classes of chemicals: PAHs, triazine, chlorinated phenol, carbamate, morpholine, organophosphorus, and biphenyl. Nine of the top 15 ranked contaminants were PAHs.

However, the frequency weighted results were different from the unweighted results. This difference was because unweighted results were obtained according to the PBT properties, which are inherent chemical properties of contaminants. Chrysene, naphthalene, terbutol, phenanthrene, fluoranthene, anthracene, pyrene, and triclosan were ranked high among the top 15 contaminants from both the weighted and unweighted results due to their inherent hazardous properties and high detection frequencies. Moreover, benzo[a]anthracene, benzo[b]fluoranthene, anilazine, trifenmorph, phenothate, benzo[k]fluoranthene, and 4-aminobiphenyl were ranked high in the unweighted results but low in the frequency-weighted results because of the low frequency of detection. Furthermore, acenaphthene, biphenyl, *o*-phenylphenol, dibenzofuran, phenol, bromopropylate, and 2-methylnaphthalene were less toxic but ranked high when weighted by frequency because of the high frequency of detection in the source water.

The top-ranked chemicals should receive more attention in source water management and further studies. However, it should be noted that the ranking results do not reflect the actual estimates of hazards or risks. This approach offers a

relative assessment of risk and identifies contaminants that show the greatest risks and should be of the most concern.

3.2.3 Uncertainty of ranking results

A good ranking method should not only identify contaminants that pose risks, but also should promote relative studies to reduce uncertainties associated with data gaps [22]. Uncertainty analysis associated with data gaps allows researchers to decide on future studies (e.g., toxicity tests, improvement of analytical methods, monitoring on a larger scale, etc.). A rough estimation was conducted for the uncertainty associated with data gaps. Briefly, for each endpoint, a value of 0 was assigned if experimental data were used to calculate the hazard scores. The uncertainty score was set at 3 if modeled data were employed and at 5 if neither experimental nor modeled data were available. The uncertainty value for each endpoint was summed to determine the total uncertainty value (UN_t). Figure 2 shows the uncertainty scores versus hazard values of the identified contaminants. Contaminants possessing high hazard values (bottom right of Fig. 2) should be listed as

Fig. 2 Uncertainty scores versus hazard values of contaminants. Refer to Table 2 for compound number in the figure, which is the ranking order according to unweighted results

priority pollutants of concern. Moreover, those contaminants that had higher uncertainty scores (top left of Fig. 2) should be focused on in future research to confirm whether these contaminants pose risks or not.

The total uncertainty was associated with data gaps of endpoints characterizing exposure potential (persistence and bioaccumulation), environmental effects (acute and chronic fish toxicities), and human health effects (acute rodent toxicity, carcinogenicity, and other specific effects). The contribution to uncertainty of different parameters for selected contaminants (with normalized uncertainty scores higher than 55) are diagrammed in Fig. 3. The contribution was equal for the three parameters for most contaminants. There is a need to strengthen studies of both hazard assessment and exposure assessment in the future to fill data gaps.

3.3 Priority pollutants

The 15 top-ranked contaminants from frequency-weighted results should be placed under risk control measures for the Danjiangkou reservoir. Among the 15 priority pollutants, only PAHs were regulated by Chinese Standards for Drinking Water [6]. No standards for the remaining priority pollutants have been established to date. More than 50% of the 15 priority pollutants are regulated by the USEPA Drinking Water Advisory, however, the standards need to be revised for use in China because of the differing consumption habits between populations [23].

PAHs are of concern because of their potentially toxic,

carcinogenic, and mutagenic effects on animals and humans [24]. They were usually related to sources such as vehicle exhaust, urban sewage, or chemical-, coke- and oil-shale industries [25]. To date, only a few studies have reported the PAH contamination in the Danjiangkou reservoir [26,27].

Phenols comprise a large group of organic contaminants in aquatic environments due to their high water solubility, strong reactivity, and poor biodegradation [28]. Three phenols were ranked high in this study: phenol, *o*-phenylphenol, and triclosan. Phenol is an important raw material in the production of pesticides, dyes, and paper. Exposure to phenol and its vapors may cause harm to the eyes, skin and respiratory tract [29]. *o*-phenylphenol is used as a fungicide, germicide, household disinfectant, and laboratory reagent. Triclosan is an antibacterial and antifungal agent used in many personal care products. Existing evidence has shown that triclosan acts as an endocrine disruptor in the environment [30,31]. Moreover, triclosan can combine with chlorine to form chloroform [32], which poses a risk of cancer.

Three pesticides, terbutol, dibenzofuran and bromopropylate, were ranked high in water from the Danjiangkou reservoir. Terbutol is used as an insecticide and an herbicide on turf grass. Reports have suggested that terbutol is cytotoxic, and the mitochondrial respiratory system and protein thiols were important targets of this pesticide [33]. Dibenzofuran, a heterocyclic organic compound, is used as an insecticide and in industrial bleaching and incineration by various industries. Accord-

Fig. 3 Contribution to uncertainty of different parameters for selected contaminants

ing to Mizukami [34], dibenzofuran is as toxic as dioxins. Bromopropylate is one of the most common acaricides used in agriculture.

Biphenyl is used extensively in medicines, dyes, and pesticides. According to the European Union (EU) classification, biphenyl is dangerous to the environment, and it is on the EU list of suspect of endocrine disruptors [35].

The Danjiangkou reservoir is subject to strict environmental management, so the identified contaminants did not enter from direct pollution by local sources. Possible routes of pollution include the migration and transport of contaminants from the upper reaches of Hanjiang and Danjiang Rivers. Shiyan, which is located in the upper reaches of the Hanjiang River, may be the main source of PAHs due to the heavy automobile industry in this region. Moreover, domestic sewage and industrial wastewater from the upper reaches of the Danjiang River may be a possible source of phenols [36]. Three pesticides (terbutol, dibenzofuran and bromopropylate) likely enter the system via agricultural non-point sources in the upper reaches of the Danjiangkou watershed [36,37]. Although there were trace amounts of pollution in the upper reaches of the Danjiangkou watershed, the water in the reservoir had good quality [38].

In conclusion, 53% of the top-ranked contaminants were PAHs, with chrysene ranked first. Of the priority pollutants, only PAHs were regulated according to their total amount or the amount of benzo[a]pyrene (BaP) in China. The pollution may be attributed to exogenous sources. Efforts are needed to derive environmental standards for these contaminants to adequately assess their risks. Additionally, data concerning the concentration, fate and behavior of contaminants in the Danjiangkou reservoir that pose risks are urgently needed. More detailed assessments should be conducted on these top-ranked

contaminants to confirm whether they pose risks to human health and the environment.

3.4 Health risk assessment of PAHs

According to the results and discussion above, PAHs were highly ranked when compared with other pollutants. Quantitative analysis was conducted to further confirm the risk of PAHs to humans. Concentrations of detected PAHs are listed in Table 3. PAH concentrations ranged from 7.36 to 179.9 ng·L⁻¹. Due to the similar mode of action of PAHs, the toxicity of PAH mixtures was calculated as the toxicity equivalent quantity based on BaP (TEQ_{BaP}), which was the sum of all individual PAH concentrations multiplied by their specific toxicity equivalence factors to BaP [39]. The TEQ_{BaP} was 4.05 ng·L⁻¹ on average, which is lower than the drinking water standard of 10 ng·L⁻¹ for BaP.

The incremental life cancer risk ($ILCR$) for PAHs was calculated according to the USEPA guidelines [40]:

$$ILCR = \frac{TEQ_{BaP} \times DR \times CSF \times EF \times ED}{BW \times AT \times 10^6}, \quad (6)$$

where DR is the daily intake of water (L·d⁻¹), CSF is the cancer slope factor for BaP (kg·d·mg⁻¹), EF is the exposure frequency per year (d), ED is the exposure duration (years), BW is the bodyweight of the exposed person (kg), and AT is life expectancy of the exposed person (d).

A consumption habit model for people in Beijing was employed in this study, since water from the Danjiangkou reservoir will be transferred to Beijing in the near future. The cancer risk of PAHs to people in young (< 20 years old), middle-aged (20–64 years old) and elderly (> 64 years old) age groups, was calculated according to different consumption habits using Eq. (6). Different

Table 3 Quantitative results of PAHs ($n = 5$; ng·L⁻¹)

contaminant	TR	range	average
naphthalene	Y	14.5–124.8	84.1
acenaphthene	Y	–	–
phenanthrene	Y	121.4–316.7	179.9
anthracene	Y	ND–15.84	7.36
fluoranthene	Y	16.8–20.3	19.5
pyrene	Y	7.48–60.1	22.2
chrysene	Y	ND–118.5	52.7
acenaphthylene		–	–
fluorene		13.1–33.8	20.4
benzo[a]anthracene		80.0–81.6	80.8
benzo[a]pyrene		–	–
benzo[b]fluoranthene		–	–
benzo[k]fluoranthene		–	–

Notes: TR, top ranked contaminants; Y, yes; ND, not detected; –, not quantified

Table 4 Parameters and incremental life cancer risk for people of different age groups and genders in summer and winter.

season	age group	gender	DR	CSF	EF	ED	BW ^{a)}	AT	ILCR/($\times 10^{-6}$)
summer	young (< 20 years old)	male	1.5			15	49.4		0.3
		female	1.0			15	46.2		0.2
	middle-aged (20–64 years old)	male	1.9	10	365	40	64.1	25550	0.7
		female	1.8			40	55.9		0.8
	elderly (> 64 years old)	male	1.8			70	58.0		1.3
		female	1.7			70	49.6		1.4
winter	young (< 20 years old)	male	1.5			15	49.4		0.3
		female	1.6			15	46.2		0.3
	middle-aged (20–64 years old)	male	2.5	10	365	40	64.1	25550	0.9
		female	2.1			40	55.9		0.9
	elderly (> 64 years old)	male	3.1			70	58.0		2.2
		female	3.2			70	49.6		2.6

Notes: a) Data of bodyweight were obtained from China Health Statistics Annuals [42]

consumption habits due to differing seasons and genders were included in this analysis. The parameters used for the calculation were retrieved from our previous studies [23,41] and listed in Table 4.

As shown in Table 4, the risk in winter was higher than that in summer. This was because more water was consumed in during winter, likely as a result of the dry and cold condition in Beijing during this time. The risk to the elderly age group was higher than that to the young and middle-aged groups due to the longer exposure duration and larger volume of water consumed by elderly people. Cancer risks associated with PAHs detected in the source water of Danjiangkou ranged from 10^{-7} to 10^{-6} , which were lower than the accepted value of 10^{-5} [43]. The cancer risks associated with PAHs in water from the Danjiangkou reservoir were comparable to those in the Luanhe River [44], and much lower than those in Jiangsu Reach of the Huaihe River [45] and Lanzhou Reach of the Yellow River [46]. Wu et al. reviewed the existing data for PAHs in the source water and drinking water of China and evaluated the health risks [47]. They found that the cancer risks of PAHs in the Danjiangkou reservoir were lower than those in most regions of China. Overall, consuming water from the Danjiangkou reservoir likely poses a low cancer risk.

4 Conclusions

In this study, we introduced an adapted version of the CHEMS-1 approach that integrated deconvolution technologies to identify and rank contaminants in the source water of the Danjiangkou reservoir. Reliability of the adapted CHEMS-1 approach was validated. The adapted CHEMS-1 approach was shown to be useful for site-specific screening of organic contaminants to identify and rank potential priority pollutants. The deconvolution

results showed that 46 contaminants from 1093 targets were present in the Danjiangkou reservoir, and 23 contaminants were detected at frequencies higher than 50%. The application of the adapted CHEMS-1 approach identified 15 contaminants as priorities. Over one half (53%) of the top 15 ranked contaminants were PAHs, with chrysene ranked first. The results from the health risk assessment for top-ranked PAHs revealed that cancer risks of the detected PAHs in the source water of Danjiangkou to different populations ranged from 10^{-7} to 10^{-6} , indicating a low cancer risk to consumers.

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