

Detection of semi-volatile organic compounds (SVOCs) in surface water, soil, and groundwater in a chemical industrial park in Eastern China

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ABSTRACT

China is suffering from serious water and soil pollution, especially in the North China Plain. This work investigated semi-volatile organic compounds (SVOCs) in surface water, groundwater and soil within a chemical industrial park in Eastern China, for which the volatile organic compound (VOC) results have been previously reported. A total of 20 samples were collected from the field, and analyzed in the laboratory. A 100% detection frequency of SVOCs in samples from this chemical industrial park was observed (same as VOCs). Moreover, the detection frequency of 113 SVOCs in each sample reached 15.93, 12.39 and 20.35% for surface water, groundwater and soil, respectively. The most detected SVOCs in the park included N-containing SVOCs, polycyclic aromatic hydrocarbons, phthalates, organic pesticides and polychlorodiphenyls. The elevated detecting frequencies and concentration levels of SVOCs identified in the groundwater were attributed to the intensive chemical production activities in the park. In addition, the agricultural activities in the area might also have contributed to the SVOCs to the groundwater. The results of VOCs and SVOCs from this and previous studies suggest that the groundwater in this industrial park has been severely contaminated, and the contamination likely spreads beyond the park. Imminent hydrogeological assessments and remedial actions are warranted to eliminate the source and mitigate the potential plume expansion beyond the park boundary.

Key words | groundwater, semi-volatile organic compounds, soil, surface water, volatile organic compounds

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INTRODUCTION

The North China Plain accounts for approximately 12% of China's gross domestic product and more than 10% of China's total grain production (Zheng *et al.* 2010). Approximately 78% of the Northern China plains rely on groundwater (Zhang *et al.* 2010a). However, surface and groundwater quality has been deteriorating in China, particularly in the northern and eastern areas. It was estimated that 90% of the groundwater in China has been contaminated and 60% seriously contaminated (Qiu 2010). Higher population density and heavy industrial activity are the dominant culprits (Foster *et al.* 2004; Zhang *et al.* 2008; Hu *et al.* 2010a). The '2014 Report on the state of the Environment in China' reported that China is also suffering from serious soil pollution (China Environmental Protection Ministry 2015).

To understand the groundwater situation in China, the first groundwater survey was conducted in the eastern plains of China in 2009 (Wen *et al.* 2012; Zhang *et al.* 2012). In this survey, major pollutants were found to be nitrogen (nitrate, nitrite and ammonia), toxic metals (arsenic, cadmium and lead) and organic chemicals (benzo[*a*]pyrene, benzene, total hexachlorocyclohexane (HCHs), carbon tetrachloride, total dichlorodiphenyltrichloroethane (DDTs), dichloromethane, 1,2-dichloropropane, hexachlorobenzene, 1,2-dichloroethane and chloroform). In further studies, Bi *et al.* (2012) investigated volatile organic compound (VOC) pollution in 130 shallow groundwater wells in East China; 36 of the 54 VOCs investigated were detected in the groundwater samples. Chen *et al.* (2014) conducted a survey of semi-volatile organic compounds (SVOCs) in Eastern Hai

River Plain, Yangtze River Delta, and Yunnan-Guizhou Plateau; 70 of the 103 SVOCs were found in the groundwater samples. Data indicate that industrial activities, especially the chemical industry, is likely one of the main sources of groundwater pollution in China (Wen *et al.* 2012; Zhang *et al.* 2012). In this study, a chemical industrial park was selected to determine the presence and distribution of VOCs and SVOCs in both surface water and groundwater in Eastern China. The distribution of VOCs in the surface water, groundwater and soil were previously reported by Liu *et al.* (2014). At least one VOC was detected in each of the 20 sampling locations, and the maximum number of VOCs detected in the surface water, groundwater, and soil were 13, 16, and 14, respectively. Two of the 10 VOCs with elevated concentrations detected in surface water, groundwater, and soil were chloroform and 1,2-dichloroethane. The characteristics of VOCs such as volatility, boiling point, and solubility could significantly affect their distribution in surface water, soil, and groundwater. For example, higher volatility of VOCs in the surface water does not necessarily result in elevated concentrations of VOCs in soil and groundwater.

This work focused on SVOCs, as a follow-up study to complement the VOC survey by Liu *et al.* (2014). The combined VOC and SVOC data were expected to establish a benchmark of contamination at this chemical industrial park, which is representative of numerous similar industrial areas in Eastern China. The results were also to be used in additional assessments and remedial actions to restore the environmental quality in the area.

EXPERIMENTAL DESIGN

Sampling

A total of 20 samples were collected from the chemical industrial park (Figure 1). Surface water samples were obtained from the outlets of an industrial wastewater treatment plant and a sewage ditch; groundwater samples were collected from irrigation wells at various depths across the site; and soil samples were collected at the surface water sampling locations. Description of sampling locations is included in Table 1. The surface water, groundwater and soil samples were collected by Jinan University (Jinan, China) by following standard sampling procedures (China Geological Survey 2008). Surface water and groundwater samples were collected in 1-L amber glass bottles fitted with polytetrafluoroethylene-lined screw cap closures, and shipped on ice within 24 h to the China University of Geoscience (Beijing) Laboratory. Soil samples of 1 kg were collected by foil encasement, sealed in bags and refrigerated at 4 °C before being processed.

Extraction methods

Extraction methods used for water and soil samples are presented in Table 2.

Water samples

The water samples were processed for SVOC analysis by following the US EPA method 3510. Hexane was used as the

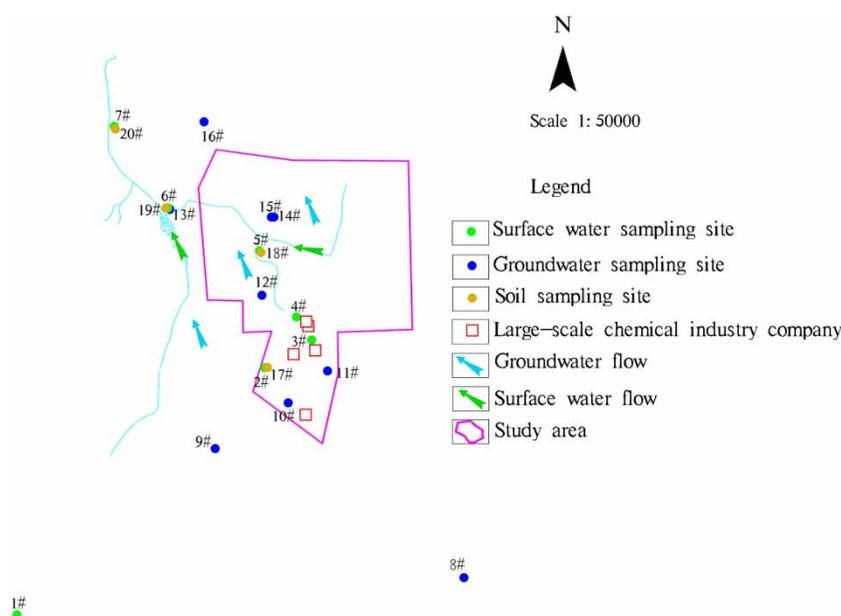


Figure 1 | Map of the chemical industrial park and sampling locations (Liu *et al.* 2014).

Table 1 | Brief description of sampling locations

ID	Sample type	Site	Well information
1#	Surface water	Upstream (reservoir)	\
2#	Surface water	Midstream (sewage ditch)	\
3#	Surface water	Outlet of industrial wastewater treatment plant	\
4#	Surface water	Midstream (sewage ditch)	\
5#	Surface water	Midstream (sewage ditch)	\
6#	Surface water	Downstream (sewage river)	\
7#	Surface water	Downstream (sewage river)	\
8#	Groundwater	Upstream	\
9#	Groundwater	Upstream	Depth 10 m
10#	Groundwater	Midstream	Depth 70 m
11#	Groundwater	Midstream	Depth 60 m
12#	Groundwater	Midstream	Depth 30 m
13#	Groundwater	Downstream	Depth 7–8 m
14#	Groundwater	Downstream	Depth 30 m
15#	Groundwater	Downstream	Depth 100 m
16#	Groundwater	Downstream	Depth 150 m
17#	Soil	Same site as 2#	\
18#	Soil	Same site as 5#	\
19#	Soil	Same site as 6#	\
20#	Soil	Same site as 7#	\

Table 2 | Extraction methods

Sample type	Reference method	Sample Volume	Extractant	Extractant volume
Water	US EPA method 3510	1 L	hexane	20 mL each time, and total 9 times under different pH conditions
Soil	US EPA methods 3500C, 3540, 3550C and 3600C	20 g	dichloromethane and hexane (V:V = 1:1)	30 mL each time, and total 3 times

extractant. The water sample (1 L) was transferred into a separating funnel after adding 30 g NaCl. Afterwards, 10 μ L of combined surrogate mixed standard CSS8250-1RPM (diluted

50 \times in acetone) was added. The CSS8250-1RPM surrogate standard, containing 2-fluorobiphenyl, nitrobenzene-d₅, *p*-terphenyl-d₁₄, 2-fluorophenol, phenol-d₆ and 2,4,6-tribromophenol, was purchased from ChemService (West Chester, PA, USA). Also added was 10 μ L of surrogate mixed standard 130023-08 (diluted 20 \times in acetone). The 130023-08 surrogate standards mixture contained decachlorobiphenyl and 2,4,5,6-tetrachloro-*m*-xylene, and was purchased from o2si smart solutions (Charleston, SC, USA). Each sample was extracted three times under unadjusted pH (\sim 7.0–7.5), pH < 2.0 (adjusted by using 18 mol/L of H₂SO₄), and pH > 10.0 (adjusted by using 10 mol/L of NaOH). For each extraction procedure, a vertical liquid–liquid extraction oscillator (Yamato Scientific Corporation, Shanghai) was used. The mixture solution was shaken for 10 minutes and settled for 10 minutes before going through the separation funnel. A total of 180 mL of hexane extractant was collected from the extraction process and purged to < 1 mL by an automatic nitrogen evaporator XT-NS1 (Shanghai Xintuo Analytical Instruments Co., Ltd, Shanghai, P.R. China). An internal standards mixture of 10 μ L (diluted 100 \times in methylene chloride) was added to the final sample. The internal standards mixture 110001-02-10PAK (including acenaphthene-d₁₀, chrysene-d₁₂, 1,4-dichlorobenzene-d₄, naphthalene-d₈, perylene-d₁₂ and phenanthrene-d₁₀) was purchased from o2si smart solutions (Charleston, SC, USA). Finally, fresh hexane was used to replenish the sample volume to 1.00 mL for analysis.

Soil samples

The soil samples were processed for SVOC analysis by following the US EPA methods 3500C, 3540, 3550C and 3600C. Soil was dried in the shade, ground, and screened by a 20-mesh sieve. Then 20 g soil was added into a 40 mL volatile organic agent bottle with 2 g Na₂SO₄ and 30 mL dichloromethane and hexane (V:V = 1:1), and 10 μ L of combined surrogate standards mixture CSS8250-1RPM (diluted 50 \times in hexane) and surrogate standards mixture 130023-08 (diluted 20 \times in methylene chloride) was added. Bottles were then shaken and ultrasonically extracted for 15 min in a KH-500E ultrasonic instrument (Kunshan Hechuangzao Ultrasonic Instrument Co., Ltd, Jiangsu, P.R. China), and centrifuged for 10 min at 1,500 rpm in an LD5-10B centrifuge (Beijing Leiboer Centrifuge Instrument Co., Ltd, Beijing, P.R. China) to collect the upper liquid. This extraction process was repeated three times, and a total of 90 mL upper liquid was collected and the solvent of this liquid was transferred to hexane in the automatic nitrogen evaporator XT-NS1. Finally, the liquid was purged to

<1 mL and the internal standards mixture PP-HC8RPM mixture of 10 µL (diluted 100× in hexane) was added, and fresh hexane was used to replenish the sample volume to 1.00 mL for analysis.

Analytical methods

As listed in Tables S1-1, S1-2, S1-3, S1-4, S1-5, and S1-6 in the Supporting Information (available with the online version of this paper), 113 SVOCs were selected as target analytes based on historic data as well as lists from the National Water-Quality Assessment by the US Geological Survey (Kolpin et al. 1998). The analytical methods are presented in Table 3. The standard solutions for the target SVOCs (including phthalates (phthalic acid esters, PAEs)), organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) were purchased from o2si smart solutions (Charleston, SC, USA).

Autosampler–gas chromatography–mass spectrometry (ALS-GC-MS) was used to analyze non-OCP SVOCs and PAEs (Agilent 7683B autosampler; Agilent 6890 gas chromatograph with HP-5MS capillary column 30 m × 0.25 mm ID × 0.25 µm; Agilent 5975 MS, Santa Clara, CA, USA). The GC temperature program was as follows: initial temperature 60 °C, holding for 5 min; increasing the temperature to 255 °C at a rate of 15 °C/min; to 300 °C at a rate of 5 °C/min and holding for 3.0 min. Helium (99.999%) was used as the carrier gas and the flow rate was set as 1.00 mL/min. The injector temperature was 270 °C with the splitless mode selected. Parameters of MS were set as follows: electron ionization source 70 eV, ion source temperature 230 °C, quadrupole rods temperature 150 °C, interface temperature 235 °C, selected ions monitoring (SIM) and scan

mode, and solvent delay 6 min. In order to obtain lower method detection limits (MDLs) of interest, three SIM methods were conducted for data acquisition. The MDLs of (i) acids mixture 8270 (17 components), (ii) base neutrals extractables mixture 8270 (30 components), (iii) acids mixture CLP-8270, semi-volatiles supplement mixture 8270B and organophosphorus pesticides mixture 8270 (36 components), and (iv) PAEs (6 components) in water and soil were in a range of 0.01–0.03 µg/L and 5–15 µg/kg, 0.01–0.2 µg/L and 5–100 µg/kg, 0.01 to 1.0 µg/L and 5–500 µg/kg, and 0.001–0.004 µg/L and 5–20 µg/kg, respectively (see Tables S1-1, S1-2, S1-3, S1-4, Supporting Information).

The same autosampler–gas chromatograph with an electron capture detector (ALS-GC-ECD) was used to detect OCPs. The GC temperature program was as follows: initial temperature 80 °C, holding for 2 min; increasing the temperature to 185 °C at a rate of 30 °C/min; to 215 °C at a rate of 3 °C/min; to 225 °C at a rate of 1 °C/min, holding for 2.0 min; to 290 °C at a rate of 20 °C/min, and holding for 10.0 min. Nitrogen (99.999%) was used as carrier gas and the flow rate was set as 1.00 mL/min. The injector temperature was 250 °C with the splitless mode selected. The temperature of ECD was set at 320 °C. The MDLs of (v) 16 OCPs in water and soil were in a range of 0.0009–0.0022 µg/L and 0.4–6.0 µg/kg (see Table S1-5, Supporting Information).

The same ALS-GC-ECD was used to detect PCBs. The GC temperature program was as follows: initial temperature 60 °C, holding for 2 min; increasing the temperature to 100 °C at a rate of 30 °C/min; to 240 °C at a rate of 15 °C/min, holding for 2 min; to 280 °C at a rate of 3 °C/min, holding for 2.0 min. Nitrogen (99.999%) was used as carrier gas and the flow rate was set as 1.00 mL/min. The injector temperature was 250 °C with the splitless mode selected. The temperature of ECD was set at 250 °C. The MDLs of (vi) eight PCBs in the water and soil were in a range of 0.0005–0.0012 µg/L and 0.3–2.6 µg/kg (see Table S1-6, Supporting Information).

Table 3 | Brief description of analytical methods

Analysis index	Reference method	Number of chemicals	Analysis instrument
Organochlorine pesticides/OCPs	US EPA method 8081A	16	ALS-GC-ECD
Polychlorinated biphenyls	US EPA method 8082A	8	ALS-GC-ECD
Other non-OCP SVOCs	US EPA method 8270D	83	ALS-GC-MS
Phthalic acid esters	US EPA method 8270D	6	ALS-GC-MS

Quality assurance and quality control

Quality assurance (QA) and quality control (QC) measures in field sampling and laboratory analyses were implemented. QA/QC controls in the laboratory analyses followed the EPA method 8270D and 8000B, in which the recovery of surrogates was kept in a range from 70 to 130%. Meanwhile, one laboratory reagent blank, one field reagent blank, one laboratory duplicate, one laboratory spiked blank, and one laboratory spiked sample matrix were included. Recovery range of all laboratory spiked blanks and the laboratory

spiked sample matrixes was 80 to 123%. The relative deviation of the laboratory duplicates was <40%. The concentrations of target compounds in all of the laboratory and field reagent blanks were less than respective MDLs. In this survey, the blanks and the recoveries of surrogates and spiked samples with target compounds were in the satisfactory range.

RESULTS AND DISCUSSION

Presence of SVOCs in surface water, groundwater and soil

Compared to the results of VOCs from this chemical industrial park (Liu *et al.* 2014), significantly different patterns of SVOCs were observed. The maximum number of the 113 SVOCs detected (>MDLs) in surface water, groundwater and soil was 18, 14 and 23, respectively (Figure 2), whereas that of VOCs was 13, 16 and 14, respectively (Liu *et al.* 2014). More SVOCs were detected in surface water and soil probably due to their lower volatility, and the number of SVOCs detected (>MDLs) in soil was about two folds higher than that of VOCs because of their lower solubility and higher adsorption by soil.

The 10 SVOCs in the samples of surface water, groundwater and soil detected at elevated concentrations are summarized in Table 4, and the highest concentrations were 1.1 µg/L, 5.0 µg/L and 1,560 µg/kg, respectively. The SVOC concentrations were the highest in soil samples followed by groundwater, and then surface water samples,

which is different from the VOC data (higher concentrations in surface water, followed by groundwater and soil samples, Liu *et al.* (2014)). The relatively lower volatility and solubility and higher density of SVOCs may be responsible for their relatively higher concentrations detected in soil than in surface water and groundwater. The 10 most frequently detected SVOC compounds are summarized in Table 5, and the detection frequency of three PCBs (PCB 1, PCB 47, PCB 100) in surface water and groundwater was 100%. The detection frequency of anthracene and bis[2-ethylhexyl]phthalate in soil also reached 100%.

Relationship analysis of SVOCs in surface water, groundwater and soil

N-containing SVOCs

N-containing SVOCs, including nitrobenzene and aniline, are the main products of this chemical industry park. As shown in Figure 3, nitrobenzene, 2,4-dinitrotoluene, 2,6-dinitrotoluene, 4-chloroaniline, 2-nitroaniline and *N*-nitrosodi-*n*-butylamine were detected with a higher detection frequency in water samples. The concentration of N-containing SVOCs in surface water, groundwater and soil were 0.02–0.97 µg/L, 0.03–0.34 µg/L, and 22.4–97.8 µg/kg, respectively.

During the production of N-containing organic chemicals, N-containing SVOCs as the raw materials, products

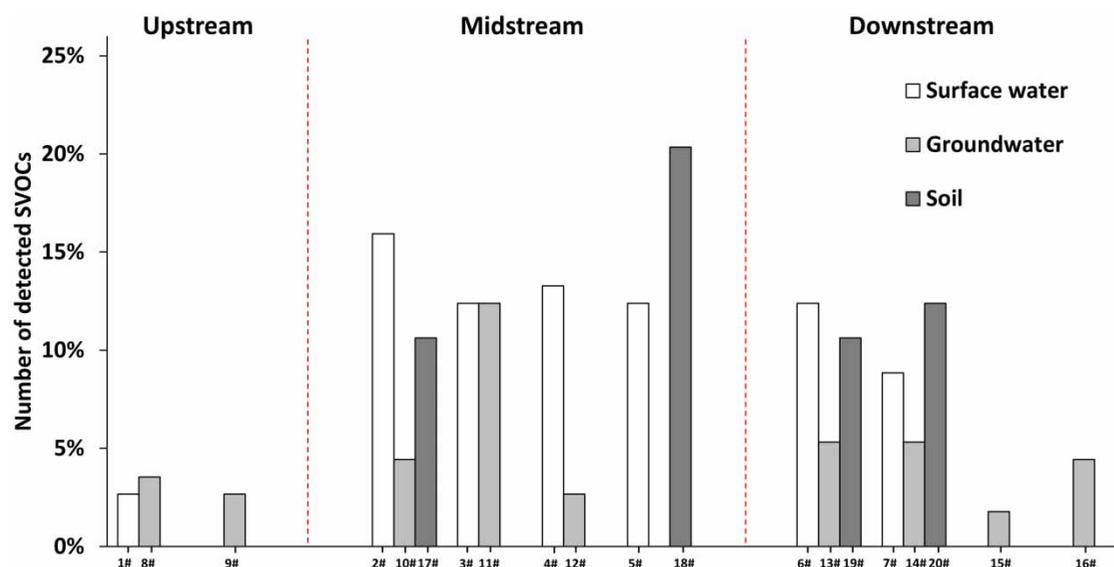


Figure 2 | SVOCs detected (>MDLs) in the chemical industrial park.

Table 4 | Ten SVOCs detected at elevated concentrations in the chemical industrial park

Surface water		Groundwater		Soil	
Contaminants	Concentration (µg/L)	Contaminants	Concentration (µg/L)	Contaminants	Concentration (µg/kg)
2-Nitrophenol	1.1	DBP	5.0	Bis[2-ethylhexyl] phthalate	1,560
Nitrobenzene	1.0	<i>O,o,o</i> -Triethylphosphorothioate	1.2	Fluoranthene	300
PCB 1	0.9	<i>N</i> -Nitrosodi- <i>n</i> -butylamine	1.0	Anthracene	288
Acenaphthylene	0.9	Total benzenehexachloride	0.9	Pyrene	266
<i>N</i> -Nitrosodi- <i>n</i> -butylamine	0.8	β -Hexachlorocyclohexane	0.7	Phenanthrene	251
PCB 47	0.6	Bis[2-chloroethoxy]methane	0.4	PCB 154	247
Isophorone	0.4	Aniline	0.4	Benzo[<i>a</i>]anthracene	110
Bis[2-ethylhexyl] phthalate	0.3	2-Nitroaniline	0.3	Benzo[<i>b</i>]fluoranthene	106
DBP	0.3	PCB 29	0.3	BBP	99
2,4-Dinitrotoluene	0.2	2,6-Dichlorophenol	0.3	<i>N</i> -Nitrosodi- <i>n</i> -butylamine	98
PCB 29	0.2	Bis[2-ethylhexyl]phthalate	0.3	/	/
2,4,6-Trichlorophenol	0.2	Bis[2-chloroethoxy]methane	0.3	/	/
2,4,5-Trichlorophenol	0.2	/	/	/	/
Total benzenehexachloride	0.2	/	/	/	/

or by-products could enter into the water and soil through leaking, discharge, and rainfall runoff. Thanks to the fast natural degradation rate of these N-containing SVOCs (Zhang *et al.* 2010b; Han *et al.* 2011; Yang *et al.* 2015), the concentration of these pollutants appeared to decrease downstream from the park.

PAHs

The US EPA considers certain polycyclic aromatic hydrocarbons (PAHs), including benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*c,d*]pyrene and dibenzo[*a,h*]anthracene, as potentially carcinogenic PAHs (US EPA 1993). A total of 15 PAHs were detected in this investigation, including acenaphthylene, acenaphthene, fluorine, phenanthrene, anthracene, fluoranthene, pyrene, benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, indeno[1,2,3-*c,d*]pyrene, dibenzo[*a,h*]anthracene, and benzo[*g,h,i*]perylene. The concentrations of the PAHs were aggregated to evaluate the distribution of PAHs in the water and soil (Figure 4). A total of 14 PAHs were detected

in the soil samples, with the total PAHs concentration between 15.9 and 1,675.5 µg/kg. Acenaphthylene and chrysene were detected in the surface water samples, and no PAHs were detected in the groundwater samples.

The PAHs in the chemistry industrial park might come from coal combustion from a coal-fired power plant located onsite. The ratios of individual PAHs in soil were used to distinguish PAHs from pyrogenic (e.g., coal/biomass combustion) and petroleum (e.g., oil spill and petroleum products) inputs. Three specific PAH ratios were calculated for the soil samples: fluoranthene/(fluoranthene + pyrene), benzo[*a*]anthracene/(benzo[*a*]anthracene + chrysene), indeno[1,2,3-*c,d*]pyrene/(benzo[*g,h,i*]perylene + indeno[1,2,3-*c,d*]pyrene) (Budzinski *et al.* 1997; Yunker *et al.* 2002; Jiang *et al.* 2009; Sun *et al.* 2014a). Those PAHs were only detected in samples 18 and 19 (center and downstream of the area), the value of these three ratios in sample 18 was 0.53, 0.59 and 0.54, respectively. Only fluoranthene was detected in sample 19 and the ratio of fluoranthene/(fluoranthene + pyrene) was 1.0. Therefore, the PAHs in the chemistry industrial park were determined to be mainly from the coal/biomass combustion.

Table 5 | Ten most detected SVOC compounds in the chemical industrial park

Surface water		Groundwater		Soil	
Contaminants	Detection frequency (%)	Contaminants	Detection frequency (%)	Contaminants	Detection frequency (%)
PCB 1	100	PCB 47	100	Anthracene	100
PCB 47	100	Bis[2-ethylhexyl]phthalate	88.9	Bis[2-ethylhexyl]phthalate	100
β -Hexachlorocyclohexane	85.7	PCB 1	33.3	PCB 154	75.0
Total benzenehexachloride	85.7	2-Nitroaniline	33.3	Phenanthrene	75.0
Hexachlorobenzene	71.4	<i>p,p'</i> -DDT	22.2	<i>N</i> -Nitrosodi- <i>n</i> -butylamine	75.0
PCB 5	71.4	Total-DDT	22.2	<i>p,p'</i> -DDE	50.0
PCB 29	71.4	PCB 29	22.2	Total-DDT	50.0
<i>p,p'</i> -DDE	57.1	Phorate	22.2	Heptachlor	50.0
Total-DDT	57.1	α -Hexachlorocyclohexane	11.1	PCB 1	50.0
Bis[2-ethylhexyl]phthalate	57.1	β -Hexachlorocyclohexane	11.1	PCB 47	50.0
4-Chloroaniline	57.1	γ -Hexachlorocyclohexane	11.1	Fluoranthene	50.0
<i>N</i> -Nitrosodi- <i>n</i> -butylamine	57.1	δ -Hexachlorocyclohexane	11.1	Benzo[<i>b</i>]fluoranthene	50.0
/	/	Total benzenehexachloride	11.1	DMP	50.0
/	/	Chrysene	11.1	DBP	50.0
/	/	DBP	11.1	BBP	50.0
/	/	Bis[2-chloroethyl]ether	11.1	Parathion	50.0
/	/	Nitrobenzene	11.1	/	/
/	/	Bis[2-Chloroethoxy]methane	11.1	/	/
/	/	Azobenzene	11.1	/	/
/	/	2,6-Dichlorophenol	11.1	/	/
/	/	4-Nitrophenol	11.1	/	/
/	/	Aniline	11.1	/	/
/	/	<i>O,O,O</i> -Triethylphosphorothioate	11.1	/	/
/	/	4-Chloroaniline	11.1	/	/
/	/	<i>N</i> -Nitrosodi- <i>n</i> butylamine	11.1	/	/

PAEs

As shown in Supporting Information Table S1-4, a total of six PAEs—dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), butyl benzyl phthalate (BBP), bis [2-ethylhexyl]phthalate (DEHP) and *n*-dioctyl phthalate – were monitored in this investigation (Figure 5). Three PAEs including DMP, DBP and DEHP were detected in surface water and groundwater, and five PAEs (all except DEP) were detected in soil. High detection frequency of DEHP was detected in surface water (57%), groundwater (88%) and soil (100%) samples. The highest concentrations were in surface water (286 ng/L) and soil (1,560 μ g/kg) samples.

Wide use of PAE-containing products resulted in higher detection frequency of PAEs in this area. DEHP is the main PAE plasticizer in polyvinyl chloride resins, to increase flexibility and transparency; DBP is widely used in cosmetic products, cellulose esters, print oils, and glues. PAE are physically mixed into products without any chemical cross-linking; therefore, they can easily leak out, particularly when the plastic is aged (Heudorf et al. 2007; Sun et al. 2014a). The spatial distribution of DEHP showed that the use of plastic film mulching in agriculture might have contributed to the PAEs (Chen et al. 2013). The wastewater from the park was another important source of PAEs, which was shown by the DBP data in the groundwater samples.

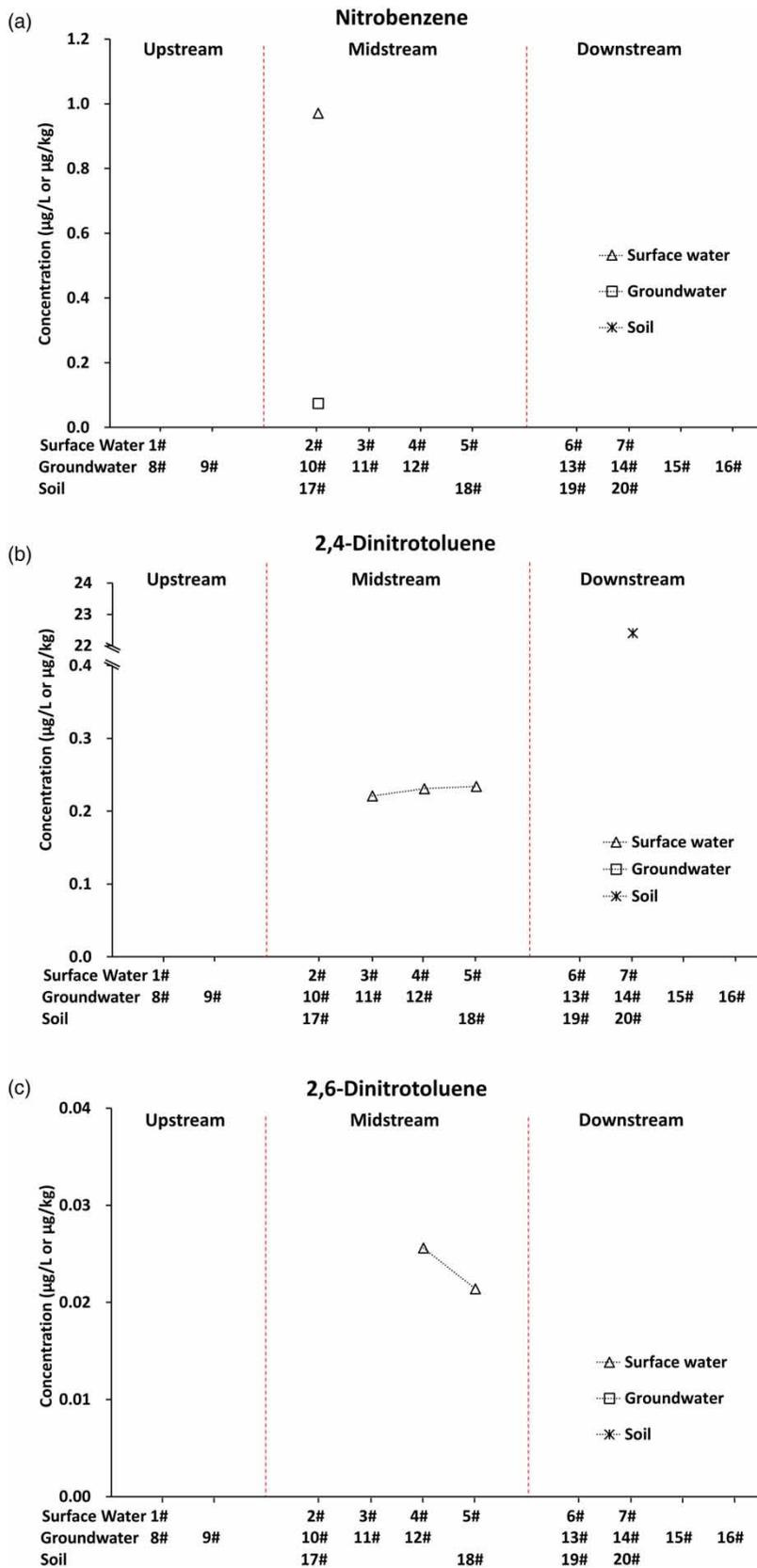


Figure 3 | Concentration of N-containing SVOCs in the chemical industrial park. (continued)

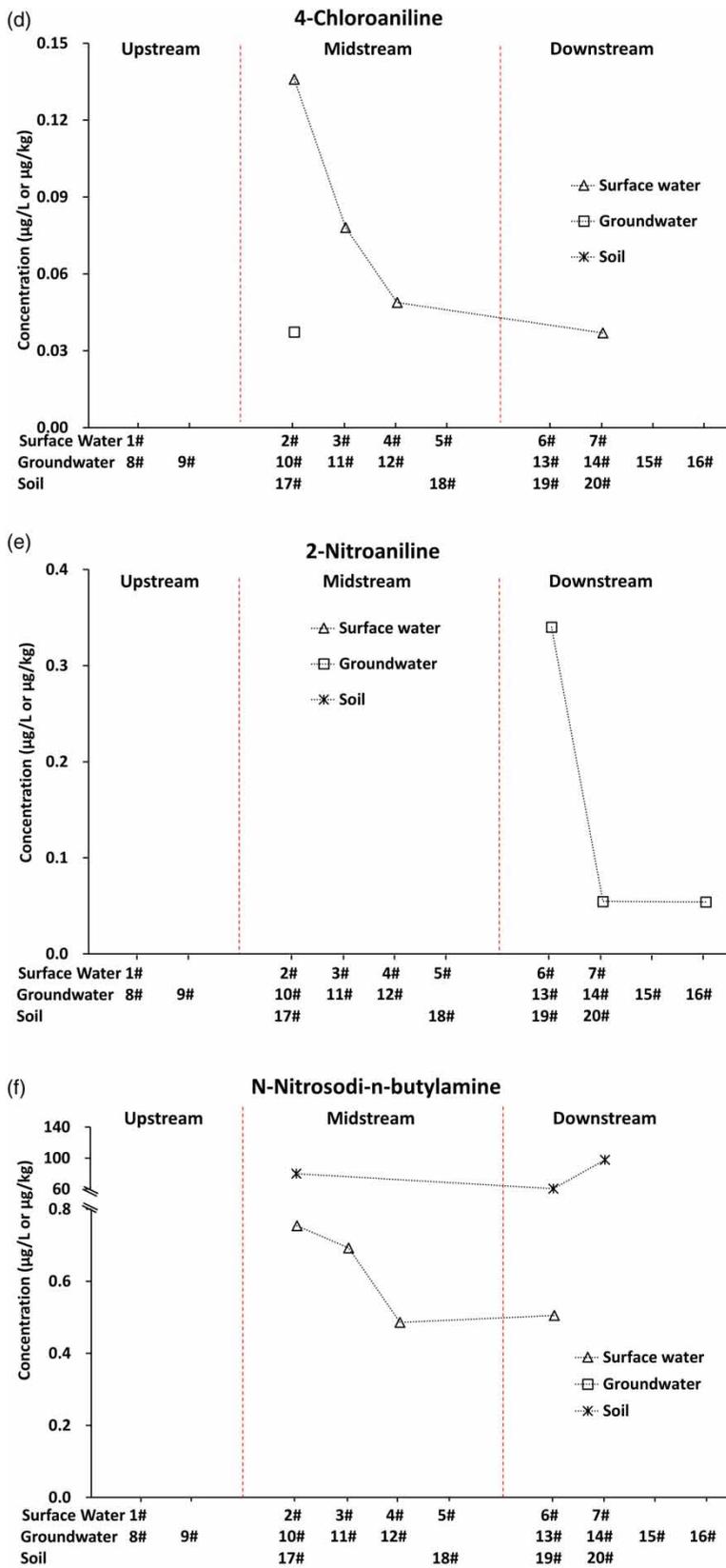


Figure 3 | continued.

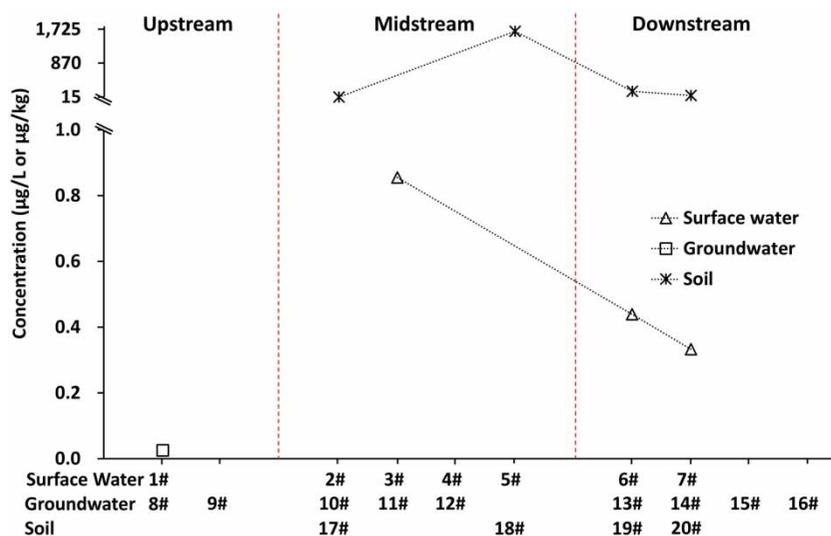


Figure 4 | Concentration of total PAHs in the chemical industrial park.

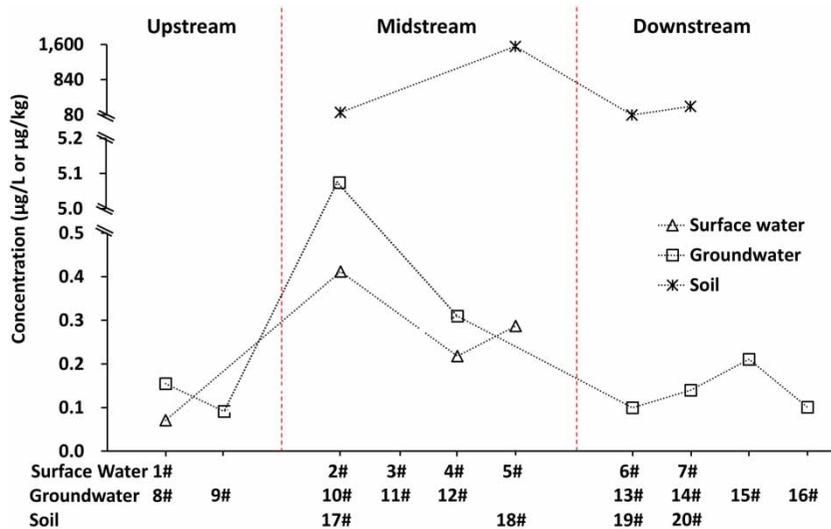


Figure 5 | Concentration of total PAEs in the chemical industrial park.

OCPs

OCPs in soils can enter surface water through effluents, atmospheric deposition and runoff (Zhou *et al.* 2008), or penetrate into the groundwater. OCPs are one of several products in the chemical industrial park under investigation. HCHs and DDTs constitute about 50% of pesticide products, and were heavily used for agricultural purposes in the 1970s (Zhu *et al.* 2005). As shown in Supporting Information Table S1-5, a total of 16 OCPs,

including α -hexachlorocyclohexane, β -hexachlorocyclohexane, γ -hexachlorocyclohexane, δ -hexachlorocyclohexane, *o,p'*-DDT, *p,p'*-DDT, *p,p'*-DDD, *p,p'*-DDE, hexachlorobenzene, heptachlor, aldrin, heptachlor epoxide, dieldrin and endrin, were investigated during this study. HCHs, DDTs, methyl parathion, parathion and phorate are the OCPs mainly found in soil and surface water (Figure 6).

The distribution of OCPs in the surface water, groundwater and soil reflects their historical usage in

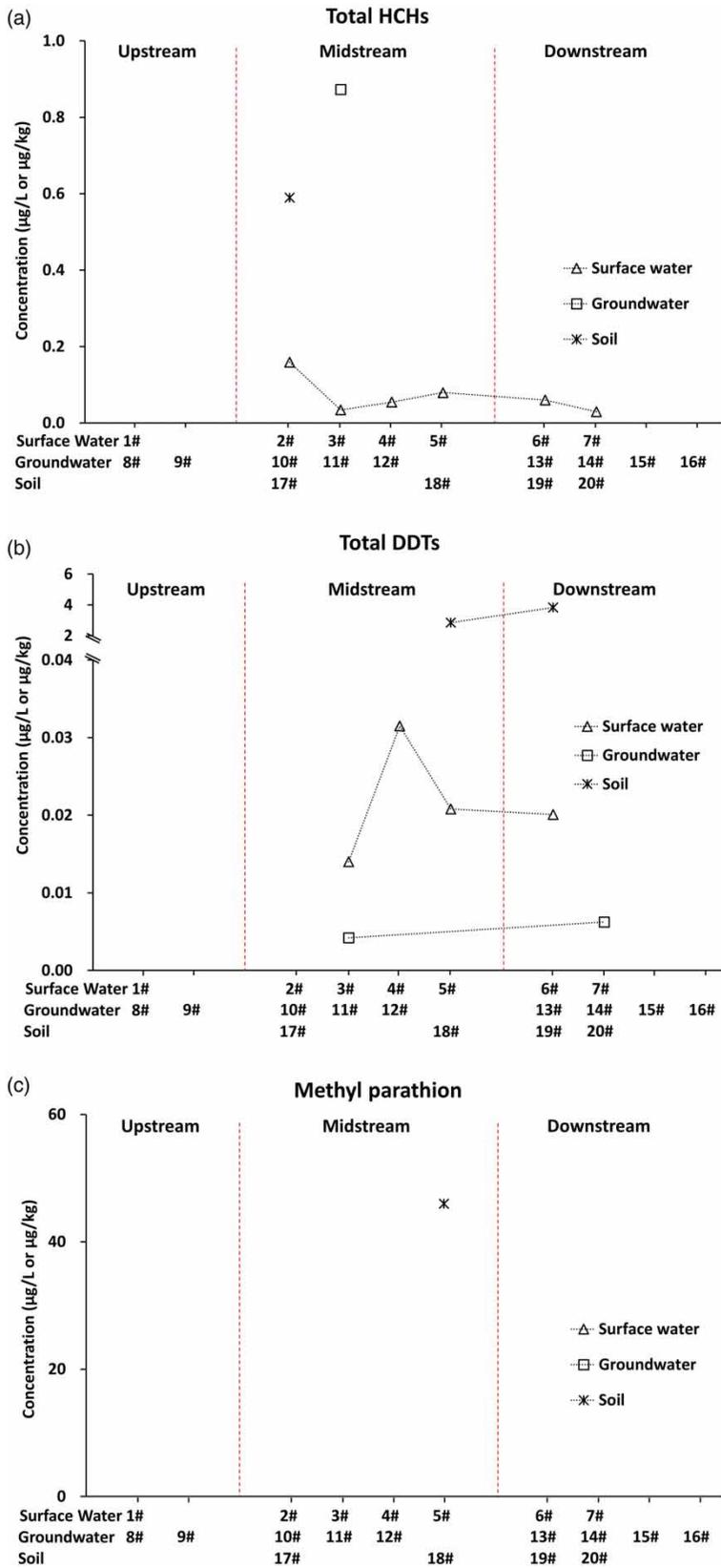


Figure 6 | Concentration of OCPs in the chemical industrial park. (continued)

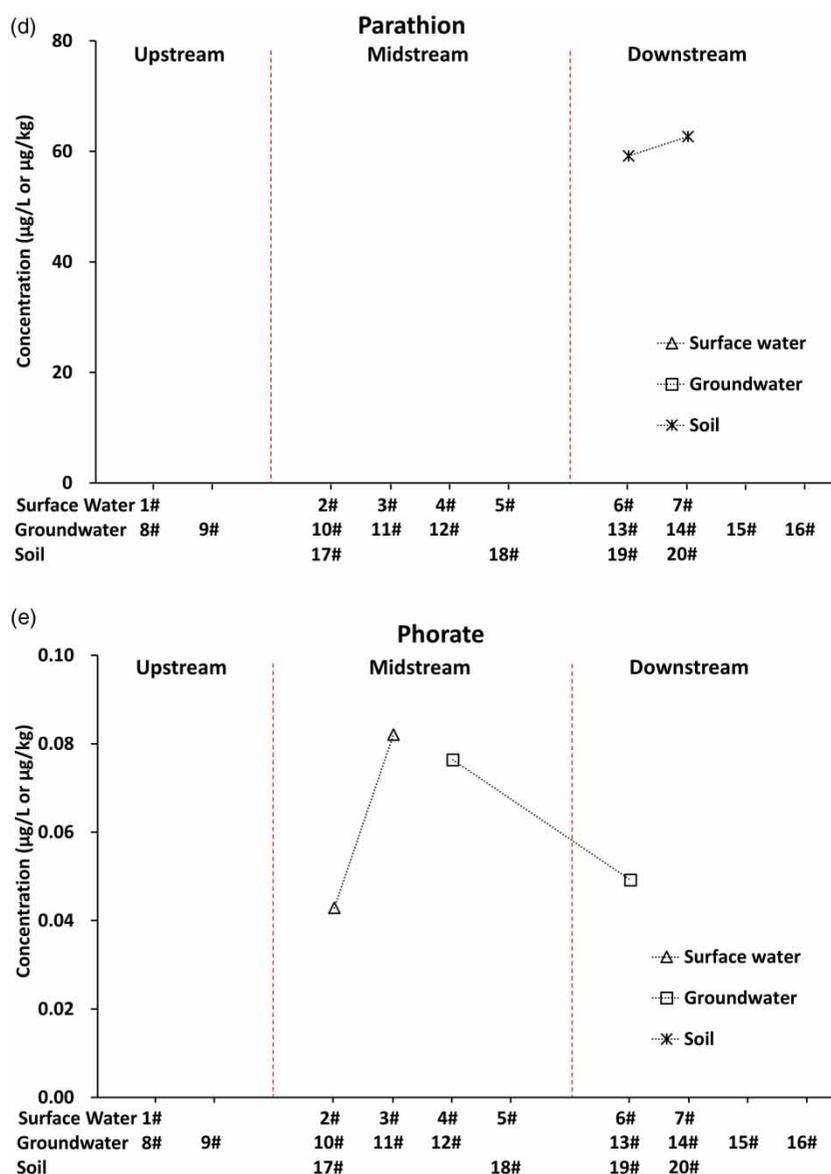


Figure 6 | continued.

the region. Although production of HCHs and DDTs has been officially banned in China since 1983 (Hu *et al.* 2010b), the detected concentration levels appeared to be too high to be merely residuals after 35 years of existence and natural degradation. For HCHs in this area, the relatively high proportion of β -HCH (45–88, 83 and 100% of total HCHs in surface water, groundwater and soil) observed indicated that the HCH was mainly due to historical use as a pesticide (Zhu *et al.* 2005; Hu *et al.* 2010b; Sun *et al.* 2014b). Compounds of DDT, *p,p'*-DDT 4.2–6.3 ng/L, were only detected in groundwater (sampling well #11 and #14), and

p,p'-DDE (sampling site #3, #4, #5 and #6) and *p,p'*-DDD (sampling site #18 and #19) were found in the soil and surface water. Most sites contained more DDE or DDD than DDT, indicating DDT residues are from 'old' sources (Zhu *et al.* 2005; Hu *et al.* 2010b; Sun *et al.* 2014a, 2014b).

PCBs

PCBs have been used widely (Qi *et al.* 2014). It was estimated that 10,000 metric tons of PCBs were produced from 1965 to 1974 (production of PCBs was banned in 1974). Some PCBs

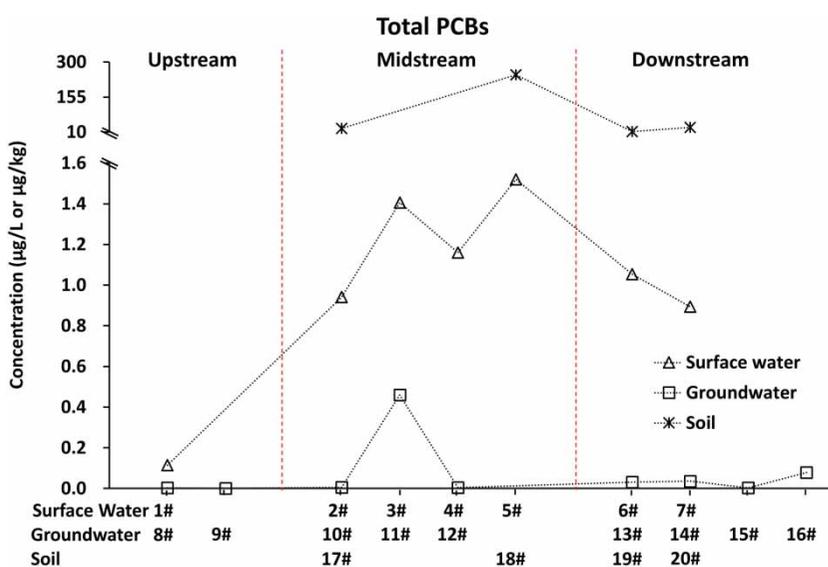


Figure 7 | Concentration of total PCBs in the chemical industrial park.

entered into the surrounding environment, especially in industrial areas (Motelay-Massei *et al.* 2004; Xing *et al.* 2005; Sun *et al.* 2014b). As shown in Supporting Information Table S1-6, a total of eight PCBs including PCB 1, PCB 5, PCB 29, PCB 47, PCB 98, PCB 154, PCB 171, and PCB 200 were analyzed in this investigation. Most PCBs were detected in this area (PCB 1, PCB 5, PCB 29, PCB 47, PCB 98 and PCB 154). The aggregated PCBs are shown in Figure 7.

Similar to the other SVOCs, more PCBs were detected in soil and surface water, with the highest concentration in soil. The sequential detection frequency and concentration of most organic chemicals in the surface water, groundwater and soil seems to be a norm for this park. Similar to the report from Xing *et al.* (2005), PCBs in this area may be from the unwanted by-products from the combustion of chlorine-containing waste through incineration and certain other chemical processes involving organochlorines.

CONCLUSIONS

As expected and similar to the VOC results reported by Liu *et al.* (2014), chemical production activities in this chemical industrial park contributed to the wide occurrence of SVOCs in the surface water, groundwater, and soil. The detection probability of SVOCs in this park was 100%. Moreover, the detection frequencies of 113 SVOCs for each sample were 15.93%, 12.39% and 20.35% for surface

water, groundwater and soil, respectively. From the sequential patterns of occurrences and concentrations, organic chemicals apparently followed the pathways of surface water, soil (with sorption), and groundwater. This is consistent with the chemical manufacturing and resultant spills during production, storage, and transportation in the park. Different from the VOC results, the relatively lower volatility and solubility and higher density of SVOCs may be responsible for their relatively higher concentrations detected in soil than surface water and groundwater.

Based on results of both VOCs and SVOCs, BTEX (benzene, toluene, ethylbenzene, and xylene), halogenated compounds, *N*-containing SVOCs, PAHs, PAEs, OCPs, PCBs and other organic compounds were all detected in the surface water, groundwater and soil in this area. These findings indicate a severe contamination of this park, which is still in operation. We expect the ongoing operation could exacerbate the threats to environmental and human health in the area. Further investigations beyond the park boundary are necessary and imminent to delineate the contaminated surface and subsurface matrices, and remedial actions are highly warranted to eliminate sources and restore environmental quality onsite and in the adjacent areas.

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