

Organochlorine pesticide residues in surface water from Sichuan Basin to Aba Prefecture profile, east of the Tibetan Plateau

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Abstract Organochlorine pesticides (OCPs) found in rivers from the Sichuan Basin to Aba Prefecture profile were analyzed to assess possible health risks to adults and children who use the river as a source of drinking water. OCP concentrations in surface water ranged between 22.29–274.28 ng·L⁻¹. Compared with other published data around the world, OCP levels in this study were moderate. Among all OCPs, hexachlorobenzene (HCB) and hexachlorocyclohexanes (HCHs) were the predominant compounds. Higher concentrations of OCPs were attributed close to the agricultural fields of the Sichuan Basin, current OCPs inputs, and long-range atmospheric transport from abroad. Various spatial patterns of OCPs in the profile might be affected by the usage and physicochemical properties of the pesticides, in addition to the adjacent geographical environment. The health risk assessment indicated that most OCPs had little impact on human health according to the acceptable risk level for carcinogens (10⁻⁶) recommended by the US EPA. However, carcinogenic effects caused by heptachlor, Aldrin, HCB, and α -HCH might occur in drinking water. The risk of negative impacts caused by OCPs is much higher for children than for adults.

Keywords organochlorine pesticides (OCPs), surface water, spatial distribution, health risk assessment, Tibetan Plateau

1 Introduction

Organochlorine pesticides (OCPs), i.e., hexachlorocyclohexanes (HCHs), dichlorodiphenyltrichloroethanes (DDTs), drins (Aldrin, Dieldrin and Endrin), chlordane, heptachlor (HEPT), hexachlorobenzene (HCB), endosulfan, mirex, and toxaphene pose significant threats to both ecosystem and human health (Darko et al., 2008). In China, Aldrin, Dieldrin, HEPT, DDTs, and toxaphene were banned in 1983, while chlordane was banned in 1999 (Wong et al., 2005). Endosulfan is still on the list of allowable insecticides on crops in China (Zhang et al., 2012). Drins were never industrially produced or used as agricultural pesticides in China (Lammel et al., 2007; Zhang et al., 2012). However, recent studies have indicated that dicofol (Qiu et al., 2005; Chen et al., 2008), lindane (Xing et al., 2010; Cai et al., 2012) and chlordane (Li et al., 2008; Zhang et al., 2012) are still used in China. On the other hand, many contaminants came from historical OCP residues (Xing et al., 2009; Wang et al., 2012; Yang et al., 2013).

The Tibetan Plateau has triggered a strong interest among the geoscience community due to its unique geographical location, unique climatic environment, in addition to relatively scarce industrial and agricultural activities. Various environmental media have been investigated for OCPs in this region, such as soil (Zheng et al., 2009; Tao et al., 2011; Wang et al., 2012), air (Gong et al., 2010; Liu et al., 2010; Wang et al., 2010a; Xiao et al., 2010), vegetation (Wang et al., 2007; Yang et al., 2008), and ice core (Wang et al., 2008; Wang et al., 2010b). It is hypothesized that cold-trapping effect for OCPs may be profound in the Tibetan Plateau because of dramatic

altitudinal gradients and its immediate vicinity to possible source regions, such as India and China. Comparatively, data is limited on OCPs found in water samples in the Tibetan Plateau. Yang et al. (2007; 2010; 2013) investigated fish samples taken from several rivers across the plateau and found various OCPs, such as DDTs, HCHs and HCB. Therefore, it is important to explore the occurrence of OCPs in water in view of the significant role of rivers in the Tibetan Plateau.

Studies on OCPs have been carried out from Sichuan Basin to Wenchuan County (Liu et al., 2010), the Balangshan region (Chen et al., 2008), and in the Jiuzhaigou Natural Scenic Area (Xing et al., 2010), all of which are high-altitude regions just east of the Tibetan Plateau. The results confirmed that many contaminants were attributed to the long-range atmospheric transport, which was most likely from Sichuan Basin. Aba Tibetan and Qiang Autonomous Prefecture (Aba Prefecture), located northwest of Sichuan province, is an important

intergrade between the Tibetan Plateau and Sichuan Basin. Aba Prefecture is also the main route for monsoon winds to the Tibetan Plateau. These traits make Aba Prefecture a perfect place to gain a better understanding of OCP transport processes from low-altitude regions to remote high-altitude regions (Wania and Westgate, 2008; Xing et al., 2010). Aba Prefecture is traversed by more than 530 rivers, including the Yellow River which flows through 126 kilometers. The main branches of the Minjiang River, Jialing River, and Fujiang River in Sichuan province originated from Aba Prefecture. Therefore, this study chose the profile from Mianzhu City to Aba Prefecture (the Aba profile) to determine OCPs in surface water. The goals were to investigate the pollution characteristics of OCPs in rivers along the Aba profile, and to assess resultant health risks for individuals caused by the OCP contamination of drinking water. A map of the sampling sites is shown in Fig. 1, and statistics of each sampling site are presented in Table 1.

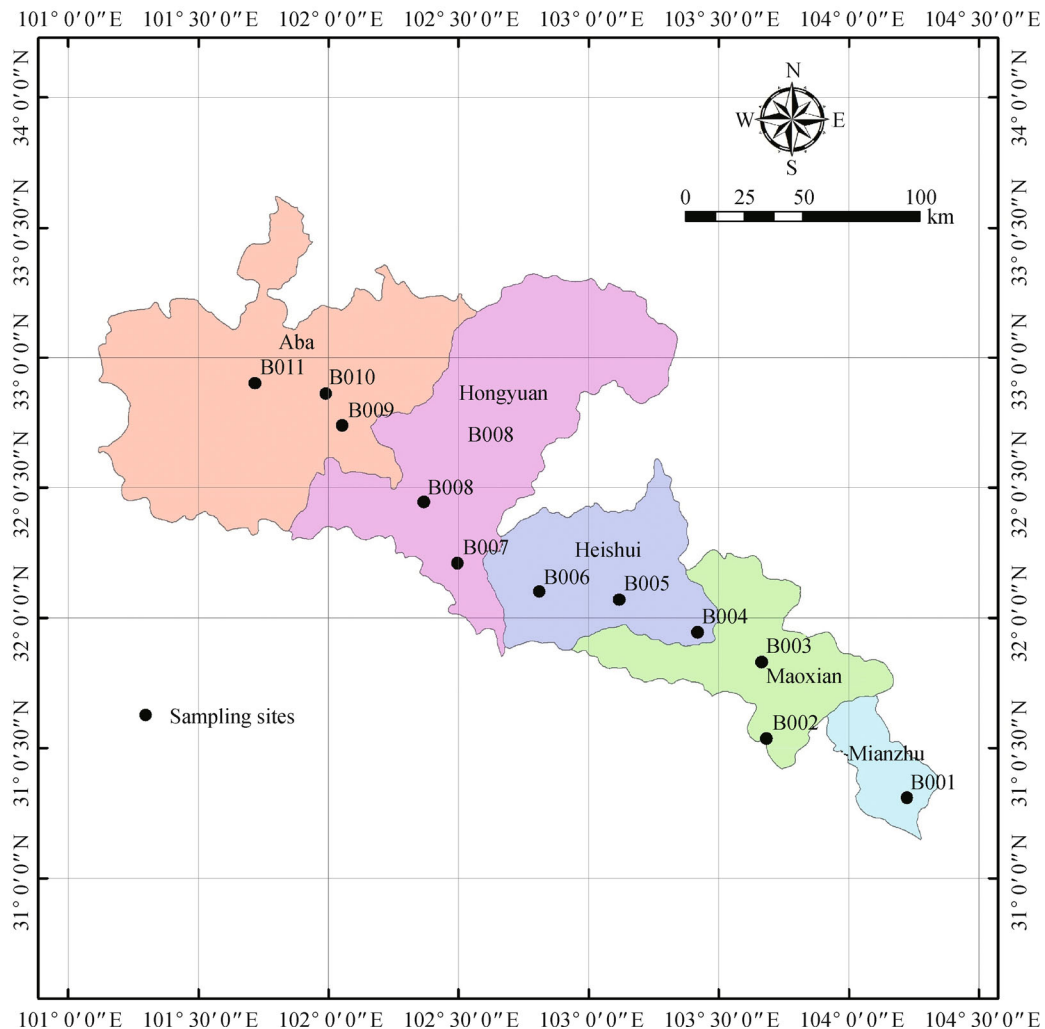


Fig. 1 Sampling sites along the Aba profile, Sichuan Province, China.

Table 1 Statistics of water sampling sites in the Aba profile, Sichuan Province, China

Site No.	Area	Altitude/m	Geographic information	Sampling site characteristics
B001	Mianzhu City of Sichuan Basin	588	N:31°18'31.6" E:104°13'25.4"	A vegetable field to the west and a large chemical plant to the south
B002	Maoxian of Aba Prefecture	1,410	N:31°32'12.6" E:103°40'59.8"	Surrounded by mountains
B003	Maoxian of Aba Prefecture	1,710	N:31°49'47.3" E:103°39'53.9"	Mountains to the south
B004	Heishui County of Aba Prefecture	1,840	N:31°56'39.9" E:103°25'02.9"	Near the Heishui River
B005	Heishui County of Aba Prefecture	2,190	N:32°04'08.9" E:103°07'01.4"	Surrounded by vegetable fields
B006	Heishui County of Aba Prefecture	2,690	N:32°06'05.6" E:102°48'39.3"	Mountains to the south
B007	Hongyuan County of Aba Prefecture	3,620	N:32°12'37.8" E:102°29'45.1"	Surrounded by mountains
B008	Hongyuan County of Aba Prefecture	3,578	N:32°26'45.2" E:102°21'57.5"	Surrounded by breeding farms
B009	Aba County of Aba Prefecture	3,320	N:32°44'26.1" E:102°03'09.4"	Valley
B010	Aba County of Aba Prefecture	3,490	N:32°51'42.3" E:101°59'24.2"	Hilly land
B011	Aba County of Aba Prefecture	3,320	N:32°54'07.9" E:101°43'01.1"	Hilly land

2 Methods

2.1 Reagents

Dichloromethane (DCM) and *n*-hexane were purchased from Tedia Co., USA. Anhydrous sodium sulfate was obtained from Sinopharm Medicine Holding Co. Ltd., China. The standard samples were purchased from Ultra Scientific, USA, including 2,4,5,6-tetrachloro-*m*-xylene (TCmX), decachlorobiphenyl (PCB-209), pentachloronitrobenzene (PCNB), HCHs (α -HCH, β -HCH, γ -HCH, δ -HCH), DDTs (*p,p'*-DDT, *o,p'*-DDT, *p,p'*-DDD, *p,p'*-DDE), drins (Aldrin, Dieldrin and Endrin), HCB, HEPT, heptachlor epoxide (HEPX), *cis*-chlordane (CC) and *trans*-chlordane (TC), *trans*-nonachlor (TN) and *cis*-nonachlor (CN), α -endosulfan (α -ES) and β -endosulfan (β -ES). Silica gel (75–150 μ m) was purchased from Qingdao Haiyang Chemical Co., China.

2.2 Sampling, extraction and cleanup

Coupled air and soil samples had been collected at the same sites to investigate residual levels, distribution characteristics, and soil-air exchange of OCPs along the profile (Liu et al., 2013a, b). In March 2011, surface water samples were collected at the same sites where coupled air and soil samples had been collected. Water samples were collected along the riverside and duplicated at each sampling site. The 1.5 L amber glass bottles were rinsed twice with water, and carefully filled without air bubbles. The samples were transferred to the laboratory and kept frozen at -4°C until further analysis.

OCPs were analyzed by the method of USEPA 8080A. Zhang et al. (2004) and Hu et al. (2011) gave detailed descriptions about the procedures for the extraction and fractionation of OCPs. Briefly, 500 mL of a water sample

was transferred into a separate funnel. Certain amounts of TCmX and PCB-209 were added to each water sample and then mixed with 25 mL of DCM. The mixture was centrifuged and the extract collected. This extraction procedure was repeated three times. The extract was concentrated by a rotary evaporator after addition of anhydrous sodium sulfate, and then subjected to a 2:1 (v/v) silica gel/alumina (both deactivated with 3% deionized water) glass column for cleanup and fractionation. Before using, neutral alumina, neutral silica gel, and anhydrous sodium sulfate were Soxhlet-extracted for 48 hr with DCM, and baked for 12 hr at 250°C , 180°C , and 450°C , respectively. The column was eluted with 30 mL of DCM/*n*-hexane (2/3, v/v) to obtain OCP fractions. The fractions were concentrated to 0.2 mL under a gentle pure nitrogen stream. PCNB was added as an internal standard prior to analysis.

2.3 Instrumental analysis

A total of 20 OCPs, including HCHs (α -HCH, β -HCH, γ -HCH, δ -HCH), DDTs (*p,p'*-DDT, *o,p'*-DDT, *p,p'*-DDD, *p,p'*-DDE), drins, HCB, HEPT, HEPX, CC and TC, TN and CN, α -ES and β -ES, were analyzed by an HP 6890 gas chromatograph equipped with ^{63}Ni electron capture detector (GC-ECD). The capillary column used for the analysis was an HP-5 (30 m length \times 0.32 mm inner diameter \times 0.25 μ m film thickness). Nitrogen was used as carrier gas at 2.5 mL/min under the constant flow mode. Injector and detector temperatures were maintained at 290°C and 300°C , respectively. The oven temperature program was as follows: the temperature started at 100°C , held for 1 min, and then increased at $4^{\circ}\text{C}/\text{min}$ to 200°C , at $2^{\circ}\text{C}/\text{min}$ to 230°C , and lastly, at $8^{\circ}\text{C}/\text{min}$ to 280°C , with a final holding time of 15 min. A 2 μ L sample was injected into the GC-ECD for analysis.

2.4 Quality control and quality assurance (QC/QA)

For each sample, procedural blanks, sample duplicates were run to check for interference and cross-contamination. No OCPs were detected in blank samples. Mean value was used as the representative for each target compound. The surrogates were added to each sample to monitor procedural performance and matrix effects. The concentrations of OCPs with retention times lower than PCNB were corrected by the recoveries of TCmX, and those with retention times higher than PCNB were corrected by the recoveries of PCB-209. The mean recoveries were $88\pm 10\%$ and $76\pm 9\%$ for TCmX and PCB-209, respectively. The correlation coefficients for the calibration curves of OCPs were all greater than 0.99. The method detection limits of most OCPs were 0.01–0.10 $\text{ng}\cdot\text{L}^{-1}$.

2.5 Health risk assessment model

A health risk assessment model derived from USEPA (IRIS, 2005) was applied to estimate the carcinogenic and non-carcinogenic risks for individuals through drinking water. Carcinogenic risk (R) is calculated as follows:

$$CDI = \frac{C \times IR \times EF \times ED}{BW \times AT}, \quad (1)$$

$$R = CDI \times SF, \quad (2)$$

where CDI = chronic daily intake ($\text{mg}\cdot\text{kg}^{-1}\cdot\text{day}^{-1}$), C = chemical concentration in water ($\text{mg}\cdot\text{L}^{-1}$), IR = water ingestion rate (1 day^{-1}) (for children: $IR = 1.0$, for adults: $IR = 2.0$), EF = exposure frequency (365 $\text{days}\cdot\text{year}^{-1}$), ED = exposure duration (year) (for children: $ED = 6$, for adults: $ED = 70$), BW = body weight (kg) (for children: $BW = 14$, for adults: $BW = 60$), AT = average lifespan (days) (for children: $AT = 2190$, for adults: $AT = 25550$), SF = slope factor ($\text{kg}\cdot\text{day}^{-1}\cdot\text{mg}^{-1}$).

To estimate non-carcinogenic risk, hazard quotient (HQ)

was calculated using the following equation:

$$HQ = \frac{CDI}{RfD}, \quad (3)$$

where RfD ($\text{mg}\cdot\text{kg}^{-1}\cdot\text{day}^{-1}$) is the reference dose of the contaminant via oral exposure route. The values of SF and RfD (Table 2) for OCPs are obtained from the USEPA Integrated Risk Information System.

3 Results and discussion

3.1 Concentrations of OCPs

Table 3 illustrates the concentrations of OCPs in water samples from the Aba profile. The residues of total OCPs were in the range of 22.29–274.28 $\text{ng}\cdot\text{L}^{-1}$. β -HCH, o,p' -DDT, HEPX, CN, α -ES, and β -ES were not detected in all samples. Mean concentrations ($\text{ng}\cdot\text{L}^{-1}$) for HCB, HEPT, HCHs, DDTs, drins, chlordane, and TN in water samples were 49.48, 27.86, 26.08, 7.97, 7.59, 6.81, and 5.15, respectively. Among all, OCPs, HCB, and HCHs were the most abundant compounds.

To understand the levels of OCPs, concentrations of contaminants in this study were compared with other published data around the world (Table 4). The total HCHs were slightly higher than those in Pearl River Delta (Guan et al., 2009), Wuhan reach of the Yangtze River (Tang et al., 2008), and Lake Chaohu (Liu et al., 2012) in China, Atoya River in Nicaragua (Castilho et al., 2000), and Lake Volvi in Greece (Fytianos et al., 2006), but were much lower than those in Tonghui River in China (Zhang et al., 2004), Selangor River in Malaysia (Leong et al., 2007), Konya Closed Basin in Turkey (Aydin et al., 2013), Gomti River in India (Malik et al., 2009), and River Chenab in Pakistan (Eqani et al., 2012). The levels of DDTs at the sampling sites were significantly lower, but a little higher than those in the Pearl River Delta (Guan et al., 2009),

Table 2 Toxicological parameters of organochlorine pesticides

Parameters	SF $/(\text{mg}\cdot\text{kg}^{-1}\cdot\text{day}^{-1})^{-1}$	RfD $/(\text{mg}\cdot\text{kg}^{-1}\cdot\text{day}^{-1})$	Parameters	SF $/(\text{mg}\cdot\text{kg}^{-1}\cdot\text{day}^{-1})^{-1}$	RfD $/(\text{mg}\cdot\text{kg}^{-1}\cdot\text{day}^{-1})$
α -HCH	6.3	8.0E-03	Aldrin	17	3.0E-05
β -HCH	1.8	–	Dieldrin	16	5.0E-05
γ -HCH	1.1	3.0E-04	Endrin	–	3.0E-04
δ -HCH	–	–	TC	0.35	5.0E-04
p,p' -DDT	0.34	5.0E-04	CC	0.35	5.0E-04
p,p' -DDD	0.24	–	TN	–	–
p,p' -DDE	0.34	–	CN	–	–
o,p' -DDT	–	–	α -ES	–	6.0E-03
HEPT	4.5	5.0E-04	β -ES	–	6.0E-03
HEPX	9.1	1.3E-05	HCB	1.6	8.0E-04

Notes: The full names (abbreviations) of toxicological parameters are: slope factor (SF), reference dose (RfD); – means no given parameter value.

Table 3 Organochlorine pesticides concentrations in water samples from the Aba profile

OCPs	Concentration/(ng·L ⁻¹)	Mean/(ng·L ⁻¹)	N (detected)
α -HCH	2.79–23.58	9.89	11/11
γ -HCH	N.D–32.22	10.37	10/11
δ -HCH	13.71–2.76	5.82	11/11
HCHs	8.79–46.54	26.08	11/11
<i>p,p'</i> -DDT	N.D–28.39	5.55	6/11
<i>p,p'</i> -DDD	N.D–6.12	0.56	1/11
<i>p,p'</i> -DDE	N.D–4.27	1.86	10/11
DDTs	N.D–38.66	7.97	10/11
Aldrin	1.63–29.00	6.71	11/11
Dieldrin	N.D–0.66	0.06	1/11
Endrin	N.D–5.38	0.82	2/11
Drins	1.63–29.66	7.59	11/11
HCB	1.88–175.60	49.48	11/11
HEPT	N.D–169.84	27.86	7/11
TC	N.D–31.14	3.88	7/11
CC	N.D–18.46	2.93	8/11
Chlordane	N.D–49.60	6.81	9/11
TN	N.D–22.69	5.15	10/11
OCPs	22.29–274.28	130.94	11/11

Notes: HCHs is the sum of α -HCH, γ -HCH, and δ -HCH; DDTs is the sum of *p,p'*-DDT, *p,p'*-DDD, and *p,p'*-DDE; chlordane is the sum of TC and CC; and OCPs is the sum of HCHs, DDTs, drins, HCB, HEPT, chlordane, and TN. N.D means not detected.

Table 4 Organochlorine pesticide concentrations in surface water from different rivers around the world (ng·L⁻¹)

Location	HCB	HEPT	HCHs	DDTs	References
Pearl River Delta, China	–	–	0.50–14.80	1.08–19.60	Guan et al., 2009
Wuhan reach, Yangtze River	–	N.D–0.69	0.55–28.07	N.D–16.71	Tang et al., 2008
Tonghui River, China	–	N.D–957.80	70.12–992.60	18.79–663.30	Zhang et al., 2004
Lake Chaohu, China	0.06–0.35	N.D–1.09	0.55–6.92	N.D–7.03	Liu et al., 2012
Atoya River, Nicaragua	–	N.D–4.00	N.D–19.00	N.D–73.20	Castilho et al., 2000
Selangor River, Malaysia	–	132.10–346.10	16.90–90.30	29.30–147.00	Leong et al., 2007
Konya Closed Basin, Turkey	–	N.D–5.00	15.00–65.00	N.D–47.00	Aydin et al., 2013
Lake Volvi, Greece	1.00–10.20	1.30–7.80	2.60–52.30	1.40–142.20	Fytianos et al., 2006
Gomti River, India	N.D–38.36	N.D–29.64	1.63–368.70	N.D–74.95	Malik et al., 2009
River Chenab, Pakistan	0.43–85.00	1.50–140.00	6.70–330.00	0.63–580.00	Eqani et al., 2012
Rivers, the Aba profile	1.88–175.60	N.D–169.84	8.79–46.54	N.D–38.66	This study

Notes: – means no available data; N.D means not detected.

Wuhan reach of the Yangtze River (Tang et al., 2008), and Lake Chaohu (Liu et al., 2012) in China. The concentrations of HCB and HEPT were obviously higher than those in other rivers, such as Lake Chaohu (Liu et al., 2012) in China, Lake Volvi in Greece (Fytianos et al., 2006), Gomti River in India (Malik et al., 2009), and River Chenab in Pakistan (Eqani et al., 2012). As a whole, OCPs concentrations in surface water from the Aba profile

were moderate in comparison with reported data from other rivers around the world.

3.2 Potential sources of OCPs

In an aquatic system, HCB is more hydrophobic ($\log K_{ow}=5.47$, Cincinelli et al., 2009) and persistent in sediment and organisms (Malik et al., 2009; Yang et al., 2013). In this

study, high levels of HCB in water samples indicated recent input. As Mianzhu and Aba Prefecture have very limited industries, HCB mostly came from incomplete combustion (Li et al., 2008; Wang et al., 2010a) and possible long-distance transport processes (Zhang et al., 2009).

The most common HCHs were α -HCH, γ -HCH, and δ -HCH (Table 3), while β -HCH was not detectable in all samples due to its low water solubility and high fat solubility (Lee et al., 2001; Feng et al., 2011). Ratios of α -HCH to γ -HCH in this study were N.D–9.34 (Fig.2(a)), reflecting recent input of lindane in the Aba profile (Feng et al., 2011; Eqani et al., 2012). Recent evidence had shown that lindane was used for pest control in rural areas of Sichuan Basin (Chen et al., 2008; Xing et al., 2009; Xing et al., 2010). Meanwhile, HCHs in the Aba profile may originate not only from direct discharges and surface runoff from surrounding agricultural soils, but also from the river bed sediment suspension (Eqani et al., 2012).

p,p' -DDT was the dominating compound accounting for 70% of total DDTs, followed by p,p' -DDE (23%) and p,p' -

DDD (7%) (Table 3). Ratios of $(p,p'$ -DDE + p,p' -DDD)/DDTs were lower than 1 in 64% of samples (Fig.2(b)), indicating fresh DDT input in the Aba profile (Eqani et al., 2012). o,p' -DDT was not detected in all samples revealing that dicofol could not be the fresh source (Chowdhury et al., 2013). The results in this study were different from the conclusion, which indicated recent dicofol input in other regions of Sichuan Basin (Chen et al., 2008; Xing et al., 2009; Xing et al., 2010). The difference in DDT concentrations between various regions may be affected by environmental factors, usage of pesticides, and physicochemical properties of the pesticides used (Chowdhury et al., 2013).

As a mixture of 147 relevant compounds, the main components of industrial chlordane are CC (11%), TC (13%), HEPT (5%), and TN (5%) (Jiang et al., 2009; Martinez et al., 2012). The ratio of industrial TC/CC is 1.56 (Bidleman et al., 2002) or 1.20 (Harner et al., 1999), which is commonly used to show the source of chlordane. The TC/CC ratios in this study were in the range of 0.78–2.44 (Fig. 2(c)), indicating new sources of chlordane.

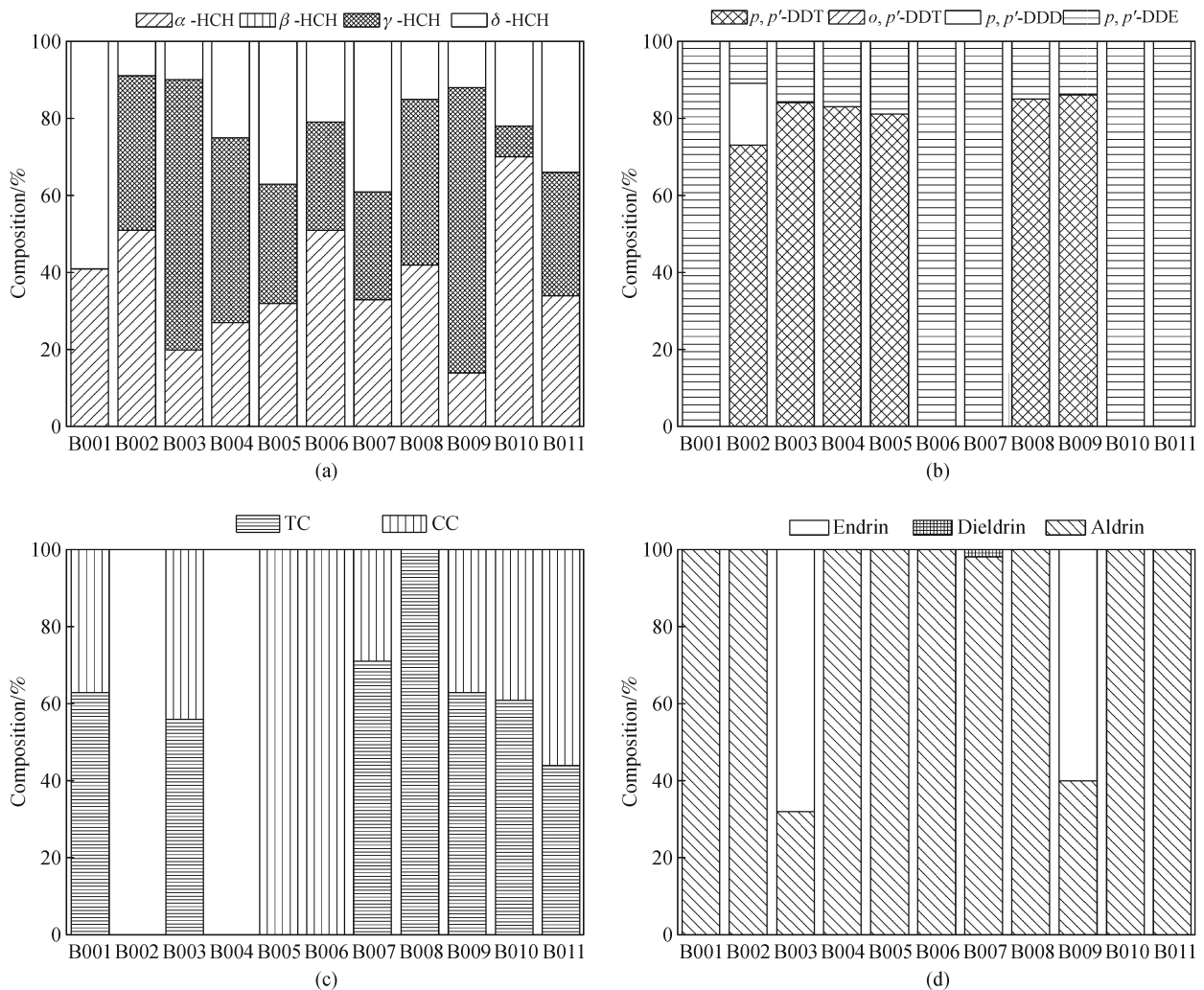


Fig. 2 Compositions of organochlorine pesticides in water samples in the Aba profile.

However, historical pollution was found in three sites (B005, B006, and B011) due to higher concentrations of CC than of TC.

High concentrations of HEPT were detected in water samples, while HEPX as a primary metabolite of HEPT was not detected in the Aba profile (Table 3). High ratios of HEPT/HEPX implied that there might be new input of this pesticide (Jiang et al., 2009). The relationship between the concentrations of chlordane and HEPT was significantly high ($R^2=0.76$, $p < 0.001$), indicating that the residues of both contaminants in this study were mainly from the same sources. In China, technical chlordane was still extensively used against termites in buildings, with an estimated amount of over $200 \text{ t} \cdot \text{year}^{-1}$ in recent years (Xu et al., 2004). Therefore, chlordane or HEPT may be widely used in the Aba profile.

Aldrin is easily oxidized to Dieldrin which is more stable and durable (Eqani et al., 2012; Aydin et al., 2013). In this study, much higher concentrations of Aldrin were observed, compared with Dieldrin (Fig. 2(d)). The fresh input of Aldrin in the Aba profile supported the hypothesis of persistent long-distance transport from neighboring countries (Jiang et al., 2009; Zhang et al., 2012). The high levels of these cyclodienes in the Aba profile reflected that great attention should be paid to tracking and monitoring the source of drins.

3.3 Spatial variation of OCPs

As shown in Fig. 3, OCP concentrations at sites B001, B002, B003, B006, and B009 reached significantly high levels. Site B001, bordering a vegetable base and a large chemical plant, was highly polluted by HEPT, chlordane, HCHs, and TN. Sites B002 and B003, located in Maoxian, an area well known for its production of fruit and rare medicinal herbs, were highly polluted by HCHs, DDTs, and HCB. Surrounded by wood-making factories and croplands in Shashiduo Town of Heishui County, site B006 was seriously contaminated by HEPT, HCB, and HCHs. Site B009 was also mainly polluted by HEPT, HCB, and HCHs.

Figure 3 clearly shows that concentrations of HEPT, chlordane, TN, and DDT decreased with increasing altitude. Concentrations of HCH in low-altitude areas was slightly lower than that in high-altitude areas, which may be attributed to their high volatility and long-distance atmospheric transport (Yang et al., 2010; Eqani et al., 2012). HCB showed higher concentrations at sites B002, B003, and B009 with increasing altitude, suggesting that it can transfer from warmer, low-altitude regions to then accumulate in colder, high-altitude regions (Simonich and Hites, 1995; Li and Macdonald, 2005; Zhong et al., 2012). Drins also showed higher concentration in high-altitude areas than in low-altitude areas. Thus, the spatial variation of drins in this study can further certify persistent long-

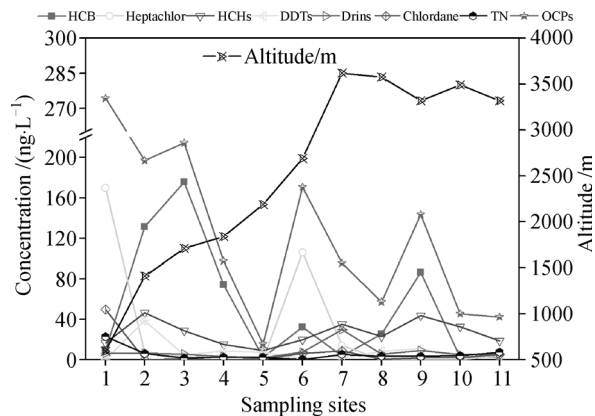


Fig. 3 Organochlorine pesticides in water samples along an altitudinal gradient in the Aba profile.

distance transport from neighboring countries (Jiang et al., 2009; Zhang et al., 2012).

OCPs can reach aquatic ecosystems by direct application, spray drift, runoff from agricultural land, and discharging of effluents from factories and sewage (Guidotti et al., 2000; Turgut, 2003). OCPs in water can act as a source to aquatic ecosystems through net deposition or as a loss via volatilization (McConnell et al., 1996; Wilkinson et al., 2005). Therefore, various spatial patterns of OCPs in water from the Aba profile may be affected by such factors as usage of pesticides, surrounding geographical environment, and physicochemical properties of the pesticides used.

3.4 Health risk assessment of OCPs

3.4.1 Carcinogenic risks

Possible health risks to adults and children caused by the drinking water in the Aba profile were calculated by using the assessment model (IRIS, 2005). The carcinogenic risks of 11 target pollutants for individuals are summarized in Fig. 4. For adults, average carcinogenic risk via oral route ranged from 4.26×10^{-9} to 4.01×10^{-6} . Average risk for children ranged from 9.14×10^{-9} and 8.59×10^{-6} . It was notable that carcinogenic risks for children were twice as high as those for adults. Evidence from other studies (Moon et al., 2009; Phan et al., 2010) found that children were more sensitive to the health risks from these pollutants. A higher intake rate and a lower body weight in children could result in a higher dose of hazardous substances per unit of body mass (Mirsadeghi et al., 2011).

Carcinogenic risk from each pollutant in all water samples was in the order of HEPT > Aldrin > HCB > α -HCH > γ -HCH > p,p' -DDT > TC > CC > Dieldrin > p,p' -DDE > p,p' -DDD (Fig. 4). Risks of HEPT, Aldrin, HCB, and α -HCH for individuals were higher than the

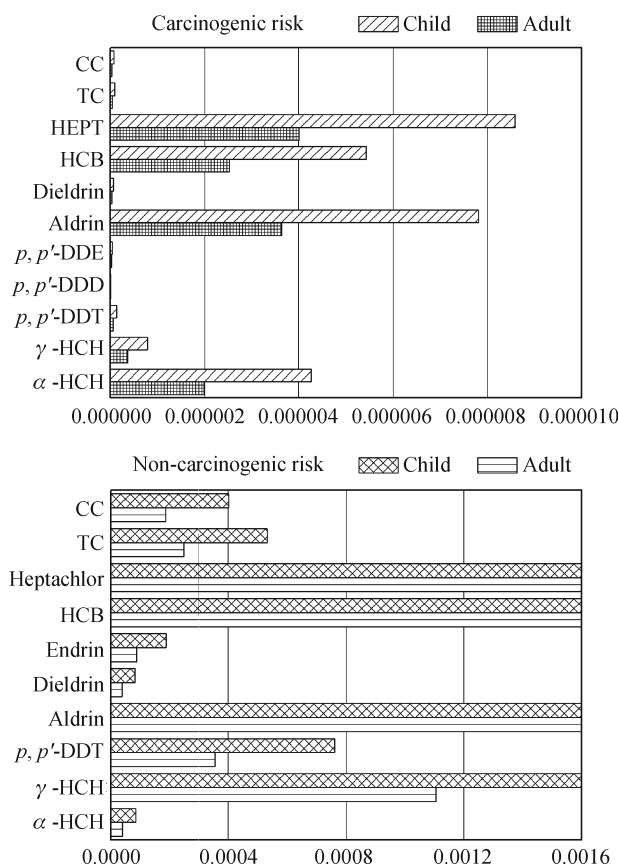


Fig. 4 Health risk assessment of organochlorine pesticides for individuals through drinking water in the Aba profile.

acceptable risk level (10^{-6}) recommended by USEPA for carcinogens, indicating potential carcinogenic risk to human health from drinking water. These four target pollutants were the main carcinogenic risk factors in the study area. Alternatively, risks caused by γ -HCH, p,p' -DDT, TC, CC, Dieldrin, p,p' -DDE, and p,p' -DDD for adults and children were lower than 10^{-6} , suggesting they did not pose any appreciable carcinogenic risk to human health through drinking water in study region.

3.4.2 Non-carcinogenic risks

The HQs of 10 target pollutants through drinking water ranged from 3.86×10^{-5} to 7.14×10^{-3} for adults, and from 8.27×10^{-5} to 1.53×10^{-2} for children, respectively (Fig. 4). Among all OCPs, Aldrin had the highest HQ, followed by HCB > HEPT > γ -HCH > p,p' -DDT > TC > CC > Endrin > α -HCH > Dieldrin. The result suggested that Aldrin was the highest priority pollutant, while Dieldrin was the least significant. According to the standards, when the HQ ratio exceeds 1, human health is adversely affected. In this study, non-carcinogenic risks from OCPs for adults and children were all less than 1, suggesting that these contaminants were unlikely to pose any adverse effects to an individuals' health. Children were exposed to higher risks for each pollutant compared to adults. Similar results were reported by Shi et al. (2011) and Hu et al. (2011), which further reflected that children were more vulnerable to these pollutants than adults. Thus, more attention should be paid to water intake for children.

Carcinogenic and non-carcinogenic risks of OCPs in this study were compared with other rivers in the world (Table 5). The carcinogenic risk of total HCHs was two or three orders of magnitude higher than those in Hanzhou (Sun et al., 2006), Jiulong River Estuary (Zhang et al., 2002) and Lake Chaohu (He et al., 2012) in China, whereas the carcinogenic risk of total DDTs was lower than the results of these reaches. The non-carcinogenic risks of total HCHs and DDTs were much lower than those in Jiulong River Estuary (Zhang et al., 2002) in China and rivers in northeastern Greece (Vryzas et al., 2009). The results showed that the risks of OCPs in surface water from the Aba profile were moderate, and were within the safety ranges of the guideline.

4 Conclusions

OCPs in surface water from the Aba profile were monitored and their spatial distribution and potential

Table 5 Risk distribution of organochlorine pesticides for individuals through drinking water in different areas

Locations	Carcinogenic risk		Non-carcinogenic risk		References
	HCHs	DDTs	HCHs	DDTs	
Huaihe River, China	1.10E-06 ^{a)}	2.17E-04 ^{b)}	— ^{h)}	— ^{h)}	Wang et al., 2009
Hanzhou, China	9.82E-10 ^{c)}	4.24E-08 ^{b)}	5.61E-06 ^{c)}	8.81E-05 ^{b)}	Sun et al., 2006
Jiulong River, China	7.4E-08 ^{a)}	6.2E-07 ^{b)}	0.010 ^{a)}	0.019 ^{b)}	Zhang et al., 2002
Lake Chaohu, China	1.45E-08 ^{a)}	3.96E-08 ^{b)}	3.22E-05 ^{d)}	1.63E-05 ^{e)}	He et al., 2012
Rivers, Greece	— ^{h)}	— ^{h)}	1.2 ^{d)}	974 ^{f)}	Vryzas et al., 2009
Ebro River, Spain	1.3E-06 ^{c)}	1.26E-07 ^{b)}	1.9E-05 ^{c)}	5.9E-06 ^{b)}	Ferré-Huguet et al., 2009
Rivers, the Aba profile	2.36E-06(for adult) ^{g)} 5.05E-06(for child) ^{g)}	8.48E-08(for adult) ^{b)} 1.82E-07(for child) ^{b)}	0.001(for adult) ^{g)} 0.002(for child) ^{g)}	0.0004(for adult) ^{e)} 0.0008(for child) ^{e)}	This study

Notes: a) Sum of α -HCH, β -HCH and γ -HCH; b) Sum of p,p' -DDE, p,p' -DDD and p,p' -DDT; c) Sum of α -HCH, β -HCH, γ -HCH and δ -HCH; d) γ -HCH; e) p,p' -DDT; f) Sum of o,p' -DDE and o,p' -DDT; g) Sum of α -HCH and γ -HCH; h) No available data.

health risks were analyzed. HCB was presented at high concentrations and was followed by HEPT, HCHs, DDTs, and other OCPs. Compared with other bodies of water throughout the world, the water in the study area was moderately polluted by OCPs. The higher concentrations of dominant OCPs were observed at sites B001, B002, B003, B006, and B009, which are all close to industrial and urban areas. The concentrations of HCH and HCB at the low-altitudes were slightly lower than those at high-altitudes, which may be attributed to high volatility and long-distance atmospheric transport. The higher drins concentration in the high-altitudes further certifies the persistent long-distance transport from neighboring countries.

Carcinogenic risks for HEPT, Aldrin, HCB, and α -HCH were greater than the acceptable risk level (10^{-6}) recommended by USEPA, suggesting potential carcinogenic risk to human health through drinking water. Non-carcinogenic risks for all studied OCPs were lower than 1, indicating that these pollutants were unlikely to pose any adverse effects to human health. However, the interactions and combined effects among different OCPs were not considered in this study (Qiao et al., 2010). Thus, it has been shown that risks caused by OCPs should not be overlooked. It is necessary in the future to validate these results through in-depth assessments.

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References

- Aydin M E, Ozcan S, Beduk F, Tor A (2013). Levels of organochlorine pesticides and heavy metals in surface waters of Konya Closed Basin, Turkey. *Scientific World Journal*, 2013: 1–6
- Bidleman T F, Jantunen L M M, Helm P A, Brorstrom-Lunden E, Juntto S (2002). Chlordane enantiomers and temporal trends of chlordane isomers in Arctic air. *Environ Sci Technol*, 36(4): 539–544
- Cai M H, Ma Y X, Xie Z Y, Zhong G C, Moller A, Yang H Z, Sturm R, He J F, Ebinghaus R, Meng X Z (2012). Distribution and air-sea exchange of organochlorine pesticides in the North Pacific and the Arctic. *J Geophys Res*, 117(D6): D06311
- Castilho J A A, Fenzl N, Guillen S M, Nascimento F S (2000). Organochlorine and organophosphorus pesticide residues in the Atoya River basin, Chinandega, Nicaragua. *Environ Pollut*, 110(3): 523–533
- Chen D Z, Liu W J, Liu X D, Westgate J N, Wania F (2008). Cold-trapping of persistent organic pollutants in the mountain soils of western sichuan, China. *Environ Sci Technol*, 42(24): 9086–9091
- Chowdhury A Z, Islam M N, Moniruzzaman M, Gan S H, Alam M K (2013). Organochlorine insecticide residues are found in surface, irrigated water samples from several districts in Bangladesh. *Bull Environ Contam Toxicol*, 90(2): 149–154
- Cincinelli A, Martellini T, Del Bubba M, Lepri L, Corsolini S, Borghesi N, King M D, Dickhut R M (2009). Organochlorine pesticide air–water exchange and bioconcentration in krill in the Ross Sea. *Environ Pollut*, 157(7): 2153–2158
- Darko G, Akoto O, Oppong C (2008). Persistent organochlorine pesticide residues in fish, sediments and water from Lake Bosomtwi, Ghana. *Chemosphere*, 72(1): 21–24
- Eqani S A M A S, Malik R N, Katsoyiannis A, Zhang G, Chakraborty P, Mohammad A, Jones K C (2012). Distribution and risk assessment of organochlorine contaminants in surface water from River Chenab, Pakistan. *J Environ Monit*, 14(6): 1645–1654
- Feng J L, Zhai M X, Liu Q, Sun J H, Guo J J (2011). Residues of organochlorine pesticides (OCPs) in upper reach of the Huaihe River, East China. *Ecotoxicol Environ Saf*, 74(8): 2252–2259
- Ferré-Huguet N, Bosch C, Lourencetti C, Nadal M, Schuhmacher M, Grimalt J, Domingo J (2009). Human health risk assessment of environmental exposure to organochlorine compounds in the catalan stretch of the Ebro River, Spain. *Bull Environ Contam Toxicol*, 83(5): 662–667
- Fytianos K, Meesters R J W, Schroder H F, Gouliarmou B, Gantidis N (2006). Distribution of organochlorine pesticides in surface water and sediments in Lake Volvi (northern Greece). *Int J Environ Anal Chem*, 86(1–2): 109–118
- Gong P, Wang X P, Sheng J J, Yao T D (2010). Variations of organochlorine pesticides and polychlorinated biphenyls in atmosphere of the Tibetan Plateau: role of the monsoon system. *Atmos Environ*, 44(21–22): 2518–2523
- Guan Y F, Wang J Z, Ni H G, Zeng E Y (2009). Organochlorine pesticides and polychlorinated biphenyls in riverine runoff of the Pearl River Delta, China: assessment of mass loading, input source and environmental fate. *Environ Pollut*, 157(2): 618–624
- Guidotti M, Giovanazzo R, Cedrone O, Vitali M (2000). Determination of organic micropollutants in rain water for laboratory screening of air quality in urban environment. *Environ Int*, 26(1–2): 23–28
- Harner T, Wideman J L, Jantunen L M M, Bidleman T F, Parkhurst W J (1999). Residues of organochlorine pesticides in Alabama soils. *Environ Pollut*, 106(3): 323–332
- He W, Qin N, He Q S, Wang Y, Kong X Z, Xu F L (2012). Characterization, ecological and health risks of DDTs and HCHs in water from a large shallow Chinese lake. *Ecol Inform*, 12: 77–84
- Hu Y, Qi S H, Zhang J P, Tan L Z, Zhang J Q, Wang Y H, Yuan D X (2011). Assessment of organochlorine pesticides contamination in underground rivers in Chongqing, Southwest China. *J Geochem Explor*, 111(1–2): 47–55
- IRIS (Integrated Risk Information System) (2005) US Environmental Protection Agency, Cincinnati, OH. Accessed at: <http://www.epa.gov/iris>, 9
- Jiang Y F, Wang X T, Jia Y, Wang F, Wu M H, Sheng G Y, Fu J M (2009). Occurrence, distribution and possible sources of organochlorine pesticides in agricultural soil of Shanghai, China. *J Hazard Mater*, 170(2–3): 989–997
- Lammel G, Ghim Y S, Grados A, Gao H W, Hühnerfuss H, Lohmann R (2007). Levels of persistent organic pollutants in air in China and

- over the Yellow Sea. *Atmos Environ*, 41(3): 452–464
- Lee K T, Tanabe S, Koh C H (2001). Distribution of organochlorine pesticides in sediments from Kyeonggi Bay and nearby areas, Korea. *Environ Pollut*, 114(2): 207–213
- Leong K H, Benjamin Tan L L, Mustafa A M (2007). Contamination levels of selected organochlorine and organophosphate pesticides in the Selangor River, Malaysia between 2002 and 2003. *Chemosphere*, 66(6): 1153–1159
- Li J, Lin T, Qi S H, Zhang G, Liu X, Li K C (2008). Evidence of local emission of organochlorine pesticides in the Tibetan plateau. *Atmos Environ*, 42(32): 7397–7404
- Li Y F, Macdonald R W (2005). Sources and pathways of selected organochlorine pesticides to the Arctic and the effect of pathway divergence on HCH trends in biota: A review. *Sci Total Environ*, 342(1–3): 87–106
- Liu H X, Qi S H, Xu F, Xing X L, Li F, Liu J, Qu C K (2013a). Contaminant characteristics of organochloride pesticides in the atmosphere of Aba Prefecture, Sichuan. *China Sciencepaper*, 8(3): 230–235
- Liu H X, Qi S H, Yang D, Hu Y, Li F, Liu J, Xing X L (2013b). Soil concentrations and soil-air exchange of organochlorine pesticides along the Aba profile, east of the Tibetan Plateau, western China. *Front Earth Sci.*, 7(4): 395–405
- Liu W J, Chen D Z, Liu X D, Zheng X Y, Yang W, Westgate J N, Wania F (2010). Transport of semivolatile organic compounds to the Tibetan Plateau: Spatial and temporal variation in air concentrations in mountainous western Sichuan, China. *Environ Sci Technol*, 44(5): 1559–1565
- Liu W X, He W, Qin N, Kong X Z, He Q S, Ouyang H L, Yang B, Wang Q M, Yang C, Jiang Y J, Wu W J, Xu F L (2012). Residues, distributions, sources, and ecological risks of OCPs in the water from Lake Chaohu, China. *Scientific World Journal*, 897697
- Malik A, Ojha P, Singh K P (2009). Levels and distribution of persistent organochlorine pesticide residues in water and sediments of Gomti River (India)—a tributary of the Ganges River. *Environ Monit Assess*, 148(1–4): 421–435
- Martinez A, Erdman N R, Rodenburg Z L, Eastling P M, Hornbuckle K C (2012). Spatial distribution of chlordanes and PCB congeners in soil in Cedar Rapids, Iowa, USA. *Environ Pollut*, 161: 222–228
- McConnell L L, Kucklick J R, Bidleman T F, Ivanov G P, Chernyak S M (1996). Air-water gas exchange of organochlorine compounds in Lake Baikal, Russia. *Environ Sci Technol*, 30(10): 2975–2983
- Mirsadeghi S A, Zakaria M P, Yap C K, Shahbazi A (2011). Risk assessment for the daily intake of polycyclic aromatic hydrocarbons from the ingestion of cockle (*Anadara granosa*) and exposure to contaminated water and sediments along the west coast of Peninsular Malaysia. *J Environ Sci (China)*, 23(2): 336–345
- Moon H B, Kim H S, Choi M, Yu J, Choi H G (2009). Human health risk of polychlorinated biphenyls and organochlorine pesticides resulting from seafood consumption in South Korea, 2005–2007. *Food Chem Toxicol*, 47(8): 1819–1825
- Phan K, Sthiannopkao S, Kim K W, Wong M H, Sao V, Hashim J H, Mohamed Yasin M S, Aljunid S M (2010). Health risk assessment of inorganic arsenic intake of Cambodia residents through groundwater drinking pathway. *Water Res*, 44(19): 5777–5788
- Qiao M, An T C, Zeng X Y, Zhang D L, Li G Y, Sheng G Y, Fu J M, Zhang G X, Guo J (2010). Safety assessment of the source water within the Pearl River Delta on the aspect of organochlorine pesticides contamination. *J Environ Monit*, 12(9): 1666–1677
- Qiu X H, Zhu T, Yao B, Hu J X, Hu S W (2005). Contribution of dicofol to the current DDT pollution in China. *Environ Sci Technol*, 39(12): 4385–4390
- Shi W, Zhang F X, Zhang X W, Su G Y, Wei S, Liu H L, Cheng S P, Yu H X (2011). Identification of trace organic pollutants in freshwater sources in Eastern China and estimation of their associated human health risks. *Ecotoxicology*, 20(5): 1099–1106
- Simonich S L, Hites R A (1995). Global distribution of persistent organochlorine compounds. *Science*, 269(5232): 1851–1854
- Sun Q, Zhu L, Dong M (2006). Risk assessment of organic pesticides pollution in surface water of Hangzhou. *Environ Monit Assess*, 117(1–3): 377–385
- Tang Z W, Yang Z F, Shen Z Y, Niu J F, Cai Y P (2008). Residues of organochlorine pesticides in water and suspended particulate matter from the Yangtze River catchment of Wuhan, China. *Environ Monit Assess*, 137(1–3): 427–439
- Tao S, Wang W T, Liu W X, Zuo Q, Wang X L, Wang R, Wang B, Shen G, Yang Y H, He J S (2011). Polycyclic aromatic hydrocarbons and organochlorine pesticides in surface soils from the Qinghai-Tibetan plateau. *J Environ Monit*, 13(1): 175–181
- Turgut C (2003). The contamination with organochlorine pesticides and heavy metals in surface water in Küçük Menderes River in Turkey, 2000–2002. *Environ Int*, 29(1): 29–32
- Vryzas Z, Vassiliou G, Alexoudis C, Papadopoulou-Mourkidou E (2009). Spatial and temporal distribution of pesticide residues in surface waters in northeastern Greece. *Water Res*, 43(1): 1–10
- Wang B, Yu G, Yu Y J, Huang J, Hu H Y, Wang L S (2009). Health risk assessment of organic pollutants in Jiangsu Reach of the Huaihe River, China. *Water Sci Technol*, 59(5): 907–916
- Wang X P, Gong P, Yao T D, Jones K C (2010a). Passive air sampling of organochlorine pesticides, polychlorinated biphenyls, and polybrominated diphenyl ethers across the Tibetan Plateau. *Environ Sci Technol*, 44(8): 2988–2993
- Wang X P, Gong P, Zhang Q G, Yao T D (2010b). Impact of climate fluctuations on deposition of DDT and hexachlorocyclohexane in mountain glaciers: evidence from ice core records. *Environ Pollut*, 158(2): 375–380
- Wang X P, Sheng J J, Gong P, Xue Y G, Yao T D, Jones K C (2012). Persistent organic pollutants in the Tibetan surface soil: spatial distribution, air-soil exchange and implications for global cycling. *Environ Pollut*, 170: 145–151
- Wang X P, Xu B Q, Kang S C, Cong Z Y, Yao T D (2008). The historical residue trends of DDT, hexachlorocyclohexanes and polycyclic aromatic hydrocarbons in an ice core from Mt. Everest, central Himalayas, China. *Atmos Environ*, 42(27): 6699–6709
- Wang X P, Yao T D, Cong Z Y, Yan X L, Kang S C, Zhang Y (2007). Distribution of persistent organic pollutants in soil and grasses around Mt. Qomolangma, China. *Arch Environ Contam Toxicol*, 52(2): 153–162
- Wania F, Westgate J N (2008). On the mechanism of mountain cold-trapping of organic chemicals. *Environ Sci Technol*, 42(24): 9092–9098
- Wilkinson A C, Kimpe L E, Blais J M (2005). Air-water gas exchange of

- chlorinated pesticides in four lakes spanning a 1,205 meter elevation range in the Canadian Rocky Mountains. *Environ Toxicol Chem*, 24(1): 61–69
- Wong M H, Leung A O W, Chan J K Y, Choi M P K (2005). A review on the usage of POP pesticides in China, with emphasis on DDT loadings in human milk. *Chemosphere*, 60(6): 740–752
- Xiao H, Kang S C, Zhang Q G, Han W W, Loewen M, Wong F, Hung H, Lei Y D, Wania F (2010). Transport of semivolatile organic compounds to the Tibetan Plateau: Monthly resolved air concentrations at Nam Co. *J Geophys Res*, 115(D16): D16310
- Xing X L, Qi S H, Odhiambo J O, Zhang Y, Liu Y P (2009). Influence of environmental variables on spatial distribution of organochlorine pesticides in Sichuan, West China. *Environmental Earth Sciences*, 59(1): 215–222
- Xing X L, Qi S H, Zhang Y, Yang D, Odhiambo J O (2010). Organochlorine pesticides (OCPs) in soils along the eastern slope of the Tibetan Plateau. *Pedosphere*, 20(5): 607–615
- Xu D D, Zhong W K, Deng L L, Chai Z F, Mao X Y (2004). Regional distribution of organochlorinated pesticides in pine needles and its indication for socioeconomic development. *Chemosphere*, 54(6): 743–752
- Yang R Q, Jing C Y, Zhang Q H, Jiang G B (2013). Identifying semi-volatile contaminants in fish from Niyang River, Tibetan Plateau. *Environmental Earth Sciences*, 68(4): 1065–1072
- Yang R Q, Wang Y W, Li A, Zhang Q H, Jing C Y, Wang T, Wang P, Li Y M, Jiang G B (2010). Organochlorine pesticides and PCBs in fish from lakes of the Tibetan Plateau and the implications. *Environ Pollut*, 158(6): 2310–2316
- Yang R Q, Yao T D, Xu B Q, Jiang G B, Xin X D (2007). Accumulation features of organochlorine pesticides and heavy metals in fish from high mountain lakes and Lhasa River in the Tibetan Plateau. *Environ Int*, 33(2): 151–156
- Yang R Q, Yao T D, Xu B Q, Jiang G B, Zheng X Y (2008). Distribution of organochlorine pesticides (OCPs) in conifer needles in the southeast Tibetan Plateau. *Environ Pollut*, 153(1): 92–100
- Zhang A P, Fang L, Wang J L, Liu W P, Yuan H J, Jantunen L, Li Y F (2012). Residues of currently and never used organochlorine pesticides in agricultural soils from Zhejiang Province, China. *J Agric Food Chem*, 60(12): 2982–2988
- Zhang L F, Dong L, Shi S X, Zhou L, Zhang T, Huang Y R (2009). Organochlorine pesticides contamination in surface soils from two pesticide factories in Southeast China. *Chemosphere*, 77(5): 628–633
- Zhang Z L, Hong H S, Wang X H, Lin J Q, Chen W Q, Xu L (2002). Determination and load of organophosphorus and organochlorine pesticides at water from Jiulong River Estuary, China. *Mar Pollut Bull*, 45(1–2): 397–402
- Zhang Z L, Huang J, Yu G, Hong H S (2004). Occurrence of PAHs, PCBs and organochlorine pesticides in the Tonghui River of Beijing, China. *Environ Pollut*, 130(2): 249–261
- Zheng X Y, Liu X D, Liu W J, Jiang G B, Yang R Q (2009). Concentrations and source identification of organochlorine pesticides (OCPs) in soils from Wolong Natural Reserve. *Chin Sci Bull*, 54(5): 743–751
- Zhong G C, Xie Z Y, Cai M H, Moller A, Sturm R, Tang G H, Zhang G, He J F, Ebinghaus R (2012). Distribution and air-sea exchange of current-use pesticides (CUPs) from east Asia to the high Arctic Ocean. *Environ Sci Technol*, 46(1): 259–267