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DOTTORATO IN
Scienze della Terra, dell'Ambiente e delle Risorse

Ph.D. in
Earth Sciences, Environment and Resources
XXIX CICLO
Ph.D. Thesis

Persistent organic pollutants in a multimedia environment, and associated human health risks: case studies in the region of Campania, Italy, and south-central China

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Abstract

Persistent organic pollutants (POPs) are notoriously toxic chemicals that pose significant threats to human health and ecosystem security. As a result of their volatility and persistence, POPs can be subject to long-range atmospheric transport (LRAT) and, as a result, may be redistributed globally. The harm of POPs to the eco-system is regarded as a global environmental problem, threatening people and animals, which has caused heavy losses economically, ecologically and socially. The environmental problems caused by POPs have finally lead the international community to address the global presence of POPs and reduce their emissions to the environment. Many treaties and laws have been enacted to eliminate or restrict the production and use of some POPs, of which the Stockholm Convention of 2004 on POPs is one of the most famous.

Soils are important POPs reservoirs due to their tremendous retention capabilities for these compounds. The huge quantities of POPs accumulated in soils have been an important reemission sources to the atmosphere even after the phasing out of these compounds decades ago. Atmospheric processes are largely responsible for the transport and deposition of polycyclic aromatic hydrocarbons (PAHs), and these compounds may adhere to both atmospheric aerosols and dustfall. Organochlorine pesticides (OCPs) can be easily adsorbed on to suspended particulate matter (SPM) as sediments. SPM can then precipitate in sediments and eventually lower the OCP concentrations in water. Under favorable conditions, sediments can be resuspended, release previously adsorbed OCPs back into the water phase, and initiate another cycle of environmental contamination.

So far, the Stockholm Convention has not been ratified by Italy, however, several other regulatory schemes, such as a European Directive in 2000, the UNECE POPs Protocol, and the Rotterdam Convention, are actively followed. The region of Campania falls within the subtropical zone and enjoys a Mediterranean climate. High temperatures in tropical/subtropical regions can facilitate the volatilization and escape of POPs from soils, sediments, and water. The lack of sufficient data on POPs residues, limits the understanding of their health effects, environmental dynamics, and the ultimate fate of these chemicals. China is one of the largest agricultural industries in the world, and was once the largest global producer and consumer of OCPs, especially in the arable southeast region.

This Ph.D. thesis presents the results of a series of investigations using a systematic sampling method and geostatistics to illustrate spatial and temporal variations in the concentrations of POPs in different environments, and associated human health risks in Campania, Italy, and south-central China.

CHAPTER 1

OVERVIEW

Introduction

Persistent organic pollutants (POPs) are organic compounds notoriously resistant to environmental degradation. Some POPs have been identified as endocrine disrupting substances (EDS) due to their ability to alter hormonal activity in humans and other living organisms. POPs are also both persistent and volatile, and because of these special physicochemical properties, POPs may be subject to long-range atmospheric transport (LRAT) from their source through various environmental media, and can be redistributed on a global scale under the actions of cold condensation and global fractionation. Recently, the attention of many scholars has been increasingly focusing on these types of pollutants. The Stockholm Convention (SC) on POPs is one of the most famous multilateral treaties, and Article 16 stipulates that the effectiveness of the measures adopted as part of the SC should be evaluated in regular intervals.

Soils are considered as important reservoirs of POPs due to their tremendous retention capabilities for these compounds. The huge quantities of OCPs accumulated in agricultural soils have been important re-emission sources to the atmosphere, even long after the phasing out of the use of these compounds. Organic pollutants in soils could influence soil microbial activity or enter the food chain directly through absorption into vegetation, thus resulting in ecosystem disturbances and/or negative impacts on human health. Therefore, it is important to understand the overall scale and impact of POP contamination in soils, by assessing their contamination profiles, distribution characteristics, and possible sources especially in seriously affected communities. The environmental fate of POPs in soils is affected by many factors, of which, the physicochemical characteristics of the agrochemicals, land use type, application history and agricultural practices, soil properties, as well as meteorological variables, are, perhaps, the most important (Yu et al., 2013; Zhang et al., 2011). Soil plays an important role in the circulation of these substances in different sectors of the environment, but the behavior and fate of OCPs in soils on a regional scale is a deeply complicated process.

The atmosphere is deemed to be a useful indicator in evaluating the POP trends on a global scale, due to its ability to respond quickly to changes in primary emissions (UNEP, 2004). Restricted by cost and logistics, in particular the local electricity supply, the high-volume active air samplers (Hi-Vol AAS) cannot be deployed at a large number of monitoring sites simultaneously, and may not be feasible for implementation during a spatial survey of POPs in remote areas (Pozo et al., 2004). Polyurethane foam-based passive air samplers (PUF-PAS) are one of the most widely used PAS for monitoring POPs. The PUF-PAS can be installed simultaneously at many sites, from a local to global scale, to assess spatial distribution and create maps (Halse et al., 2011; Harner et al., 2004; Pozo et al., 2006), and temporal trends can be obtained by deployment of PUF-PAS over several seasons and years (Pozo et al., 2009; Ren et al., 2014). After considering the advantages of PUF-PAS in monitoring spatiality and seasonality of atmospheric POPs, we have used this method to measure the variations in concentration of atmospheric POPs during this PhD research programme.

OCPs can enter the aquatic environment through different pathways, such as industrial discharge, runoff from agriculture farmland, and deposition (dry or wet). Given their relatively high lipophilicity, as reflected by elevated n-octanol/water partition coefficients (log K_{OW} values: 3.7–6.95), and low water solubility (0.096–17 ppm) (Willett et al., 1998; Shen and Wania, 2005), OCPs can be easily adsorbed on to the surface of suspended particulate matter (SPM) as sediment (Montuori et al., 2014). SPM can then precipitate in sediments and eventually lower the OCP concentration in water. Under certain conditions (e.g., turbulence from ship movement or by flooding), sediments can be resuspended, releasing previously adsorbed OCPs back into the water phase, and initiate another cycle of environmental contamination (Feng et al., 2011; Zhou et al., 2014). When OCPs enter the water, they can also be transferred into the food chain by bioaccumulation in aquatic organisms. Subsequently, OCPs may reach humans by their consumption of contaminated water and marine life (Zhou et al., 2008). There is increasing research focusing on OCP pollution in Chinese estuaries and rivers (e.g., Luo et al., 2004; Tang et al., 2008; Wang et al., 2010; Wei et al., 2014).

Research aims

The primary aim of my research is to achieve a more detailed understanding of the fate mechanisms of POPs in the environment focusing, on the synergistic effects of physical, chemical, and biological processes within different media, including soil, sediment, air, and dustfall. In this Ph.D. thesis, I investigate the concentration and spatial distribution of POPs, to identify and quantitatively assess source contributions to POP populations, with the ultimate aim of evaluating the potential cancer risk to human health from POPs. This work is an investigation of POP residues in a multimedia environment that can serve as a blueprint for informed policy decision making, with the aim of evaluating public health risk due to exposure to POPs.

Article in this Ph.D. thesis

1. **Qu Chengkai, Albanese Stefano, Chen Wei, Lima Annamaria, Doherty Angela L., Piccolo Alessandro, Arienzo Michele, Qi Shihua, and De Vivo Benedetto, 2016. The Status of Organochlorine Pesticide Contamination in the Soils of the Campanian Plain, Southern Italy, and Correlations with Soil Properties and Cancer Risk. Environmental Pollution 216: 500-511.**

The main objective of this paper is to investigate the distribution, inventory, and potential risk of OCPs, including Hexachlorocyclohexanes (HCHs) and Dichlorodiphenyltrichloroethanes (DDTs), and their correlation with soil properties and anthropogenic factors in soils of the Campanian Plain. We found that (1) agriculture is a significant source of OCPs being released into the environment; (2) the distribution of OCPs in soils is a typical secondary distribution pattern; (3) there is no strong evidence for a link between OCPs distribution and the incidence of cancer; (4) the incremental lifetime cancer risk for residents exposed to OCPs is negligible.

2. **Qu Chengkai, Albanese Stefano, Sun Wen, Lima Annamaria, Qi Shihua, and De Vivo Benedetto. Residues of hexachlorobenzene and chlorinated cyclodiene pesticides in the soils of the Campanian Plain, southern Italy. (In progress to be submitted to science of the total environment)**

The main objective of this article is to investigate the distribution, inventory, and potential risk of hexachlorobenzene and chlorinated cyclodiene pesticides, and their correlation with soil properties and anthropogenic factors in soils of the Campanian Plain.

3. **Qu Chengkai, Qi Shihua, Yang Dan, Huang Huanfang, Zhang Jiaquan, Chen Wei, Yohannes Keleta Habtom, Sandy Edward Hinga, Yang Junhua, and Xing Xinli, 2015. Risk Assessment and Influence Factors of Organochlorine Pesticides (OCPs) in Agricultural Soils of the Hill Region: A Case Study from Ningde, Southeast China. Journal of Geochemical Exploration 149: 43-51.**

The aim of the research is to elucidate contamination profiles, distribution characteristics, influencing factors, and carcinogenic risks of these compounds in this rugged region by assessing surface soil samples from farmlands in Ningde. We found that (1) HCHs, DDTs and Endosulfans were the most dominant contaminant among the 20 OCPs; (2) the OCP residues especially DDTs were remarkably influenced by land-use type; (3) the residue levels of OCPs in agricultural soils were slightly controlled by TOC; (4) the agricultural soils polluted by OCPs may pose a high carcinogenic risk for exposed populations.

4. **Qi Shihua, Zhang Yuan, Xing Xinli, Yang Dan, Devi Ningombam Linthoingambi, Qu Chengkai, Liu Hongxia, Zhang Jiaquan and Zeng Faming, 2017. Legacies of Organochlorine Pesticides (OCPs) in soil of China - A Review, and cases in Southwest and Southeast China. In the book: Environmental Geochemistry: 21st Century Solutions to Old and New Environmental Problems (De Vivo B., Belkin H. E. and Lima A., Eds), Elsevier, Amsterdam (Accepted, in press).**

The article reviews the history and the present of OCPs in soil in China, and enclosed cases on OCPs distributions and influencing factors in soil of Chengdu Economic Region in Sichuan Province and Zhangzhou in Fujian Province, representatives of the Southwest and Southeast of China, respectively. As the majority of OCPs are not the POPs currently in use in various industries, the main targets of the research on OCPs may shift to aspects further than simply their concentration and distribution. The experience of battling with such POPs may give examples on how to avoid or terminate such chemicals pollutants.

5. **Qu Chengkai, Doherty Angela L., Xing Xinli, Sun Wen, Albanese Stefano, Lima Annamaria, Qi Shihua and De Vivo Benedetto, 2017. Polyurethane foam-based passive air samplers in monitoring persistent organic pollutants: Theory and application. In the book: Environmental Geochemistry: 21st Century Solutions to Old and New Environmental Problems (De Vivo B., Belkin H. E. and Lima A., Eds), Elsevier, Amsterdam (Accepted, in press).**

The article makes a survey on the principles of passive air samplers (PAS) techniques and progress of the polyurethane foam-based PAS (PUF-PAS) in monitoring POPs from a local to global scale. The calibration method of the site-specific sampling rate (R_s) on the basis of the loss of depuration compounds (DCs) from the PUF disk is explained, and the factors (i.e., temperature, wind speed, and atmospheric particle) that influence R_s are also discussed. The future research prospects in the development and application of PUF-PAS have been discussed.

6. **Qu Chengkai, Xing Xinli, Albanese Stefano, Doherty Angela L., Huang Huanfang, Lima Annamaria, Qi Shihua and De Vivo Benedetto, 2015. Spatial and seasonal variations of atmospheric organochlorine pesticides along the plain-mountain transect in central china: regional source vs. long-range transport and air–soil exchange. Atmospheric Environment 122: 31-40.**

The aim of the article was to make a preliminary explorative study of the source-sink relationship of OCPs and their association with the monsoon by deploying PUF-PAS to measure spatiality and seasonality of atmospheric OCPs in Jianghan Plain (JHP) and Western Hubei Mountain (WHM). The major conclusions include: (1) variations in spatial and seasonal concentration of atmospheric OCPs were observed; (2) since 2005, levels of atmospheric legacy OCPs decreased while Endosulfan increases; (3) the plains act as an OCP contaminant emitter to atmosphere; (4) seasonal fluctuation of atmospheric OCPs are linked to the East Asian monsoon.

7. **Zhang Jiaquan, Qu Chengkai (co-first author), Qi Shihua, Cao Junji, Zhan Changlin, Xing Xinli, Xiao Yulun, Zheng Jingru and Xiao Wensheng, 2015. Polycyclic Aromatic Hydrocarbons (PAHs) in Atmospheric Dustfall from the Industrial Corridor in Hubei Province, Central China. Environmental Geochemistry and Health 37: 891-903.**

Thirty atmospheric dustfall samples collected from an industrial corridor in Hubei Province, central China, were analyzed for 16 USEPA priority PAHs to investigate their concentrations, spatial distributions, sources, and health risks. We found that (1) individual PAH concentrations were not significantly correlated with total organic carbon; (2) the PAHs were mainly from motor vehicles and biomass/coal combustion; (3) potentially serious carcinogenic risks for exposed populations in the industrial corridor should be considered furture.

8. **Liu Jia, Qi Shihua, Yao Jun, Yang Dan, Xing Xinli, Liu Hongxia and Qu Chengkai, 2016. Contamination Characteristics of Organochlorine Pesticides in Multimatrix Sampling of the Hanjiang River Basin, Southeast China. Chemosphere 163: 35-43.**

This field study of the research examined the distribution of different HCH- and DDT-related compounds in multimatrix samples taken from various sites along a major Chinese river. Highlights include (1) dissolved phase, SPM, and surface sediment in Hanjiang River Basin were analyzed for OCPs; (2) K_d was used to determine the partition between SPM and water on horizontal profile; (3) transport was predicted based on fugacity model.

Highlights on PhD program: POPs in soils of Campania, Italy

In the framework of a wide reaching project aiming at characterizing the environmental conditions of the region of Campania in southern Italy, within the regional Project Campania Trasparente, managed by IZSM Portici (Napoli), water, soil, air and biological samples from different sources were collected to assess the ecological and the human health risk for the local population.

Among the different sampled media, 400 soil samples were collected across the whole regional territory with an average density of 1 sample per 6 square km with the aim of determining the distribution patterns of PAHs, OCPs and PCBs concentrations (Figs. 1 and 2).

Sampling sites were established on the basis of a systematic approach by means of a regular grid; a judgmental criteria was used within each sampling cell to enhance the representativeness of the results.

At each sampling site, soil samples were formed by mixing 5 subsoil samples collected within a radius of 5-10 meters. During the whole process of transportation and shipment of samples to the Pacific Rim Laboratory (Canada) the temperature was kept below -10°C to avoid the degradation of organic compounds in soils.

All samples were processed using an ASE 350 extractor, analyzed on a Thermo Scientific DFS HRMS, and quantified using isotope dilution methodology. Approximately 10 g dry weight of sample was loaded into a 100 mL s.s. cell, spiked with 13C-labeled standards (27 PCB congeners @ 5 ng, 18 OCP @ 25 ng) and deuterated PAH (11 @ 500 ng) and extracted with 75:25 hexane:acetone. The resulting extract was split into three fractions for separate clean-up and analysis using the following columns/resolution:

- PCB – 60 m x 0.25 mm i.d., SGE HT8, tuned to 10,000 resolution
- OCP – 30 m x 0.25 mm i.d., Zebron Pesticide I, tuned to 8,000 resolution
- PAH – 60 m x 0.25 mm i.d., Zebron Semivolatiles, tuned to 3000 resolution.

Preliminary results show that, on a side, the distribution of analyzed compounds strongly depends on the presence of human activities and, on the other side, they are not always predictable on the basis of preliminary assumptions.

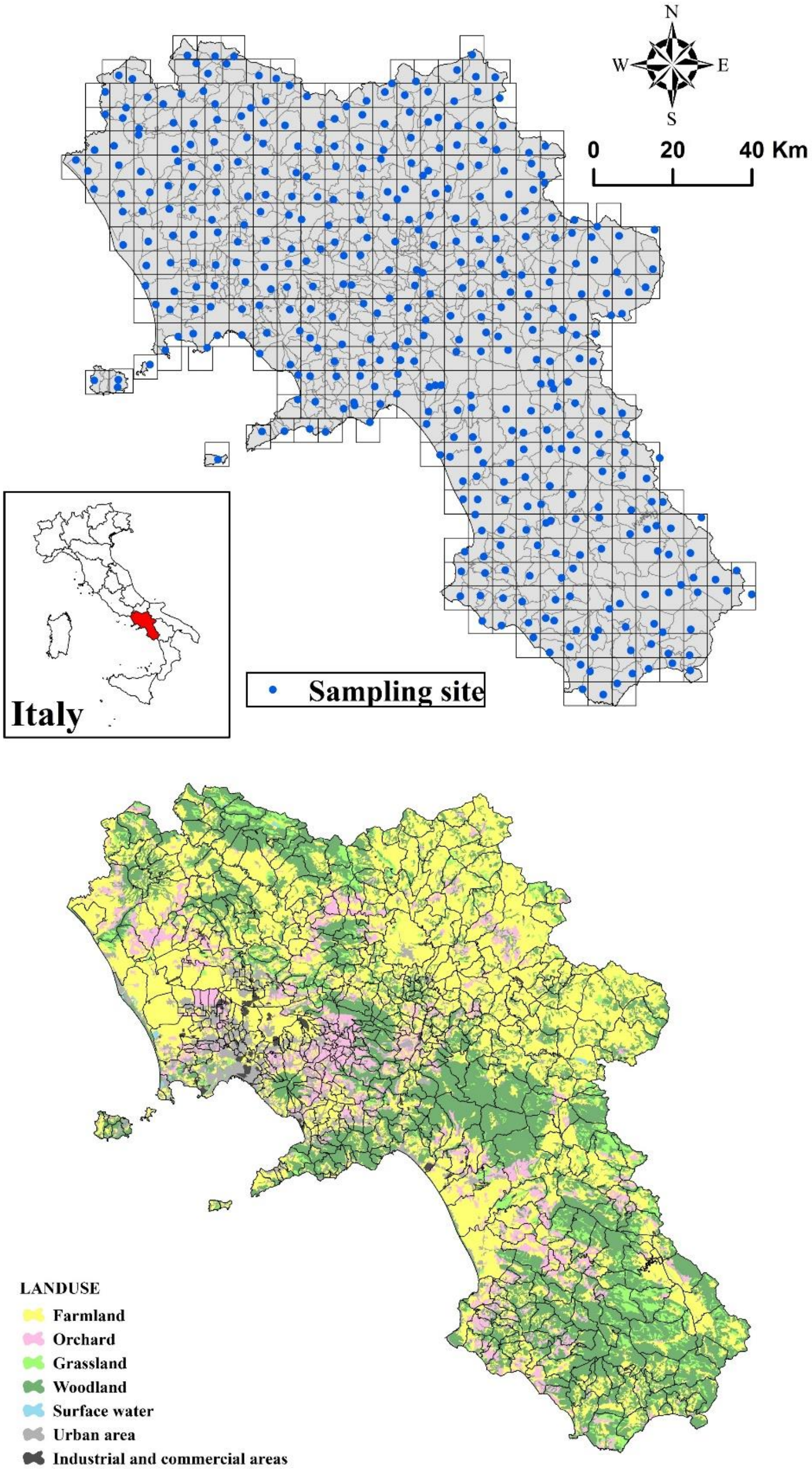

Fig. 1. Map of the different land uses within the study area and location of soil sampling sites.

Fig. 2. Photographs showing the local conditions at selected sampling sites.

Highlights of Ph.D. program: POPs in air and particle deposition in the region of Campania, Italy

Campania covers approximately 13,600 km^2, and is one of the most densely populated regions in Italy (approximately 6 million inhabitants). Many detailed research projects have illustrated that Campania faces an arduous challenge in mitigating increasing environmental pollution by POPs. For example, our recent research confirmed that the PAH and OCP contamination in the soils of the Campania Plain persist which, while at a low level of risk, requires attention (Albanese et al., 2015; Qu et al., 2016).

Campania falls within the subtropical zone and enjoys a Mediterranean climate, and thus, the high temperatures experienced here may facilitate the volatilization and escape of POPs from soils, sediments, and water. Our findings suggested that the distribution of OCPs in soils appears to be a typical secondary distribution pattern (i.e., soils act as the re-emission source to atmosphere) (Qu et al., 2016). However, this should be confirmed with further study, implementing a monitoring program of atmospheric POPs in Campania.

A large-scale field campaign, managed by Istituto Zooprofilattico Sperimentale del Mezzogiorno (IZSM), Portici, Italy, is being implemented with the purpose of characterizing the environmental conditions of Campania, within the framework of Project Campania Trasparente. In this program, samples from several target environmental media including, water, soil, air, and organisms, are being collected, with the aim of evaluating the potential ecological and human health risk of POPs, including OCPs, PCBs and PAHs. As one of the design and implementation partners of the project, we use PUF-

PAS to monitor the spatiality and seasonality of atmospheric POPs in a subproject, namely the Campania Atmospheric Monitoring Project (CAMP).

The monitoring network is performed at approximately 150 sites using PUF-PAS, and particle deposition is collected at 40 sites (Fi. 3.). The PUF-PAS project is divided into two stages: first, a pilot study in the metropolitan area of Naples, which will be followed by an investigation of atmospheric POPs in the territory of Campania. The entire sampling campaign lasts from July 2015 to March 2017 in 3 month integrated periods; the sampling period lasts an initial three seasons in the first stage, and subsequent four seasons in the second stage.

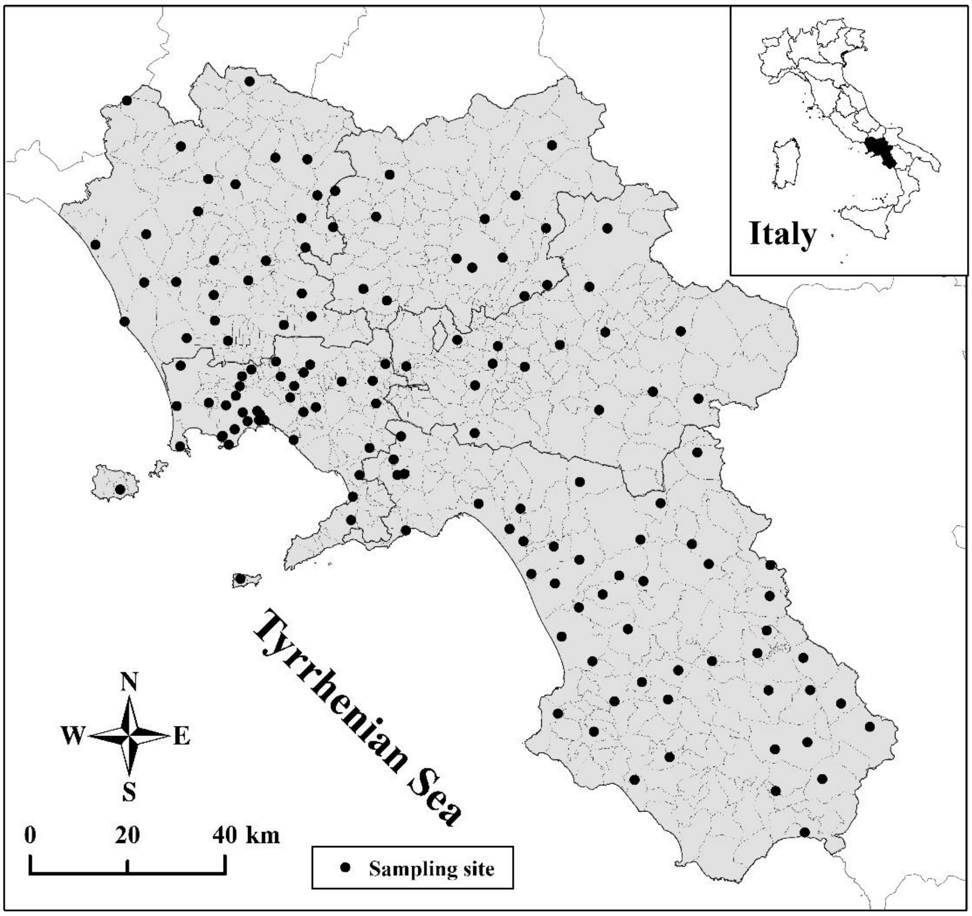

Fig. 3. Map showing the study area and locations of passive air sampling sites

PCB congeners 54, 104, and 188 were added to the PUF disks to calculate the R_S. in the first season of the first stage, and $^{13}C_{12}$-labeled PCB congeners 31, 70, 95, 153, and 180 were used as the DCs in the subsequent sampling campaign.

In the project, the three types of POPs are measured:

OCPs: *α*-, *β*-, *γ*-, and *δ*-HCH, *p,p'*-DDE, *p,p'*-DDD, *o,p'*-DDT, *o,p'*-DDE, *o,p'*-DDD, and *p,p'*-DDT, HCB (Hexachlorobenzene), *a*-Endosulfan, *β*-Endosulfan, Endosulfan sulfate, cis-Chlordane, trans-Chlordane, cis-Nonachlor, tran-Nonachlor, Aldrin, Dieldrin, Endrin, Heptachlor, Mirex, Methoxychlor.

PAHs: Acenaphthene, Acenaphthlyene, Anthracene, Benz(a)anthracene, Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(ghi)perylene, Benzo(k)fluoranthene, Chrysene, Dibenz(a,h)anthracene, Dibenzo(a,e)pyrene, Dibenzo(a,h)pyrene, Dibenzo(a,i)pyrene, Dibenzo(a,l)pyrene, Fluorene, Indeno(1,2,3-cd)pyrene, Naphthalene, Phenanthrene, Pyrene.

PCBs: PCB 81, PCB 77, PCB 123, PCB 118, PCB 114, PCB 105, PCB 126, PCB 167, PCB 156, PCB 157, PCB 169, PCB 189, PCB 28, PCB 52, PCB 101, PCB 153, PCB 138, PCB 180.

CAMP aims to present spatial and seasonal variations in the concentrations of POPs in the atmosphere of the metropolitan area of Naples, and the territory of the Campania region; the contamination status, possible sources, and human health risk of POPs will also be demonstrated. The relationship between epidemiological data and carcinogenic risk of air POP residues in the study area will also be explored.

The research is a pioneering investigation of POP residues in the atmosphere and particle deposition of Campania by adopting a sampling plan of high spatial resolution and may be as a blueprint for formulating informed policy related to the evaluation of public health risk due to POP exposure.

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Chapter 2: Soil

Section 2.1

The status of organochlorine pesticide contamination in the soils of the Campanian plain, southern Italy, and correlations with soil properties and cancer risk

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Section 2.1

The status of organochlorine pesticide contamination in the soils of the Campanian plain, southern Italy, and correlations with soil properties and cancer risk

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The status of organochlorine pesticide contamination in the soils of the Campanian Plain, southern Italy, and correlations with soil properties and cancer risk

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Highlights:

- Systemic data on OCPs concentrations in soils of the Campanian Plain are presented.
- Agriculture is a significant source of OCPs being released into the environment.
- The distribution of OCPs in soils is a typical secondary distribution pattern.
- No strong evidence for a link between OCPs distribution and the incidence of cancer.
- The incremental lifetime cancer risk for residents exposed to OCPs is negligible.

Abstract: The distribution, inventory, and potential risk of organochlorine pesticides (OCPs), including Hexachlorocyclohexanes (HCHs) and Dichlorodiphenyltrichloroethanes (DDTs), and their correlation with soil properties and anthropogenic factors were investigated in soils of the Campanian Plain. The total concentrations of HCHs and DDTs ranged from 0.03 to 17.3 ng/g (geometric mean: GM= 0.05 ng/g), and 0.08 to 1231 ng/g (GM= 14.4 ng/g), respectively. In general, the concentration of OCPs in farmland and orchards was higher than on land used for non-agricultural purposes. There are significant differences in the concentration of OCPs in the soils across the region, more specifically, the Acerra-Marigliano conurbation (AMC) and Sarno River Basin (SRB) are recognized as severely OCP-contaminated areas. The recent application of technical HCHs and DDTs in large quantities appears unlikely in light of the ratio of α-HCH/β-HCH and *p,p'*-DDT/*p,p'*-DDE, and the prohibition of the use of these chemicals in Italy nearly forty years ago. The clear correlation between the concentration of DDTs and organic carbon suggests a typical secondary distribution pattern. The mass inventory of OCPs in soils of the Campanian Plain is estimated to have a GM of 17.3 metric tons. There is no clear evidence linking the impact of geographical distribution of OCPs on the incidence of cancer, and the 95% confidence interval of total incremental lifetime cancer risk (TILCR) data falls below the internationally accepted benchmark value of 1 x 10^{-5}.

"Capsule": The contamination status of OCPs, and their correlations with soil properties and cancer risk are assessed in soils of the Campanian Plain using a grid sampling method and geostatistics.

Keywords: Organochlorine pesticides; Soil property; Mass inventory; Risk assessment; Campanian Plain

1. Introduction

While the prolific use of organochlorine pesticides (OCPs) over the last few decades has greatly decreased the incidence of agricultural and vector-borne diseases, it has raised new concerns regarding the potential dangers of OCPs to human health and the environment (Yadav et al., 2015). Many treaties and laws have been enacted to eliminate or restrict the production and use of some OCPs, of which the Stockholm Convention on Persistent Organic Pollution (POPs) is one of the most famous. Two of the most representative OCPs are Dichlorodiphenyltrichloroethanes (DDTs) and Hexachlorocyclohexanes (HCHs), which were used extensively worldwide from the 1950s to the 1980s as agricultural and domestic pesticides (Tieyu et al., 2005). In the latter half of the 20th century, the total global production of HCHs and DDTs reached at 2 and 3 million metric tons, respectively, and the consumption rate of these both pesticides in Mediterranean countries reached approximately 2000 t/yr (Bacci, 1993 and references therein).

OCPs generally break down in the environment over time, however, as they are persistent and have an affinity for organic matter, a considerable quantity of these chemicals may remain stored in soils (Zhang et al., 2012). These OCPs tend to accumulate in organisms and are biomagnified through the food chain (Naso et al., 2003). The soil then becomes a reemission source as the OCPs are released into the atmosphere (Tao et al., 2008). A large quantity of OCPs in agricultural soils can be transported into the surface water by farm drainage and surface runoff, and into groundwater via farmland sewage irrigation (Montuori et al., 2014). The environmental fate of OCPs in soils is affected by many factors, of which, the physicochemical characteristics of agrochemicals (e.g., vapor pressure, water solubility), land use type, application history and agricultural practices (e.g., flood irrigation, superphosphate application, and tilling), soil properties (e.g., organic carbon [OC], pH, texture, and moisture content), as well as meteorological variables (e.g., temperature, wind direction), are, perhaps, the most important (Yu et al., 2013; Zhang et al., 2011). As a result, soil plays an important role in the circulation of these substances in different sectors of the environment, but the behavior and fate of OCPs in soils on a regional scale is a complicated process.

Many recent studies have produced ecological risk assessments in soils contaminated with OCPs (e.g., Yu et al., 2013; Zhang et al., 2009), however, literature regarding the carcinogenic risk of human exposure to OCPs is limited. While the risk to human health from exposure to soil-borne OCPs has recently been evaluated by calculating the incremental lifetime cancer risk (Ge et al., 2013; Hu et al., 2014; Qu et al., 2015), in general, the research into environmental epidemiology of OCPs, determining possible links between the incidence of specific diseases (including various forms of cancer) and the distribution patterns of OCPs, is scarce. For examples, Albanese et al. (2013) observed a clear spatial correlation between the incidence of some types of cancer and the distribution of certain toxic metals in stream sediments, while other research has demonstrated a close relationship between human cancers of the pancreas, breast, uterus, and liver with OCPs (Botella et al., 2004). Studying the impact of geographical distribution and ultimate fate of OCPs on the incidence of cancer is especially critical to the potential mitigation and/or remediation of the contaminated area.

So far, the Stockholm Convention has not been ratified by Italy, however, several other regulatory schemes, such as a European Directive in 2000, the UNECE POPs Protocol, and the Rotterdam Convention, are actively followed (Estellano et al., 2012). Italy was one of the main consumers of DDTs in late 20th century Europe, with consumption of DDTs reaching 2178, 1570, 197, 103, and 55 t/yr in 1970, 1975, 1980, 1985, and 1990, respectively (Pacyna et al., 2003). The Campania region is a very important area for Italian agriculture where fruits and vegetables are the predominant agricultural product, and uses a greater quantity of pesticides (28.4 kg/ha in 1978) relative to other Italian regions (Berardi, 1983). Recent studies have reported the levels of OCP contamination in the water, sediment and organisms of the Campania region (e.g., Ferrante et al., 2010; Montuori et al., 2014; Naso et al., 2005), however, a regional study of the soil contamination is still lacking. The Campania region falls within the subtropical zone and enjoys a Mediterranean climate. High temperatures in tropical/subtropical regions can facilitate the volatilization and escape of OCPs from soils, sediments, and water (Yadav et al., 2015). However, the lack of sufficient data on the residual concentration of OCP in soils, limits the understanding of the health effects, environmental dynamics, and ultimate fate of these chemicals.

This paper presents the results of an investigation using a systematic grid sampling method and geostatistics to illustrate spatial variations in the concentrations of OCPs in the soils of the Campanian Plain. The main objectives of this study were: (I) to investigate the residual levels, distribution, and possible sources of OCPs, and their subsequent mass inventories in soils of the Campanian Plain, (II) to analyze the impact of soil properties on contaminant distribution, and (III) to evaluate the potential ecological and health risks of OCPs and preliminarily explore whether there is a significant correlation between epidemiological data and carcinogenic risk of OCP residues.

2. Study area

The study area covers approximately 2,400 km^2, and roughly corresponds to the Campanian Plain, defined as a wide coastal belt that extends from the Volturno River Plain to the Sarno River Basin (Fig. 1A). Large urban settlements are located within the study area. These are densely populated and industrialized, and adjacent to extensive areas dedicated to agriculture. Recently, this area has become infamous for the illegal disposal of toxic/radioactive waste by local criminal organizations (Senior and Mazza, 2004). The study area consists of three idealized territorial units based on land use (Fig. 1A) and morphology (Fig. 1B): (1) the Domizio-Flegreo Littoral (DFL) and Agro Aversano (AA) areas, (2) the metropolitan area of Naples (NAP), and (3) the Sarno River Basin (SRB) and Sorrento Peninsula (SP).

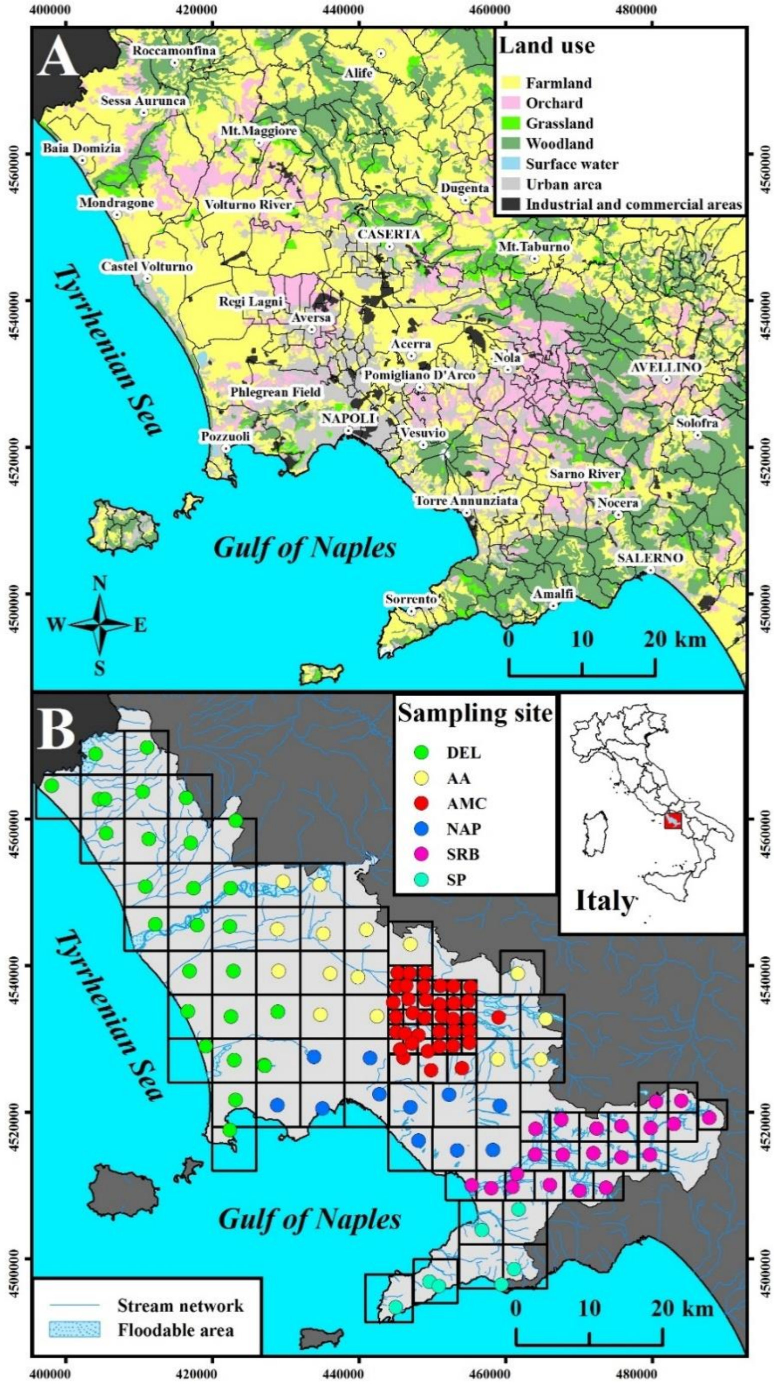

Fig. 1. (A) Map of the different land uses within the study area; (B) Location of soil sampling sites. Note: DFL: Domitizio-Flegreo Littoral, AA: Agro Aversano, AMC: Acerra-Marigliano Conurbation, NAP: Metropolitan area of Naples, SRB: Sarno River Basin, SP: Sorrento Peninsula.

2.1.Domizio-Flegreo Littoral, Agro Aversano and Acerra-Marigliano Conurbation

The Domitizio-Flegreo Littoral (DFL) and Agro Aversano (AA) areas (including the Volturno River Plain, the Regi Lagni Basin, and the Phlegrean volcanic field) have been declared as Sites of National Interest by the Italian Government due to their high potential for contamination. Chemical industries, intensive agriculture and buffalo farms are the main productive activities in the Volturno River Plain and the Regi Lagni Basin, and are also considered the main sources of heavy metal and organic pollution in both stream waters and soils (Bove et al., 2011; Grezzi et al., 2011). Across the DFL and AA areas, illegal waste dumping and uncontrolled burning of agricultural and industrial wastes continue to affect the overall environmental equilibrium.

Within the Agro Aversano territory, the Acerra-Marigliano conurbation (including the municipalities of Acerra, Pomigliano d'Arco, Castelcisterna, Marigliano, Mariglianella and Nola, collectively known as the AMC) was once an important agricultural heartland, and remains the home of important chemical (Montefibre) and automotive (FIAT) industries. In the northern sector of the Acerra municipal territory, an urban waste incinerator started activity in 2009, burning, at the start of its operation, un-differentiated waste from the metropolitan area of Naples. Additionally, the AMC is known as part of the infamous “Triangle of Death”, the region where Senior and Mazza (2004) found an abnormal incidence of cancer in the local population, and postulated a link to the widespread illegal dumping (and burning) of waste.

The AMC also belongs to a huge territorial meta–entity, comprising 57 municipalities, and approximately two and half million inhabitants, renamed by Italian media as the "Land of Fires", due to the almost daily unauthorized burning of industrial waste of unknown origin across these territories.

2.2.Naples Metropolitan Area

Naples, the third-largest municipality in Italy with a high density of both population and industry, faces a serious challenge in mitigating the increasing environmental contaminants caused by persistent toxic substances (Albanese et al., 2015a). The metropolitan area of Naples (NAP), extending from the Phlegrean Fields in the west, to the Mt. Vesuvius volcanic complex in the east, is surrounded on three sides by agriculture (Fig. 1A).

2.3.Sarno River Basin and Sorrento Peninsula

The Sarno River Basin (SRB), comprising the alluvial plain of the Sarno River and the valleys of the Solofrana and Cavaiola tributaries, is the largest and most important economic area in Campania due to its fertile soil and favorable climate.

Productive activities within the alluvial plan of the SRB include dairies processing milk from local farms, canneries associated with local agricultural production (mostly tomatoes), paper mills and chemical (or pharmaceutical) plants.

The inner sector of the SRB, also dominated by the presence of farms, is well known for the area of Solofra, where about 160 tanneries are located, and as a base for trucking companies (Arienzo et al., 2015).

Due to high population density, the extensive application of agricultural fertilizers and pesticides, and widespread industrial development, the Sarno River itself has long suffered from pollution, and is considered "the most polluted river in Europe" (Montuori et al., 2014). Furthermore, agricultural soils close to the river bed are often overloaded with contaminants by the frequent floods of the river, which is also used as a water supply for local intensive agriculture (Albanese et al., 2015a).

The Sorrento Peninsula (SP), located in the southeast of the SRB, is mostly mountainous with rugged coasts and small beaches attracting thousands of tourists annually.

3. Methodology

3.1.Sample collection

One hundred and nineteen soil samples were collected from the Campanian Plain between April and May 2011. Each sampling site was selected at the center of the squared cells of an ideal grid superimposed onto the study area. The cells have variable dimensions, and sampling density varied acaccordingly, from the 36 km^2 of the Domizio–Flegreo Littoral, to 4 km^2 of the Acerra–Marigliano conurbation (Fig. 1B). At each site, a composite sample of 0.5 kg was collected by mixing together five aliquots taken at the center and at the corners of an ideal square with a side of 5 m. After every 20 sampling sites, a duplicate sample in the same cell was collected, in order to allow a blind control of the analytical quality. At each sampling site, spatial coordinates, soil and air temperatures, local geology, type and main properties of soils, land use, and any additional details related to anthropic activities in the surroundings were recorded. All samples were stored in plastic bags and kept at a temperature of 4°C using a portable cooler during the transportation from the collection sites to the Environmental Geochemistry Laboratory (LGA) at the University of Naples Federico II. Subsequently, all samples, packed in polystyrene boxes together with dry ice pellets (to maintain a low temperature) were sent to the State Key Laboratory of Biogeology and Environmental Geology at China University of Geosciences, for the analysis of OCPs.

3.2.Analytical procedures for OCPs and soil properties

The concentration of OCPs including HCH isomers (α-β-γ- and δ-HCH), and DDT and its metabolites (*p,p′*-DDD, *p,p′*-DDE, *o,p′*-DDT and *p,p′*-DDT) were quantified in each sample. Soil physiochemical properties including particle-size distribution, pH, and organic carbon (OC) content were measured for 41 samples, which were selected as representative of the soil units of the study area, including 21 samples from the SRB. Analytical procedures for OCPs and the determination of soil properties are as following:

3.2.1 OCPs

Extraction and cleanup

The extraction/clean-up procedure for the soil samples has been described previously (Chen et al., 2011; Qu et al., 2015; Zhang et al., 2013). Briefly, soil samples were spiked with 2,4,5,6-tetrachloro-m-xylene (TCmX) and decachlorobiphenyl (PCB209) and then Soxhlet extracted with dichloromethane for 24 hours. Anhydrous Na_2SO_4 and activated copper were added for dehydration and desulfurization, respectively. The extracts were concentrated and solvent-exchanged to hexane by rotary evaporator. The hexane solution was purified by an alumina/silica (1:2, v/v) gel column. The column was eluted with 30 mL of dichloromethane/hexane (2:3, v/v). The eluate was concentrated to 0.2 mL under a gentle nitrogen stream and spiked with penta-chloronitrobenzene (PCNB) as an internal standard for instrument analysis.

Instrumental analysis

The quantitative analysis was performed using an Agilent 7890A gas chromatograph with a 63Ni electron capture detector (GC-μECD) and a DB-5 capillary column (30.0 m×320 μm×0.25 μm film thickness). Nitrogen was used as carrier gas at 2.5 mL/min under constant-flow mode. Injector and detector temperatures were maintained at 290°C and 300°C, respectively. The oven temperature started from 100°C (with an equilibration time of 1 min), and rose to 200°C at a rate of 4°C/min, then to 230°C at 2°C/min, and finally reached 280°C at 8°C/min, and was held for 15 min. 2.0 μL of each sample was injected into the GC-μECD system for the analysis. The individual OCPs was identified by comparison of their retention times (previously confirmed with GC/MS) and quantified using an internal standard. An Agilent 6890GC-5975MSD system was employed. The chromatographic conditions were the same as described above. The MS was operated using electron impact (EI) ionization at 70 Ev and in the selected ion monitoring (SIM) mode.

Quality control/Quality assurance

Analytical procedures were monitored using strict quality control measures, as follows:

(1) TCmX and PCB 209 were spiked as surrogate standards to judge procedural performance. The surrogate recoveries for TCmX and PCB 209 were 77.8 ± 19.0 % and 89.3 ± 20.3 %, respectively;

(2) The target compounds were identified by the comparison of their retention times, and quantified by a six-point internal standard calibration curve obtained from the OCP standard regents with concentration of 200, 150, 100, 50, 20 and 10 μg/L;

(3) A procedural blank and a parallel sample were run to check for interferences and cross contamination in every set of 16 samples. No significant peaks overlapping the OCP standards appeared in the chromatograms of the procedural blanks. For more than 97% of target com-pounds in parallel samples, the relative errors (RE, %) of concentration was less than 50%;

(4) A solvent blank sample and an OCP standard solution (100 μg/L) was injected daily before analyzing the soil samples extracts. No target OCPs were detected in the solvent blank sample. The OCPs standard solution was analyzed for instrument calibration, and the deviation was less than ±15 %;

(5) The samples of different concentrations were injected 10 times, and the relative standard deviation (RSD) was calculated. RSD for all the target compounds ranged from 2.7% to 8.3%.

The limits of detection (LOD) and quantification (LOQ) were determined as the concentrations of analytes with a signal-to-noise-ratio of 3 and 10, respectively. Reported values were corrected by the surrogate recoveries and were subtracted of the blank samples results.

3.2.2 Physicochemical analysis of soil

Forty-one samples selected as representative of the soil units of the study area, including twenty-one samples from SRB, were sent to the Agricultural and Environmental Analytical Laboratory of the

University of Naples Federico II for the measurement of soil physicochemical properties. Particle-size distribution was determined by the pipette method (Gee and Bauder, 1986). Soil pH was measured in water with the soil to water ratio of 1:2.5 (w/v) using a potentiometric glass electrode (Pansu and Gautheyrou, 2007). Organic carbon (OC) content was measured by using the Walkley-Black method (Walkley and Black, 1934) and converted to organic matter (OM) by multi-plying for 1.724 (Nelson and Sommers, 1996).

3.3.Data processing and elaboration

3.3.1. Geochemical mapping

Geochemical maps showing the spatial distribution of HCHs and DDTs were generated by means of the multifractal inverse distance weighted (MIDW) algorithm with the GeoDAS^{TM} software (Cheng, 2003). As already demonstrated by previous studies at regional and continental scale (Albanese et al., 2007; Albanese et al., 2015b; Lima et al., 2003), the MIDW was chosen as an interpolation method as it preserves high frequency information (anomalies), while taking into account both spatial associations and local singularity in geochemical data (Cheng, 1999). The concentration–area (C–A) fractal method (Cheng et al., 1994) was applied to set the concentration intervals of the interpolated surfaces generated by the MIDW method, and ArcGIS^{TM} software was used for the graphical presentation of the results.

3.3.2. Mass inventory

To assess the potential influence of OCPs on the agricultural products and the terrestrial environment, the mass inventory of particular OCPs in the soils of the Campanian Plain were estimated using the following equation (Zou et al., 2007):

$$I=\sum_{i=1}^{n} kC_iA_id\rho \qquad (1)$$

where C_i is the soil concentration of OCPs within segment i (ng/g dw); A_i is the land area of segment i (km^2); d is the thickness of the soil sampled (cm); ρ is the dry mass density of soils (g/cm^3); and k is the unit conversion factor.

Considering the inherent problem of uncertainty/variability of the parameters in Eq. (1), the calculation of the pollutant inventory using a single deterministic value has some limitations (Wang et al., 2010). In this study, the OCP inventory was calculated using Monte Carlo simulations to select the variables using the following steps:

(I) In Eq. (1), the C_i value was selected randomly based on its probability distribution; the A_i value was chosen from a uniform distribution based on land-type (Table 1); the d value was selected from a uniform distribution using an estimated thickness of 0-20 cm; the ρ value was chosen from the normal distribution using a soil density of 1.15±0.0507 g/cm^3 (Ciollaro and Romano, 1995). And finally, the product of C_i, A_i, d and ρ was calculated.

(II) Subsequently, step (I) was repeated n times (n being the number of soil samples), and Eq. (1), $\sum_{i=1}^{n} k\, C_i A_i d\rho$ was used to calculate the OCP inventory.

(III) Step (II) was repeated 20,000 times to generate the frequency distribution of OCP inventory.

The Microsoft Excel add-in Crystal Ball (Oracle software, Version 11.1.2.3) was used to calculate the OCP inventory using Monte Carlo simulations.

Table 1 Total land area and extent of area prone to flooding within the sub-areas of the Campanian Plain.

	Campanian Plain [a]	DFL	AA	AMC	NAP	SP	SRB
Total area (km^2)	2624	936	624	132	396	216	320
Floodable area (km^2) [b]	113	34	27	5	3	2	42

[a] the Campanian Plain is divided into six areas, including Domizio-Flegreo Littoral (DFL), Agro Aversano (AA), Acerra-Marigliano Conurbation (AMC), Naples (NAP), Sarno River Basin (SRB) and Sorrento Peninsula (SP).

[b] The "Total area" less the "Floodable area" is used as the lower limit of a uniform distribution to calculate land area during Monte Carlo OCP mass inventory simulations.

3.3.3. Cancer risk model and mapping

In this study, the incremental lifetime cancer risk (ILCR) was calculated by means of a Preliminary Quantitative Risk Assessment (PQRA) procedure, with the intent of estimating the cancer risk for human beings exposed to environmental OCPs. Considering inhalation of fugitive dust, inadvertent ingestion, and dermal contact from contaminated soil as exposure pathways, the ILCRs was calculated using the following equations (Health Canada, 2010):

$$ILCR_{Ing}=\frac{C_S \cdot IR_S \cdot RAF_{Oral} \cdot D_2 \cdot D_3 \cdot D_4}{BW \cdot LE} \cdot CSF_{Ing} \tag{2}$$

$$ILCR_{Inh}=\frac{C_S \cdot P_{Air} \cdot IR_A \cdot RAF_{Inh} \cdot D_1 \cdot D_2 \cdot D_3 \cdot D_4}{BW \cdot LE} \cdot CSF_{Inh} \tag{3}$$

$$ILCR_{Derm}=\frac{[(C_S \cdot SA_H \cdot SL_H)+(C_S \cdot SA_O \cdot SL_O)] \cdot RAF_{Derm} \cdot D_2 \cdot D_3 \cdot D_4}{BW \cdot LE} \cdot CSF_{Derm} \tag{4}$$

where C_S is the concentration of contaminant in soil (mg/kg); IR_S is the receptor soil ingestion rate (kg/d); RAF_{Oral} is the relative absorption factor from the gastrointestinal tract (unitless); D_1 is the hours per day exposed/24 hours; D_2 is the days per week exposed/7 days; D_3 is the weeks per year exposed/52 weeks; D_4 is the total years exposed to site; BW is the body weight (kg); LE is the life expectancy (yr); P_{Air} is the particulate concentration in air (kg/m^3); IR_A is the receptor air intake (inhalation) rate (m^3/d); RAF_{Inh} is the relative absorption factor by inhalation (unitless); SA_H is the surface area of hands exposed for soil loading (cm^2); SA_O is the surface area exposed other than hands (cm^2); SL_H is the soil loading rate to exposed skin of hands (kg/cm^2-event); SL_O is the soil loading rate to exposed skin other than hands (kg/cm^2-event); RAF_{Derm} is the relative dermal absorption factor (unitless); and CSF is the carcinogenic slope factor (1/mg/kg/d).

The values of the *CSF* and exposure parameters used to derive the ILCR are presented in Tables 2 and 3. The total incremental lifetime cancer risks (TILCRs), were estimated as the sum of individual risks of the three exposure pathways, for 5 specific age groups (infant, toddler, child, teen, and adult) on the basis of their behavioral, biological, and morphometric characteristics (Table 3).

Calculated TILCR values associated with each soil sampling point were then georeferenced, and mapped after undergoing MIDW interpolation. Value intervals in maps were constructed to facilitate the comparison of results using the internationally accepted benchmark value of 1 x 10^{-5} (1 case of cancer in 100,000 exposed people), deemed to be the most appropriate for considering an essentially negligible carcinogenic risk.

Table 2 The carcinogenic slope factor (1/mg/kg/d) of OCPs through ingestion, dermal contact and inhalation.

Compound	$CSF_{ingestion}$	CSF_{dermal}	$CSF_{inhalation}$
p,p'-DDE	3.40E-01	4.86E-01	NA
p,p'-DDD	2.40E-01	3.43E-01	NA
p,p'-DDT	3.40E-01	4.86E-01	3.40E-01

NA indicated that a value was not available

Table 3 Parameters for estimating of the incremental lifetime cancer risk

Receptor Characteristic	Units	Infant	Toddler	Child	Teen	Adult	Source
Age	yr	0–6 mo.	7 mo.–4 yr.	5–11 yr.	12–19 yr.	≥ 20 yr.	Health Canada (1994)
Age group duration	yr	0.5 yr.	4–5 yr.	7 yr.	8 yr.	60 yr.	Based on an 80-year lifespan
Body weight (BW)	kg	8.2	16.5	32.9	59.7	70.7	Richardson (1997)
Life expectancy (LE)	yr	80	80	80	80	80	Health Canada (2010)
Soil ingestion rate (IR_S)	kg/d	0.00002	0.00008	0.00002	0.00002	0.00002	CCME (2006); MassDEP (2002); Wilson Scientific and Meridian (2006)
Relative oral absorption factor (RAF_{Oral})	unitless	1	1	1	1	1	OMOE (2011)
Particulate concentration in air (P_{Air})	kg/m^3	0.76×10^{-9}	0.76×10^{-9}	0.76×10^{-9}	0.76×10^{-9}	0.76×10^{-9}	US EPA (1992)
Inhalation rate (IR_A)	m^3/d	2.2	8.3	14.5	15.6	16.6	Allan et al., (2008, 2009)
Relative inhalation absorption factor (RAF_{Inh})	unitless	1	1	1	1	1	OMOE (2011)
Skin surface area (SA)	cm^2						Richardson (1997)
Hands		320	430	590	800	890	
Arms (upper and lower)		550	890	1480	2230	2500	
Legs (upper and lower)		910	1690	3070	4970	5720	
Soil loading to exposed skin	kg/cm^2/event						Kissel et al., (1996, 1998)
Hands (SL_H)		1×10^{-7}	1×10^{-7}	1×10^{-7}	1×10^{-7}	1×10^{-7}	
Surfaces other than hands (SL_O)		1×10^{-8}	1×10^{-8}	1×10^{-8}	1×10^{-8}	1×10^{-8}	
Relative dermal absorption factor (RAF_{Derm})[a]	unitless	0.03	0.03	0.03	0.03	0.03	OMOE (2011)
Dermal exposure events per day	event/d	1	1	1	1	1	Health Canada (2010)

[a] The relative dermal absorption factor (RAF_{Derm}) is 0.03 for DDT.

3.3.4. Statistical analysis

All statistical analysis was performed using SPSS 19.0, Origin 8.0 and CANOCO 4.5 for Windows with significance level of p=0.05. The data deviated from a normal distribution (Kolmogorov–Smirnov test, p<0.05), therefore non-parametric tests were employed. The correlation between the concentrations of individual OCPs, and between the concentration of OCPs and the soil physicochemical properties, was analyzed using Spearman's rank correlation coefficients. Distribution patterns of individual OCPs in soil from different areas and different land use types, were compared using the Kruskal–Wallis and Mann-Whitney tests. Redundancy Analysis (RDA) was performed to quantitatively identify any association between the concentration of OCPs and soil physicochemical properties using the CANOCO 4.5 program, as described by Ter Braak and Smilauer (2002). Before conducting RDA, a detrended correspondence analysis (DCA) was used to obtain the length of the ordination gradient along the first axis. The gradient length resulting from DCA was below 3, thus the RDA model was considered appropriate for this data set (Lepš and Šmilauer, 2003). Monte Carlo analysis using 499 unrestricted permutations was performed to determine the variability and statistical significance of each soil physicochemical property.

4. Results and discussion

4.1. General comments regarding soil concentration

The majority of individual OCP concentrations did not obey a normal, or lognormal distribution, therefore, the geometric mean (GM) was used over arithmetic mean (AM) to eliminate the influence of some "outlier" values throughout the data analysis.

Table 4 summarizes the descriptive statistics of OCPs in soils of the Campanian Plain. The large standard deviation indicates significant spatial heterogeneity in the measured concentrations of OCPs (Table 4). Thus, the Campanian Plain is divided into six areas, namely the aforementioned DFL, AA, AMC, NAP, SRB, and SP (Fig. 1B).

In general, the concentrations of ∑HCHs in our study area ranged from 0.03 to 17.3 ng/g with GM= 0.05 ng/g and AM= 1.37± 2.81 ng/g, and ∑DDTs ranged from 0.08 to 1231 ng/g with GM= 14.4 ng/g and AM= 107± 204 ng/g (Table 4). This indicates that the residual levels of DDTs are significantly higher than those of HCHs, which is consistent with results of similar regions, such as in Mexico and the Haihe Plain (Table 5). The highest values of ∑DDTs (up to 1231 ng/g) and ∑HCHs (up to 17.3 ng/g) were found in soil samples from the farmland/orchards of the Sarno River Plain within the SRB (Fig. 2A), and from the southwest sector of DFL (Fig. 2B), respectively.

Table 4 Descriptive statistics of HCHs and DDTs in the soils of the Campanian Plain (ng/g).

		Campanian Plain (n=119)			Farmland (n=56)			Grassland (n=13)			Orchard (n=29)			Woodland (n=16)			Uncultivated (n=5)		
	LOD	Range	AM±SD	GM	Range	AM±SD	GM	Range	AM±SD	GM	Range	AM±SD	GM	Range	AM±SD	GM	Range	AM±SD	GM
α-HCH	0.01	0.01-2.41	0.12±0.26	0.06	0.01-2.41	0.17±0.35	0.07	0.01-1.11	0.12±0.30	0.04	0.01-0.23	0.08±0.06	0.06	0.01-1.36	0.09±0.11	0.05	0.02-0.12	0.06±0.05	0.04
β-HCH	0.01	N.D.-17.1	0.79±2.40	0.18	N.D.-15.4	1.03±2.57	0.29	N.D.-17.1	1.55±4.71	0.10	N.D.-5.15	0.42±1.06	0.14	N.D.-3.29	0.21±0.27	0.10	0.01-1.06	0.29±0.44	0.09
γ-HCH	0.01	N.D.-9.56	0.31±1.00	0.10	N.D.-9.56	0.55±1.43	0.17	N.D.-0.67	0.10±0.17	0.06	N.D.-0.46	0.12±0.12	0.08	N.D.-1.11	0.07±0.05	0.06	0.05-0.11	0.07±0.02	0.07
δ-HCH	0.01	N.D.-1.79	0.14±0.25	0.07	N.D.-1.79	0.21±0.34	0.09	N.D.-0.45	0.08±0.12	0.04	N.D.-0.38	0.09±0.10	0.07	0.01-1.64	0.10±0.11	0.06	0.01-0.17	0.06±0.06	0.04
∑HCHs	-	0.03-17.3	1.37±2.81	0.50	0.03-16.0	1.95±3.28	0.75	0.05-17.3	1.84±4.72	0.34	0.11-5.26	0.71±1.10	0.38	0.04-7.42	0.46±0.43	0.33	0.11-1.34	0.48±0.52	0.30
p,p'-DDE	0.02	N.D.-589	46.9±97.8	5.03	0.08-589	77.0±125	12.5	0.04-13.1	3.97±5.16	1.24	0.07-295	37.4±74.2	3.53	0.10-117	7.28±16.6	1.48	N.D.-15.8	4.08±6.64	2.43
p,p'-DDD	0.01	N.D.-53.4	5.02±9.51	0.97	0.03-53.4	7.28±11.1	1.93	0.01-5.61	0.87±1.58	0.23	N.D.-39.9	5.51±10.2	0.90	N.D.-16.7	1.04±1.87	0.38	N.D.-1.72	0.50±0.69	0.41
o,p'-DDT	0.02	N.D.-48.0	3.46±8.60	0.44	N.D.-47.7	5.11±10.1	0.86	N.D.-3.00	0.48±0.91	0.12	N.D.-45.0	3.31±9.52	0.34	N.D.-7.80	0.49±1.08	0.14	N.D.-15.8	3.20±7.05	0.21
p,p'-DDT	0.02	N.D.-962	51.1±126	8.29	N.D.-697	63.8±121	13.7	N.D.-95.2	13.9±27.4	4.17	N.D.-962	75.0±186	7.64	N.D.-141	8.83±21.2	2.65	N.D.-5.92	2.18±2.45	3.30
∑DDTs	-	0.08-1231	107±204	14.4	0.18-948	153±218	32.2	0.08-98.5	19.3±30.4	4.58	0.41-1231	121±258	12.8	0.12-282	17.7±40.2	3.35	2.80-23.5	9.97±9.25	6.90

N.D.: not detectable

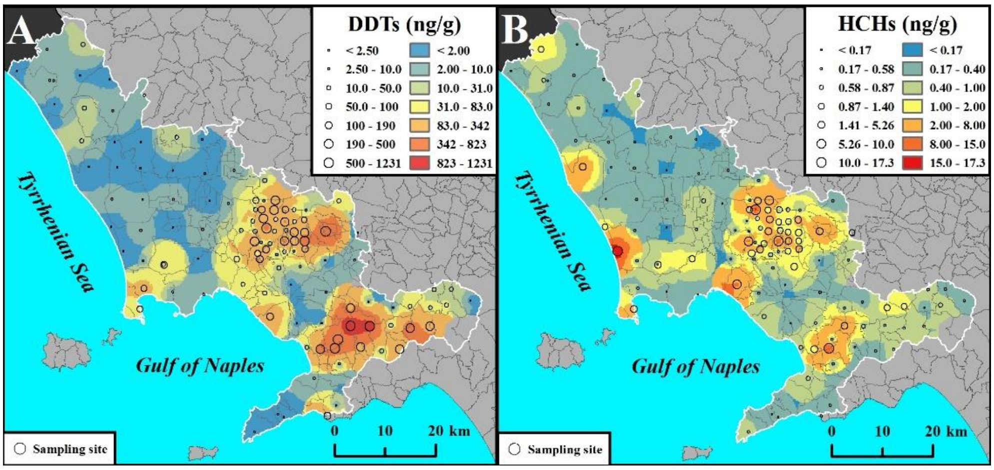

Fig. 2. Spatial distribution of DDTs and HCHs (ng/g) in soils of the Campanian Plain.

Among the HCHs, β-HCH is the predominant isomer contributing to 57.7% of the total, followed by γ-HCH>δ-HCH>α-HCH. Among DDTs, *p,p'*-DDE and *p,p'*-DDT were observed as the dominant chemicals, with concentrations reaching up to 589 ng/g (*p,p'*-DDE) and 962 ng/g (*p,p'*-DDT), accounting for 44.1% and 48.0% of the total DDT, respectively. The application of DDT and HCH in Italy has been severely restricted, with their application as agricultural chemicals prohibited for nearly forty years (Estellano et al., 2012). As this study is the first of its kind for the study area, there was little data with which to construct historical trends regarding the residual concentration of OCPs. However, as HCH and DDT can be considered typical OCPs, and have not had fresh application in decades, a decreasing trend can be speculated based on relative proportions of their isomers and metabolites (β-HCH and *p,p'*-DDE, respectively; Zhu et al., 2014).

Overall, the measured ∑HCHs and ∑DDTs values in this study were comparable or slightly higher than those reported for Yangtze River Delta, Haihe Plain, and Mexico (Table 5). In particular, research on the soils in the Haihe Plain and Mexico, have shown their gradual change into a reemission source of OCPs into the atmosphere (Tao et al., 2008; Wong et al., 2010). The enormity of OCP pollution in southern China and India has also been confirmed (Tieyu et al., 2005; Yadav et al., 2015). Compared with these severely OCP-contaminated areas, the concentrations of ∑HCHs and ∑DDTs were lower than those observed in Dibrugarh and Nagaon, in NE India, and Zhejiang, SE China (Table 5). Moreover, the concentration of OCPs appears to be of a relatively low level compared to the values of Midway Atoll and Galicia, NW Spain (Table 5). The comparative results indicate that although the concentration of OCPs in the soils of the Campanian Plain persist at only low levels, their potential as a secondary emission source to the atmosphere still exists.

Table 5 Concentrations of HCHs and DDTs in soils from different countries, including the area of study (ng/g).

Study region	Sampling year	∑HCHs				∑DDTs				Reference
		Range	AM	SD	GM	Range	AM	SD	GM	
Campania Plain	2011	0.03-17.3	1.38	2.83	0.50	0.08-1231	107	204	14.4	This study
Yangtze River Delta	2004	N.D.-99.0	3.23	10.3	-	N.D.-600	88.8	119	-	Hu et al. (2014)
Haihe Plain, Northern China	2004	0.02-349	3.90	26.0	0.44	0.40-2350	63.6	256	8.68	Tao et al. (2008)
Mexico	2005	N.D.-0.14	0.039	0.038	0.027	0-360	19	67	1.6	Wong et al. (2010)
Zhejiang, Southeast China	2006-2007	N.D.-50.6	6.81	10.2	2.82	4.0-529	82	86	31	Zhang et al. (2011, 2012)
North-East India										
Dibrugarh	2009-2010	178-1701	705	389	-	75-2296	757	455	-	Mishra et al. (2012)
Nagaon		98-1945	825	445	-	166-2288	903	494	-	
Midway Atoll	2006	N.D.-127	23.5	-	-	1.4-643	191	-	-	Ge et al. (2013)
Galicia, NW Spain	2003	N.D-2305	200	327.8	53.8	-	-	-	-	Calvelo Pereira et al. (2010)

N.D.: not detectable

4.2. Variation and distribution of the residual concentration of OCPs in soils

A significant spatial heterogeneity (Kruskal-Wallis test, $p<0.05$) of OCP concentrations in soils was observed between the six sub-areas, and differences in most OCPs were observed in the five land use types (Table 6).

Table 6 Spearman’s correlation coefficients among the residual levels of individual OCPs in soils of the Campanian Plain (n = 119), between the OCPs residues and soil physicochemical properties in Sarno River Basin (n = 21), and multiple-statistical analyses (labelled p^{a} and p^{b}) of OCPs in soils from land-use types and different areas (n = 119).

	Campanian Plain (n=119)										Sarno River Basin (n=21)						p^{a}	p^{b}
	α-HCH	β-HCH	γ-HCH	δ-HCH	HCHs	*p,p’*-DDE	*p,p’*-DDD	*o,p’*-DDT	*p,p’*-DDT	DDTs	pH	Coarse sand	Fine sand	Silt	Clay	OC		
α-HCH	1	0.33^{**}	0.62^{**}	0.50^{**}	0.65^{**}	0.46^{**}	0.42^{**}	0.13	0.34^{**}	0.42^{**}	0.08	0.06	0.26	-0.02	0.35	0.24	0.190	<0.001
β-HCH		1	0.50^{**}	0.33^{**}	0.77^{**}	0.30^{**}	0.21^{*}	0.06	0.16	0.23^{*}	0.11	0.02	-0.17	-0.09	-0.20	-0.01	0.038	<0.001
γ-HCH			1	0.43^{**}	0.74^{**}	0.47^{**}	0.45^{**}	0.22^{*}	0.38^{**}	0.46^{**}	0.39	0.12	0.13	-0.02	0.39	0.10	0.029	<0.001
δ-HCH				1	0.63^{**}	0.27^{**}	0.26^{**}	0.16	0.16	0.21^{*}	-0.12	0.46^{*}	-0.13	-0.28	-0.14	0.22	0.429	0.390
HCHs					1	0.49^{**}	0.46^{**}	0.23^{*}	0.37^{**}	0.45^{**}	0.23	0.16	0.13	-0.13	0.00	0.34	0.029	<0.001
p,p’-DDE						1	0.94^{**}	0.57^{**}	0.80^{**}	0.92^{**}	0.24	0.07	0.33	-0.06	0.00	0.40	0.001	<0.001
p,p’-DDD							1	0.59^{**}	0.86^{**}	0.93^{**}	0.23	0.10	0.32	-0.06	-0.10	0.53^{*}	0.001	<0.001
o,p’-DDT								1	0.60^{**}	0.63^{**}	-0.08	0.19	0.36	-0.31	-0.29	0.22	0.071	0.003
p,p’-DDT									1	0.93^{**}	0.16	0.16	0.32	-0.13	-0.02	0.51^{*}	0.008	<0.001
DDTs										1	0.25	0.10	0.29	-0.06	-0.04	0.44^{*}	0.003	<0.001

Significant correlation at $^{*}p< 0.05$, and at $^{**}p< 0.01$.

[a] values result from the comparison among land-use types (n=119; Kruskal-Wallis test).

[b] values result from the comparison among six different areas (n=119; Kruskal-Wallis test).

4.2.1. Variation in OCP distribution with land use

The systematic consideration of land-use associated with the soil collection points reveals the highest concentrations of OCPs (both ∑HCHs and ∑DDTs) are generally found in farmland and orchards, and then with decreasing concentrations in grassland, woodlands, and uncultivated areas for ∑HCHs, and uncultivated areas, grassland, and woodlands for ∑DDTs (Table 4). Further testing using the Mann-Whitney test indicates that concentrations of DDT and its metabolites were particularly higher in farmland and orchards than the other land uses.

It is widely accepted that the major source of pesticide contamination of soil is their direct application in agriculture, and the discharge from pesticide manufacturing facilities (Tao et al., 2008). Since there has been no pesticide manufacture in the Campania region in the last decade that would produce DDT and/or HCH, their presence in the environment may be predominantly associated with the agricultural application.

Our results prove that DDT was mostly used in agricultural activities in the Campanian Plain, and is in general agreement with Estellano et al. (2012), who considered agricultural use as the prevailing source of DDT in the atmosphere across the Tuscany region, in central Italy.

However, the concentration of ∑HCHs and HCH isomers varied only slightly between the soils of the five land use types, which may be attributed to their moderately high vapor pressure (Mackay et al., 1997). This generally results in a tendency of HCHs to volatilize from soil to atmosphere, and return to soil by dry/wet deposition after atmospheric transport, such as observed by Zhang et al. (2006) in Hong Kong.

4.2.2. Geographic distribution

The higher concentrations of OCPs were found in both AMC (with elevated concentrations of HCHs and DDTs, GM = 1.22 ng/g and 68.3 ng/g, respectively), and SRB (characterized by elevated concentrations of DDTs, GM = 60.8 ng/g; Fig. 2A and B). Although extensively farmed, the DFL and AA are characterized by relatively low concentrations of OCPs, more in line with concentrations of the non-agricultural areas of NAP and SP.

The AMC was once an important agricultural heartland, but has long been used as a site of the illegal dumping of waste, now known as part of the “Triangle of Death” (Senior and Mazza, 2004). Our results suggest that serious pollution of OCPs, as a result to some extent of agricultural application, may have been instrumental in contributing to the high-level of cancer mortality in the AMC.

As extremely hydrophobic contaminants (log K_{ow}>3), HCHs and DDTs are predominantly transported in association with suspended particulate matter in water (Zou et al., 2007). Not only do floods and mudslides happen frequently in the SRB, but the Sarno River is still partially exploited for agriculture irrigation. Exceptionally elevated concentrations of OCPs are possibly being washed into the Sarno River from the land surrounding the SRB, and recently, Montuori et al. (2014) reported discharge of approximately 326 g/day from the Sarno River into the Tyrrhenian Sea. Consequently, soil erosion, together with surface runoff, is recognized as an important mode of OCP transportation from terrestrial sources to the coastal zone of the gulf of Naples.

4.3. Source identification

Two formulations of commercial HCHs are technical HCH and lindane. In general, the α/γ-HCH ratio, which is often used to determine the source and history of HCHs, is a constant value in technical HCH (between 5 and 7) (Zhang et al., 2011), and nearly zero for lindane. In this study, the α/γ-HCH ratio ranged between 0 and 7.71 with an AM= 0.71, which indicates the application of both technical HCH and lindane. Among the HCH isomers, γ-HCH may be transformed into α-HCH by sunlight and through biological degradation in soil (Li et al., 2006). β-HCH is the most stable isomer, and tends to accumulate and isomerize from α-HCH, or γ-HCH via α-HCH, in the source area (Jiang et al., 2009). The α-HCH/β-HCH ratios in all soil samples (AM= 0.69) were below that of technical HCHs (i.e., 11.8) (Zhang et al., 2011). This means, our results preclude the possibility of the fresh application of technical HCHs on large scale in the study region. We noted significant correlation among HCHs and HCH isomers ($p< 0.01$) (Table 6). This likely reflects the degradation of γ-HCH to α-HCH, and also implies the sources originated from the use of lindane. Our conclusion is coincident with the widespread trend of commercial HCH application (Calvelo Pereira et al., 2010; Ge et al., 2013; Yadav et al., 2015), where lindane was widely applied as substitute for technical HCH, after it was officially banned around the globe.

Technical DDT is generally composed of about 65 - 85% *p,p'*-DDT and 15 - 21% *o,p'*-DDT. Once introduced into environment, DDT can biodegrade to DDE under aerobic conditions, and to DDD under anaerobic conditions (Tao et al., 2008). Significant positive correlations were observed between *p,p'*-DDT and *p,p'*-DDE ($p< 0.01$, $R_s= 0.80$), and *p,p'*-DDD ($p< 0.01$, $R_s= 0.86$) (Table 6). The fraction of *p,p'*-DDE is greater than *p,p'*-DDD (44.1% and 4.27%, respectively), which indicates the aerobic breakdown of p,p'-DDT is most dominant, however, anaerobic degradation processes cannot be completely disregarded. The *p,p'*-DDT/*p,p'*-DDE ratio in this study fluctuated greatly, ranging from 0.08 to 16.1 with 98 soil samples having a ratio of <3.5. Assuming a ratio value of fresh DDT of 15 (Zhang et al., 2012), our results indicate that the DDT residues are mainly the result of historical use, although recent inputs can be inferred at several sites. Naso et al. (2003; 2005) determined no recent input of technical DDT on the basis of the analysis of tissue from bird and marine species. However, studies of the European eel by Ferrante et al. (2010), suggested a recent, although not extensive, input from the banned pesticides. At present, the use of dicofol is not reported in the Campania region, however, it was banned by the Italian government in 2009 (Governo Italiano, 2009). The *o,p'*-DDT/*p,p'*-DDT ratio ranges from 0.2 to 0.3 in technical DDT, and from 1.3 to 9.3, or higher, in dicofol (Qiu et al., 2005). The *o,p'*-DDT/*p,p'*-DDT ratios ranged from 0 to 0.92 with AM=0.11, suggesting no fresh application of dicofol. The strong correlation between *o,p'*-DDT and *p,p'*-DDT ($p< 0.01$, $R_s= 0.60$) also supports this conclusion (Table 6).

4.4. Influence of soil properties

The influence of soil properties on the concentration of OCPs was evaluated using a multivariate method of redundancy analysis (RDA). The physicochemical properties (pH, components of coarse sand, fine sand, silt, clay, and OC) of 21 soil samples from the Sarno River Basin (SRB) were analyzed, and the detailed measurements are listed in Arienzo et al. (2015). Spearman's coefficients between OCPs and soil properties are presented in Table 6. The RDA results revealed that 32.6% of the variation was explained by soil properties, implying that they exert at least some control on OCP concentrations (Fig. 3). The first two RDA axes accounted for 31.6% and 1.0% of the total variation, respectively. Using the forward selection of soil properties within a Monte Carlo permutation test (n= 499, unrestricted permutations), the RDA indicated that OCP concentrations showed strong correlations to the content of OC ($p< 0.05$; which explain 17% of the variation), however, they showed no other significant correlation with other soil properties.

As illustrated in Fig. 3, DDT and its metabolites show a positive correlation with OC, suggesting that OC is an important factor influencing the persistence of DDTs in soils. While the primary distribution appears dependent on the use of the chemical, the secondary distribution pattern (that is, the distribution of sources that are created by the transport of a chemical away from the primary source and the subsequent deposition, accumulation, and reemission in another area) is generally controlled by soil OC content and temperature (Jia et al., 2010). Zhang et al. (2012; 2011) concluded that the secondary distribution pattern for chemicals with a low vapor pressures (for example, DDT) is driven by total OC content whereas the secondary distribution pattern of chemicals with a high vapor pressure (for example, α-HCH) is controlled by temperature. In this study, temperature cannot be used in correlation analysis as it lacks significant variation due to the limited territory of SRB. There was no significant correlation between HCHs and soil properties (Table 6). As the use of HCHs and DDTs have been phased out, our observations are consistent with the secondary distribution pattern.

Soil pH has significant impact on OCPs residues by changing the structure of humus (Wenzel et al., 2002). Soil pH varies from moderately acidic to alkaline in Sarno area, but it was generally neutral with a mean of 7.03, in our study area (Arienzo et al., 2015). The lack of correlation between pH and OCPs in this study may be the result of slight variations in soil pH, however, unlike OC, correlations between soil pH and the concentration of OCPs are rarely found in the literature (Hao et al., 2008; Yu et al., 2013; Zhang et al., 2012). Additionally, soil textures show no obvious impact on the concentration of OCPs in our study, a result mirrored in other studies (e.g., Hao et al., 2008; Zhang et al., 2011). An additional twenty samples were randomly selected from other places in the study area to look for similar correlations (see *Table 2* from Albanese et al. (2015a)), however, in general, we found no meaningful correlation between the concentration of OCPs and soil properties. Our findings support the idea that the environmental fate of OCPs cannot be predicted by using a single soil-geochemical factor on a regional scale (Hao et al., 2008).

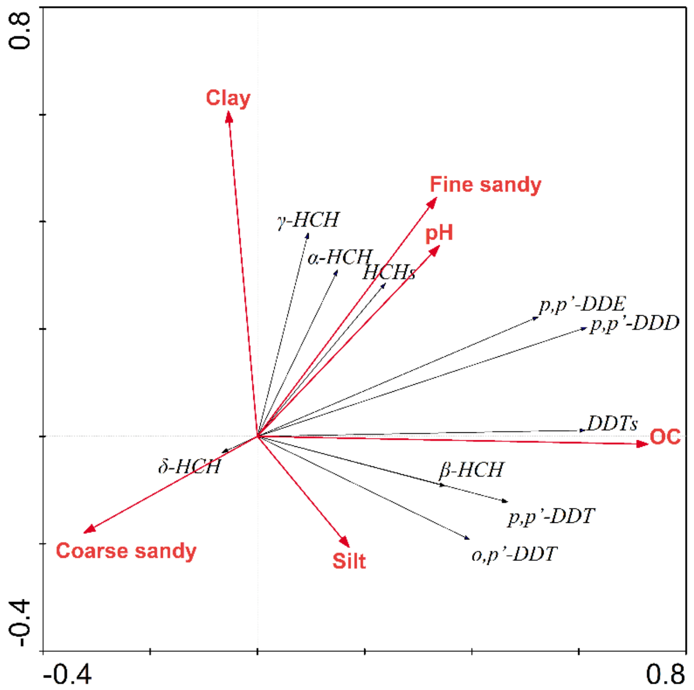

Fig. 3. Redundancy analysis (RDA) of the concentrations of OCPs and soil physicochemical properties in the Sarno River Basin (SRB) (n = 21). The lengths of arrows reveal the relationship strength between the explanatory variable and the response variable, and the intersection angles between the arrows (cosine value) represents their correlation.

4.5. Preliminary estimation of OCP inventory

The frequency distribution of the OCP inventory in soils of the Campanian Plain obtained using the Monte Carlo simulation obeys a lognormal distribution (Fig. 4); a summary of the simulation results is presented in Table 7. The OCP inventories ranged from 8.11 to 109 metric tons in the Campanian Plain, where GM= 17.3 metric tons and AM= 17.8±4.45 metric tons. Globally, the reported data concerning the OCP inventory in soils are scarce. However, a study of the soils of Shouguang (honored as the "Chinese home of the vegetable"), revealed approximately 12.9 metric tons of HCH and 11.8 metric tons of DDT residue after their ban in 1983 (Zhu et al., 2014). The estimated inventory of DDTs residing in soils of the Campanian Plain contributes up to 98.3% of the total OCP inventory (GM= 17.0 metric tons for DDTs and GM= 0.28 metric tons for HCHs; Table 7), and were higher than those in Shouguang which has a similar land area of 2180 km^2. The GM of mass inventories of OCPs in the soils of DFL, AA, AMC, NAP, SRB, and SP were 1.04, 2.93, 2.29, 1.06, 8.05 and 0.51 metric tons of DDTs, and 0.10, 0.04, 0.04, 0.04, 0.01, and 0.01 metric tons of HCHs, respectively. Considering the weight of the land area, the OCP burden per unit area in soils of the SRB is much heavier than that in other areas, while the minimum burden is found in the DFL.

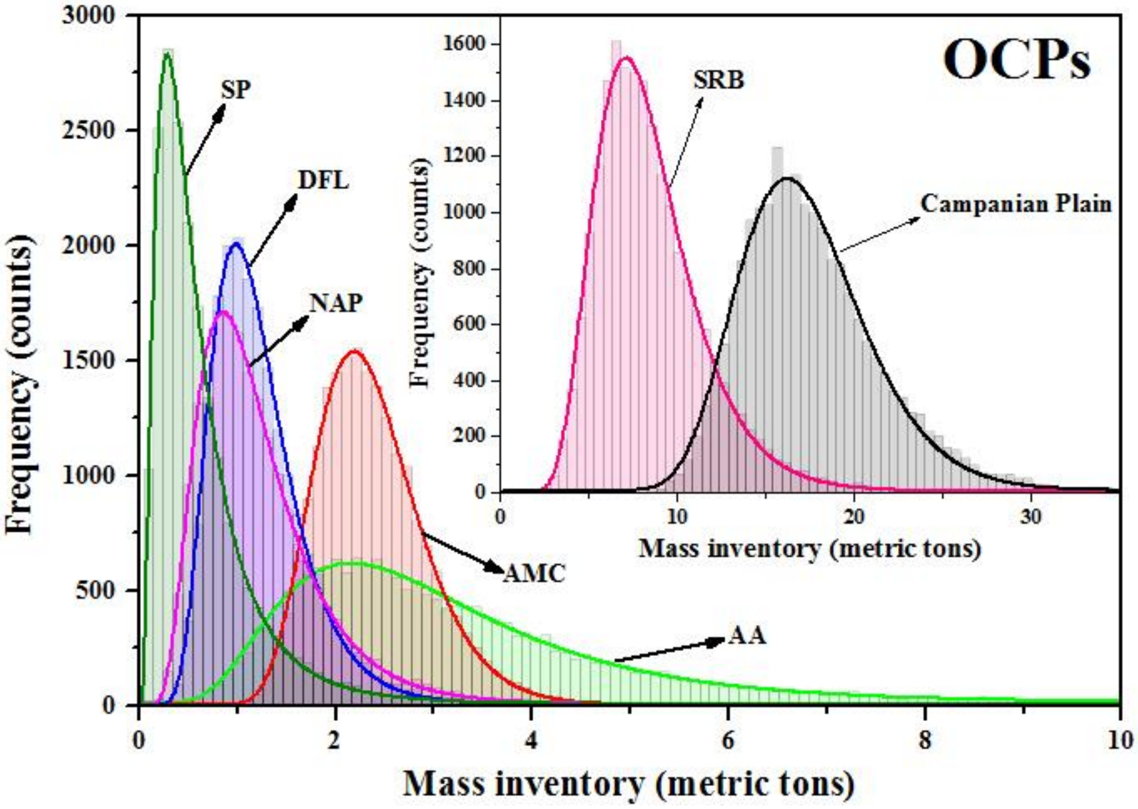

Fig. 4. Frequency distributions of the OCP inventory (metric tons) in the soils of the Campanian Plain, based on the results of 20,000 Monte Carlo simulations.

Table 7 The mass inventories of OCPs in soils of the Campanian Plain.

		Minimum	Maximum	AM±SD	GM
OCPs	AA	0.43	94.0	3.57±2.73	2.98
	AMC	0.95	8.96	2.39±0.58	2.32
	DFL	0.29	14.0	1.27±0.59	1.17
	NAP	0.16	45.6	1.26±0.78	1.10
	SP	0.02	29.7	0.71±0.76	0.51
	SRB	2.18	41.4	8.62±3.25	8.09
	Campanian Plain	8.11	109	17.8±4.45	17.3
DDTs	AA	0.48	102	3.52±2.83	2.93
	AMC	0.84	7.77	2.36±0.58	2.29
	DFL	0.26	21.2	1.14±0.56	1.04
	NAP	0.12	28.9	1.22±0.75	1.06
	SP	0.02	33.8	0.71±0.81	0.51
	SRB	2.26	51.4	8.57±3.23	8.05
	Campanian Plain	7.78	120	17.5±4.55	17.0
HCHs	AA	0.01	0.28	0.04±0.02	0.04
	AMC	0.01	0.18	0.04±0.01	0.04
	DFL	0.02	3.29	0.12±0.08	0.10
	NAP	0.00	1.09	0.05±0.04	0.04
	SP	0.00	0.03	0.01±0.00	0.01
	SRB	0.01	0.44	0.05±0.02	0.04
	Campanian Plain	0.12	3.41	0.30±0.09	0.28

4.6. Environmental significance

4.6.1. Epidemiology

In the early 1960s, Carson (1962) highlighted the detrimental effects of DDTs on human health and the environment. Pesticides, including OCPs, are toxic substances. When intentionally released into the environment, they can affect human health, producing chronic diseases such as various different types of cancers, diabetes, neurodegenerative disorders like Parkinson’s Disease, Alzheimer’s Disease, and Amyotrophic Lateral Sclerosis (ALS), birth defects, and reproductive disorders (Mostafalou and Abdollahi, 2013 and the references therein).

Epidemiological studies of OCPs have revealed that lindane (γ-HCH) could be associated with an elevated incidence of non-Hodgkin's lymphoma (Purdue et al., 2007) and prostate cancer (Band et al., 2011), and DDTs are potentially associated with prostate (Band et al., 2011) and pancreatic cancers (Garabrant et al., 1992).

In a large-scale project focusing on the Campania region, Albanese et al. (2008), using epidemiological data produced by Montella et al. (1996), showed the trend of mortality (Standard Mortality Ratio: SMR) for pancreatic cancers are markedly higher in the NAP region, and for a sector in the south of AA (which lies at the northern margin of NAP). The SMR was slightly higher or equivalent to the regional average in the northern sector of DFL, the southern sector of NAP (along the coastline facing Mt. Vesuvius), and the alluvial plain of SRB and the SP. The SMR was below the regional trend in the southern sector of DFL, the eastern sector of AA, all of AMC, and the inner sector of SRB (generally corresponding with the Solofrana tributary sub-Basin).

In the same study, the SMR for prostate cancer was calculated to be, again, higher for the city of Naples, and slightly higher than, or in line with, the regional average for the rest of the study area, except the eastern sector of AA and in AM, which were characterized by values below the reference value.

A study of cancer distribution on the municipality-scale, showed that the middle zone of SRB, belonging to the Province of Salerno (southern Campania), is characterized by an abnormal incidence (Standard Incidence Ratio: SIR) of liver cancer, while many prostate cancer values, are just slightly above the provincial trend (Albanese et al., 2013).

In an update of the National Epidemiological Study On The Territories And Settlements Exposed To Risk Of Pollution (S.E.N.T.I.E.R.I. Project, in Italian), Pirastu et al. (2014) reported, in DFL and AA, average mortality values for pancreatic cancer and non-Hodgkin's lymphoma in line with the regional standards, with only slight increases in rates in women. In the same study, the prostate cancer mortality rate is reported as slightly higher than the regional trend.

4.6.2. Hazard and preliminary quantitative risk assessment (PQRA)

The Italian environmental law D. Lgs.152/06 establishes trigger limits values for DDE/DDD/DDT in soil, of 10 ng/g and 100 ng/g, for the safety of the human beings in residential and commercial/industrial areas, respectively (Lgs, 2006). Fig. 5 shows that the 10 ng/g and 100 ng/g limits are exceeded for DDT and its metabolites in a considerable number of samples. In a comparison with

Chinese soil quality criterion (GB15618-1995), ∑DDT concentrations were higher than the primary standard value (50 ng/g in 36) soil samples, and 7 exceeded the secondary standard value (500 ng/g) (SEPA, 1995). Only 54 samples were lower than the Dutch target value (10 ng/g) (Dutch, 2000), and 31 were lower than the United States target value (2.5 ng/g) (USEPA, 2001). Jongbloed et al. (1996) have published maximum permissible DDT concentrations for the protection of plants and invertebrates (10 ng/g), small birds and mammals (11 ng/g), and birds and animals that eat birds (190 ng/g), based on a model described by Traas et al. (1996). The ∑DDT concentrations in over half of samples surpassed 10 ng/g, and are greater than 190 ng/g in 22 samples. In contrast, the concentration of HCHs only exceed the Italian trigger limits for residential land use (10 ng/g) in 4 samples (Lgs, 2006). HCH contamination may be categorized as nonexistent, but DDTs should be considered as low pollution in the majority of soil samples.

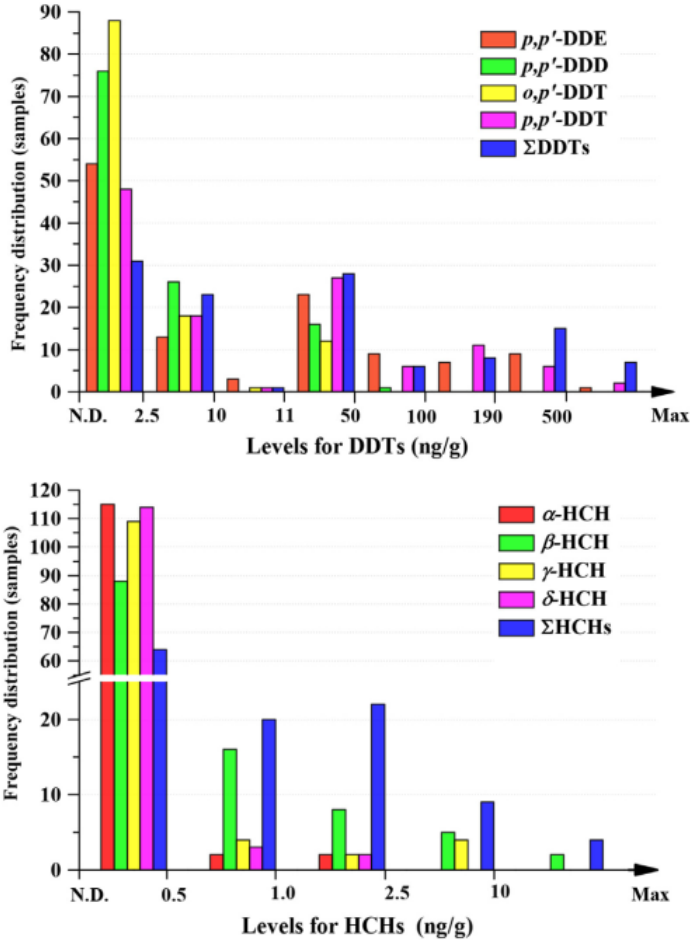

Fig. 5. Frequency distribution of the concentration of HCH and DDT in soils of the Campanian Plain (ng/g).

Usually, the highest risk from pesticides is provided by the long-term occupational exposure of farmers, although exposure to these pollutants for the end-consumers of the agricultural products cannot be excluded. However, as the sales network of agricultural products is complex with several distribution channels, the increased incidence of a specific disease in a population cannot be related solely to the consumption of locally produced food. As surficial soil is one of the preferential sinks for contaminants released into the environment, a human health risk assessment for population living in agricultural areas (even if not involved in farming activities), could be based on ingestion, dermal contact, and inhalation, as they are all effective and reliable exposure pathways for OCPs especially in the young (Simcox et al., 1995).

In Italian environmental law, surpassing the trigger limits (D. Lgs.152/06) implies the need to assess the health risk of the local population exposed to carcinogenic contaminants. The spatial distribution of the TILCR was calculated for soil-borne OCPs based on ingestion, dermal contact, and inhalation (Simcox et al., 1995). As, under a common risk assessment framework, an essentially negligible cancer risk level of 1 x 10^{-5} is recommended (Health Canada, 2010), and the 95% confidence interval of TILCR data for OCPs in Campanian Plain soils falls below this value, the cancer risk for residents exposed to these pollutants should not be considered extraordinarily high (Table 8). The cancer risk via inhalation was commonly 10^4 to 10^5 times less than through ingestion and dermal contact (Table 8), thus one can assume, the inhalation of OCP particulates through the mouth and nose was almost negligible. This conclusion has been reached in other comparable research (e.g., Hu et al., 2014; Qu et al., 2015; Wang et al., 2011).

On the basis of the increasing trend of the TILCR, toddlers were identified as the most sensitive sub-population, followed by the adults, children, teens and infants (Fig. 6; Table 8). The areas with the highest risks associated with OCPs were determined to be the AMC and SRB, where for a very small area, the TILCR for toddlers and adult falls within the 1 x 10^{-6} and 1 x 10^{-7} interval (Fig. 6). More specifically, the cancer risk of inadvertent ingestion for toddlers was significantly higher (Mann-Whitney test, $p<0.01$) than that for all other age groups, and the risk through dermal contact was greater (Mann-Whitney test, $p<0.01$) in adults. The contaminated soil is readily ingested by toddlers as the result of hand-to-month activity (Wang et al., 2011). Additionally, as toddlers have a lower body weight than adults, the OCP intake (mg/kg bw/day) of a toddler is considered to be greater than that of an adult. Young children are more vulnerable to pesticides, as the developing organs of children are more sensitive to cancers and their bodies lack the ability to detoxify the pesticides from their systems (Man et al., 2014). It follows that the cancer risk for toddlers exposed to soils OCP are thought to be greater than that of adults. However, because of their greater skin surface area and exposure duration, adults have the highest levels of cancer risk through dermal contact (Table 8). In particular, the cancer risk via dermal contact in adults was of the same order of magnitude as ingestion (Table 8), suggesting that these two pathways greatly contribute to the overall cancer risk.

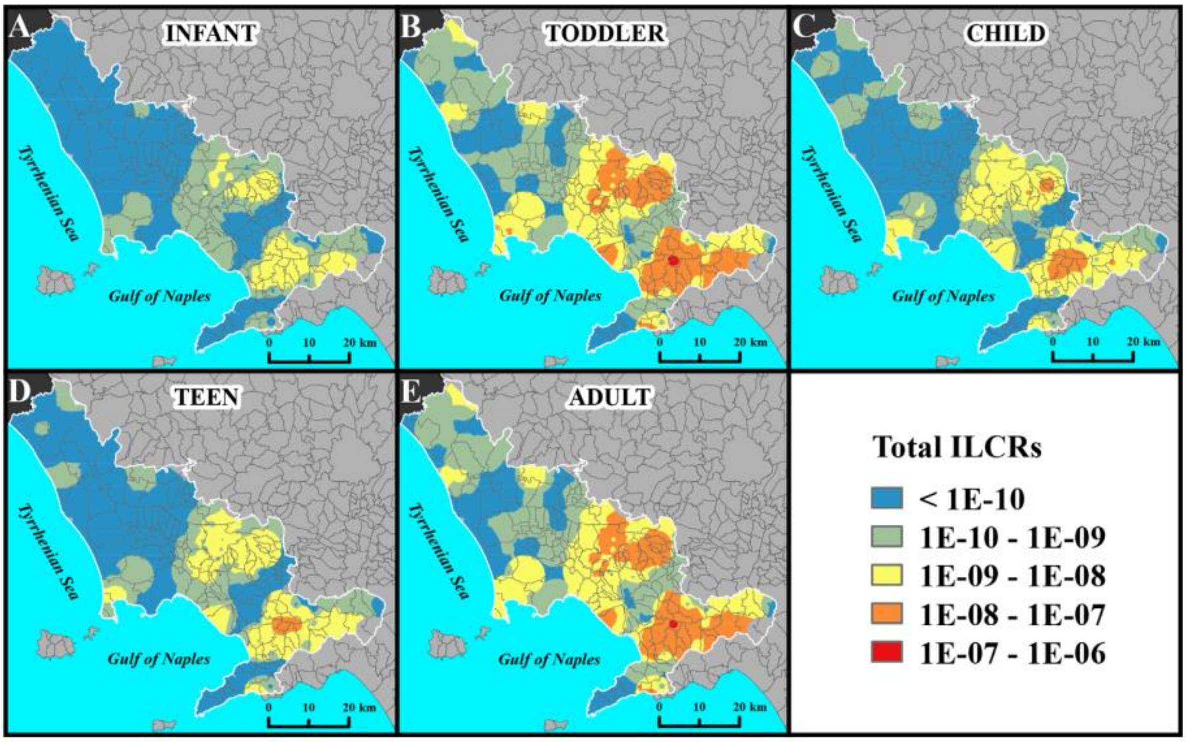

Fig. 6. Map showing the spatial distribution of total incremental lifetime cancer risks (TILCRs) separated by age group, in soils of the Campanian Plain.

Table 8 Cancer risk due to human exposure to OCPs via soil.

Exposure pathways		Minimum	Maximum	Mean	Median	LCL (95%)[a]	UCL (95%)[b]
Infant	Ingestion	4.20E-13	6.07E-09	5.16E-10	5.83E-11	3.34E-10	6.98E-10
	Dermal contact	4.19E-14	6.07E-10	5.16E-11	5.82E-12	3.34E-11	6.97E-11
	Inhalation	3.51E-17	4.17E-13	2.21E-14	2.77E-15	1.22E-14	3.21E-14
	Cancer risk	4.62E-13	6.68E-09	5.68E-10	6.41E-11	3.68E-10	7.67E-10
Toddler	Ingestion	8.35E-12	1.21E-07	1.03E-08	1.16E-09	6.65E-09	1.39E-08
	Dermal contact	3.08E-13	4.45E-09	3.78E-10	4.27E-11	2.45E-10	5.11E-10
	Inhalation	6.58E-16	7.82E-12	4.15E-13	5.19E-14	2.29E-13	6.01E-13
	Cancer risk	8.65E-12	1.25E-07	1.06E-08	1.20E-09	6.89E-09	1.44E-08
Child	Ingestion	1.46E-12	2.12E-08	1.80E-09	2.03E-10	1.17E-09	2.43E-09
	Dermal contact	3.28E-13	4.75E-09	4.03E-10	4.56E-11	2.61E-10	5.45E-10
	Inhalation	8.07E-16	9.59E-12	5.09E-13	6.37E-14	2.81E-13	7.37E-13
	Cancer risk	1.79E-12	2.59E-08	2.20E-09	2.49E-10	1.43E-09	2.98E-09
Teen	Ingestion	9.23E-13	1.33E-08	1.13E-09	1.28E-10	7.35E-10	1.53E-09
	Dermal contact	3.01E-13	4.35E-09	3.70E-10	4.17E-11	2.40E-10	5.00E-10
	Inhalation	5.47E-16	6.50E-12	3.45E-13	4.32E-14	1.90E-13	5.00E-13
	Cancer risk	1.22E-12	1.77E-08	1.50E-09	1.70E-10	9.75E-10	2.03E-09
Adult	Ingestion	5.84E-12	8.45E-08	7.18E-09	8.11E-10	4.65E-09	9.71E-09
	Dermal contact	2.14E-12	3.10E-08	2.64E-09	2.98E-10	1.71E-09	3.56E-09
	Inhalation	3.69E-15	4.38E-11	2.33E-12	2.91E-13	1.28E-12	3.37E-12
	Cancer risk	7.99E-12	1.16E-07	9.82E-09	1.11E-09	6.36E-09	1.33E-08

[a] The lower 95% confidence limit.

[b] The upper 95% confidence limit

5. Conclusions

This preliminary study has raised some important points. The residual concentrations of OCPs in the soils of the Campanian Plain have persisted at a low level, and the residual concentration of DDT may be considered as low-level pollution, which requires attention. The AMC and SRB regions, exhibit particularly high residual concentrations of OCPs, and this fact is mirrored in their notorious reputation for serious pollution. However, the recent application of technical HCHs and DDTs in large quantities appears unlikely, and their presence in the soils may be predominantly associated with historic agricultural applications. The residual concentration of OCPs in agricultural land (i.e., farmland and orchards) is generally higher than in land used for non-agricultural purposes. However, the agricultural areas of DFL and AA have relatively low OCP concentrations, of the same order of magnitude as the non-agricultural areas of NAP and SP. The OCP inventories are estimated at GM = 17.3 metric tons, and the OCP burdens per unit area are highest in the SRB and lowest in the DFL. The distribution of OCPs in soils appears to have a typical secondary distribution pattern. Based on the available literature, we cannot connect the high mortality rate of some cancer types to the presence and spatial correlation of OCPs across the study area. This is also consistent with the results of the PQRA, which indicates that while the sensitivities of the population age groups to these contaminants differs, the TILCR for OCPs in the study area is always negligible. Further study is needed to critically analyze the role of agricultural soil as a reemission source, and further explore the relationship between the incidence of cancer and the distribution of these harmful compounds on a regional scale.

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Conflict of Interest

The authors declare no conflict of interests.

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Section 2.2

Residues of hexachlorobenzene and chlorinated cyclodiene pesticides in the soils of the Campanian Plain, southern Italy

The paper is in progress to be submitted in the journal (March 2017):

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Residues of hexachlorobenzene and chlorinated cyclodiene pesticides in the soils of the Campanian Plain, southern Italy

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1. Methodology

1.1. Sampling

One hundred and nineteen soil samples were collected from the Campanian Plain between April and May 2011, as described in detail by Albanese et al. (2015). Briefly, a systematic grid sampling approach was implemented, and the density of sampling grid varied from 6 × 6 km of the Domitizio-Flegreo Littoral (DFL), to 2 × 2 km of the Acerra-Marigliano conurbation (AMC), as shown in Fig. 1. At each site, soil samples were obtained by mixing five aliquots taken at the center and at the corners of an ideal square with a side of 5 m. Samples were wrapped in aluminum foil, sealed in polyethylene zipped bags, and immediately stored at 4°C until analysis.

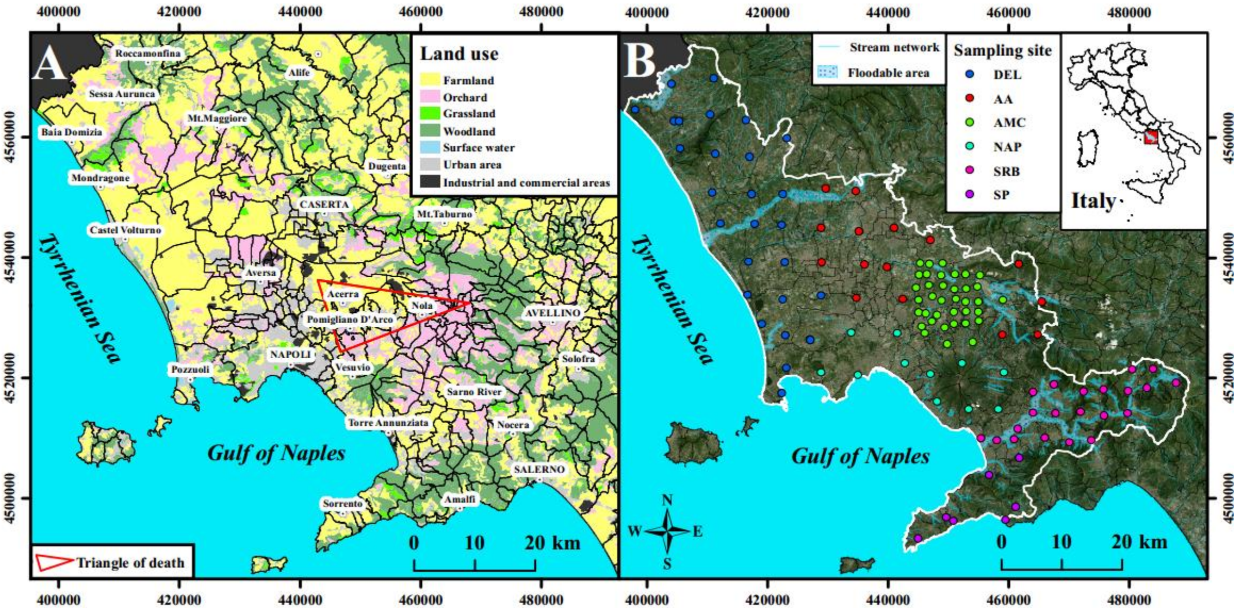

Fig. 1. (A) Map of the different land uses within the study area; (B) Location of soil sampling sites. Note: DFL: Domitizio-Flegreo Littoral, AA: Agro Aversano, AMC: Acerra-Marigliano Conurbation, NAP: Metropolitan area of Naples, SRB: Sarno River Basin, SP: Sorrento Peninsula.

1.2. Chemical analysis

The eleven compounds were measured for all samples, and they were divided into four chemical sub-groups including HCB (Hexachlorobenzene), SULPHs (α-Endosulfan, β-Endosulfan, and Endosulfan sulfate), CHLs (Heptachlor, Heptachlor epoxide, trans-Chlordane, and cis-Chlordane), and DRINs (Aldrin, Dieldrin, and Endrin). The analytical procedures of OCPs are presented by Qu et al. (2016). A brief description of chemical analysis is as following:

1.2.1. Extraction and cleanup

A surrogate standard consisting of 2,4,5,6-tetrachlorom-xylene (TCmX) and decachlorobiphenyl (PCB209) was spiked to the soil sample before Soxhlet-extracted with dichloromethane (DCM) for 24 hours. The extract was concentrated and solvent-exchanged with hexane by rotary evaporator, and then purified by an alumina/silica (1:2, v/v) gel column together with the elution solvent (DCM/ hexane, 2/3, v/v). The eluate was concentrated to 0.2 mL under a gentle nitrogen stream and spiked with penta-chloronitrobenzene (PCNB) as an internal standard for instrument analysis.

1.2.2. Instrumental analysis

The measurements of target compounds were performed using an Agilent 7890A gas chromatograph with a ^{63}Ni electron capture detector (GC-μECD) equipped with a DB-5 capillary column (30.0 m length, 0.32 mm i.d., 0.25 μm film thickness). Nitrogen was used as the carrier gas at a constant flow of 2.5 mL/min. Injector and detector temperatures were maintained at 290 °C and 300 °C, respectively. The oven temperature started from 100°C for 1 min, and rose to 200°C at 4°C/min, then to 230°C at 2°C/min, and finally reached 280°C at 8°C/min, and held for 15 min. A 2.0 μL of sample was injected into the GC-μECD under the splitless mode. The individual target OCPs was quantified by a six-point internal standard calibration curve.

1.2.3. Quality assurance/Quality control

For every set of 16 samples, a procedural blank and parallel sample was run to check for interferences and cross contamination. A standard OCPs solution and solvent blank was injected into the GC-μECD daily before analyzing the soil samples extracts. The surrogate recoveries for TCmX and PCB209 were 77.8 ± 19.0 % and 89.3 ± 20.3 %, respectively. Reported concentrations were corrected by the surrogate recoveries. A signal-to-noise-ratio (S/N) of 3 was described as the limit of the detection (LOD), which ranged from 0.009 to 0.064 ng/g for the target compounds. The relative standard deviation (RSD) ranged from 2.7% to 8.3%.

1.3.Statistics

Statistical analysis was performed using SPSS 19.0, Origin 8.0 and CANOCO 4.5 for Windows with significant probability of $p < 0.05$. The data deviated from a normal, or lognormal distribution (Kolmogorov-Smirnov test, $p < 0.05$), therefore, non-parametric tests were employed, and geometric mean (Gmean) was used over arithmetic mean (AM) throughout the data analysis.

2. Results and discussion

2.1. Residual levels

Table 1 and Fig.2 summarizes the statistical results of HCB and cyclodienes in soils of the Campanian Plain. A quantifiable amount of OCPs is measured in all analyzed samples, HCB, α-Endosulfan, Heptachlor, and Aldrin being the most frequently observed compounds. The large coefficient variations (CV, range: 0.78 - 4.10) reflects significant difference in spatial variations of these OCPs. Among the four chemical sub-groups, the Gmean concentration of CHLs was the highest (0.82 ng/g), followed by DRINs (0.62 ng/g), SULPHs (0.57 ng/g), and HCB (0.22 ng/g).

Significant difference of most OCP concentrations ($p < 0.05$) was observed between the six subareas, and recorded simultaneously in the five land use types except chlordane-related compounds (Table 1). The concentrations of Endosulfan and its metabolites, Aldrin, Dieldrin, and Endrin in agricultural soils (Farmland & Orchard) were prevalent higher than the other land uses ($p < 0.05$). Our recent article pointed out that agricultural application may be a major source of DDT and HCH (Qu et al., 2016). No broader generalization for spatial difference of individual compounds in the six subareas can be inferred by Mann-Whitney test, and thus, geochemical maps illustrating the spatial distribution of HCB, SULPHs, CHLs, and DRINs were produced by means of the multifractal inverse distance weighted (MIDW) interpolation associating with the concentration-area fractal method (C-A), as shown in Fig. 3.

Table 1 Basic statistical parameters of HCB and chlorinated cyclodiene pesticides in the soils of the Campanian Plain (n=119, ng/g dw) [a].

	Mean ± SD	CV	Gmean	Min	Max	Percentiles							DF (%)	p^{b}	p^{c}
						P05	P10	P25	P50	P75	P90	P95			
HCB	0.36 ± 0.28	0.78	0.22	0.013	1.19	0.035	0.044	0.067	0.42	0.59	0.70	0.77	100	0.010	<0.001
α-endosulfan	0.41 ± 0.96	2.36	0.14	N.D.	9.33	N.D.	0.022	0.048	0.13	0.38	1.02	1.71	91.6	0.001	<0.001
β-endosulfan	0.50 ± 1.32	2.64	0.065	N.D.	11.7	N.D.	N.D.	N.D.	0.052	0.38	1.87	2.22	58.8	0.094	0.383
Endosulfan sulfate	1.06 ± 2.60	2.46	0.19	N.D.	15.8	N.D.	N.D.	N.D.	0.16	0.55	3.06	7.07	67.2	0.006	0.004
SULPHs	1.96 ± 3.75	1.91	0.57	N.D	19.4	N.D.	N.D.	0.20	0.50	1.34	6.79	11.9	95.8	0.004	<0.001
Heptachlor	1.20 ± 1.33	1.11	0.50	N.D.	8.11	N.D.	N.D.	0.28	0.73	1.88	3.04	3.49	87.4	0.475	0.271
Heptachlor epoxide	0.08 ± 0.23	2.80	0.015	N.D.	1.30	N.D.	N.D.	N.D.	N.D.	N.D.	0.31	0.52	23.5	0.703	0.380
trans-chlordane	0.06 ± 0.12	1.87	0.025	N.D.	0.69	N.D.	N.D.	N.D.	N.D.	0.063	0.17	0.27	40.3	0.043	0.542
cis-chlordane	0.04 ± 0.09	2.10	0.017	N.D.	0.55	N.D.	N.D.	N.D.	N.D.	0.028	0.14	0.20	31.9	0.099	0.077
CHLs	1.39 ± 1.44	1.04	0.82	N.D.	9.02	N.D.	0.18	0.43	0.90	2.02	3.22	3.75	58.0	0.421	0.117
Aldrin	0.42 ± 0.52	1.25	0.18	N.D.	3.22	N.D.	0.016	0.075	0.27	0.53	1.06	1.47	91.6	<0.001	0.015
Dieldrin	1.69 ± 6.93	4.10	0.084	N.D.	64.1	N.D.	N.D.	N.D.	0.048	0.33	2.16	12.7	61.3	0.076	0.213
Endrin	0.34 ± 0.81	2.37	0.092	N.D.	7.19	N.D.	N.D.	N.D.	N.D.	0.29	0.98	1.88	47.9	0.015	0.711
DRINs	2.45 ± 7.71	3.15	0.62	N.D.	72.4	N.D.	0.092	0.19	0.59	1.45	3.70	13.9	95.8	<0.001	0.002

[a] SD: standard deviation; CV: coefficient variation; Gmean: geometric mean; DF: detection frequency; N.D.: not detectable; SULPHs: sum of α-endosulfan, β-endosulfan and endosulfan sulfate; CHLs: sum of heptachlor, heptachlor epoxide, trans-chlordane and cis-chlordane; DRINs: sum of aldrin, dieldrin and endrin.

[b] Values result from the comparison among land-use types (n = 119; Kruskal-Wallis test).

[c] Values result from the comparison among six different areas (n = 119; Kruskal-Wallis test).

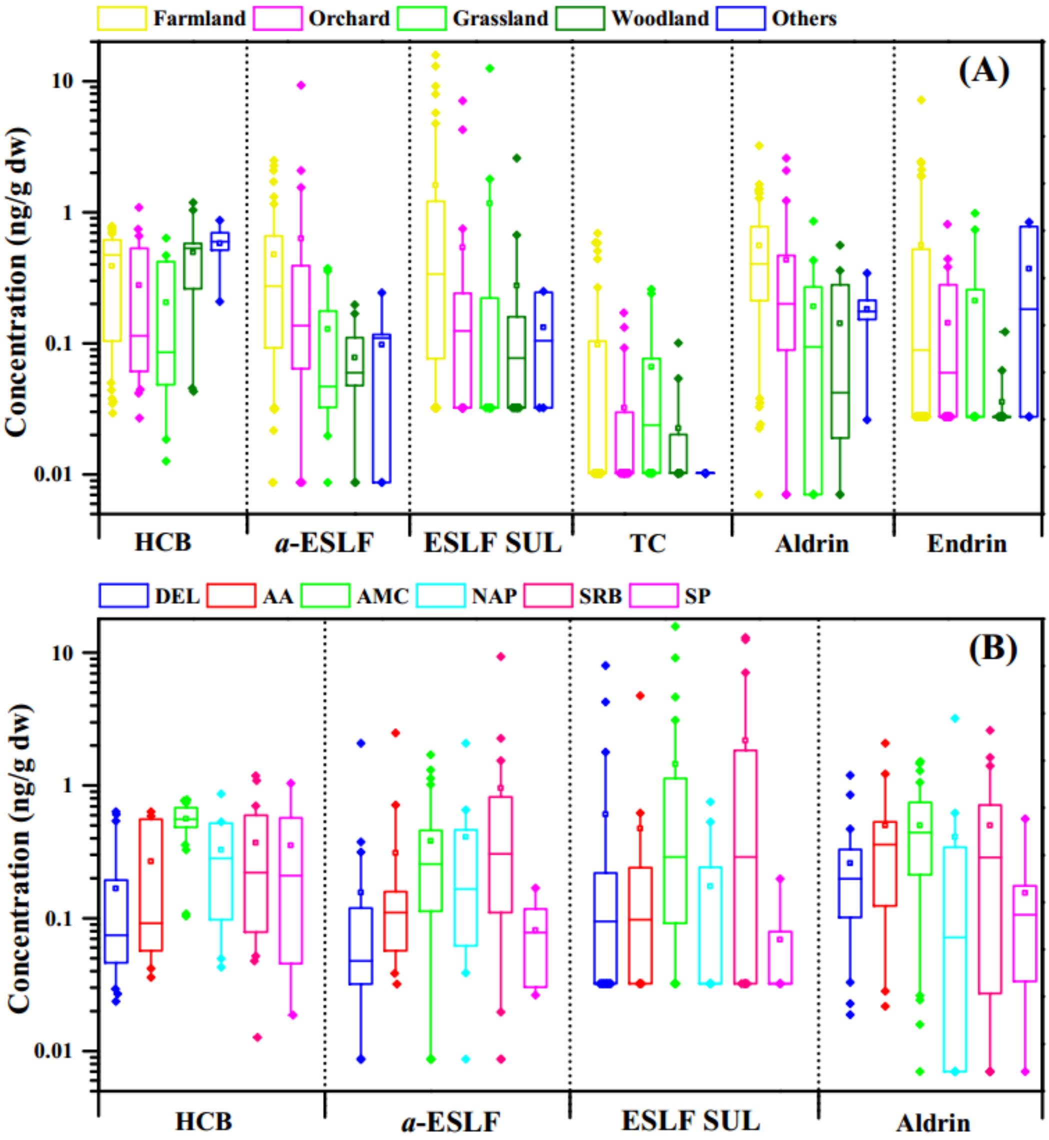

Fig. 2. Box-and-whisker plots of hexachlorobenzene and chlorinated cyclodiene pesticides in soils of the Campanian Plain

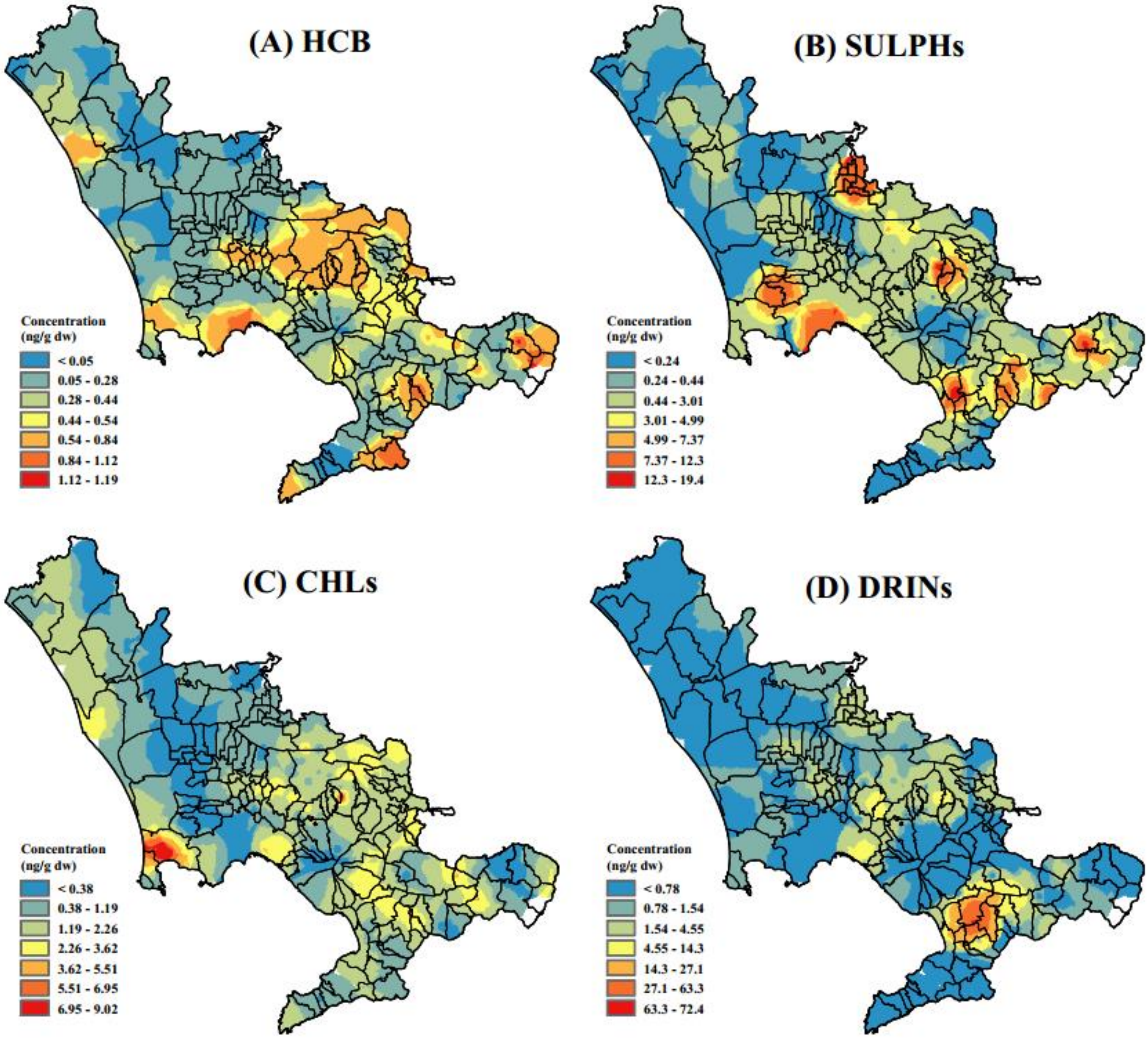

Fig. 3. Spatial distribution of hexachlorobenzene and chlorinated cyclodiene pesticides (ng/g) in soils of the Campanian Plain.

2.1.1. Hexachlorobenzene (HCB)

The usage of HCB as a fungicide was banned in European Union in 1978 (Barber et al., 2005), and subsequently, its emissions in Italy significantly decreased from 20123 kg/year in 1979 to 795 kg/year in 1995 (Pacyna et al., 2003). The HCB concentrations ranged from 0.013 to 1.19 ng/g with Gmean = 0.22 ng/g in this study (Table 1), and the residual level was similar to that in Hongkong soils (Zhang et al., 2006), but lower than for Germany (Aichner et al., 2013) and Shanghai (Jiang et al., 2009). Significant variations ($p < 0.05$) of HCB in regional distribution and land use types were observed, however, it just varied slightly in the soils of the Campanian Plain (CV = 0.78) (Table 1), which may be attributed to its high vapor pressure (Mackay et al., 2010). The atmospheric transport potential of HCB resulted in an extraordinary high detection frequency (DF = 100%) and relatively homogenous distribution (Table 1), such as observed by Jiang et al. (2009) in agricultural soil of Shanghai, and Qu et al. (2015b) in air of central China.

Currently, several pathways to introduce HCB into environment are mainly manifested on the impurities as byproduct from chemical synthesis processes, and fuel combustion/waste incineration (Aichner et al., 2013). In our study area, a power plant fueled by palm oil and an urban waste incinerator are located in northern Acerra, AMC, and the almost daily unauthorized burning of agricultural and industrial wastes of unknown origin has existed on territories of the AMC (Albanese et al., 2015). Significantly high levels of HCB in the AMC may be attributed to combustion processes (Fig. 3). Naso et al. (2003, 2005) concluded that HCB concentrations in birds from Campania and marine organisms of the Gulf of Naples originated from its previous use as a fungicide and the impurities as byproduct of chlorine products. Studies of red foxes suggested that agriculture was a dominant use for HCB in Italy (Corsolini et al., 2000). The significant amount of HCB remained in agricultural areas, particularly in the SRB (Fig. 2), supports the opinion. The NAP is mostly occupied by urban and industrial settlements, including chemical industries, refineries, and an abandoned steelwork factory (Albanese et al., 2015). Thus, higher HCB concentrations in the NAP were expected (Fig. 2), and consistent with the decreased tendency from urban to rural areas (Barber et al., 2005).

2.1.2. Endosulfan

Endosulfan was pervasive in soils of the Campanian Plain, and at least one of two endosulfan isomers and their metabolite was detected in 95.8% of the soil samples (Table 1). The SULPHs concentrations in this study ranged from N.D. to 18.4 ng/g (Gmean = 0.57 ng/g), and the result was higher than those in agricultural soils across China (Niu et al., 2016), Mexico (Wong et al., 2010), and remarkably were lower than those measured in agricultural soils of southeast China, such as Zhejiang (Zhang et al., 2012) and Ningde (Qu et al., 2015a).

The concentrations of α-endosulfan and Endosulfan sulfate were significantly higher in farmland and orchards than the other land uses ($p < 0.05$). This reflects that endosulfan was mainly used for agricultural activities in the Campanian Plain, and agrees with Estellano et al. (2012), which displayed a close relationship between intensive farming practices (e.g., olives, vineyards, sunflower) and higher α-endosulfan concentrations in the atmosphere of the Tuscany region, Italy.

Technical endosulfan consists of approximate 70% α-endosulfan and 30% β-endosulfan (Qu et al., 2015a). α-endosulfan is more easily volatilization and degradation than β-endosulfan in soil (Jia et al., 2010). In 57 out of the total soil samples in which α- and β-endosulfan were simultaneously detected, the $\alpha/(\alpha+\beta)$-endosulfan ratios ranged from 0.01 to 0.96 with a Gmean value of 0.39, and were less than the ratio value of fresh endosulfan of 0.7 in most samples. The results indicate that the endosulfan residues are mainly the result of historical application, however, a recent input of technical endosulfan still exists at several sites.

Endosulfan sulfate was the dominant component, with arithmetic mean value reaching up to 1.06 ng/g, contributing to 54.1% of the total endosulfan. This reflected that endosulfan sulfate is more recalcitrant than its parent isomers in soils (Niu et al., 2016). Statistically significant correlations were observed between endosulfan sulfate and its parent isomers, namely α-endosulfan ($p < 0.01$, $R_s = 0.51$), and β-endosulfan ($p < 0.01$, $R_s = 0.61$) (Table 2). This implies that endosulfan sulfate most likely originates from historical application of technical endosulfan.

2.1.3. Chlordane-related compounds

The concentrations of trans-chlordane (TC) displayed statistically significant differences in land use types. Beyond that, however, neither regional variations nor land use types for cis-chlordane (CC), Heptachlor (HEPT), and Heptachlor epoxide (HEPX) were observed (Table 2).

The concentrations of TC and CC ranged from N.D. to 0.69 ng/g (Gmean = 0.025 ng/g), and N.D. to 0.55 ng/g (Gmean = 0.017 ng/g), respectively. They were similar to those recorded in agricultural soils across China (Niu et al., 2016), and far below those reported in the U.S. corn belt (Aigner et al., 1998). The main components of technical chlordane are 13% TC, 11% CC, 5% HEPT and 5% trans-nonachlor (Bidleman et al., 2002). TC is easier to degrade than CC in the environment, and thus the TC/CC ratio can be used to ascertain the "weathering degree" (Jiang et al., 2009). TC and CC was detected in 40.3 and 31.9% soil samples, respectively (Table 1), and almost half of TC/CC ratios in these samples were above that of technical chlordane (i.e., 1.18). This implies the ongoing use of technical Chlordane.

HEPT exhibited the highest Gmean concentration (0.50 ng/g), however, its soil oxidation product, HEPX, has the lowest value (0.015 ng/g) (Table 1). The DF of HEPX is well lower than HEPT (23.5% and 87.4%, respectively). Zhang et al. (2012) appeared opposite tendencies, and interpreted it as being the result of the rapid transformation of HEPT (Aigner et al., 1998). However, a certain quantity of Italian honey was detected only HEPT and no HEPX (Panseri et al., 2014). HEPT was isolated from technical chlordane in 1946, and its commercial product contains 72% HEPT and 28% related compounds, including about 20% TC (Zhang et al., 2012). No significant correlation ($p > 0.05$) was found between HEPT and Chlordane (Table 2). The fact indicated that the higher level of HEPT was found, originating from technical Heptachlor.

2.1.4. Aldrin, Dieldrin, and Endrin

Aldrin and dieldrin were widely used as insecticides in agriculture such as corn and citrus fruit, and as termiticides for wooden structures. Italy was a major consumer of aldrin/dieldrin, with their consumption reaching approximately 913 metric tons annually from 1974 to 1976, and has formally banned as agricultural chemical in 1988 (Newton, 1988). Aldrin can slowly transform into dieldrin in soil; dieldrin is more resistant to chemical degradation and metabolic breakdown in the environment; Endrin is a stereoisomer of dieldrin, and it is mainly used in controlling cotton pests. Special attentions need to be paid due to their higher toxicity than other OCPs (ATSDR, 2002).

The concentrations (ng/g) of aldrin, dieldrin and endrin ranged from N.D. to 3.22 (Gmean = 0.18), N.D. to 64.1 (Gmean = 0.084) and N.D. to 7.19 (Gmean = 0.092), respectively (Table 1). Their residual levels were correspondingly higher than those observed in Chinese agricultural soils, such as the national scope, Shanghai and Zhejiang (Jiang et al., 2009; Niu et al., 2016; Zhang et al., 2012), and lower than those in the U.S. corn belt and German forest soils (Aichner et al., 2013; Aigner et al., 1998). The comparative results were understandable: these chemicals have never been industrially produced and used for agriculture in China, their residues in Chinese soils were mainly transported atmospherically from other regions (Zhang et al., 2012); aldrin use in United States reached 4,720 metric tons in 1970 (ATSDR, 2002), and Germany is the second largest consumer of pesticides in Europe after France (Zhang et al., 2011b).

Significant difference ($p < 0.05$) for aldrin and endrin in land use types was found (Table 1), and significant high levels ($p < 0.05$) were measured in farmland (Fig. 2). The Gmean concentration of dieldrin in farmland was the highest (0.14 ng/g), followed by uncultivated areas (0.089 ng/g), orchard (0.072 ng/g), grassland (0.051 ng/g), and woodland (0.024 ng/g), though no significant difference ($p < 0.05$) for dieldrin among different land use types was displayed (Table 1). In fact, the higher concentrations of aldrin/dieldrin/endrin in farmland were consistent with the study of OCPs in liver of birds from coastal areas of Campania which noted dieldrin contamination caused by their abundant agricultural use from the 1960s up until 1973 (Naso et al., 2003).

Studies of the European eel by Ferrante et al. (2010), suggested a recent, direct use of dieldrin in the areas along the Garigliano river, Campania region. Significant positive correlations ($p < 0.05$) were observed among aldrin, dieldrin and endrin (Table 2); the relative abundance of aldrin and dieldrin in 44 out of the total soil samples were below unity. This evidence may imply that the usage of aldrin, to a large extent, was a major pollution source, and subsequently the biological metabolism of aldrin to dieldrin in soil got under way. Aldrin is rapidly metabolized to dieldrin in plants and animals, and then only in small amounts (ATSDR, 2002). This explains why aldrin was not detected in liver of birds from the Campania region, but dieldrin presented in 56% of the samples with the range of <1 to 356 ng/g (Naso et al., 2003). Moreover, the higher DF of aldrin (DF = 91.6%) reveals the possibility of long-range atmospheric transport (Table 1).

Table 2 Spearman’s correlation coefficients among the residual levels of individual OCPs in soils of the Campanian Plain (n = 119), between the OCPs residues and soil physicochemical properties in Sarno River Basin (n = 21) [a].

	Campanian Plain (n = 119)														Sarno River Basin (n = 21)					
	HCB	α-ESLF	β-ESLF	ESLF SUL	SULPHs	HEPT	HEPX	TC	CC	CHLs	Aldrin	Dieldrin	Endrin	DRINs	pH	Coarse sand	Fine sand	Silt	Clay	OC
HCB	1	***0.27***	0.06	0.15	***0.24***	***0.48***	0.14	-0.03	0.08	***0.51***	0.16	0.08	0.03	0.17	0.37	-0.15	0.18	0.09	0.14	-0.18
α-ESLF		1	***0.50***	***0.51***	***0.79***	-0.02	**0.20**	***0.37***	**0.21**	0.11	***0.41***	***0.36***	***0.29***	***0.51***	0.16	0.34	0.38	**-0.44**	-0.03	**0.50**
β-ESLF			1	***0.61***	***0.78***	-0.11	0.11	***0.32***	***0.28***	-0.01	***0.40***	**0.21**	**0.21**	***0.42***	-0.29	0.23	0.24	-0.27	-0.16	0.18
ESLF SUL				1	***0.79***	-0.01	0.06	***0.25***	***0.30***	0.05	***0.43***	***0.32***	***0.24***	***0.53***	-0.02	**0.46**	-0.06	-0.33	**-0.49**	0.28
SULPHs					1	-0.08	0.15	***0.36***	***0.32***	0.04	***0.50***	***0.33***	***0.27***	***0.57***	0.11	**0.46**	0.17	**-0.49**	-0.35	0.27
HEPT						1	0.04	-0.07	0.08	***0.93***	-0.07	0.17	0.11	0.03	0.39	-0.40	0.33	0.19	0.20	-0.10
HEPX							1	***0.31***	0.17	**0.19**	0.03	0.11	0.08	0.04	0.05	-0.28	0.32	0.17	0.15	0.11
TC								1	***0.45***	0.14	***0.30***	**0.23**	***0.36***	***0.38***	-0.14	0.36	0.18	-0.25	0.06	0.38
CC									1	***0.24***	***0.24***	***0.24***	**0.22**	***0.30***	0.01	0.38	0.29	-0.33	0.01	0.28
CHLs										1	0.01	**0.21**	0.12	0.11	0.30	-0.32	0.42	0.20	0.36	0.03
Aldrin											1	***0.25***	***0.31***	***0.83***	0.20	0.39	0.20	-0.43	-0.27	**0.52**
Dieldrin												1	**0.22**	***0.59***	0.22	0.34	0.31	**-0.46**	-0.17	0.37
Endrin													1	***0.50***	0.11	**0.54**	0.28	***-0.57***	-0.09	0.41
DRINs														1	0.21	**0.44**	0.23	**-0.48**	-0.30	**0.55**

[a] Spearman's coefficients at significance level of $p < 0.05$ and $p < 0.01$ are shown in bold, and italic plus bold, respectively. Note: HEPT (heptachlor), HEPX (heptachlor epoxide), CC (cis-chlordane), TC (trans-chlordane), α-ESLF (α-endosulfan), β-ESLF (β-endosulfan), ESLF SUL (endosulfan sulfate).

2.2. Effects of soil properties

Twenty-one soil samples from the SRB were analyzed for soil textures, pH, and organic carbon (OC), and the detailed analytical procedures and measurements are presented in Arienzo et al. (2015). On the whole, HCB and Chlordane-related compounds were not significantly correlated with any soil properties ($p > 0.05$), and no significant correlations were observed between pH, fine sand, and any chemicals ($p > 0.05$) (Table 2).

The lengths of first ordination gradient resulting from detrended correspondence analysis (DCA) were below 3 for the soil samples, thus redundancy analysis (RDA) was performed to quantify the influence of soil properties on the concentration of HCB and cyclodienes. Significant variables were determined by forward selection procedure, using Monte Carlo permutation test (n = 499, unrestricted permutations).

RDA revealed that 33.2% of the variation was explained by soil properties. The remaining unexplained variation was probably because of other influence factors unaccounted for in the RDA, such as microbial community, temperature, precipitation, land use type, and other soil properties, like moisture, redox potential, carbon biomass, cation exchange capacity, total nitrogen, and phosphorous (Zhang et al., 2012; Zhang et al., 2006). The first two RDA axes accounted for 18.9% and 7.78% of the variation, respectively. The OC content was highly significant in the forward selection procedure ($p = 0.012$), explaining 15.0% of the variation, however, soil textures and pH did not significantly correlate with HCB and cyclodienes.

2.2.1. pH

Soil pH did not significantly influence HCB and cyclodienes, perhaps because of its slight variations from moderately acidic to alkaline in this study (see Table 1 from Arienzo et al. (2015)). Soil pH can affect OCPs residues by changing the humus structure, however, significant correlation between pH and OCPs is difficult to be observed at field sites (Hao et al., 2008; Qu et al., 2016). The further research about the effect of pH on OCP concentration is still needed. For instance, the increase of pH value could promote the degradation of endosulfan (Awasthi et al., 2000). Zhao et al. (2013) observed that soil pH (AM = 8.5) around a pesticide factory had negative effect on endosulfan ($p < 0.05$). Certain soil sampling sites still display a high pH value in our study, especially in the DFL (Albanese et al., 2015; Arienzo et al., 2015).

2.2.2. Organic carbon (OC)

Soil organic matter is a significant variable that influences OCP behavior, and a great deal of field investigation approved it (Hao et al., 2008; Jiang et al., 2009; Qu et al., 2015a). The close relationship between OC content and endosulfan, chlordane, and aldrin/dieldrin/endrin was exhibited (Fig. 4). The secondary distribution pattern of chemicals depends largely on soil OC content and temperature, unlike the usage of these chemicals for primary distribution pattern (Jia et al., 2010). Thus, some legacy OCPs in the Campanian Plain may belong to the secondary distribution pattern. Temperature is an important driven power of the secondary distribution of chemicals with higher vapor pressure (for example α-HCH) (Zhang et al., 2011a). However, as a volatile chemical substance being different from legacy HCHs, the origin of HCB is too complicate to discriminate its distribution pattern.

2.2.3. Soil textures

The soil texture of most of selected soils in this study varied from sandy to sandy loamy with an average content of silt in the range from 10 to 30 % (Albanese et al., 2015). Coarse sand positively correlated with several chemicals, whereas silt and clay negatively correlated ($p < 0.05$) (Table 2). The moisture and organic materials between sandy soil and loamy soil may result in the differences of absorption and degradation of OCPs. In fact, Hu et al. (2010) assumed that land use types, compared with soil textures, have greater impact to the absorption of HCH and DDT. The degradation of endosulfan in wet soils was faster than those in the flooded soils (Awasthi et al., 2000). The agricultural irrigation and frequent flooding in the SRB may cause the variations in the concentrations of chemicals.

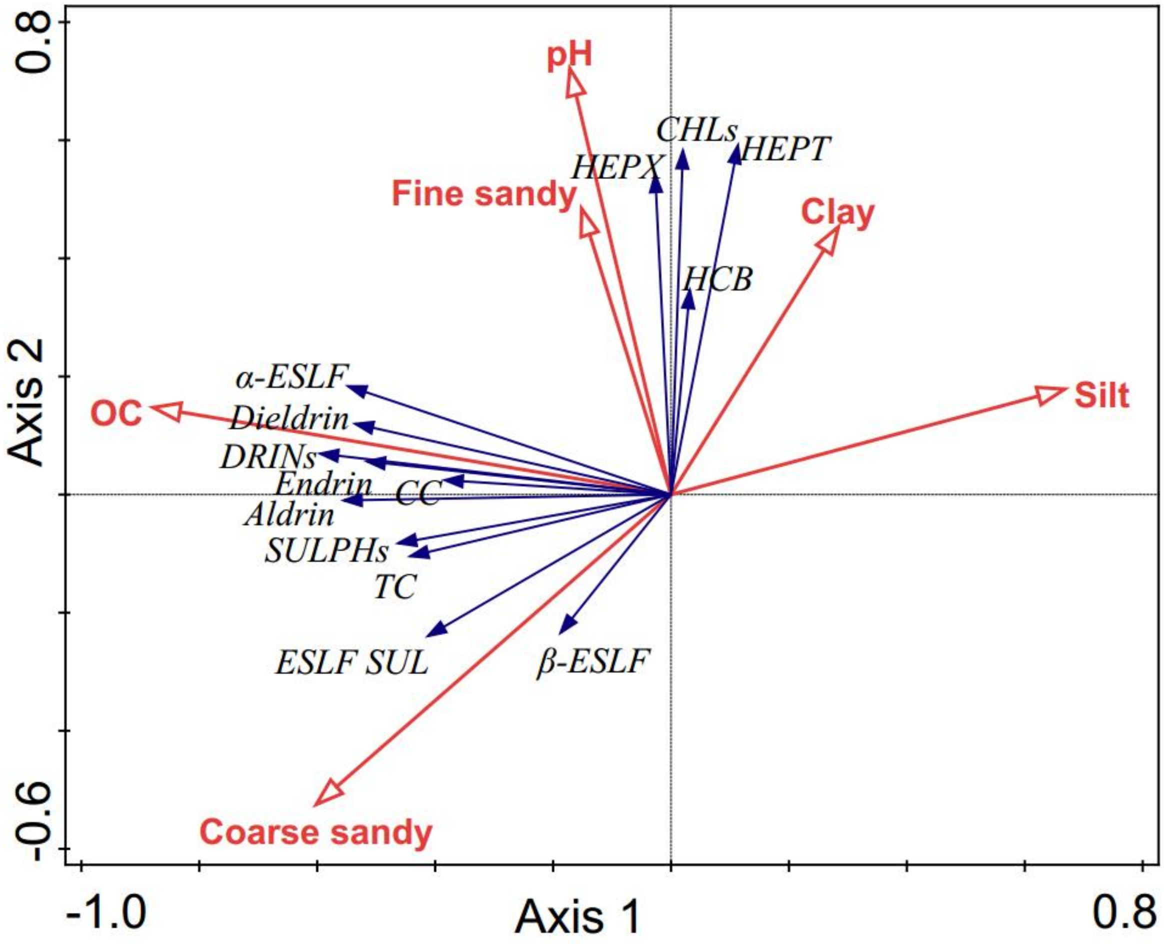

Fig. 4. Redundancy analysis (RDA) of the concentrations of OCPs and soil physicochemical properties in the Sarno River Basin (SRB) (n = 21). The lengths of arrows reveal the relationship strength between the explanatory variable and the response variable, and the intersection angles between the arrows (cosine value) represents their correlation.

2.3. Mass inventory

After the use of some OCPs being prohibited for decades, soils have been gradually converted to a secondary source of these legacy pesticides, and the remission continues to damage to the ecological environment (Qu et al., 2015b). To assess the possibility of soil as a source, the inventories (I, metric tons) of HCB and cyclodienes were calculated by the following equation:

$$I = \sum_{i=0}^{n} kC_iA_id\rho \qquad (1)$$

where n is the land segment number, C_i is the soil concentration of chemicals within segment i (ng/g dw), A_i is the land area of segment i (km^2), d is the thickness of the soil sampled (cm), ρ is the soil bulk density (g/cm^3), and k is the unit conversion factor.

To eliminate the uncertainty/variability of the parameters in Eq. (1), Monte Carlo simulation was used to estimate the mass inventory in this study, and the procedures in detail for the simulation calculation were presented in Qu et al. (2016). In the soils of the Campanian Plain, the Monte Carlo-based target compound inventory was of logarithmic normal distribution (Fig. 5).

The Gmean inventory of HCB, SULPHs, CHLs and DRINs in the Campanian Plain was 0.081, 0.41, 0.36 and 0.41 metric tons, respectively, and they were similar to HCHs (GM = 0.28 metric tons), but lower by one order of magnitude than that of DDTs (GM = 17.0 metric tons) (Qu et al., 2016). The reported data concerning the soil residue inventories of HCB and cyclodienes are extremely limited. The Gmean of EULPHs inventory in this study is lower than those in soil of Huai'an, China (Gmean = 1.5 metric tons), where industrial production and agricultural use were identified as the major input pathways (Wang et al., 2012).

In terms of the six subareas, the SULPHs and DRINs burden in soils of the SRB exhibited the highest value, and HCB and CHLs was observed in AA and DFL, respectively (Fig. 5). If the weight of the land area was considered, the HCB and CHLs burden per unit area in soils of AMC were the highest, and the SULPHs and DRINs are still in the SRB. The SRB has been plagued by floods and mudslides, and the Sarno River is still partially exploited for agriculture irrigation. The higher level of SULPHs and DRINs inventory in the SRB is extremely important for the coast environment because of their continuous dispersal via runoff. Qu et al. (2016) concluded that soil erosion and surface runoff play a major role in transporting DDTs and HCHs from the SRB to its coastal zone. The high-level of cancer mortality in the AMC probably related to the higher HCB and DFL burden.

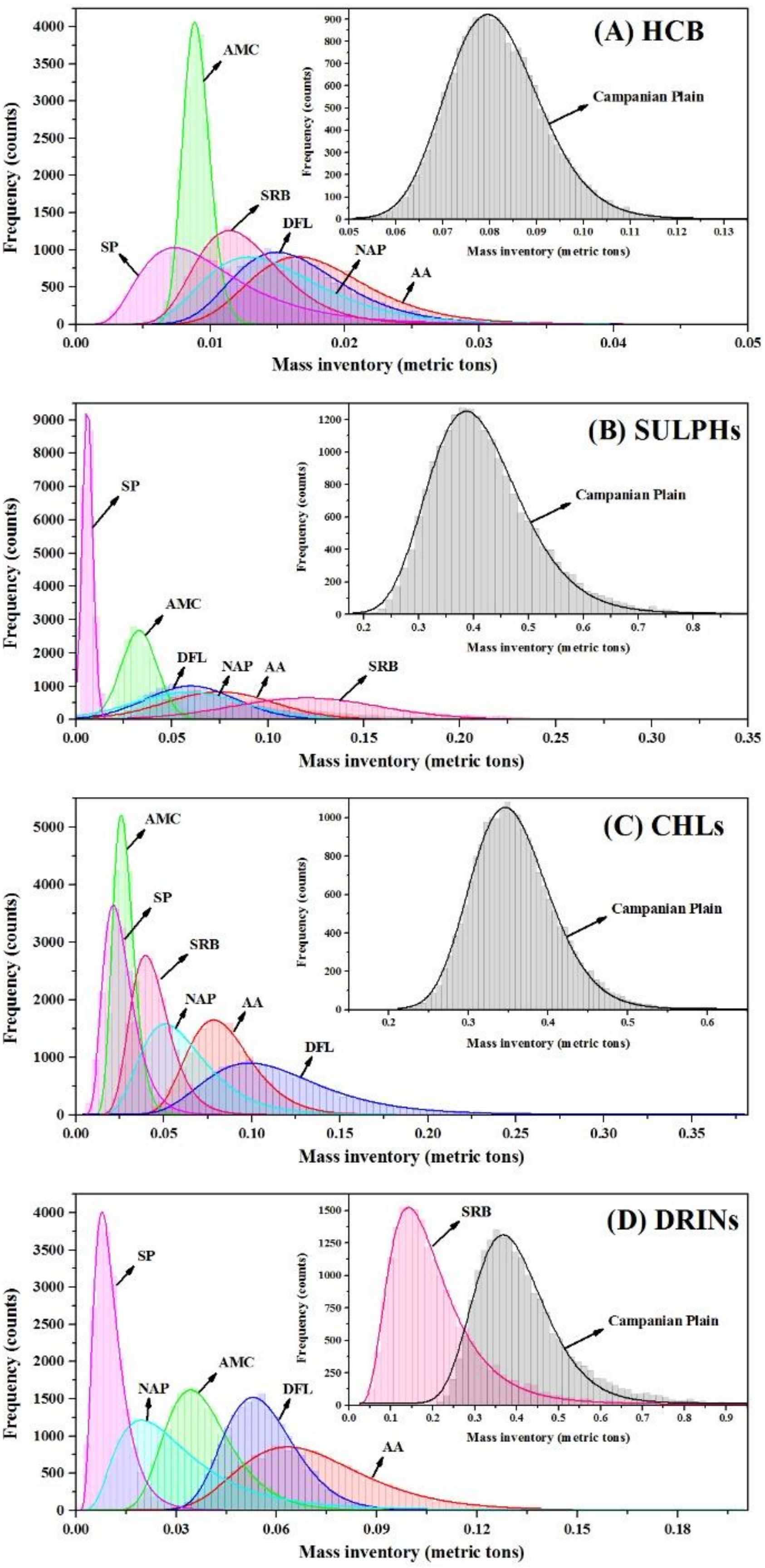

Fig. 5. Frequency distributions of the OCP inventory (metric tons) in the soils of the Campanian Plain, based on the results of 20,000 Monte Carlo simulations.

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Section 2.3

Risk assessment and influence factors of organochlorine pesticides (OCPs) in agricultural soils of the hill region: a case study from Ningde, southeast China

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Risk assessment and influence factors of organochlorine pesticides (OCPs) in agricultural soils of the hill region: A case study from Ningde, southeast China

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Highlights:

- The OCP residues in agricultural soil from Ningde were investigated and assessed for the first time.
- HCHs, DDTs and Endosulfans were the most dominant contaminant among the 20 OCPs.
- The OCP residues especially DDTs were remarkably influenced by land-use type.
- The residue levels of OCPs in agricultural soils were slightly controlled by TOC.
- The agricultural soils polluted by OCPs may pose a high potential carcinogenic risk for exposed populations.

Abstract: Surface soil samples from farmlands in Ningde were analyzed for 20 organochlorine pesticides (OCPs) with the aim of elucidating contamination profiles, distribution characteristics, influencing factors and carcinogenic risks of these compounds in this hilly region. The total concentrations of OCPs ranged from 3.66 to 658.42 ng/g, with a mean of 78.83 ng/g. HCHs, DDTs and Endosulfans were the predominant contaminants in agricultural soils. The residual levels of OCPs on vegetable farmlands were significantly higher than those of corresponding counterparts on paddy farmlands, mainly attributed to variations in pesticide application and OCP degradation in the soils. Potential source analysis traced the occurrence of high residual levels of DDTs and HCHs to historical applications. Spearman correlation analysis pointed to TOC as a significant variable controlling OCP distribution, and artificial influences possibly contributed to the fate of OCPs in the soils. The OCP contamination levels in the agricultural soils based on national standards are generally considered safe for crop production, but they however, pose significant carcinogenic risks to exposed populations based on the calculated results of the incremental lifetime cancer risk (ILCR) parameters.

Keywords: Organochlorine pesticides; Agricultural soils; Hill region; Health risk assessment

1. Introduction

Organochlorine pesticides (OCPs) are classified as persistent organic pollutants (POPs) due to their ubiquity, persistence and bioaccumulation in the environment (Jones and de Voogt, 1999 and Willett et al., 1998). Their high toxicity to humans and non-target organisms poses significant threats to human health and biodiversity (Jiang et al., 2009). Soil media are important reservoirs for OCPs due to their tremendous retention capabilities for these compounds (Harner et al., 2001). Consequently, huge amounts of accumulated pesticides in agricultural soils have been important re-emission sources to the atmosphere even after the phasing out of these compounds over decades ago (Tao et al., 2008). Organic pollutants in soils could influence soil microbial activity or enter the food chain directly through absorption into vegetation, thus resulting to ecosystem disturbances and/or negatively impacting human health (Cai et al., 2008). Some OCPs have been identified as endocrine disrupting substances (EDS) due to their tendency to alter hormonal activity in humans and other living organisms (Ge et al., 2013). Thus, an assessment of the pollution levels of OCPs in agricultural soils and their impact on human health is crucial for developing effective environmental remediation, abatement strategies, and predictive models regarding OCPs. Previous studies have considered the ecological risk assessment of OCP contamination in soil (Gao et al., 2013, Jiang et al., 2009 and Yu et al., 2013), but less attention has been given to the health risk due to exposure to OCPs in soils, especially agricultural soils, which serve as reservoirs of agrochemical OCPs.

China is one of the largest agricultural industries in the world with productivity accounting for 10.6% of the Gross Domestic Product in 2009. The country has once been the biggest producer and consumer of OCPs, especially in the arable southeast region (Tieyu et al., 2005). Although the production and use of OCPs including DDT, HCH, Aldrin, Dieldrin, Heptachlor, HCB and Chlordane have been phased out about three decades ago, the widespread usage of these persistent OCPs during the agricultural revolution had resulted to high residual levels in agricultural soil even now (Fu et al., 2003, Jiang et al., 2009 and Qu et al., 2010). The residual levels of OCPs at regional scale show large spatial variability in the country that is embodied in a regional distribution pattern of south > central > north (Hao et al., 2008). The estimated amounts of OCP active ingredients in pesticide mixtures used in southeast China ranged between 2.4 and 4.5 kg/ha (Cao et al., 2007). The foregoing sheds light on the enormity of OCP pollution in China. This obviously demands an in-depth research to determine the overall scale and problems of OCP contamination in agricultural soils by assessing their composition, distribution and public health risk especially in the severely affected communities of southeast China.

Ningde, located in Fujian Province, southeast China (between 26°18′–27°4′ N and 118°32′–120°44′ E; as shown in Fig. 1), is an area of typical subtropical hilly landform and moderate climate. This region with an arable land per capita of ca 0.72 hm^2 (a quarter of the world's average; 2.88 hm^2) is subject to intensive farming practices with an unprecedented use of agrochemicals. Although numerous studies have been done on the residual levels of OCPs in soils from other regions in China (Gao et al., 2013, Jiang et al., 2009, Yu et al., 2013, Zhang et al., 2006, Zhang et al., 2011, Zhang et al., 2012a and Zhang et al., 2012b), there is very little literature regarding the OCP distribution in agricultural soils of this hilly region. The non-availability of sufficient data on this subject constrains the evaluation of risk owing to OCP contamination of agricultural products and development of adequate policies regarding abatement measures. This work is therefore a pioneering investigation of OCP residues in selected agricultural soils of Ningde that should serve as a blueprint for the purpose of formulating informed policies with the aim of evaluating public health risk due to OCP exposures.

The study reports the level of OCP residues in agricultural soil collected at 67 locations in Ningde, China. The specific objectives of this research are to analyze the impact of the influence factors (total organic carbon, elevation and land-use type on the distribution patterns and fate of OCPs) and to evaluate the potential ecological and health risks due to exposure to OCPs in agricultural soils of the hill region (an area subject to intensive farming practices).

2. Methodology

2.1.Sampling

The locations of the sampling sites are shown in Fig. 1. Sixty-seven surface soil samples at depths between 0 and 20 cm were collected from agricultural soils of the study area during November 2009. Based on crop cultivation practices, the soil samples were divided into two categories, forty-five soil samples from paddy farmland and twenty-two samples from vegetable farmland. At each location, four subsamples were collected within a 50 m × 50 m plot, and thoroughly mixed to form a homogeneous composite sample using a pre-cleaned stainless steel scoop. All samples were wrapped in aluminum foil, packed into sealed polythene bags and immediately stored at − 4 °C until ready for analysis. Prior to OCP extraction, soil samples were air-dried and sieved through a 1 mm steel sieve.

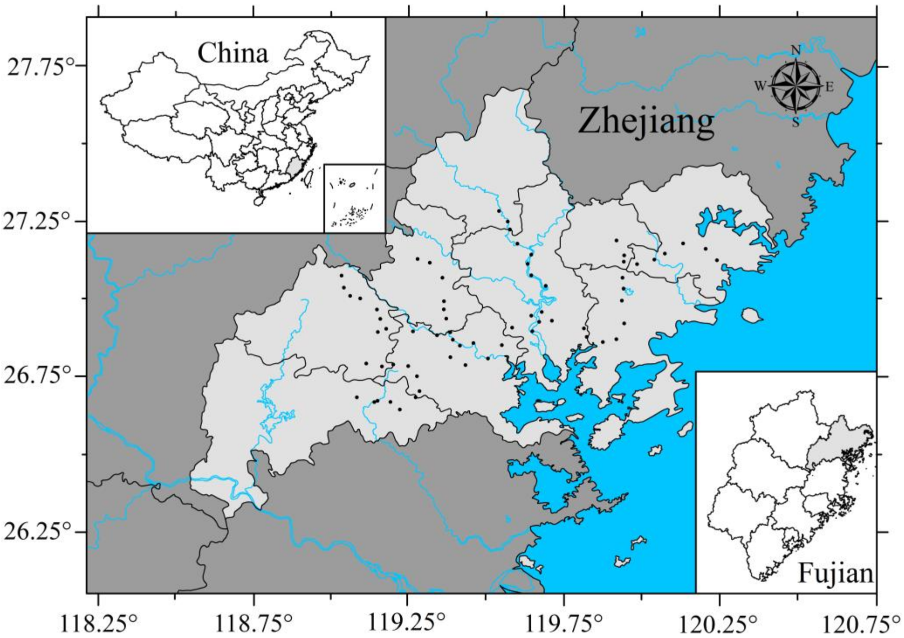

Fig.1. Locations of soil sampling sites in Ningde, China

2.2.Extraction and analysis

Extraction and quantification was done targeting twenty OCPs listed as follows: α-β-γ- and δ-HCH, p,p′-DDD, p,p′-DDE, p,p′-DDT, o,p′-DDT, α-Endosulfan, β-Endosulfan, Endosulfan sulfate, cis-Chlordane, trans-Chlordane, Aldrin, Dieldrin, Endrin, Heptachlor, Heptachlor epoxide, Methoxychlor, and HCB.

The US-EPA recommended 8080A method was used for the OCP analysis of the soil samples (Chen et al., 2011, Yang et al., 2013 and Zhang et al., 2013). Portions of 10 g air-dried soils were spiked with 20 ng mixed recovery surrogates containing 2,4,5,6-tetrachloro-m-xylene (TCmX) and decachlorobiphenyl (PCB209) before Soxhlet-extracted with dichloromethane (DCM) for a period of 24 h. Activated copper granules were added to the collection flask to remove elemental sulfur. The OCP extracts were first solvent exchanged to hexane and the final volume reduced to 2–3 mL by rotary evaporation. The alumina/silica (v/v = 1:2) gel column (48 h extraction with DCM, then 180 °C and 240 °C muffle drying for 12 h, both 3% deactivated with H_2O) was used to purify the extract and OCPs were eluted with 30 mL of DCM/hexane (2/3, v/v). The eluent was concentrated to 0.2 mL under a gentle nitrogen stream. A known quantity of penta-chloronitrobenzene (PCNB) was added as an internal standard prior to instrument analysis.

The samples were analyzed on an Agilent 7890A gas chromatograph coupled to a Ni electron capture detector (GC-ECD). The capillary column used for the analysis was a DB-5 (30 m, 0.32 mm i.d., 0.25 μm film thickness). Nitrogen was used as carrier gas at 2.5 mL/min under the splitless mode. The injector and detector temperatures were maintained at 290 °C and 300 °C, respectively. The temperature program was as follows: The oven initial temperature held at 100 °C (equilibrium time 1 min) raised to 200 °C at 4 °C/min, then to 230 °C at 2 °C/min, and at last reached to 280 °C at a rate of 8 °C/min, held for 15 min. A 2 μL sample was injected into the GC-ECD for analysis. Concentrations of individual target OCPs were quantified according to a six-point internal standard calibration curve.

To determine the total organic carbon (TOC), 3 g of the freeze-dried soil was treated with 1 mol/L HCl for 24 h to thoroughly remove any inorganic carbon. The treated soil was then dried overnight at 85 °C until a constant weight was reached. Portions of 50 mg treated soil were used to determine TOC by conventional standard procedures (liquiTOC, Elementar, Germany).

2.3.**Quality assurance/quality control**

The target compounds were identified based on the retention times (previously confirmed by GC–MS) and quantified using an internal standard. Selected samples were analyzed on GC–MS to confirm the concentration. A standard OCP solution was analyzed for daily instrument correction of the calibration, and the deviation was less than ± 15%. Surrogate standards were spiked to each of the sample to monitor procedural performance and matrix effects. No significant peaks overlapping the OCP standards appeared in the chromatograms of the blanks. The method detection limits (MDLs) of OCPs were described as a signal-to-noise (S/N) of three. The spiked recoveries of OCPs using 20 ng of composite standards were in the range of 72–103%. The relative standard deviation (RSD) ranged from 4% to 10%.

2.4.Carcinogenic risk model

The incremental lifetime cancer risk (ILCR) represents the incremental probability that an individual will develop cancer during his lifetime as a result of exposure to a potential chemical carcinogen (Chiang et al., 2009). We evaluated the ILCR of population groups in Ningde influenced by exposures to OCPs. The three pathways of human exposure to OCPs through soil contamination are: (a) direct ingestion of substrate particles; (b) dermal absorption of trace elements in particles adhered to exposed skin; and (c) inhalation of re-suspended particles emitted from soil through the mouth and nose (De Miguel et al., 2007). Therefore, the ILCR of the three pathways within the scope of the study was calculated using the following equations adapted from the USEPA standard models (Hu et al., 2014, Peng et al., 2011, USEPA, 1991 and Wang, 2007):

$$\mathrm{ILCRs_{ingestion}} = \frac{\mathrm{C_{soil}} \cdot (\mathrm{CSF_{ingestion}} \cdot \sqrt[3]{(\mathrm{BW}/70)}) \cdot \mathrm{IR_{soil}} \cdot \mathrm{EF} \cdot \mathrm{ED}}{\mathrm{BW} \cdot \mathrm{AT} \cdot \mathrm{CF}}$$

$$\mathrm{ILCRs_{dermal}} = \frac{\mathrm{C_{soil}} \cdot (\mathrm{CSF_{dermal}} \cdot \sqrt[3]{(\mathrm{BW}/70)}) \cdot \mathrm{SA} \cdot \mathrm{FE} \cdot \mathrm{AF} \cdot \mathrm{ABS} \cdot \mathrm{EF} \cdot \mathrm{ED}}{\mathrm{BW} \cdot \mathrm{AT} \cdot \mathrm{CF}}$$

$$\mathrm{ILCRs_{inhalation}} = \frac{\mathrm{C_{soil}} \cdot (\mathrm{CSF_{inhalation}} \cdot \sqrt[3]{(\mathrm{BW}/70)}) \cdot \mathrm{IR_{air}} \cdot \mathrm{EF} \cdot \mathrm{ED}}{\mathrm{BW} \cdot \mathrm{AT} \cdot \mathrm{PEF}}$$

where C_{soil} is the concentration of the contamination in soil (mg/kg); CSF is the carcinogenic slope factor (1/(mg/kg/d)); BW is the average body weight (kg); IR_{soil} is the ingestion rate of soil (mg/d); EF is the exposure frequency (d/yr); ED is the exposure duration (yr); AT is the average life span (d), SA is the surface area of the skin that contacts the soil (cm^2/d); FE is the fraction of dermal exposure ratio to soil; CF is the conversion factor (106 mg/kg); AF is the skin adherence factor for soil (mg/cm^2); ABS is the dermal absorption factor (chemical specific); IR_{air} is the inhalation rate (m^3/d); and PEF is the particle emission factor (m^3/kg).

Because several exposure parameters, such as body weight, ingestion rate, and inhalation rate, changed with age growth, the cancer risk was categorized and estimated for three age groups: childhood (0–10 yr), adolescence (11–18 yr), and adulthood (19–70 yr). Details of exposure parameters and the values used to derive the incremental lifetime cancer risk are presented in Table 1. The carcinogenic slope factors of OCPs obtained from the Integrated Risk Information System (IRIS) are listed in Table 2. The total risks in different age groups were estimated as the sum of individual risk for the three exposure pathways.

Table 1 Values of the parameters for the estimation of the incremental lifetime cancer risk

Exposure parameters	Unit	Childhood	Adolescence	Adulthood	References
Body weight (BW)	kg	13.95	46.75	58.75	MHC, 2007
Ingestion rate (IR_{soil})	$mg \cdot d^{-1}$	200	100	100	USDOE, 2011
Exposure frequency (EF)	$d \cdot yr^{-1}$	350	350	350	USDOE, 2011
Exposure duration (ED)	yr	6	14	30	Wang, 2007
Average life span (AT)	d	LT×365	LT×365	LT×365	USDOE, 2011
Lifetime (LT)	yr	72	72	72	WHO,2006
Surface area (SA)	$cm^2 \cdot d^{-1}$	2800	2800	5700	USDOE, 2011
Dermal exposure ratio (FE)	unitless	0.61	0.61	0.61	Wang, 2007
Dermal surface factor (AF)	$mg \cdot cm^{-2}$	0.2	0.2	0.07	USDOE, 2011
Dermal absorption factor (ABS)	unitless	0.13	0.13	0.13	USEPA, 2001
Inhalation rate (IR_{air})	$m^3 \cdot d^{-1}$	10.9	17.7	17.5	Wang, 2007
Particle emission factor (PEF)	$m^3 \cdot kg^{-1}$	1.36×10^9	1.36×10^9	1.36×10^9	USDOE, 2011

Table 2 The carcinogenic slope factor $(mg \cdot kg^{-1} \cdot d^{-1})^{-1}$ of OCPs through ingestion, dermal contact and inhalation

Compound	$CSF_{ingestion}$	CSF_{dermal}	$CSF_{inhalation}$
α-HCH	6.30E+00	4.49E+00	6.30E+00
β-HCH	1.80E+00	1.98E+00	1.86E+00
γ-HCH	1.30E+00	1.34E+00	1.80E+00
δ-HCH	1.80E+00	NA	1.80E+00
p,p’-DDE	3.40E-01	4.86E-01	NA
p,p’-DDD	2.40E-01	3.43E-01	NA
p,p’-DDT	3.40E-01	4.86E-01	3.40E-01
Aldrin	1.70E+01	1.70E+01	1.72E+01
Dieldrin	1.60E+01	1.60E+01	1.61E+01
Heptachlor	4.50E+00	6.25E+00	NA
Chlordane	3.50E-01	7.00E-01	3.50E-01
HCB	1.60E+00	3.20E+00	NA

NA indicated that a value was not available

2.5.Statistical analysis

Statistical analyses were performed using SPSS Statistics version 19.0. Values below the limit of detection were reckoned as zero. The data significantly deviated from a normal probabilistic distribution (Shapiro–Wilk Text, $P > 0.05$), therefore nonparametric statistical test were applied to these data. Spearman's non-parametric test was performed to determine the relationship between OCPs and TOC. The principal component analysis (PCA) was applied to examine the source and degradation behavior of OCPs in the two distinct land-use types. A P-value below 0.05 (two tail) was considered in identifying statistically significant differences, with $P < 0.01$ defined as extremely significant throughout the study.

3. Results and discussion

3.1.Residual levels

The results of the OCP levels in the agricultural soils from Ningde are summarized in Fig. 3. The detection frequencies of OCPs in all samples were all over 86.57%, except for o,p′-DDT. The high detection frequencies of OCPs indicated that they are pervasive in the different regions of Ningde. The total OCP concentrations varied between 3.66 and 658.42 ng/g, with a mean value of 78.83 ng/g. The mean value was in the order of DDTs > HCHs > Endosulfans > the rest OCPs. The total concentrations of DDTs, HCHs and Endosulfans accounted for 78.28% of the OCPs making them the predominant OCPs in the study area. This statistics warrants special attention on these 3 OCPs in this study and any futuristic abatement strategies should focus on them. Compared with other organochlorine pesticides, HCH isomers exhibit moderately high vapor pressures and lower octanol–water coefficient (K_{ow}), making them easier to transport for long distances (Walker et al., 1999). This fact resulted in lower soil concentration of HCHs than DDTs in study regions, consistent with previous studies on OCP residues in agricultural soil from different areas as shown in Table 3. In addition, the concentrations of the rest OCPs were in the range of 0.84–147.28 ng/g, with a mean of 17.12 ng/g. Although, the respective concentrations of the rest OCPs have been kept in low levels, the detection frequencies were all much higher than 86.57%. This fact indicated that the rest of OCPs had been widely used in the region's agricultural production, but their amounts of application probably were relatively lower than DDTs, HCHs and Endosulfans.

The residual levels of HCHs, DDTs and Endosulfans in Ningde were compared with those in other agricultural surface soils from various regions (Table 3). The residual levels of HCHs and DDTs were similar to those reported for agricultural soil samples collected from Hongze Lake (Gao et al., 2013), and they were both higher than for other regions in China, such as Shanghai, Pearl River Delta, Zhangzhou and Hong Kong (Jiang et al., 2009, Yang et al., 2012, Yu et al., 2013 and Zhang et al., 2006), and relatively lower than those in Taihu and Nagaon, India (Mishra et al., 2012 and Wang et al., 2007). The concentration of HCHs in the present study was higher than those recorded for Haihe Plain, Zhejiang and Hanoi, Vietnam (Tao et al., 2008, Toan et al., 2007 and Zhang et al., 2011), but remarkably lower than those in A Coruña, NW Spain (Calvelo Pereira et al., 2010). Whereas, the concentration of DDTs in this study was inverse to HCHs, and it was lower than those recorded in Haihe Plain, Zhejiang and Hanoi, Vietnam (Tao et al., 2008, Toan et al., 2007 and Zhang et al., 2012a). In addition, the residual levels of Endosulfans were higher than those from Shanghai, Hong Kong, Zhejiang, and Zhangzhou (Jiang et al., 2009, Yang et al., 2012 and Zhang et al., 2012b). The result showed that the concentrations of HCHs and DDTs in the agricultural soils of Ningde were in medium level, whereas the residual levels of Endosulfans had been maintained at the highest level compared with those reported.

Table 3 Comparisons of OCPs residual levels in agricultural surface soils from different areas (dry weight ($ng \cdot g^{-1}$))

Study region	Sampling year	HCHs[b]		DDTs[c]		Endosulfan		Reference
		Range	Mean	Range	Mean	Range	Mean	
Ningde	2009	0.45-151.21	14.51	0.51-241.30	29.61	0.14-453.96[d]	17.59[d]	this study
Shanghai	2007	N.D[a]-10.38	2.41	0.44-247.45	21.41	N.D-3.68[e]	_	(Jiang et al., 2009)
Taihu	2004	0.73-60.97	24.06	3.10-166.55	57.04	_	2.04[f]	(Wang et al., 2007)
Around Hongze Lake	2009	N.D-42.59	8.85	N.D-184.02	24.82	_	_	(Gao et al., 2013)
Pearl River Delta	2006	N.D-62	3.4	N.D-110	8.8	_	_	(Yu et al., 2013)
Zhangzhou	2009	0.72-30.16	9.79	0.64-78.07	3.86	0.30-110.24[d,h]	3.93[d,h]	(Yang et al., 2012)
Haihe Plain	2004	0.02-349	3.9	0.40-2350	63.6	_	_	(Tao et al., 2008)
Zhejiang	2006-2007	N.D-50.6	2.82	3.13-529	75.65	N.D-39[d]	7.9[d]	(Zhang et al., 2011; Zhang et
Hong Kong	2000	_	0.52	_	6.19	N.D[d]	N.D[d]	(Zhang et al., 2006)
Hanoi, Vietnam	2005	0.05-20.57	8.03	0.02-171.83	89.86	_	_	(Toan et al., 2007)
A Coruña, NW Spain	2003-	1 –2305	337	_	_	_	_	(Calvelo Pereira et al., 2010)
Nagaon, India	2009-2010	98-1945	825	166-2288	903	_	_	(Mishra et al., 2012)

[a] Not detected; [b]sum of *α*-HCH, *β*-HCH, *γ*-HCH and *δ*-HCH; [c] sum of *p,p'*-DDE, *p,p'*-DDD, *p,p'*-DDT, *o,p'*-DDT; [d] sum of α-Endosulfan, β-Endosulfan and Endosulfan-sulfan; [e] Endosulfan: sum of *α*- and *β*-Endosulfan; [f] concentration of *α*-Endosulfan; [h] Unpublished results

3.2.Distribution characteristics

3.2.1. Geographical distribution

The spatial distributions of OCPs, HCHs, DDTs, and Endosulfans are presented in Fig. 2. The spatial distributions showed a strong gradient in selected OCP concentrations, with variation coefficients of all OCPs in this study area exceeding 113.04%. The spatial distribution of OCPs was under the double influence of global distillation effect and the usage of OCPs (Jiang et al., 2009). Due to agricultural activities, the distribution of OCPs might change in the hilly area. With an increase in elevation (1 m–1067 m), the environmental effects of human activities are reduced, and no correlation coefficients (R2) were observed between elevation and residues of OCPs based on Spearman's non-parametric test. Therefore, this observation could be due to the indiscriminate use and poor management practices regarding OCPs. High levels of OCPs were found in the central and eastern parts of the study area. The high residual sampling point of OCPs had a low concentration of the rest OCPs, which indicated that HCHs, DDTs or Endosulfans were the predominant contributor to the heavy contamination area of OCPs. HCHs were featured with high local residue. The variation tendencies of DDTs coincided with OCPs, which indicated that DDTs were the favored OCPs used on farmlands. Endosulfan concentrations in soil samples from central Ningde were remarkably higher than in other parts of Ningde. Higher residual sampling points of Endosulfans had corresponding higher concentrations of DDTs, which was not the situation for HCHs residual concentrations. This observation could be attributed to local pesticide practices specific to pest control needs or crop type and the differences in the properties of these pesticides in these areas, despite the fact that they were considered to be the main OCPs.

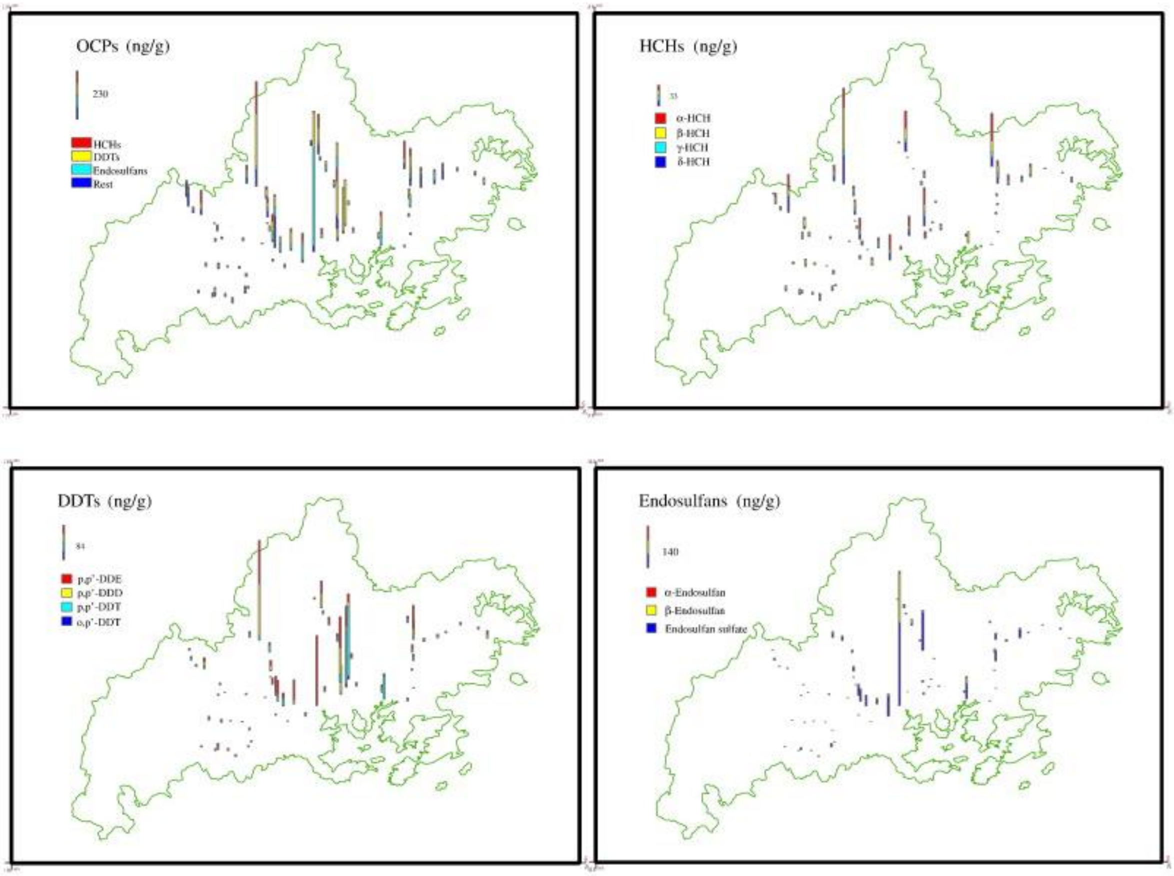

Fig. 2. Distribution of individual component of OCPs, HCHs, DDTs and Endosulfans in agricultural soils collected from Ningde. Rest: sum of cis-Chlordane, trans-Chlordane, Aldrin, Dieldrin, Endrin, Heptachlor, Heptachlor epoxide, Methoxychlor, and HCB.

3.2.2. Distribution of OCPs in different land-use types

Land-use type, which has a direct impact on the application history and the dissipation of OCPs by changing the soil conditions, is considered to be an important factor to influence the residues of individual OCPs in soil (Gao et al., 2013 and Hao et al., 2008). Fig. 3 shows the box-and-whisker plots for the concentrations of selected OCPs in paddy farmland and vegetable farmland. The concentrations of individual OCPs in vegetable farmland were generally higher than those in paddy farmland, an observation akin to those of previous studies done in other parts of South and Central China (Tieyu et al., 2005). Vegetables were especially prone to damage by insects compared to grain crops and thus are subject to higher pesticide application per unit area in the field. Furthermore, the alternation of anaerobic and aerobic conditions of paddy land was beneficial for the microbial degradation of OCPs (Hao et al., 2008).

The concentrations of DDTs in paddy farmland were remarkably lower than those in vegetable farmland, and this observation reflects the difference in pesticide application and their decomposition in these two land-use types. Regarding the decomposition of DDTs, Boul (1996) made the following assertion regarding DDT decomposition, stating that flooded soils have higher capacity to transform p,p′-DDT to p,p′-DDD through a 42-day laboratory microcosm experiment. Moreover, it has been shown that the effect of waterlogged soil for paddy farmland makes DDTs more prone to biodegradable through reductive dechlorination under anaerobic condition (Xu et al., 1994). On the other hand, DDTs have shown sluggish rates of degradation under aerobic conditions notable for vegetable planting (Hao et al., 2008). The foregoing rationalizes the enhanced degradability of DDTs in paddy farmland or the reverse in vegetable farmland and invariably explains the variations in the residual concentrations of DDTs in the two land-use types.

Unlike paddy farmland, we observed that β-HCH was not the dominant isomer of HCH in vegetable farmland (Fig. 3). This result does not corroborate the results reported in other previous studies (Gao et al., 2013, Yu et al., 2013 and Zhang et al., 2011). The microbial transformation of α-HCH and γ-HCH by microbes to β-HCH coupled by its enhanced soil stability due to its molecular structure could explain its high levels or accumulation in soils (Hao et al., 2008). We however speculate that the residual differences of individual HCH isomers on vegetable land could be due to the illegal use of technical HCH or the difference in the degradation of HCH in specific conditions. Endosulfan-sulfate which is the dominant metabolite of Endosulfan degradation in soil (Jia et al., 2010) was detected in higher concentrations than those of α-Endosulfan and β-Endosulfan, which indicated that Endosulfan had a tendency of degradation in this region.

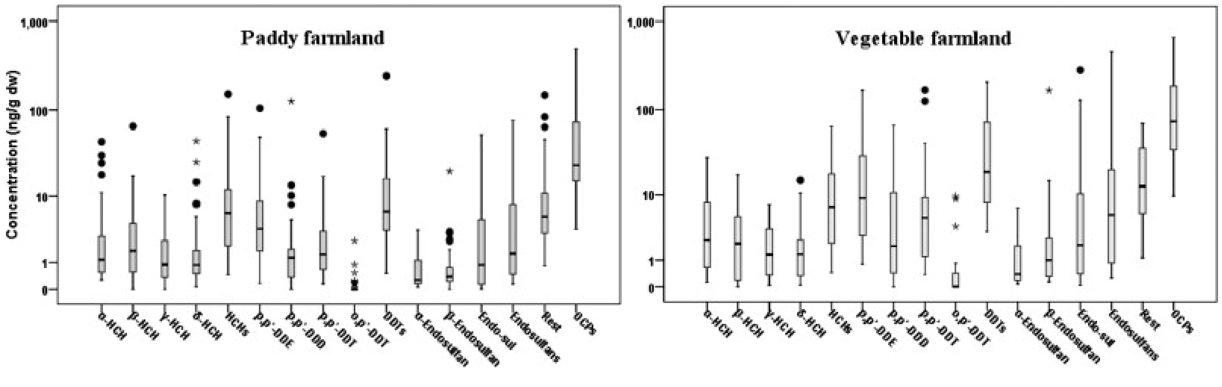

Fig. 3. Box-and-whisker plots of HCHs, DDTs, Endosulfans (Endo-sulfate: Endosulfan sulfate) and OCPs in paddy and vegetable farmland. The box represents the interquartile range, containing the middle half of the data. The whiskers extending from the box represent the minimum values and maximum values. The upper and the lower edge of the box represent the 75th and 25th percentilesof the data set. The median value is designated by the horizontal black line inthe box. "●" represents outliers, whichwere beyond1.5 times the interquartile range, and "*" represents extreme values, which were beyond the triplication of the interquartile range.

3.3.Source apportionment of HCHs, DDTs and Endosulfans

3.3.1. Molecular composition analysis

Several isomeric ratios of selected compounds were used to distinguish whether the sources are from the historical usage or fresh application on agricultural soils in the study area. The principle of molecular indices as tracing signatures had been described in previous papers (Ge et al., 2013, Jiang et al., 2009 and Yu et al., 2013). Fig. 4 shows the scatter plots for isomeric ratios of selected OCPs.

In China, technical HCH (α-HCH 71%, β-HCH 6%, γ-HCH 14%, δ-HCH 9%) was in widespread use for agriculture since the 1950s until they are officially banned in 1983 (Tao et al., 2008). Subsequently, lindane was applied in agriculture as a substitute, which contained almost 100% of the γ-HCH (Li et al., 2001). Regardless of land-use types, α-/γ-HCH ratios were less than 3 in most of sample locations, which indicates fresh application of lindane in recent years. Most of the samples with high residues of HCHs (> 20.0 ng/g) also showed higher α-/γ-HCH ratio, suggesting that the heavy pollution of HCHs in the soil was mainly due to historical use.

The major source of DDT pollution in China was through the application of technical DDTs and dicofol in agriculture (Yang et al., 2013). Technical DDT contains higher than 85% of p,p-DDT and less than 15% of o,p-DDT (Yang et al., 2012). The small ratio of (p,p′-DDE + p,p′-DDD)/p,p′-DDT(< 1.0) indicates historical DDTs and a ratio more than 1.0 is indicative of aged DDTs (Jiang et al., 2009). The high concentration of DDTs (> 10.0 ng/g) was a common situation that (p,p′-DDE + p,p′-DDD)/p,p′-DDT ratios for most of sample locations were far greater than 1, suggesting that the heavy pollution of DDTs was derived from the historical application of technical DDT.

Previous studies suggest that a ratio of o,p′-DDT/p,p′-DDT in the range of 1.3 to 9.3 or higher than 9.3 is indicative of dicofol source while a range of 0.2–0.3 is indicative of technical DDT source (Qiu et al., 2005). Judging by this perspective, our study showing predominantly o,p′-DDT/p,p′-DDT ratios ranging between 0 and 0.39, is indicative of technical DDT as the prime source of DDT. However, the results here do not conform to those reported by Qiu et al. (2005) who speculated dominant dicofol type DDT pollution in a south China.

The technical Endosulfan consists of ~ 70% α-Endosulfan and ~ 30% β-Endosulfan (Rice et al., 1997). In vegetable farmland, α-/β-Endosulfan ratio in all samples was below 2.33, suggesting that there may not be a recent application of Endosulfan in the study area. A few sample locations in paddy farmland showed higher α-/β-Endosulfan ratios, indicating continual use of Endosulfan in such localities within the study area. It is noteworthy that the four samples contained β-Endosulfan below the limit of detection, but with appreciable levels of α-Endosulfan and Endosulfan-sulfate. This is attributed to the fact that the vapor pressure and Henry's law constant of α-Endosulfan are higher than β-Endosulfan, thus having a greater tendency to evaporate from surface media to air (Jia et al., 2010), a major reason for its transport over long-ranges in the environment.

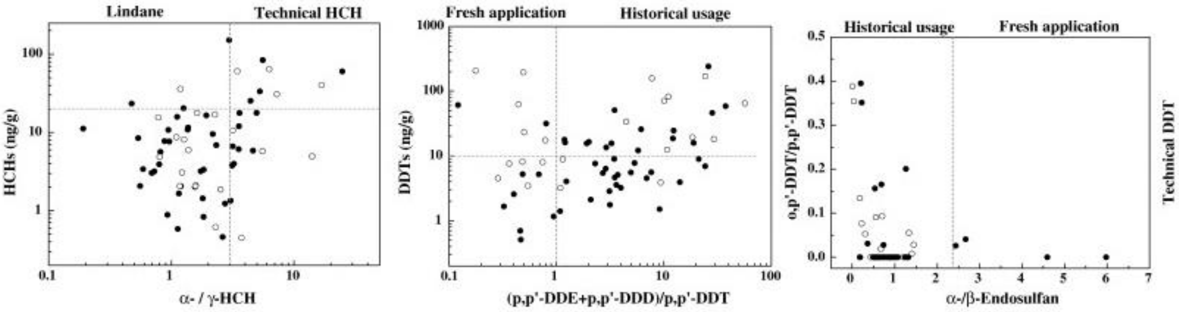

Fig. 4. Scatter plots of molecular indices to identify OCP contamination sources. “●” and “○” represent soil samples from paddy farmland and vegetable farmland, respectively.

Table 4 The selected OCPs on the principal rotated component matrix (factor loadings greater than 0.5 are shown in bold)

Variable	Paddy field (n=45)			vegetable field (n=22)		
	PC1	PC2	PC3	PC1	PC2	PC3
α-HCH	0.33	-0.02	**0.85**	**0.87**	0.12	-0.18
β-HCH	**0.84**	0.15	0.42	**0.90**	-0.10	-0.11
γ-HCH	0.42	-0.02	**0.81**	**0.83**	-0.03	-0.12
δ-HCH	**0.75**	-0.02	**0.56**	**0.95**	0.01	-0.14
p,p’-DDE	**0.80**	0.16	0.35	0.25	**0.88**	0.19
p,p’-DDD	**0.95**	0.02	0.27	**0.84**	0.02	0.20
p,p’-DDT	0.10	**0.95**	-0.03	-0.08	-0.05	**0.98**
o,p’-DDT	**0.95**	0.00	0.08	-0.15	-0.01	**0.97**
α-Endosulfan	0.18	**0.60**	**0.69**	0.10	**0.91**	-0.14
β-Endosulfan	-0.10	**0.94**	0.10	-0.17	**0.95**	-0.06
Endosulfan sulfate	0.11	**0.87**	0.01	-0.15	**0.95**	-0.05
Eigenvalues	4.07	2.93	2.55	4.01	3.44	2.08
% of Variance	37.02	26.66	23.20	36.41	31.24	18.92
Cumulative %	37.02	63.68	86.89	36.41	67.66	86.58

3.3.2. Principal component analysis

Principal component analysis (PCA) was performed to further determine the possible sources and degradation behavior of selected OCPs. The majority of the variance (> 86%) for the two land-use types were explained using three eigenvector factors (as seen in Table 4). In the case of paddy farmland, PC1 was highly associated with β-HCH, δ-HCH, p,p′-DDD, p,p′-DDE and o,p′-DDT, but β-HCH was the predominant isomer in this farmland type resulting from the decomposition and transformation of other HCH isomers over time (Hao et al., 2008). However, p,p′-DDD and p,p′-DDE were the two major degradation products of p,p′-DDT. Thus, this observation suggested that these compounds appeared to have a similar origin and represented the degradation of DDT and HCH. PC2 had a high positive loading for p,p′-DDT, α-Endosulfan, β-Endosulfan and Endosulfan sulfate, indicating a similar source for all of them. PC3 principally described the characteristics of α-γ-δ-HCH and α-Endosulfan, showing that these compounds had similar physicochemical properties, such as relatively high volatility in comparison to other OCPs. In the case of the vegetable farmland, PC1 was highly associated with

HCH group and p,p′-DDD. PC2 correlated well with p,p′-DDE, α-Endosulfan, β-Endosulfan and Endosulfan sulfate, which suggests that they were of a similar source. PC3 had a strong positive correlation with p,p′-DDT and o,p′-DDT, suggesting that they originated from the same source. Based on the composition analysis of DDT as mentioned above, the main source of DDT then ascertained to be technical DDT rather than dicofol. It is worthy to note that p,p′-DDT was separated from p,p′-DDE and p,p′-DDD in the two land-use types. The results suggested that DDT degradation behavior and the historical/current inputs of technical DDT in soil cannot be easily deciphered.

3.4.Effect of total organic carbon (TOC)

OCPs have the tendency to be adsorbed by soil organic matter (SOM) due to their hydrophobicity, and high soil organic matter content provides adequate carbon for soil microbes to facilitate the degradation of OCPs. Consequently, TOC is a clearly significant variable that influences OCP behavior in soil. TOC content in soil samples of this study varied between 0.65% and 7.46% and the concentrations of several OCPs (even after logarithmic transformation) do not follow a normal distribution. Thus, Spearman's non-parametric test was used to investigate the relationship between OCPs and TOC in soils of paddy farmland and vegetable farmland. The result of the Spearman's correlation analysis between OCPs and TOC is given in Table 5.

Table 5 Spearman’s Coefficients (Rs) between the residual levels of OCPs and TOC in soils of Paddy farmland and vegetable farmland.

Compound	Paddy field (n=45)		vegetable field (n=22)	
	P-value	R_s	P-value	R_s
α-HCH	<0.001	0.545^{**}	0.230	0.267
β-HCH	<0.001	0.532^{**}	0.104	0.356
γ-HCH	0.016	0.356^{*}	0.801	0.057
δ-HCH	<0.001	0.626^{**}	0.236	0.264
HCHs	<0.001	0.572^{**}	0.255	0.254
p,p’-DDE	0.559	0.089	0.962	0.011
p,p’-DDD	0.089	0.257	0.543	0.137
p,p’-DDT	0.918	-0.016	0.318	-0.223
o,p’-DDT	0.261	0.171	0.245	-0.259
DDTs	0.372	0.136	0.658	-0.100
α-Endosulfan	0.134	0.227	0.157	-0.312
β-Endosulfan	0.389	0.132	0.112	-0.348
Endosulfan sulfate	0.325	0.150	0.029	-0.466^{*}
Endosulfans	0.261	0.171	0.049	-0.424^{*}
OCPs	0.004	0.421^{**}	0.420	-0.181

*. Correlation is significant at the 0.05 level (2-tailed). **. Correlation is significant at the 0.01 level (2-tailed).

The concentrations of OCPs, HCHs and its isomers in paddy farmland exhibited a significant positive correlation with TOC contents, while significantly negative correlations were observed between TOC and Endosulfans (P = 0.029, Rs = − 0.466), Endosulfan-sulfate (P = 0.049, Rs = − 0.424) in vegetable farmland. This result indicates that TOC was an important variable that controls the distribution of these compounds in soils. However, there were no significant correlations ($P > 0.05$) between TOC and other individual OCPs, especially DDTs. OCP concentrations are expected to be proportional to SOM for a soil–air system in equilibrium (Kannan et al., 2003). No correlation is shown for individual OCPs and TOC, suggesting that the geographical distribution pattern of these compounds does not approach the adsorption equilibrium status with TOC in soils. Because of their relatively high log K_{ow} and easier absorption to the soil, DDT isomers are less likely to volatilize from soil to air after application, thus not permitting the easy attainment of equilibrium in soil. This fact supports the observed non-correlation among DDTs and TOC in the two land-use types considered in this work. Gao et al. (2013) observed an insignificant positive correlation between TOC and OCPs, and attributed this observation to certain artificial influences which possibly contributed to the disequilibrium relationships. Vegetable farmlands are subject to more frequently changes in crops cultivated especially with the robust agricultural activities in the area, which, results in different usage of manure and pesticides. This probably could be the reason for poor correlation between TOC and OCPs in vegetable farmland.

3.5.Risk assessment

3.5.1. Potential ecological risk

To illustrate the potential ecological risk of OCP residues in the soil environment, the risk was evaluated by comparing the concentrations of OCPs with related guidelines of soil environmental quality standard. According to the Dutch target values (Netherlands Ministry of Housing, 2002), the residues of HCHs exceeded the target value for unpolluted soil (10 ng/g) at 25 sites. For DDTs, only 8 soil samples were lower than the target value for unpolluted soil (2.5 ng/g). In addition, the concentrations of HCB and Endrin in most samples were lower than their target values for unpolluted soil (2.5 ng/g). The concentrations of both HCHs and DDTs in all soil samples were lower than the guideline (GB 15618-1995) of the second level (500 ng/g) recommended by the Chinese government to guarantee the safety of agricultural products so as to uphold human health (Science &Technology Department of State Environmental Protection Administration, 1995). For the protection of plants and invertebrates, small birds and mammals, the maximum permissible concentrations of DDTs in soil are 10, 11, and 190 ng/g, respectively (Yu et al., 2013). The concentrations of DDTs in half soil samples exceeded 11 ng/g and in 3 of samples higher than 190 ng/g. Therefore, the OCP levels are categorized as moderate contaminations, but yet posing potential ecological risks. For the reason that the soil in this region is suitable for agricultural products, it does not need to adopt some corresponding ecological restoration measures based on the Chinese target values.

3.5.2. Carcinogenic risk

The ILCR was calculated as a means for interpreting the integrated lifetime risks of exposure to soil-borne OCPs through the pathways of ingesting, dermal contact and inhalation (Chen and Liao, 2006). For most regulatory programs, an ILCR between 10^{-6} and 10^{-4} denoted potential risk, whereas the virtual safety was indicated by an ILCR of 10^{-6} or less and a potentially high health risk was estimated by ILCR larger than 10^{-4} (Chen and Liao, 2006, Peng et al., 2011 and Wang et al., 2011).

As shown in Table 6, the 95% confidence interval ILCRs of total cancer risk for different age groups exposed to the selected OCP concentration of agricultural soils were higher than the baseline value of potential risk (10^{-4}), indicating a high potential carcinogenic risk. It is worthy to note that this result may be a complement with respect to the Chinese soil quality standards (GB 15618-1995), which focuses on soil affecting the safety of agricultural products but neglects the immediate negative effects of contaminated soils on public health especially peasants. This problem is magnified here due to the increased number of the compounds considered for carcinogenic risk assessment in our research. For different exposure pathways, the increasing trend in cancer risk for OCPs is determined as follows: inhalation < dermal contact < ingestion. The carcinogenic risk through inhalation of OCPs containing soil particulates is 10^4–10^5 times less than that through ingestion and dermal contact with OCPs containing soil, thus comparably, inhalation of OCP particulates is almost negligible of the these three exposure pathways.

Table 6 Cancer risk due to human exposure to OCPs via agricultural soil

Exposure pathways		Minimum	Maximum	Mean	Median	UCL (95%) [a]	LCL (95%) [b]
Childhood	Ingestion	1.70E-05	6.19E-03	4.04E-04	1.50E-04	6.11E-04	1.97E-04
	Dermal contact	3.00E-06	1.38E-03	8.70E-05	3.40E-05	1.33E-04	4.20E-05
	Inhalation	5.66E-10	2.49E-07	1.45E-08	4.94E-09	6.33E-09	2.27E-08
	Cancer risk	2.00E-05	7.56E-03	4.91E-04	1.81E-04	7.43E-04	2.39E-04
Adolescence	Ingestion	9.00E-06	3.22E-03	2.10E-04	7.80E-05	3.18E-04	1.03E-04
	Dermal contact	3.00E-06	1.43E-03	9.10E-05	3.50E-05	1.38E-04	4.40E-05
	Inhalation	9.58E-10	4.22E-07	2.46E-08	8.37E-09	3.84E-08	1.07E-08
	Cancer risk	1.20E-05	4.66E-03	3.02E-04	1.14E-04	4.56E-04	1.47E-04
Adulthood	Ingestion	1.60E-05	5.93E-03	3.87E-04	1.44E-04	5.85E-04	1.89E-04
	Dermal contact	4.00E-06	1.88E-03	1.19E-04	4.60E-05	1.82E-04	5.70E-05
	Inhalation	1.74E-09	7.67E-07	4.47E-08	1.52E-08	6.99E-08	1.95E-08
	Cancer risk	2.10E-05	7.81E-03	5.07E-04	1.89E-04	7.67E-04	2.47E-04

[a] The upper 95% confidence limit; [b] The lower 95% confidence limit

4. Conclusions

The present study has provided the first systemic data on the contamination status of OCPs in agricultural soils in Ningde, China. The high detection frequencies of OCPs in soil samples indicated their wide spread in agricultural soil of the study area, with DDTs, HCHs and Endosulfans being the most dominant OCPs. The residual level of OCPs in vegetable farmland is generally higher than those of corresponding counterparts in paddy farmland. Potential source analysis indicated that the residues of OCPs in most samples were derived from historical application, with evidence showing current application of lindane and DDT pesticide formulations in some parts of the study area. The close relationship between TOC and a part of OCPs indicates that the former is an important factor influencing the persistence of these OCPs in soils. Compared to the published guidelines and previous studies, the residual OCPs in Ningde may be classified as slight contamination, making soils in the study area and it is somehow suitable for agricultural production. However, there is still a high potential of carcinogenic risk for exposed populations, especially agricultural producers/farmers.

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Section 2.4

Legacies of Organochlorine Pesticides (OCPs) in soil of China - A Review, and cases in Southwest and Southeast China.

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Legacies of Organochlorine Pesticides (OCPs) in soil of China - A Review, and cases in Southwest and Southeast China

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Abstract: Organochlorine Pesticides (OCPs) are the major Persistent Organic Pollutants (POPs) in China. China has a history of intensive application and production of OCPs between the 1950s and the 1980s for agricultural use and vector control. Since the early 1980s, China began to ban the agricultural use of OCPs and then signed the Stockholm Convention on POPs in the 21st century. By 2009, majority of OCPs were restricted and eliminated in China but for emergency. However, residual OCPs can still be detected in various environmental media and even in great quantity in some sites in recent years. This article briefly introduced the origin and environmental chemistry of OCPs, reviewed the history and present of OCPs in soil of China, and also enclosed cases on OCPs distributions and influencing factors in soil of Chengdu Economic Region in Sichuan Province and Zhangzhou in Fujian Province, representatives of the Southwest and Southeast of China, respectively. Moreover, as majority of OCPs are not the currently used POPs, the main targets of the research on OCPs may shift to aspects further than their concentration and distribution. The experience of battling with such POPs may give the examples on how to avoid or terminate such chemicals pollutions.

Keywords: Organochlorine Pesticides, Persistent Organic Pollutants, soil contamination, China

1. Introduction

Organochlorine pesticides (OCPs) are Persistent Organic Pollutants (POPs) that have received world-wide attentions due to their mutagenic, teratogenic or carcinogenic characters and resistance to degradation in the environment. 9 OCPs were initially listed in the "dirty dozen" of POPs regulated by the Stockholm Convention on POPs in 2001 (Unep, 2009), including Aldrin, Dieldrin, Endrin, Dichloro-Diphenyl-Tricgloroethane (DDT), Chlordane, Hexachlorobenzene (HCB, also classified as industrial chemical), Mirex, Toxaphene, and Heptachlor.

OCPs were intensively produced and consumed between the 1950s to the 1980s for agricultural use and vector control, and the major POPs in China. Till 1993, the total productions of technical HCH and DDT in China were estimated 4.9 million tones and 0.4 million tones, which accounted for 33%

and 20% of the global output, respectively (Hua & Shan, 1996) The application of technical HCH in agriculture has been banned since early 1980s, and DDTs and Lindane early 1990s (Devi, 2009). Most OCPs were banned till 2001, while a small amount of DDT, Chlordane, Mirex, and HCB were exempted for a 5-year production and use for vector control, pest control and industrial materials, based on Prior Informed Consent (PIC) procedures established under the Convention on POPs. By 2009, these OCPs were restricted and eliminated in China but in emergency (Mep, 2009). However, residual OCPs can still be detected in various environmental media in many areas after banned (Gong et al., 2003; Ma et al., 2003; Zhao & Ma, 2001).

This article aims to briefly introduce the origin and environmental chemistry of the OCPs, review the history and their present of OCPs in soil of China, and also here enclosed cases on OCPs in regional soil of China. Hence, if there were any similarity between the follow-up fluent of chemicals that may be harmful to the environment and organisms, the experience on the battle with OCPs and other POPs may give us the hint and alert.

2. The origin and environmental chemistry of OCPs

2.1. Origins and properties of specific OCPs

2.1.1. Dichloro-Diphenyl-Tricgloroethane (DDT)

DDT was initially utilized to eliminate anopheles that spread malaria and also to control other vectors around the WWII. Henceforth, DDT was used in agriculture and health control. In 1962, *Silent Spring* written by Rachel Carson was published and conveyed deep worries about the abuse of DDT in US and the emission of the great quantity of chemicals to the environment. This iconic book aroused world efforts on environment and ecology preservation.

This compound is formed by acetochloral and chlorobenzene under acidic condition, and the synthesis efficiency and purity of DDT slightly varied in different producing process (She et al., 2010). The synthetized DDT normally presented commercially in the form of emulsion and is diluted at a certain ratio as to spray onto crops. Among the synthetic products, *p,p'*-DDT is the main effective component, and *o,p'*-DDT is the by-product which has chiral isomers.

DDT also comes from the impurities of Dicofol product since DDT is the raw material for producing Dicofol (Tang, 2001). The technical DDT contains ca. 85% *p,p'*-DDT and ca. 15% *o,p'*-DDT , while compositions of Dicofol are just has more *o,p'*-DDT than *p,p'*-DDT as impurity (Qiu et al., 2005a).

Generally in agricultural soils, the half-life of DDT is 4–35 years (average 10–10.5 years) (Dimond & Owen, 1996; Harner et al., 1999) DDT can be dehydrochlorinated to DDE and reductively dechlorinated to DDD in the environment, and these degradants are still toxic — even more persistent than the parent compound (Meijer et al., 2001a; Quensen et al., 1998)

2.1.2. Hexachlorocyclohexane (HCH)

HCH, also known as “BHC” or “666”, was firstly confirmed for the pesticide activity by Dupire and Raucourt (Dupire & Raucourt, 1943) and Slade (Slade, 1945) in the 1940s. HCH is mainly synthetized by reaction between chlorine gas and benzene in the industrial production (Liao, 1980). The technical HCH is often a blend of several stereoisomers, which commonly contains 4 isomers, namely *α*-HCH, *β*-HCH, *γ*-HCH and *δ*-HCH, accounting for 67–70%, 5–6%, 13–15 and 6% of the technical HCH respectively, and *γ*-HCH, also named Lindane, is the main active ingredient (Bai, 1983). The ratio of *α*-HCH/*γ*-HCH in technical HCH ranges from 4 to 7 (Iwata et al., 1993).

The half-lives of *γ*-HCH and *α*-HCH in agricultural soils are 20–50 days and 20 weeks, respectively (Dimond & Owen, 1996; Harner et al., 1999). *δ*-HCH and *β*-HCH are more stable against environmental degradation than *α*-HCH and *γ*-HCH, while *α*-HCH can be converted to *β*-HCH (Piao et al., 2004; Zhang et al., 2007). And thus *δ*-HCH and *β*-HCH could be the indicator to historical usage and residues in the environment (Yang et al., 2012). In 2009, *α*, *β*, and *γ* isomers of HCH were added to the list of POPs for elimination.

2.1.3. Other OCPs listed as POPs in the Stockholm Convention

Chlordane, with two common isomers *α*(*cis*) and *β*(*trans*), and Mirex were mainly used to prevent and control termite, and these two types of pesticides were commonly produced in the same factory (Wang et al., 2007c). The ratio of industrial *trans*-Chlordane(TC)/*cis*-Chlordane(CC) was reported above 1 (reported as 1.56 (Bidleman et al., 2002) or 1.20 (Harner et al., 1999)), which can be used to retrieve the source of Chlordane. TC has a higher volatility than CC and tends to degrade in the environment, and a high TC/CC ratio suggests fresh chlordane sources (Martinez et al., 2012).

Technical Heptachlor which contains 20–22% TC is a broad spectrum pesticide and it can be used as sprays onto crops, dressing seeds for prevention from pests in soil, and killing termite and household insects (Bidleman et al., 1998). Commercial chlordane product usually has about 10% heptachlor (Manz et al., 2001b). Heptachlor can be metabolized in the soil through epoxidation, hydrolysis and dechlorination. The primary metabolite Heptachlor epoxide is more stable and durable than Heptachlor (Murano et al., 2009; Xiao et al., 2011) and of similar toxicity to Heptachlor (Zhang, 2000)

Endosulfan with two common isomers *α*(*cis*) and *β*(*trans*) is a broad spectrum pesticide of stomach toxicity and contact toxicity, and used for fumigation, to prevent cotton, vegetables, tobacco and tea trees from pests and also used as an acaridae (Ding & Lirong, 2001) Commercial product contains more than 95% of *α*-Endosulfan and *β*-Endosulfan (the ratio of *α*/*β* is 7:3), with *α*-Endosulfan having a higher volatility, toxicity, and rapid degradation rate compared with *β*-Endosulfan (Gong et al., 2010; Mukherjee, 2012). The environmental metabolite Endosulfan sulfate is also toxic.

HCB, are normally reported in three major categories, i.e., a precursor to some pesticide (PCP and PCP-Na) (Mep, 2009), a byproduct of chlorination processes (as in the manufacture of chlorinated solvents, chlorinated aromatics and pesticides) (Holoubek et al., 2009; Li et al., 2008), and a released substance in incomplete combustion and old dump sites (Qu et al., 2015; Tremolada et al., 2008).

2.2.The environmental transport and degradation of OCPs

2.2.1. The environmental transport of OCPs

Soil is the main reservoir of POPs (Harrad et al., 1994; Li, 2005; Zhang et al., 2013). These less degradable organics could be absorbed to soil and stay there for years(Li, 2005). The levels and distribution of POPs in soil could be related to the time, the physiochemical characteristics, soil properties (i.e. soil organic matter content, pH, and granularity), environmental temperature, etc. (Barra et al., 2005; Daly & Wania, 2005; Falloon et al., 2007; Gong et al., 2003; Grimalt et al., 2004; Hassanin et al., 2004; Meijer et al., 2002a, 2002b; Ruzickova et al., 2008; Sweetman et al., 2005; Valle et al., 2007; Wang et al., 2006a; Wang et al., 2007b; Wang et al., 2006b; Zhang et al., 2007; Zhang et al., 2006).

The levels of POPs residues in soil could be further studied for the secondary emission and atmospheric deposition (Sweetman et al., 2005). Being semi-volatile, POPs have close relationship with atmosphere temperature, and thus can be transported by air from warm regions and condense in cold regions. The evaporating-condensing may repeat along the pathway from low latitude to high latitude, from warm areas to cold areas and thus was illustrated as the global distillation model of POPs (Iwata et al., 1994; Wania & Mackay, 1996).

The transport of POPs can also be described by the fugacity variation of the chemicals in different environmental media. The chemical mass balance model that based on the fugacity (Waller et al., 1999) could be applied in judging the equilibrium status of POPs between phases. The fugacity equations of POPs in soil and atmosphere are shown as follows:

$$f_s = \frac{C_s RT}{0.411 \Phi_{om} K_{oa}}$$

$$f_a = C_a RT$$

f_s and f_a refer to the fugacity values of certain pollutants in soil and air respectively; C_s and C_a refer to the concentration of the pollutants in soil and air respectively, Φ_{om} is the concentration of organic matters in soil; K_{oa} is the octanol-air partition coefficient; R is the ideal gas constant, and T is the temperature in Kelvin. When $f_s > f_a$, the pollutants tend to evaporated from soil to the air, while $f_s > f_a$ the pollutants tend to enter soil from the air, and hence $f_s = f_a$ indicates the pollutants are at the equilibrium between soil-air.

On the basis of this fugacity theory, Ma et al (Ma et al., 2013) reported the air-soil transport of HCHs and DDTs in Hami Prefecture, Xinjiang, which showed HCHs are mainly from soil to the air while predominant DDTs reversed due to the physio-chemical characteristics variation; Wang et al (Wang, 2009) reported OCPs were relative homogeneous in the air but varied significantly in the soil in Harbin, China, and HCB and HCHs were at the equilibrium between soil-air exchange while atmospheric precipitation dominated in the transport of endosulfan and chlordane according to the fugacity model.

The wet deposition is one of the main pathway of POPs remove from the air, and thus precipitate into soil and waters. Howell et al (Howell et al., 2011) reported in their study OCPs in the air decrease by 25–75% during the wet deposition, and PCBs removed in the wet deposition is higher than in a dry deposition. The transport efficiency is also related to the concentration of POPs in different phases, the environmental temperature, and physio-chemical properties per se (Wu, 2009; Zhu et al., 2003).

Soil erosion and surface runoff may also redistribute POPs between soil, sediment and water. Zhang et al. (2002) reported that the sudden rise of HCH and DDT in the sediment of Pearl River Delta in 1990s was mainly caused by the soil transported by surface runoffs. Da et al. (2014) also reported that the levels of HCHs and DDTs in the sediment of old Yellow River Estuary were correlated with their soil residues and the historical use and emission. POPs entering the waters, partly dissolved, are mainly absorbed onto the suspended particles and finally entre sediment by gravity sedimentation, and thus the concentration of OCPs in the sediment can be more orders of magnitude than that in the water (Zhu et al., 2003). Therefore, the sediment is considered as one of the major destinations of POPs. However, with bioturbation, the change of the hydrodynamic and other environmental conditions, secondary release of POPs from sediment may occur (Da et al., 2014; Malarvannan et al., 2014; Wu, 2009)

2.2.2. The environmental degradation of OCPs

Affected by the environmental conditions and the characteristics of POPs per se, the natural degradation of POPs is usually complicated, and it features in complex intermediate products of POPs' degradation (Zhang, 1979). As shown in Fig. 1, the pathways of DDT degradation vary in different environmental conditions, and thus yield various intermediate products, among which many are also biotoxic (Wetterauer et al., 2012). For instance, DDT can be de-chlorinated and reduced to DDD and a few amounts of DDMU, DDMS and DDNU in the oxygen-deficient environment, while dehydrochlorinated to DDE and DBP in the aerobic environment (Heberer & Dunnbier, 1999). Actually, as the degradation path and the physio-chemical properties of POPs vary, the yield of these intermediate products (Kale et al., 1999) and commonly occur in varied types of environmental media (Heberer & Dunnbier, 1999).

A number of laboratory studies were carried out on OCPs degradation technology and mechanism. Yu et al. (2007) used nano-TiO_2 as a catalyst to photocatalytic degrade OCPs with a 400w high pressure lamb light (HPML), and reported that at 365 nm UV, HCH, Dicofol, and cypermethrin were efficiently degraded on a TiO_2 film (2.24 mg/cm^2) while 20μg of α-HCH degraded completely with 20 min. Ren (2013) researched the oxidation degradation of Dicofol, Diuron, and 2-methyl-4-chlorphenoxyaceticacid (MCPA), and elaborated the mechanism of ·OH-induced degradation. Chen (2008) reported with a absorbed dose of irradiation of 17 kGy, the degradation rate of HCB can reach 95 %, and the free radical ·OH plays an important role in oxidizing HCB in processes of ring-open and dechlorination and final mineralization. Langenhoff et al. (2013) carried out a test on in-situ bioscreen degradation of HCH, in which the methanol was added in intermittently as electron donor, and the results showed HCH decreased when passing though anaerobic infiltration zone of the bioscreen and the degradation products benzene and chlorobenzene increased.

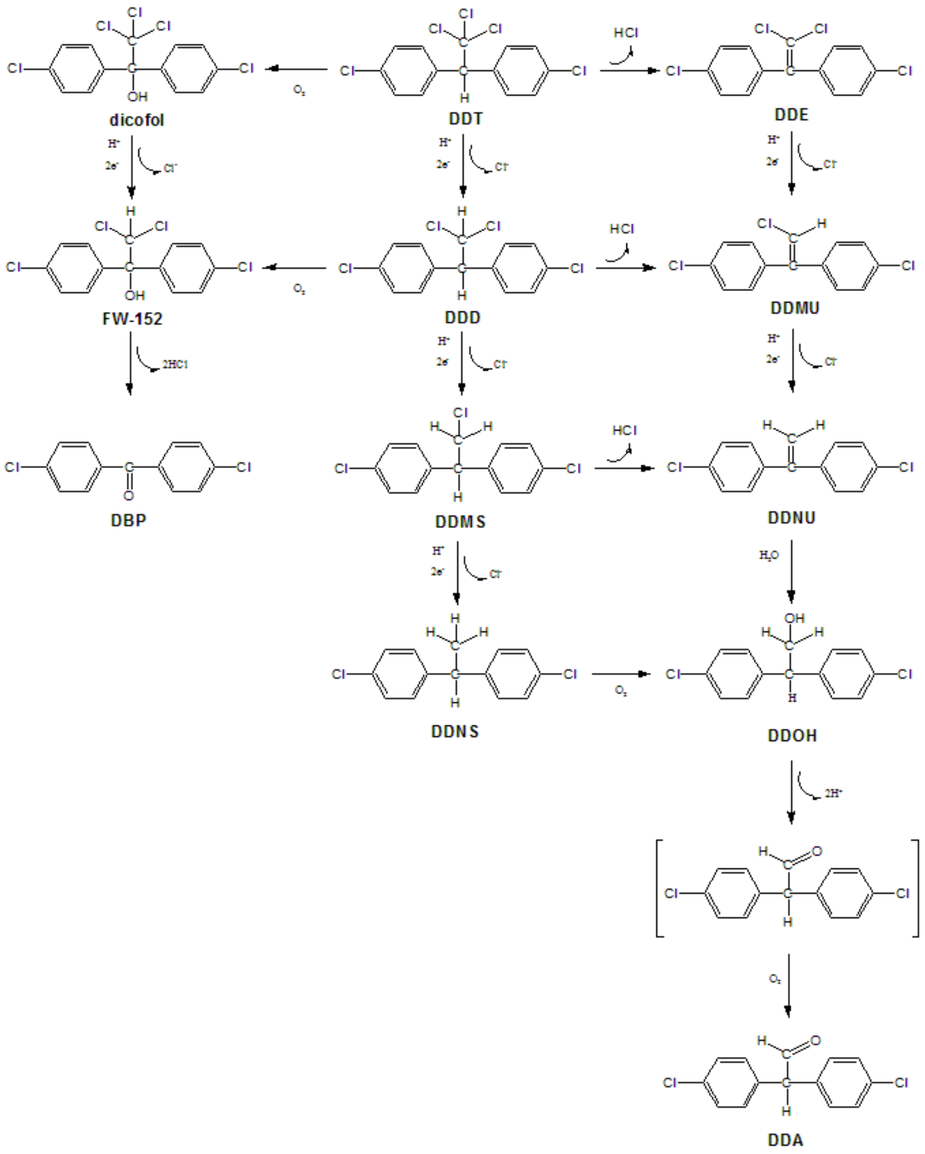

Fig. 1 Possible degradation pathways of DDT(Zhang, 1979)

However, the natural attenuation of POPs might be slower than the artificial method developed in laboratories. And in actual environment, the POPs degradation is usually complicated and the intermediate products are various till the final mineralization as the environmental conditions are varying. For instance, Kale et al. (1999) observed the degradation of ^{14}C labelled DDT in the sea sediment and marine ecological system, and reported that DDD dominated in metabolites of DDT in sediment, while DDMU was the major metabolite in clam samples. The polar degradation product DDA is mainly reported in waters, e.g., Heberer and Dunnbier (1999) reported DDA in a canal of Berlin, Germany reached to several microgram per litre.

Up to date, the research difficulties of POPs degradation mainly focused on following aspects: 1) There are uncertainties on the various degradation pathways, when it is involved in actual environment and special generation mechanism of some degradation products (Xing et al., 2009b); 2) the initial reaction of some POPs is still in dispute, with lack of degradation pattern of chemical with similar structural as to comparatively study (Ren, 2013); 3) the natural attenuation of POPs may be much slower than artificial processes—not to mention the complicated reactions. Therefore, the fate and the attenuation of POPs in reality still require accumulation of sample cases and in-depth research.

3. The history and present of OCPs in China

3.1. The production and application history of OCPs in China

The major species of POPs in China, as in the great agricultural country that has a long history of using large amount of pesticides, are OCPs. In 1983 the Chinese government started to ban the production of HCH (Li et al., 1998). In 2001, the signing year of the Convention on POPs, China banned most of the production and use of OCPs except for Chlordane, HCB, Mirex, and DDT that got an exemption period of 5 years. Till 2009, DDT was mainly used for emergency vector control, and the production of Dicofol and anti-fouling paint; Chlordane and Mirex for termite prevention; and HCB for production of Sodium pentachlorophenol (PCP-Na) in China (Mep, 2009). The other pesticide POPs, Heptachlor, Aldrin, Dieldrin, and Endrin, in the first “dirty dozen”, had only been produced with a small yield or never produced in China (Die et al., 2015)

In 2010, the Ministry of Environmental Protection of China proclaimed that all these POPs shall be prohibited for their production, circulation, use, import, or export in China, and the emergency use of DDT for vector control should be consulted with related authorities (Mep, 2009). However, the residues of OCPs are still in the environment, though the implement of elimination of OCPs in decades, due to these chemicals’ persistence. Especially, DDT and HCH were the most abundantly used OCPs in China and they are detected at a high residual level in some places.

In the 30 years of application of OCPs since 1950s, the amount of consumed HCH reached to 4,900,000 tones, that is 3 times of the amount used in aboard in the same period; and the amount of DDT used in China was estimated of a grand total of 400,000 tones that accounts for 20% of the gross amount used in the world (Devi, 2009; Hua & Shan, 1996). As the biggest consumer in the country, the province of Zhejiang was reported used 1,123,000 tones OCPs in 1952–1983, and 91.38% of the total was HCH (Cao et al., 2005)

HCH was the most produced and consumed OCP in China before 1983 (Devi, 2009; Hua & Shan, 1996). China began to produce and use technical HCH in 1952 and became the largest producer and user of technical HCH in the world during the 1970s and early 1980s (Fig. 2) (Li et al., 1998). HCH was widely used in agriculture in China to control pests to crops and mainly on rice paddies (Li et al., 1998). The level of technical HCHs has decreased in China as technical HCH was substituted by γ-HCH (over 90% of Lindane) in 1991 (Lammel et al., 2007).

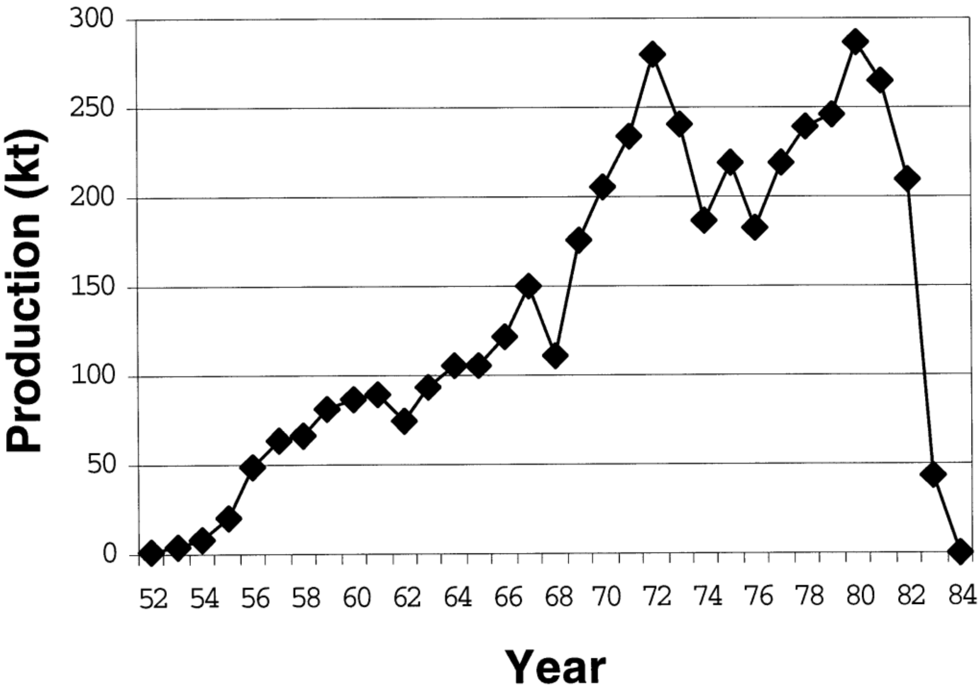

Fig. 2 Annual technical HCH production in China from 1952 to 1984 (Li et al., 1998)

DDT consumed in agricultural production was about 0.26 million tons in total from 1952 to 1983 in China (Li & Macdonald, 2005). Historical DDT residues and its metabolites were still detected at high rate in the surface soil in some agricultural regions after 2001 (An et al., 2005; Gong et al., 2002; Ma et al., 2010a; Ma et al., 2010b). In recent years, DDT pollution contributed by Dicofol in China has been significant(Qiu et al., 2004; Yang et al., 2008), as Dicofol contains noticeable level of *o,p'*-DDT as an impurity (Fujii et al., 2011). Statistically, the total technical DDT production was about 84,000 tones from 1988 to 2002, of which nearly 80% was for Dicofol production (Qiu et al., 2005b). Given that Dicofol was restricted in 1996 (Zhao et al., 2004), later than the restriction of DDT, the Dicofol may be a recent source of DDTs. In a case, around 5–10% of DDT had been detected in the final Dicofol product (Tao et al., 2007). Until China carried out two chemical industry sector standards in 2003, which require DDT impurity ≤ 0.5% in technical Dicofol or ≤ 0.1% in formulated Dicofol (containing 20% Dicofol) (Qiu et al., 2005b), Dicofol products with impurity DDTs above these standards were still available in the Chinese market. And thus in a period, the application of Dicofol elevated the DDT residues in environment (Dimuccio et al., 1988; Gillespie et al., 1994). As was reported (Zhao et al., 2004), DDT residues in tea leaves grown in Fujian had increased and the over-limit ratio raise up to 65%, after DDT was banned but Dicofol was largely put into use until 1996; and till 2003 when 7 years after the prohibition year of Dicofol, the over-limit rate of DDT in tea leaves had fallen to 13%.

For other banned pesticide POPs, HCB has never been registered as a pesticide in China (Liu et al., 2015), where HCB was mainly used to produce Pentachlorophenol (PCP) and PCP-Na. In practice it is often investigated together with other OCPs (Die et al., 2015). Chlordane and Mirex were widely used in preventing termite in the south of China (Wang et al., 2007c). Heptachlor was also massively produced in 1960s–1980s in China (Li & Li, 2004), but Heptachlor in the environment of China were majorly from impurities of Chlordane (Li et al., 2007). Chlordane was on a 5 year exemption in China and phased out in 2009 under the Stockholm Convention, when technical chlordane was still extensively used against termites in buildings, with an estimated amount of over 200 t year^{-1} in recent years (Xu et al., 2004).

Endosulfan is still in use in many countries including China, Europe, Canada, and India (Barrett & Jaward, 2012; Jia et al., 2009; Weber et al., 2010). Its global yield was reported 308,000 tones during 1950–2000, and India contributed 113,000 tones in 1958-2000. In 1998–2004, world yield of Endosulfan was at a rate of 12,800 tones yearly, and India and China were the main contributor who yielded 5,400 tones and 2,800 tones per year respectively (Weber et al., 2010).

3.2.Distributions and levels of OCPs in soil of China

Majority of OCPs in soil at present are residues from historical use. The field with high-yield of grains have become place with the intensive use of pesticides in China (El-Shahawi et al., 2010). These regions are located in the southeast of the country including Zhejiang, Shanghai, Fujian, and Guangzhou provinces, which accounted for 36.7% of the nationwide consumption (El-Shahawi et al., 2010). Zhejiang Province consumed about 9.96 kg/hm^2 — 3.7 times of the national average (2.71 kg/hm^2), and 28 times more than that in Inner Mongolia that was the lightest user of the pesticides (El-Shahawi et al., 2010). The distribution pattern of pesticide application in China shown in Fig. 3, where the sequence of consumption as follows: southeast > central > northwest (Tieyu et al., 2005).

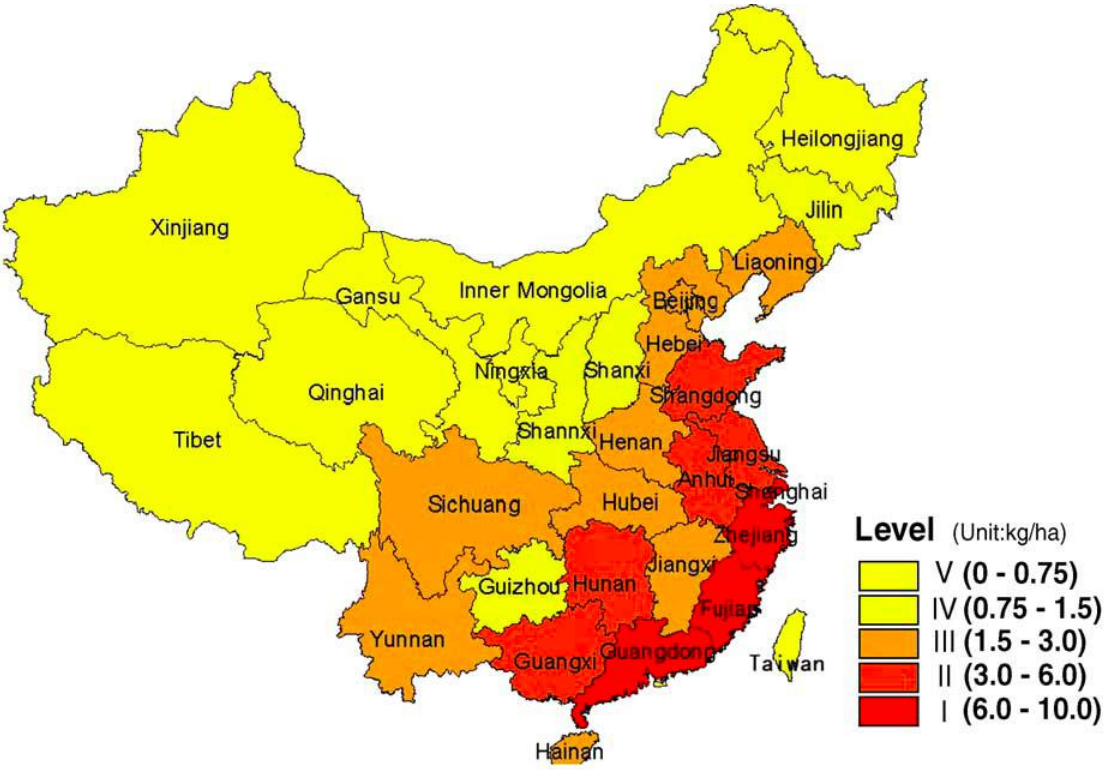

Fig. 3 Classification of pesticide in China in 1996(Tieyu et al., 2005)

Accordingly, levels and distribution patterns of specific OCPs are varied throughout the country. It was reported concentrations of DDT in the north and east of China were generally higher than that of the south and the southwest, while the magnitudes of concentration of HCH in the south and southwest of the territory are 2–4 times of that in the north; and the pesticide levels are higher in the lands growing vegetables than corps (Cai et al., 2008).

The concentrations of OCPs in various uses of soils in different areas of China, as well as other countries are listed in Table. 1.

Table. 1 OCPs levels in soils of various usages in China and other regions (excerpted from (Yang et al., 2012))

Region	Land usage	HCHs a)	DDTs b)	Reference
		ng g^{-1}	ng g^{-1}	
Nantong, China	Cotton field		183.07 ± 171.68 c)	(Yang et al., 2008)
Taihu Lake, China	Vegetable lands	21	82 c)	(Gao et al., 2005)
Taihu Lake, China	Paddy field	28.53 ± 10.77	50.23 ± 28.70 c)	(Wang et al., 2007a)
Beijing, China	Irrigated soils	3.70 ± 0.52	31.27 ± 6.65	(Sun et al., 2009)
Shanghai, China	Agricultural land	2.41±2.32	21.41±22.43	(Jiang et al., 2009)
Fujian, China	Tea land	3.7	8.3	(Sun et al., 1997)
Hong Kong, China	Farmland	6.53 ± 0.17	1.85 ± 1.64	(Zhang et al., 2006)
South Korea	Rice growing	5.22	2.93 f)	(Kim & Smith, 2001)
Corn Belt， US	Agricultural land		9.63	(Aigner et al., 1998)
Southern US	Cotton field	0.30 e)	211±343 c)	(Bidleman & Leone, 2004)
Southern Ontario, Canada	Agricultural land		18500 d)	(Kurt-Karakus et al., 2006)
Leipzig–Halle, Germany	Agricultural land	23.7--173	4.60--10.00 f)	(Manz et al., 2001a)
UK	Background in 1986	<0.88 e)	0.34	(Meijer et al., 2001b)

a) HCHs = sum of α-HCH, β-HCH, γ-HCH and δ-HCH.

b) DDTs = sum of *p,p′*-DDT, *p,p′*-DDE, *p,p′*-DDD and *o,p′*-DDT.

c) DDTs = sum of *p,p′*-DDT, *p,p′*-DDE, *p,p′*-DDD *o,p′*-DDT and *o,p′*-DDE.

d) DDTs = sum of *p,p′*-DDT, *p,p′*-DDE, *p,p′*-DDD *o,p′*-DDT *o,p′*-DDE and *o,p′*-DDD.

e) HCHs = sum of α-HCH and γ-HCH.

f) DDTs = sum of *p,p’*-DDD, *p,p’*-DDE and *p,p’*-DDT.

3.3.Site Pollution and Secondary emission of OCPs

Up to date, the research on OCPs mainly focused on the farmland, woods, and such non-point source pollution, and the surface 0–20cm of the soil were mostly concerned (An et al., 2005; Ma et al., 2010a; Tao et al., 2005; Wang et al., 2006d; Wang et al., 2006e). In recent years, some point source pollution has been concerned, i.e. the abandoned field of factories that manufacturing pesticide or related chemical have become a focus.

The factory field can be contaminated by spilling, discharge, and penetration around the production facilities and warehouses (Die et al., 2015). Cong et al. (2009) researched the vertical distribution of OCPs in soil of an abandoned factory and reported DDT was mainly historical residues. Wang et al. (2007c) surveyed the spatial distribution of the Chlordane and Mirex in the contaminated field of a factory in Beijing with more than 10 years of production history and reported that the Chlordane has an observable horizontal transfer pattern and Chlordane and Mirex had diffused into deeper soil, and Chlordane was at levels of 0.75–5.18mg·kg^{-1} at 10m depth, and Mirex 0.02–0.65 mg·kg^{-1}. As the residues can stay in the field for long time, some left in the soil at high residual levels that even the air samples at adjacent points showed contaminated (Zhou et al., 2009).The contaminated field with high level of residues may continuously release OCPs into the environment (Die et al., 2015). And if these sites field shall be developed for other residential use, e.g. as excavated for housing develop, the re-emission of bulked OCPs from deep soil may be another secondary emission.

Another concern may come from pesticide wastes in China which has a complex situation in large land area, with a scattered distribution; and few POPs were still used restrictedly in China in special locations with exemptions, which may cause environmental risks (Die et al., 2015).

Above all, if the land contaminated by chemical factory were switched for other use, the contamination should be considered cautiously on the re-emission of the chemicals. Especially, in the POPs factory field, the long life POPs may accumulate long-period residues in the soil, and even effected the surface and underground waters. What is more, there were also unawareness in the environmental protection in last decades of years when some of the POPs production could be widely open to the environmental media and thus the production activities were accompanied with continuous emissions of POPs and other pollutants. So the contamination and secondary emission of POPs were even sophisticated in or beyond the bounds of the factory. These problems may become disturbing in the monitoring, excavation, remediation of the contaminated lands and even would “haunt” when they are recycled for residential use without feasible treatment.

3.4.Related controlling plans

The chemical pollution roots from the demand of related chemicals, or rather the abuse use and unintentional spread. As the first step to control OCPs and other POPs, China has banned OCPs in agriculture use since 1980s. After signed the Stockhlom Convention China had carried out schedules on elimination of the target POPs. And in 2007 the nation deliberated a total budget of 34 billion RMB on works of controlling POPs until 2015 (Daily, 2007).

On May 28th, 2016, China carried out *the program of prevention and controlling the soil pollution*, issued as the State Council Document [2016] No. 31(China, 2016). The major quantitative index with schedule to this plan includes: the rate of safely utilization of the contaminated arable soil to be up to around 90% by 2020, and over 95% by 2030; and the rate of safely utilization of polluted land parcels to be up to over 90% by 2020, and over 95% by 2030. In this plan, pesticides and other chemical pollution are the aspects from concerned issues, from source control to remediation.

4. Regional distributions and influencing factors of OCPs — cases on OCPs in soil of the Southwest and the Southeast of China

Since 1999, the eco-geochemical surveys were carried out in many provinces, municipalities and autonomous regions in China. The survey was to research mechanisms of transportation and transformation of elements and compounds in eco-systems to assess and forecast their ecological effects nationwide, covering interdisciplinary and services as ecology, environment, agriculture, etc. In this survey, OCPs were determined as one class of important geochemical indicators due to their persistent, toxic and residual level.

To date, we have undertaken a series of surveys within this scheme, and based on the previous studies some new missions on OCPs and other POPs have been extended. The following sections are compiled from our publications from these surveys, based on the regional study cases in Sichuan and Fujian, in the Southwest and the Southeast of China, respectively

4.1.Chengdu Economic Region, Sichuan—the case of Southwest of China[1]

Chengdu Economic Region, the most developed region in Western China (Chen, 1999), locates in the center of Sichuan Province, west of Sichuan Basin. It includes six cities, Chengdu, Deyang, Mianyang, Meishan, Leshan and Ya'an. The climate in Sichuan Province varies from the subtropical plain zone in the east to the subfrigid plateau zone in the west. Typically, there is abundant rainfall and a high humidity of 70–80% (Shi et al., 2007). The landform is elevated in the west, lower in the east, and can be divided into four parts: corrosive tectonic mountain of Tibet Plateau east slope, Longmen Orogenic belt piedmont depression accumulation plain, corrosive tectonic hills of East Sichuan Basin and corrosive and denuded tectonic mountain of Southwest Sichuan Basin (unpublished report by Geological Survey of Sichuan Province, China).

The sampling campaign was carried out in April 2006. Totally 245 samples were collected from every square grid of 15 km × 15 km covering the study region, and in each grid a sampling site were chosen, mainly including farmlands. The surface 0–20 cm of the soil were collected and analyzed. More details available in the source article (Xing et al., 2009a).

1) General comments on soil concentrations in study area

The spatial distribution of HCHs and DDTs in the Chengdu Economic Region, were illustrated in Fig. 4. Detectable rate of HCHs and DDTs were all above 90% except for δ-HCH. Concentrations of HCHs were less than DDTs. Among the four isomers of HCHs, the concentration of δ-HCH and β-HCH were most elevated, which indicates HCHs are mainly historical residues. More DDT were observed in Leshan and Meishan City that were near pesticide factories.

2) OCPs in different climatic zones

The concentrations of HCH in the subtropical and temperate zones were higher than in the frigid zone where OCPs may be transported from remote area e.g. the subtropical and temperate zones (Meijer et al., 2001a).

The ratio of *p,p'*-DDD/*p,p'*-DDT presented higher in the low temperature zone than in subtropics, while *p,p'*-DDE/*p,p'*-DDT ratios appeared an opposite trend. And the oxygen level may effect — oxygen becomes scarce at high altitude, where more DDT likely degrade to DDD (Gong et al., 2007; Piao et al., 2004).

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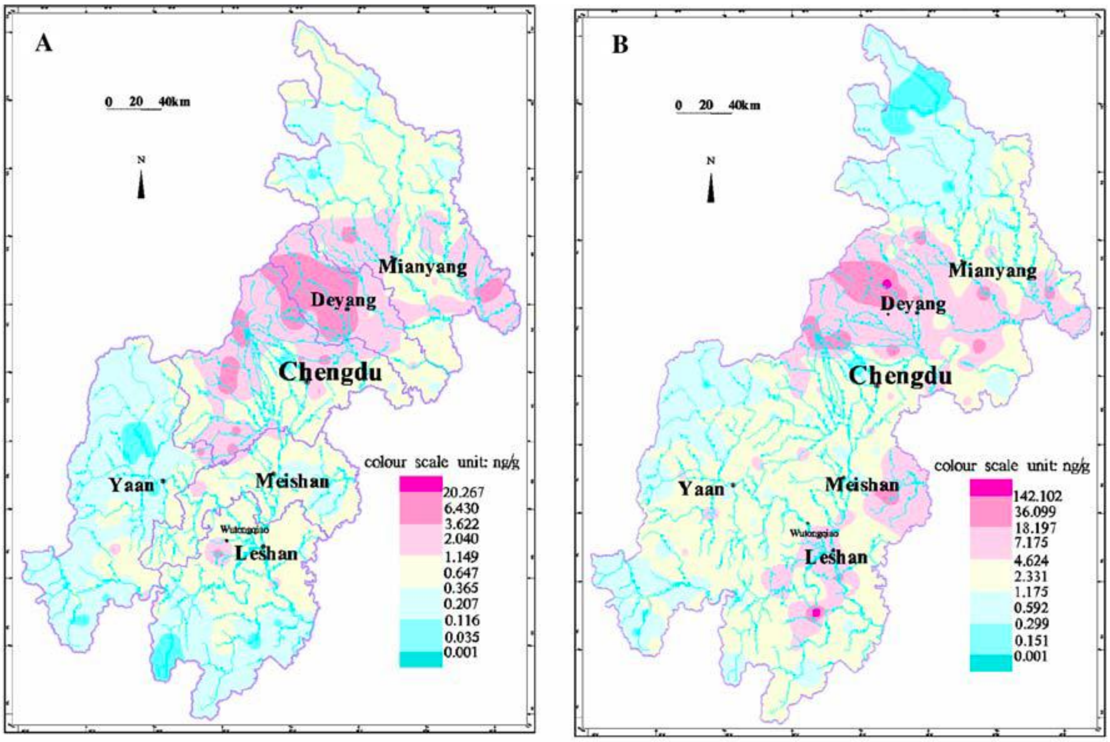
[1] The beginning 4 sections were abridged and re-edit from the article by Xing et al. (2009a)



HCHs DDTs

Fig. 4 Spatial distribution of HCHs and DDTs in the Chengdu Economic Region, Sichuan, China(Xing et al., 2009a)

3) OCPs in different landform regions

The concentrations of HCHs in the surface soil of the plain and the upland were higher than in the mountain area, while DDTs were higher in the surface soil of the mountain regions. Historical HCHs might have be drained into the lower horizons by percolating water from the heavy precipitation in this area. Lindane may contribute the local HCHs since the low ratio of α-HCH/γ-HCH were observed in some areas (Meijer et al., 2001a; Piao et al., 2004).

DDTs may have accumulated over years in the mountains, and the manufacturing plants may contribute too, i.e. high DDT levels found in Emei and Xichang-Shimian Mountains may be from the pesticide factory releasing DDT in the neighbor city Leshan. Moreover, the high density of tree cover, and soil organic matter content could have enhanced the accumulation of DDTs (more hydrophobic than HCHs) (Meijer et al., 2002a; Sweetman et al., 2005).

4) OCPs in soil of different types

In the present study OCPs concentrations were higher in the soil samples with low pH and high water content i.e. paddy soil, clay, and brown taiga soil. With regard to the brown coniferous forest soil that is preferred by termites and many insects, more pesticides might have been used there than other soil types. Moreover, forest soil contains high organic matter content that is a factor in accumulating OCPs.

The concentration of *p,p'*-DDE presented highest in dry lands and grasslands where prevailing aerobic conditions enhance the DDT degradation to DDE. The elevated levels of *p,p'*-DDT in paddy and forest land indicated the recent use of technical DDT.

5) Extended research

Based on the above work, Qu et al. (2013) researched the vertical distribution and transport of HCHs and DDTs in the high level sites located in Mianzhu and Mianyang in Chengdu Economic Region, and reported that the concentration of OCPs decreased in soil core with surface soil of high organic matters, and increased in that with sandy surface. It also pointed out that organic matters, soil texture and voidage may be important factors affecting the soil adsorption of OCPs. Moreover, soil priority current may be a key factor for vertical transport of OCPs, and thus may contaminate the groundwater.

As a potential pathway in which POPs may transport to the Tibetan Plateau, Mianzhu—Aba transect profile (shown as in Fig. 5) was selected to study the occurrence of OCPs along the altitudinal gradient (Liu et al., 2013). Higher OCP concentrations in the profile were attributed to the adjacent agricultural fields in the Sichuan Basin, with current Lindane and fresh non-Dicofol DDTs inputs, and also long-range atmospheric transport from other countries. Seasonal variations were observed, with higher levels of DDTs in winter and higher levels of HCHs and Drins (Aldrin, Endrin and Dieldrin) in summer, which may be caused by climatic conditions, i.e, the summer monsoon, and physico-chemical properties of OCPs. HCHs and Drins showed increasing trend, while DDTs evidently decreased with increasing altitude. The fugacity analysis on OCPs soil-air exchange indicated that the profile may be secondary sources for HCHs and Endrin, and both the secondary source and sink for DDTs, Aldrin, and Dieldrin.

Liu et al. (2015) also researched the “currently used pesticides” in this transect, and determined the transport direction of the OCPs depicted in fugacity ratio f_s/f_a (Fig. 5) and reported the transect may be not only a sink of OCPs from the air, but also a secondary source for *trans*-Chlordane, α-Endosulfan and β-Endosulfan to the air, and for HCB and Heptachlor, this transect may be a secondary source, but a sink for *cis*-Chlordane.

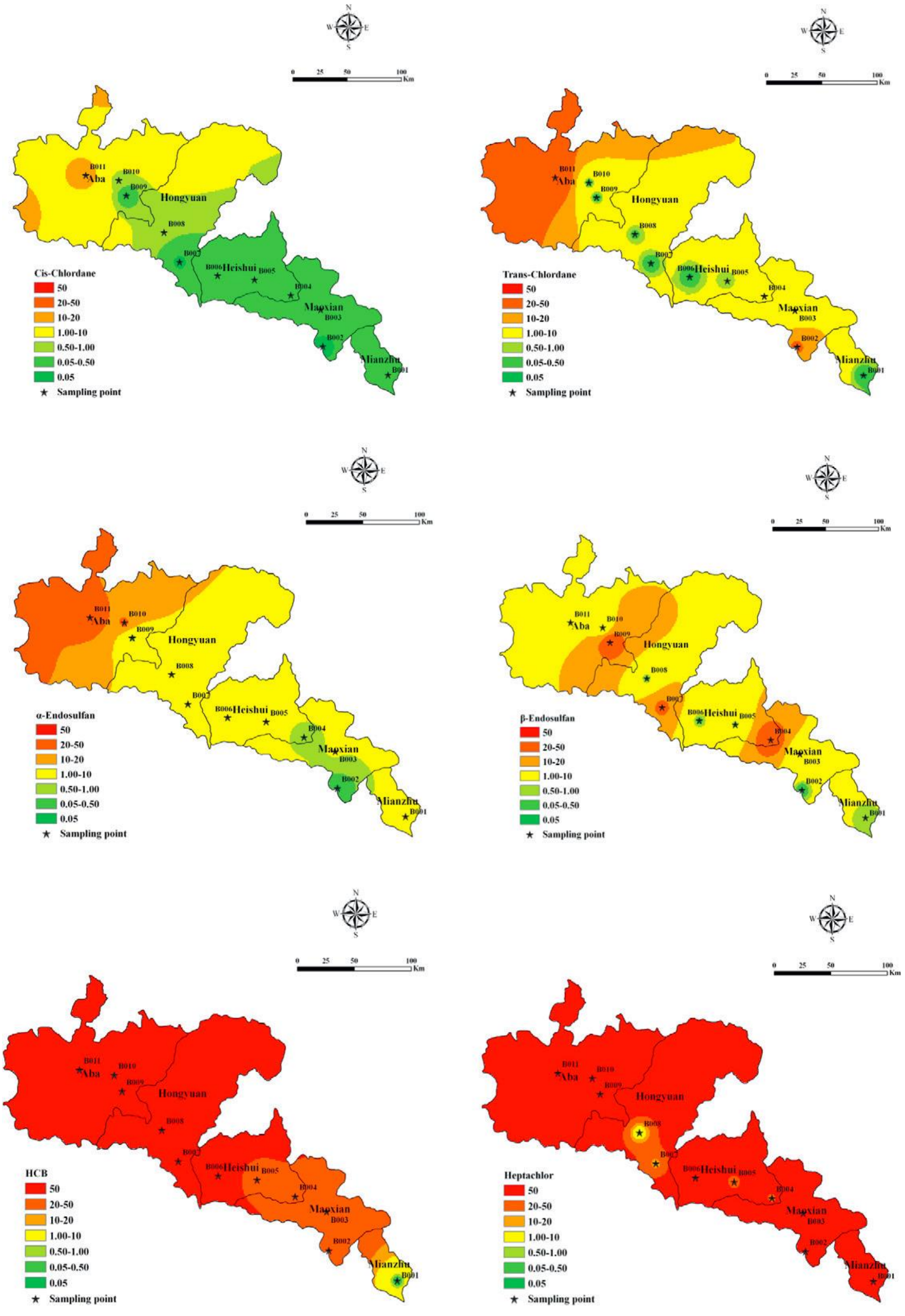


Fig. 5 The contour maps of f_s/f_a for the concerned OCPs in summer at Mianzhu-Aba prefecture transect(Liu et al., 2015)

4.2.Zhangzhou, Fujian—the case of southeast of China[2]

Zhangzhou City is an important agricultural region in Fujian Province. The landforms of Zhangzhou vary with estuaries, coastal and valley plains, and the altitude of regional highest mountain is 1,544 m. The range of altitudes of all sampling sites in this study was approximately 800 m.

Totally 93 surface soil samples (0–20 cm) were collected in March 2009 from every 12 km × 12 km sampling grid covering the whole region of Zhangzhou. Samples were mainly taken from four different land use types, including paddy fields, vegetable lands, orchards and tea plantations. And also a vertical soil column was collected and discussed. More details available in the source article (Yang et al., 2012).

1) General OCPs in soils of study region

Both DDTs and HCHs were of high detectable ratios. Concentrations of DDTs were higher than those of HCHs. The highest concentration of HCHs was found in Pinghe, while concentrations of DDTs were highest in Longhai, Longwen and Zhangpu (Fig. 6). As OCPs residues could stay in soil for long time, and thus act as a point source of pollution continuously emitting to the atmosphere, the secondary release of OCPs at high level in Longhai might influence the spatial distribution of OCPs in Zhangzhou.

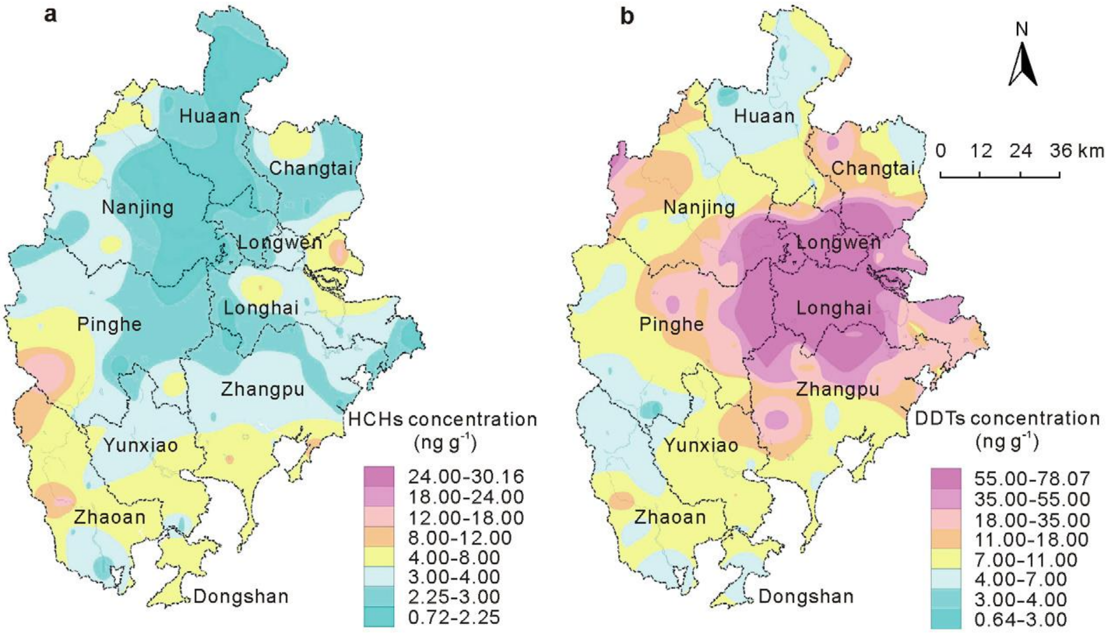


Fig. 6 Spatial distribution of (a) HCHs and (b) DDTs in soils of Zhangzhou(Yang et al., 2012)

2) OCPs in soils under four land uses

Concentrations of HCHs in the soils ranged in the order paddy fields > vegetable lands > tea plantations > orchards, and DDTs ranged as tea plantations > orchards > paddy fields > vegetable lands. The variation may partly relate to the pesticides specified to land types and their usage. The higher

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[2] Abridged and re-edit from the article by Yang et al. (2012)

solubility of HCHs than DDTs (Bommanna & Kannan, 1994) may lead more HCHs accumulation in wet paddy fields. DDTs levels were significantly higher in tea plantation soils than the others, and so were the ratios of *o,p'*-DDT/*p,p'*-DDT. The aerobic soil conditions in the tea plantations and orchards increased DDT degradation, and lead high *p,p'*-DDE/*p,p'*-DDD values.

The concentrations of HCHs and DDTs varied slightly with increasing altitude in paddy and orchard field. However, the correlation between HCHs and DDTs was significant in paddy fields ($r=0.883$, $p<0.01$) but poor in orchard field($r<0.1$). In vegetable lands, both HCHs and DDTs concentrated in the plain regions that were below the altitude of 100 m; and HCHs showed correlated with DDTs ($r=0.562$, $P<0.05$), but did not show more correlated to the altitude than DDTs did — this could owe to the greater solubility and volatility of HCHs (Bommanna & Kannan, 1994).

No obvious relationship was observed between the POPs accumulation and the TOC in soil of Zhangzhou. This is similar to the reports on the agricultural land in the suburb of Beijing (Chen et al., 2005) and the eastern slope of the Tibetan Plateau (Xing et al., 2010). Frequent ploughing, crop alternative and the irrigation water may all affect the fate of OCPs in agricultural soil. It is therefore difficult to assign a single soil-geochemical factor to predict distribution of OCPs in the soil at regional scale (Hao et al., 2008).

3) The estimation on Dicofol use

The DDT fraction from Dicofol formulation (FD) (Qiu & Zhu, 2010) and principal component analysis (PCA) combined with multiple linear regression analysis (MLRA) were used to estimate the source of DDTs(Larsen & Baker, 2003; Yang et al., 2008) (Table. 2). These two methods give out varied results, as reported by Qiu and Zhu (2010) (Qiu & Zhu, 2010). The FD calculated from the *o,p'*-DDT/*p,p'*-DDT ratios may be influenced by complex factors over time; and the PCA can be influenced by arbitrary explanations and negative values. Average results from both methods showed that the Dicofol-type DDT may dominate the contribution to tea plantations (73%).

Table. 2 Contributions of Dicofol-type DDT to each type of land (Yang et al., 2012)

Method [a]	**Contribution of Dicofol-type DDT (%)**				
	Paddy fields	Vegetable lands	Orchards	Tea plantations	Zhangzhou region
F_D [b]	58±39	50±32	58±34	79±64	57 ±31
PCA/MLRA	23	26	82	66	74
Mean	41	38	70	73	66

a) F_D = fraction of DDT from dicofol formulation; PCA-MLRA = PCA combined with MLRA.

b) Mean±standard deviation.

4) Vertical distribution of OCPs in agricultural soil

Both of HCHs and DDTs showed decreasing from topsoil to subsoil with a rapid decline at the depth of 50 cm in the soil core from the paddy field (Fig. 7) — similar to the report on soil profiles of cultivated land in Tianjin (Wang et al., 2006c) and paddy fields in the Yangtze River Delta Region (Zhang et al., 2009), where it was attributed to the plough pan of Stagnic Anthrosols, which probably retard OCPs transporting downward.

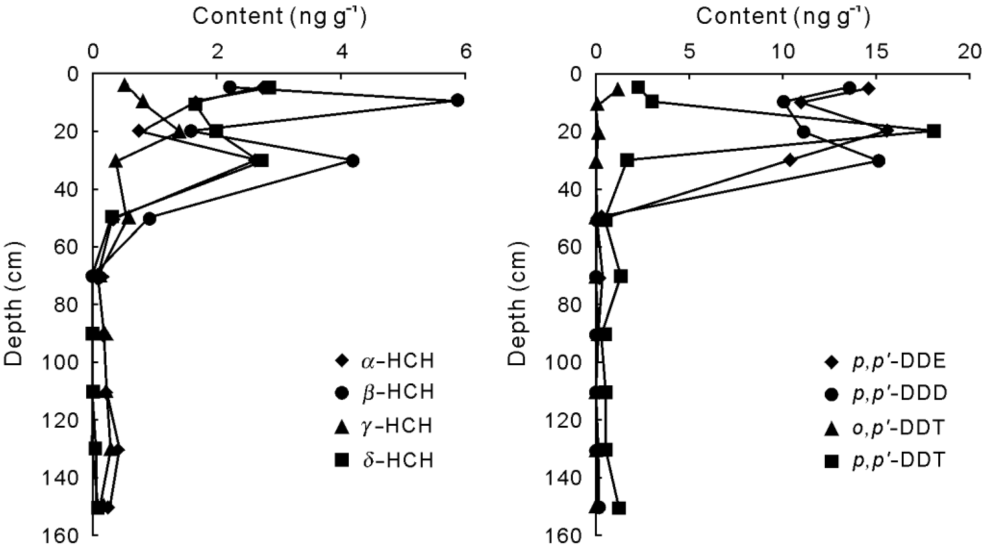

Fig. 7 Vertical distributions of OCPs in soil profile in Zhangzhou(Yang et al., 2012)

In the surface 0–50cm section, the burden of *γ*-HCH was much lower than other HCH isomers, since *γ*-HCH has a shorter half-life (Willett et al., 1998), and a greater degradation rate in the waterlogged soil i.e. paddy fields (Zhang et al., 1983). More *β*-HCH was observed than the other isomers, indicating high degradation of technical HCHs in the shallow agricultural soils, while the isomerization *α*- to *β*-HCH and *γ*- via *α*- to *β*-HCH may occur (Manz et al., 2001b).

The ratios of *p,p'*-DDE/*p,p'*-DDD were greater than 1 at depths above 30 cm and less than 1 in deeper soil, possibly due to the decreasing oxygen with depth. The *o,p'*-DDT appeared only concentrated a bit in the topsoil.

4.3.Summaries and new missions

Chengdu and Zhangzhou are both important grain producing areas in China and both had the overlapping peak period for production and application of OCPs in the 1950s to the 1980s that was even likewise nationwide. The influencing factors as land use, temperature, latitude have effects in common. In the case of Zhangzhou, we recognized a point pollution source of OCPs that may be a secondary source of OCPs influencing adjacent areas, and also found lately forbidden spices of pesticide (i.e. Dicofol) that may introduce fresh OCPs pollutions. In the case of Chengdu plain close to the Tibetan Plateau that has vulnerable ecological environment, the residual OCPs may cause pollution through long range transport. And therefore the missions for regulation, monitoring, and remediation of OCPs and other POPs should not cease.

Based on previous geochemistry surveys, especially the Sichuan surveys, one of our projects funded by National Natural Science Foundation of China (NSFC)[3] launched from 2014 on the environmental media along the profile of Sichuan Basin - West Sichuan Plateau - Zhaling Lake and Eling Lake (Fig. 8), source area of the Yellow River. This profile with a span of about 1000 km, has

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[3] NSFC No. 41473095, “The intermediate degradation products in the long range transport of Organochlorine Pesticides and the environmental significance”

various geological conditions from the temperate moist basin to the cold dry plateau, and diverse climatic conditions from the normal to the lower atmospheric pressure, which is also from aerobic ambient to the one of relative reducibility. And thus it will be of great interests to observe the degradation product series along with parent OCPs in the routine of long range transport from pollution source (i.e., Sichuan Basin) to the reservoir (i.e. the Tibetan Plateau). Whether and to what extend the current residual status of OCPs and their intermediate metabolites may be the indicators to environmental events will be emphasized issues.

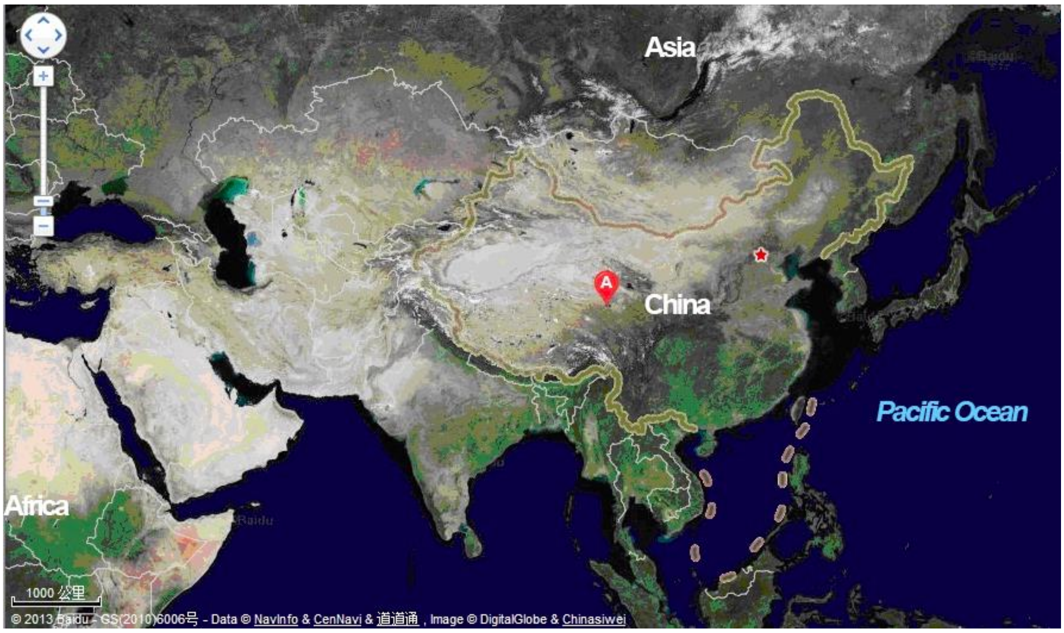

Fig. 8 Location of Zhaling Lake and Erling Lake

Future missions may no longer focusing on the concentration and distribution of OCPs. As majority of OCPs are not the currently used POPs, the main targets of research on OCPs may shift. For instance, the remediation of the heavy polluted sites could be a practical engineering attempt. For another instance, the dynamics of the residues in the environmental media could be indicators for the historical event and give us examples on how to eliminate such POPs and remedy their pollutions.

5. Conclusions

Until 2011, 22 chemicals or chemical categories have been listed as POPs in the Stockholm Convention. However, as more new chemicals invented and found according to the definition, there will be more chemicals enrolled as POPs. And this could inevitably recall the history of use and elimination of OCPs in China

The history of OCPs in China is the one of its origin, mass production and use, till elimination process. As a former useful chemical for agriculture and disease vector control in the early time, the massive and intensive use without control is the major cause to the heavy residues of environmental toxicants, though they helped the world with certain success. For future development and use of the functional chemicals, the controlling and monitoring work should be arranged ahead and throughout the full life cycle of chemicals in the environment.

To date, many surveys and researches have done a lot on the concentration and distribution of OCPs in China, and these are indispensable works on controlling POPs pollution. As majority of OCPs are not the currently used POPs, the main targets of research on OCPs may shift. For instance, the remediation of the heavy polluted sites could be a practical engineering attempt. For another instance, the dynamics of the residues in the environmental media could be indicators for the historical event and give us examples on how to end and remedy such POPs.

The major challenges may come from the following aspects:

1) The residues of OCPs and other POPs in special areas like related industrial zones are still at high levels and require remediation.

2) Site with few POPs that were still used restrictedly in special locations with exemptions, are of potentially environmental risks.

3) With the rapid grow of the chemical industry more chemical are found or suspected potential toxic and could be enrolled into the list of POPs. The production, use and circulation of the new chemicals should be carefully monitored and regulated as to avoid any abuse or unintentional spread.

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Chapter 3: Atmosphere

Section 3.1

Polyurethane foam-based passive air samplers in monitoring persistent organic pollutants: Theory and application

Section 3.2

Spatial and seasonal variations of atmospheric organochlorine pesticides along the plain-mountain transect in central china: regional source vs. long-range transport and air-soil exchange

Section 3.1

Polyurethane foam-based passive air samplers in monitoring persistent organic pollutants: Theory and application

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Polyurethane foam-based passive air samplers in monitoring persistent organic pollutants: Theory and application

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Abstract: This chapter reviews the principles of passive air samplers (PAS) techniques and progress of the polyurethane foam-based PAS (PUF-PAS) in monitoring persistent organic pollutants (POPs) from a local to global scale. The calibration method of the site-specific sampling rate (R_s) on the basis of the loss of depuration compounds (DCs) from the PUF disk is explained, and the factors (i.e., temperature, wind speed, and atmospheric particle) that influence R_s are also discussed. A case history is presented to help explain the atmospheric transport of organochlorine pesticides (OCPs) from plain to mountain, as well as to demonstrate the feasibility of using PUF-PAS for achieving spatially and seasonally resolved data for POPs. And lastly, the future research prospects in the development and application of PUF-PAS will be discussed.

Keywords: Persistent organic pollutants; Passive air sampler; Polyurethane foam; Application theory; Sampling rate; Depuration compounds

1. Introduction

The environmental toxicity, persistence, and bioaccumulation of persistent organic pollution (POPs) have recently began to arouse great concern (Pozo et al., 2006). They are capable of undergoing long-range atmospheric transport (LRAT) from source to remote areas (Jaward et al., 2005a), further threatening the global ecological environment and human health. Considering their potential deleterious effects, the international community is now beginning to establish specific treaties and laws to eliminate or restrict the production and use of POPs. The Stockholm Convention (SC) on POPs is one of the most famous multilateral treaties, and its Article 16 stipulates that the effectiveness of the measures adopted as part of the SC is evaluated in regular intervals. Due to the ability to respond quickly to changes in primary emissions, the atmosphere is deemed to be a useful indicator to evaluate the effectiveness of the measures prescribed by the SC, and is recommended for assessing the trends of POPs on a global scale (UNEP, 2004).

The conventional approach of air monitoring for POPs is based on the periodic collection of high-volume active air samplers (Hi-Vol AAS). Restricted by cost and logistics, in particular the local electricity supply, the Hi-Vol AAS cannot be deployed at a large number of monitoring sites simultaneously, and may not be feasible for implementation in a spatial survey of POPs in remote areas (Pozo et al., 2004). To overcome these drawbacks, many different types of passive air samplers (PAS) have been developed, validated, and used in the monitoring of POPs in recent years. The fundamental principle of PAS is to utilize a sampling medium to trap POPs by a passive uptake mechanism, that is, advection and diffusion (Moeckel et al., 2009). Because of their low-cost and the non-reliance on electricity, PAS are very suitable for achieving spatially resolved data for POPs on a regional or even global scale. In addition, PAS continuously integrate data relating to the air burden of POPs over the sampling period, making it possible to complement the sometimes intermittent information provided by Hi-Vol AAS (Harner et al., 2006b).

Polyurethane foam-based passive air samplers (PUF-PAS) are one of the most widely used PAS for monitoring POPs. In the terms of its design structure (Figure 1), the PUF disk is mounted in two stainless steel domed chambers, which shield it from precipitation, UV sunlight, and the deposition of other particles, and act to buffer the air flow within the chamber (Jaward et al., 2004). The advantage of PUF-PAS lies in that they are simple, easy to operate, inexpensive, and independent of electrical power. The PUF-PAS can be installed simultaneously at many sites, from a local to global scale, to assess spatial distribution and create maps (Halse et al., 2011; Harner et al., 2004; Pozo et al., 2006), and temporal trends can be obtained by deployment of PUF-PAS over several seasons and years (Pozo et al., 2009; Ren et al., 2014). In recent years, a large number of research projects have been implemented all over the world (Figure 2), investigating a range of POPs in the atmosphere by using PUF-PAS including organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), polychlorinated naphthalenes (PCNs), polybrominated diphenyl ethers (PBDEs), polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). This paper summarizes the theory of uptake by PAS and progress of the PUF-PAS for monitoring POPs.

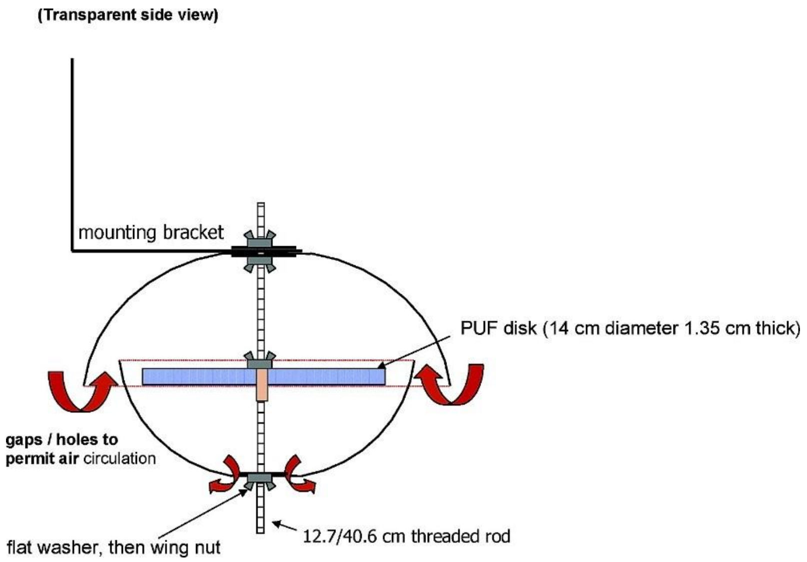

Figure 1. Schematic of the polyurethane foam-based passive air samplers (PUF-PAS) (Jaward et al., 2004).

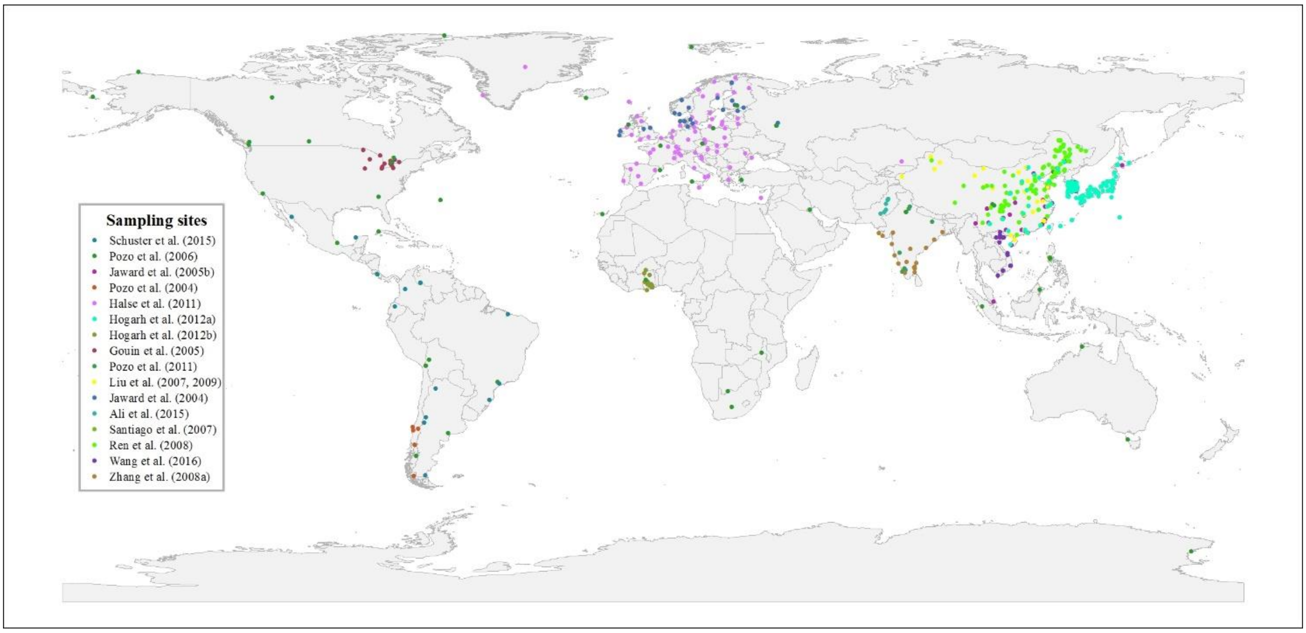

Figure 2. Sampling sites of the polyurethane foam-based passive air samplers (PUF-PAS) in all the world.

2. Principles

2.1.Theory of uptake by PAS

The principles of passive air sampling for POPs have been discussed in detail elsewhere (Bartkow et al., 2005; Harner et al., 2003), and are only briefly described here. The uptake of gaseous chemicals by a passive sampling medium (PSM) is based upon mass transport by molecular diffusion, as described by Fick's first law. Mass flux, F (units of ng/s), from ambient air to the PSM, can be calculated as:

$$F = k_{\mathrm{O}} A_{\mathrm{PSM}} (C_{\mathrm{A}} - C_{\mathrm{PSM}} / K_{\mathrm{PSM\text{-}A}}) \tag{1}$$

where C_{PSM} and C_{A} are the concentrations of analyte (ng/m^3) in the PSM and air, respectively, A_{PSM} is the planar area of the exposed portion of the PSM (m^2), and $K_{\mathrm{PSM\text{-}A}}$ is the PSM-air partition coefficient. The overall mass transfer coefficient (MTC), k_{O} (units of m/s), is given by using the Whitman two-film approach:

$$1/k_{\mathrm{O}} = 1/k_{\mathrm{A}} + 1/(k_{\mathrm{PSM}} K_{\mathrm{PSM\text{-}A}}) \tag{2}$$

where k_{A} and k_{PSM} are the air-side and PSM-side MTCs (m/s).

For nonpolar organic chemicals, $K_{\mathrm{PSM\text{-}A}}$ probably has the same order of magnitude as the octanol-air partition coefficient, K_{OA}. Therefore, if a chemical has a large value of K_{OA} (i.e., $K_{\mathrm{OA}}>10^6$), then the term $1/(k_{\mathrm{PSM}}K_{\mathrm{PSM\text{-}A}})$ is insignificant, and the uptake of chemical is mainly dominated by mass transfer via the air-side boundary layer (i.e., k_{O} is approximately equal to k_{A}). Thus, the accumulation of chemical by the PSM can be described as:

$$V_{\mathrm{PUF}} (\mathrm{d}C_{\mathrm{PSM}} / \mathrm{d}t) = k_{\mathrm{A}} A_{\mathrm{PSM}} (C_{\mathrm{A}} - C_{\mathrm{PSM}} / K_{\mathrm{PSM\text{-}A}}) \tag{3}$$

where V_{PSM} is the volume of the PSM (m^3).

The net flux of chemical accumulation in the PSM can be defined as the uptake rate minus the elimination rate. Thus, Eq. (3) can be rewritten on the basis of rate constant:

$$\mathrm{d}C_{\mathrm{PSM}} / \mathrm{d}t = k_{\mathrm{u}} C_{\mathrm{A}} - k_{\mathrm{e}} C_{\mathrm{PSM}} \tag{4}$$

where the uptake constant k_{U} (units of reciprocal time) and the elimination constant k_{e} (units of reciprocal time) are given by:

$$k_{\mathrm{U}} = k_{\mathrm{A}} A_{\mathrm{PSM}} / V_{\mathrm{PSM}} \tag{5}$$

$$k_{\mathrm{e}} = k_{\mathrm{A}} A_{\mathrm{PSM}} / (V_{\mathrm{PSM}} K_{\mathrm{PSM\text{-}A}}) \tag{6}$$

The schematic diagram of the uptake described by Eq. (3) is presented in Figure 3. The process of a chemical uptake by the PSM includes three phases, namely, the linear uptake, the curvilinear region, and the equilibrium or plateau phase. The accumulation of chemical by the PSM, in its initial phase, when the term $C_{\mathrm{PSM}}/K_{\mathrm{PSM\text{-}A}}$ is negligible (because C_{PSM} is small, and $K_{\mathrm{PSM\text{-}A}}$ is large), the uptake is a linear and a function of k_{A}, A_{PSM}, and C_{A}:

$$V_{\mathrm{PSM}} (\mathrm{d}C_{\mathrm{PSM}} / \mathrm{d}t) = k_{\mathrm{A}} A_{\mathrm{PSM}} C_{\mathrm{A}} \tag{7}$$

In the linear portion of the uptake curve, the amount (M, ng) of chemical sequestered by the PSM can be described by

$$M_{\mathrm{PSM}} = k_{\mathrm{A}} A_{\mathrm{PSM}} C_{\mathrm{A}} t = bt \tag{8}$$

where t is the sampling time (s), and b is the mass sampling rate (ng/s) determined by taking the slope of the plot of M_{PSM} versus t (i.e., $b = k_{\mathrm{A}} A_{\mathrm{PSM}} C_{\mathrm{A}}$). The term $k_{\mathrm{A}} A_{\mathrm{PSM}}$ is defined as the sampling rate, R_{s}, which represents the volume of air sampled by the PSM per unit of time (e.g., cm^3/s). The k_{A} can be related to chemical's diffusion coefficient (D_{a}) and the "effective" thinness of the boundary/diffusion layer (δ_{FILM}) (i.e., $k_{\mathrm{A}} = D_{\mathrm{a}}/\delta_{\mathrm{FILM}}$), and thus the R_{s} also equal to $A_{\mathrm{PSM}} D_{\mathrm{a}}/\delta_{\mathrm{FILM}}$.

As chemicals accumulate over time in the PSM, the term $C_{\mathrm{PSM}}/K_{\mathrm{PSM\text{-}A}}$ in Eq. (3) becomes increasingly important with increasing C_{PSM}. When C_{PSM} has increased to a certain value, the uptake process enters the curvilinear phase, and finally the net uptake ($\mathrm{d}C_{\mathrm{PSM}}/\mathrm{d}t$) will approximate to zero as it arrives at the equilibrium phase. In the equilibrium phase, C_{PSM} becomes constant, C'_{PSM}, and can be calculated as:

$$C_{\mathrm{A}} = C'_{\mathrm{PSM}} / K_{\mathrm{PSM\text{-}A}} \tag{9}$$

The generalized uptake profile based on rate constants can be provided by integrating Eq. (4) to yield:

$$C_{\mathrm{PSM}} = C_{\mathrm{A}} (k_{\mathrm{u}} / k_{\mathrm{e}})[1 - \exp(-k_{\mathrm{e}} t)] \tag{10}$$

Eq. (10) is a first-order rate expression of the form $C = C_{\mathrm{o}}\exp(-k_{\mathrm{e}}t)$ or equivalently $\ln(C/C_{\mathrm{o}}) = -k_{\mathrm{e}}t$. The time to effective equilibrium (t_{eq}), being defined as when C_{PSM} reaches 99% of its true equilibrium value, can be calculated as:

$$t_{\mathrm{eq}} = 4.605 / k_{\mathrm{e}} \tag{11}$$

In summary, when the uptake is in the linear uptake phase, once the R_{S} value is obtained, C_{A} can be derived from Eq. (8), (i.e., $C_{\mathrm{A}}=M_{\mathrm{PSM}}/(R_{\mathrm{S}}t)$). If the uptake is in the equilibrium phase, once the $K_{\mathrm{PSM\text{-}A}}$ is obtained, C_{A} can be calculated by Eq. (9) (i.e., $C_{\mathrm{A}}=C'_{\mathrm{PSM}}/\mathrm{K}_{\mathrm{PSM\text{-}A}}$). Owing to their operating model (kinetic model or equilibrium model), passive sampling techniques are classified into two types: kinetic sampling device and equilibrium sampling device. PUF, as an organic polymer material, has a very large sorption capacity for organic chemicals, and thus PUF-PAS belongs in the kinetic passive sampler classification.

It should be emphasized that, generally speaking, this analysis considers the gas-phase transfer of chemicals only, and ignores particle-associated chemicals, which may be scavenged by the PSM and finally incorporated into the total amount of chemical sequestered. In particular, the particle-scavenging effect has a greater impact on chemicals with $K_{OA}>10^{10}$, where it starts to partition appreciably onto particles. Some of the chemicals, such as PAHs and PBDEs, are able to undergo photodegradation when exposed to solar radiation. The air-side MTCs, k_A, is sensitive to wind, thus causing the fluctuation of uptake rate under various wind conditions. As shown in Figure 1 and described above, the PUF disks are deployed within sheltered chambers designed to alleviate the effect of particle impact onto the PSM surface and environmental variables, such as sunlight, precipitation and wind.

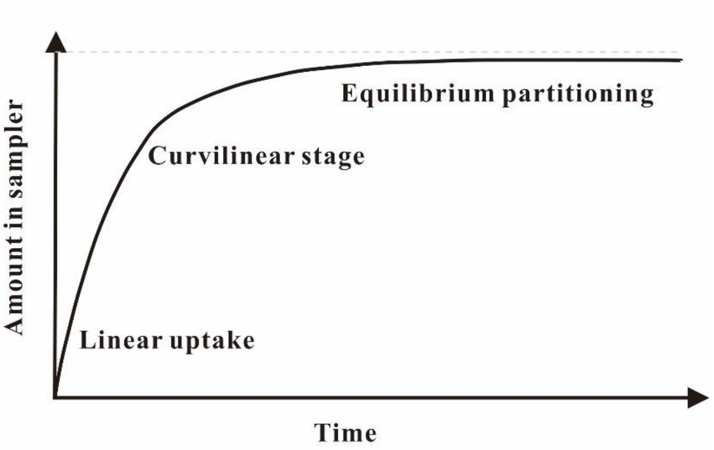

Figure 3. The passive sampler operates in three phases of uptake: linear uptake, curvilinear region, and equilibrium or plateau phase.

2.2.Influence factors of sampling rate

Continuing from the discussion above, the R_s is a function of k_A (k_A is related to D_a and δ_{FILM}, i.e., $k_A = D_a/\delta_{FILM}$) and A_{PSM}, and can be calculated as:

$$R_s = k_A A_{PSM} = A_{PSM} D_a / \delta_{FILM} \tag{12}$$

When the A_{PSM} is the same, environmental variables including temperature and wind speed, are the main influencing factors on the variability in the R_s, as a result of k_A, D_a and δ_{FILM} related to these environmental variables.

(i) Temperature

In the relatively still air, the k_A is likely to be similar to the D_a (Shoeib and Harner, 2002):

$$D_a = \{10^{-3} T^{1.75} [(1/m_{air}) + (1/m)]^{1/2}\} / P[V_{air}{}^{1/3} + V^{1/3}]^2 \tag{13}$$

where T is the absolute temperature (K), m_{air} is the average molecular mass of air (28.97 g/mol), m is the molecular mass of the chemical (g/mol), P is the gas-phase pressure (atm), V_{air} is the average molecular volume of the gases in the air (20.1 cm^3/mol), and V is the molecular volume of the chemical (cm^3/mol).

As shown in Eq. (13), the D_a is proportional to the T, however, due to it having an increase by only 13% over a 20°C temperature range (e.g., 0~20 °C), it is not particularly sensitive to variations in temperature.

The K_{OA} has a strong dependence on temperature, and can be calculated by the regression equation given by

Harner and Mackay (1995):

$$\log K_{\mathrm{OA}} = A + B / T = A + \Delta H_{\mathrm{OA}} / RT \tag{14}$$

where ΔH_{OA} is the enthalpy of phase change (J/mol), and R is the ideal gas constant.

The K_{OA} decreases with increasing the T, accordingly the $K_{\mathrm{PSM\text{-}A}}$ also decreases, which reduces the sorption capacity of the PSM.

While T can have an effect on D_a and K_{OA}, this can be complicated and may vary by compound. However, in warmer climates, these effects may result in an overall underestimation of the concentration, as opposed to the same sampling period in cooler climates (Melymuk et al., 2014).

Finizio et al. (1997) developed an equation that uses K_{OA} to clarify the relationship between the concentrations of airborne POPs and their equilibrium values on aerosols:

$$\log K_{\mathrm{P}} = \log K_{\mathrm{OA}} + \log f_{\mathrm{om}} - 11.91 \tag{15}$$

where K_{P} is the particle-gas partition coefficient (m^3/μg), and f_{om} is the fraction of organic matter on aerosol.

K_{P} is controlled by T, highlighting the transfer of chemicals from gas- to particle-phase with decreasing temperature. Melymuk et al. (2011) found that the R_{S} for chemicals with lower volatility increased significantly over the deployment time as a result of the increase of their gas-phase proportion with increasing T. The effect of particle-associated chemicals on the R_{S} is significant, which may be aggravated at lower temperatures (discussed below).

One of the fundamental assumptions of PAS is that there is a constant concentration of the element of interest in the air, over the entire sampling period. However, variations in T can lead to varying degrees of volatilization of elements from their source, and therefore changes in their concentrations in the air.

(ii) Wind speed

The uptake of a chemical is controlled by mass transfer via the air-side boundary layer, and thus, wind speed can influence the R_{S} by changing the δ_{FILM}.

In the PUF disk, Tuduri et al. (2006) found that the average δ_{FILM} for all PCBs was estimated to be 0.28 mm in still air and 0.028 mm at an air velocity of approximately 1.75 m/s. The R_{S} gradually rose from 4.5 to 14.6 m^3/d with an increase in the wind speed from 0 to 0.9 m/s, and then rose sharply to ~42 m^3/d at 1.75 m/s. A significant exponential correlation between the R_{S} and wind speed was also observed by Moeckel et al. (2009).

Some experimental field studies observed a clearly positive relationship between the R_{S} and wind speed. Gouin et al. (2008) found that the R_{S} in the windier dry season was higher than the value observed in the rainy season. Klánová et al. (2008) concluded that higher R_{S} values at colder temperatures can be attributed to variations in the R_{S} with increasing wind speed. In particular, the R_{S} for the particle-associated chemicals with higher K_{OA}, has a clear correlation with wind speed, whereas no such correlation exists for gas-phase chemicals (Melymuk et al., 2011).

Considering the effect of wind speed, the structure of the “flying saucer” PUF-PAS (i.e., two stainless steel domed chambers enclosing the PUF disk) is designed to weaken the air flow within the chamber as much as possible. The “flying saucer” device is effective up to an external wind velocity of ca. 3.5~4 m/s, maintaining an internal wind velocity of less than 1 m/s (Tuduri et al., 2006). When wind speeds exceed 5 m/s, the PUF-PAS is unable to effectively dampen external winds, this may cause rapid increase in the R_{S} as a result of a higher air velocity within the chamber (Melymuk et al., 2014; Tuduri et al., 2006).

The terrain of the sampling site in the field may affect the incidence angle between the PUF-PAS and wind direction. For example, deploying PASs on a slope, may preferentially direct wind towards them at an angle, due to prevailing winds blowing typically up-slope from the valley to the mountain (Daly et al., 2007). May et al. (2011) found the R_s may be influenced significantly by the angle of the ambient wind, which means that the variations in the air flow field, caused by azimuth misalignment between the PUF-PAS and wind direction, or the “shelter” effect of obstacles around the PUF-PAS, may lead to uncertainty in the R_s value.

Higher wind speeds may promote the transfer of particles from the ambient air to the PUF disk (Melymuk et al., 2011). The influence of particles on the R_s is discussed below.

(iii) Particles

Particle-associated chemicals can be trapped by the PUF-PAS, and thus, the influence of atmospheric particles is one of the most significant causes of difference in estimating air concentration of POPs between PUF-PAS and AAS.

Generally, atmospheric particles transfer to the PUF disk in different ways, including sedimentation, impaction, interception, and diffusion (Bohlin et al., 2010). Smaller particles (<2 mm) are believed to be trapped by diffusive uptake in the PUF, in a similar way to gas-phase chemicals, so the theory of PAS uptake may also be used to interpret the sampling rate of these particles (Melymuk et al., 2011). However, other deposition mechanisms (i.e., sedimentation, impaction, or interception), are affected by factors such as, wind speed, chamber design and PUF density to a greater extent (Chaemfa et al., 2009), and it follows that quantitatively estimating these methods of particle uptake is very difficult.

The key influence mechanism of particles on sampling rates has not yet been clearly recognized. Some studies with PUF-PAS suggest similar or even higher sampling rate for particle-associated chemicals (Harner et al., 2013; Melymuk et al., 2011), while others found higher sampling rate in gas-phase chemicals (Bohlin et al., 2014; Klánová et al., 2008). However, it is most likely that this debate may actually be caused by differences in site characteristics, PUF types, or analytical processes (Melymuk et al., 2014).

So far, there is still no consensus on what proportion of atmospheric particles are trapped by the PUF. Chaemfa et al. (2009) found that the diameter of particles up to 1 mm are consistently trapped by the PUF, while Bohlin et al. (2010) found that particles less than 2 mm are sampled. However, Klánová et al. (2008) observed that approximately 10% of ambient particles are trapped, regardless of particulate size.

The influence of particle-associated chemicals, among other factors, is perhaps the most difficult to quantitatively describe as the particles are unable to be separated from the PUF, making their measurement and type even harder to discern. This difficulty, existing in the PUF-PAS, may lead to considerable error, thereby decreasing the reliability and comparability of data for all sites in a monitoring network, especially in a global or regional-scale study. This debate reinforces the need for further research on particle trapping by the PUF-PAS.

2.3.Estimation of sampling rate using Depuration compounds

Understanding the R_s is essential for estimating a volumetric air concentration (pg/m^3) from the amount of chemical sequestered in the PUF-PAS (pg/PAS). Meteorological parameters at field sites, most notably wind speed and temperature, can be difficult to replicate and maintain over an extended period experimentally, making it complicated if not impossible to generate experimentally determined R_s values that represent the actual circumstances of sampling. Currently, R_{s} is obtained *in situ* by two primary methods: one using an active air sampler (AAS) (Shoeib and Harner, 2002), and another using depuration compounds (DCs), also called performance reference compounds (PRCs) (Gouin et al., 2005; Moeckel et al., 2009). The operating principle of the former is to draw air through the PSM with an electric pump, thereby trapping the target chemicals. Consequently, this method requires specialized sampling equipment, which limits its application and feasibility in simultaneous sampling campaigns at different locations, especially in remote sites. The DC method depends on the hypothesis of isotropic exchange, whereby chemical uptake and desorption are theoretically equally influenced by meteorological conditions (Huckins et al., 2002). DCs are added to the PUF disk prior to deployment, to calibrate the site-specific R_{s} by calculating the elimination rate of DCs (R_{sDC} equals R_{s}), addressing the influence of site effects on PUF-PAS sampling rates.

Some points of interest using the DC method in calculating site-specific R_{s} are as follows (Ahrens et al., 2013; Moeckel et al., 2009):

(i) DCs are not generally present in the environment, and they do not interfere with analytical processes of target compounds.

(ii) DCs cannot degrade in the PUF disk during the sampling period. The DC losses would only be attributed to their direct desorption (i.e., air-side mass transfer).

(iii) Only DCs that experience losses between 20% and 80% can be used to calibrate the R_{s} value. This not only ensures quantitative accuracy (the amount of retained DCs should be higher than detection limit), but would also avoid quantifying insignificant dissipation (i.e., the DC loss must exceed 20%).

(iv) An average R_{sDC} determined by several DCs may be adopted to mitigate variability in the analysis of individual compounds.

Considering that the atmospheric concentration of DC is zero, the desorption of DC from the PUF disk can be calculated by integrating Eq. (3) to yield:

$$-V_{\mathrm{PUF}}(\mathrm{d}C_{\mathrm{DC}}/\mathrm{d}t) = k_{\mathrm{A}}A_{\mathrm{PUF}}C_{\mathrm{DC,0}}/K_{\mathrm{PUF\text{-}A}} \tag{16}$$

where $C_{\mathrm{DC,0}}$ is the initial concentration (ng/sampler), A_{PUF} is the planar area of the PUF disk (m^2), V_{PUF} is the volume of the PUF disk (m^3), and $K_{\mathrm{PUF\text{-}A}}$ is the PUF-air partition coefficient.

By analogy with Eq. (6), the depuration rate constant k_{eDC} (units of reciprocal time) of DC can be described as:

$$k_{\mathrm{dDC}} = k_{\mathrm{A}}A_{\mathrm{PUF}}/(V_{\mathrm{PUF}}K_{\mathrm{PUF\text{-}A}}) \tag{17}$$

Combining Eq. (16) and (17), the concentration of the DC (ng/sampler) at time, t, can be calculated as

$$C_{\mathrm{DC,t}} = C_{\mathrm{DC,0}}\exp(-k_{\mathrm{dDC}}t) \tag{18}$$

Since the R_{sDC} is defined as $k_{\mathrm{A}}\mathrm{A}_{\mathrm{PUF}}$, it can be calculated by rearranging Eq. (17) and (18)

$$R_{\mathrm{sDC}} = -\mathrm{In}(C_{\mathrm{DC,t}}/C_{\mathrm{DC,0}})K_{\mathrm{PUF\text{-}A}}V_{\mathrm{PUF}}/t \tag{19}$$

Two important issues should be considered for Eq. (19):

(i) A stable DC, non-volatilized from the PUF disk, can be used to correct the $C_{\mathrm{DC,t}}$ value to compensate for variations in the sources for all DCs (e.g., loss during spiking, loss of pieces of sampler material during collection, losses during the cleanup, matrix effects) (Moeckel et al., 2009).

(ii) Theoretically, $K_{\text{PUF-A}}$ is defined on a dimensionless basis, and yet a $K'_{\text{PUF-A}}$ on a mass basis is intuitive (i.e., $K'_{\text{PUF-A}} = C_{\text{PUF}}$ (ng/g) / C_{A} (ng/m^3), with units of m^3/g). $K_{\text{PUF-A}}$ can transform to $K'_{\text{PUF-A}}$ by multiplying the bulk density of the PUF, ρ_{PUF} (unit of g/m^3; i.e., $K_{\text{PUF-A}} = K'_{\text{PUF-A}}\ \rho_{\text{PUF}}$). According to the regression equation given by Shoeib and Harner (2002), $K'_{\text{PUF-A}}$ can be calculated as:

$$\log K'_{\text{PUF-A}} = 0.6366 \log K_{\text{OA}} - 3.1774 \quad (r^2 = 0.87) \tag{20}$$

Thus, the R_{sDC} can be calculated as:

$$R_{\text{sDC}} = -\text{In}(C_{\text{DC,t}}^{\text{corr}} / C_{\text{DC,0}}) K'_{\text{PUF-A}}\ \rho_{\text{PUF}} V_{\text{PUF}} / t \tag{21}$$

with:

$$C_{\text{DC,t}}^{\text{corr}} = C_{\text{DC,t}} / (C_{\text{DC-stable,t}} / C_{\text{DC-stable,0}}) \tag{22}$$

where $C_{\text{DC-stable,0}}$ is the initial concentration of stable DC. $C_{\text{DC,t}}^{\text{coor}}$, and $C_{\text{DC-stable,t}}$ are the concentrations of corrected DC and stable DC at time (t), respectively.

In conclusion, the site-specific sampling rate, R_{s} (m^3/day), is equal to R_{sDC}, therefore the atmospheric concentration of a chemical, C_{A} (pg/m^3), can be derived by the following equation:

$$C_{\text{A}} = M_{\text{PUF}} / (R_{\text{s}} t_{\text{s}}) \tag{23}$$

where M_{PUF} is the concentration of chemical sequestered by the PUF (pg/PUF), and t_{s} is the sampling time (days).

3. Progress of the PUF-PAS in monitoring POPs

3.1. Investigation of atmospheric POPs on a continental and global scale

(i) Global Atmospheric Passive Sampling (GAPS) network

The Global Atmospheric Passive Sampling (GAPS) network was the only global PAS program under the Global Monitoring Plan (GMP) for POPs, and gained the support of the United Nations Environment Program (UNEP). The GAPS network, led by Tom Harner, emerged in response to the need for an effective evaluation of the SC on POPs. The GAPS study, launched in December 2004, deployed the PUF-PAS for 3 monthly integration periods at more than 40 background sites on 7 continents, with the aim of demonstrating the feasibility of using PAS for assessing the spatial and seasonal variations of POPs on a worldwide basis (Pozo et al., 2009; Pozo et al., 2006). The published results of the GAPS research so far, have had a profound impact on understanding of baseline trends at the global background sites, and long-range transport and transboundary flows of POPs.

(ii) European PUF-PAS monitoring network

Jaward et al. (2004) first described the success in the application of PUF-PASs in monitoring the spatial distribution of PCBs, PBDEs, and OCPs in the European atmosphere in 2002. In the program, the PUF-PASs were deployed at 71 sites during a six-week period from June 15 to July 30, 2002 across 22 European countries, with the aim of providing a promising new opportunity for an inexpensive large-scale deployment exercise, and obtaining ambient data in order to satisfy the needs of a European-scale multimedia model. In fact, the monitoring campaign implemented by Jaward et al. (2004) is, in a sense, the precursor of the European Monitoring and Evaluation Programme (EMEP) PAS program (discussed below), but while the former focuses on remote/rural/urban locations, the latter targets background sites only (Halse et al., 2011).

A European network of PUF-PAS, with emphasis on background/remote sites, has been established under the patronage of the EMEP program. A network of PUF-PASs was deployed at 86 sites in 34 European countries for approximately 3 months during late summer of 2006. This research had the following aims: (i) obtaining meaningful interpretation of spatial patterns of POPs in the background European air, (ii) demonstrating the feasibility of PAS under the EMEP, (iii) exploring the limitations of spatial coverage on the current EMEP measurement network (Halse et al., 2011).

(iii) Asian Atmospheric Monitoring Project

The initial survey of Asian-scale PAS was conducted in four Asian countries (i.e., China, Japan, South Korea, and Singapore) by simultaneously deploying PUF-PAS at 77 sites in 2004 (Jaward et al., 2005b). This study was completed under stable meteorological conditions (between September 21 and November 16, 2004) without the interference of monsoon and dust storms, thus, providing knowledge about regional distribution of POPs across Asia. Additionally, Hogarh et al. (2012a) investigated spatial distribution of PCBs and PCNs across East Asia by deploying PUF-PASs at 106 sites across 3 countries (i.e., China, Japan, South Korea) from March 21 to May 16, 2008. Subsequently, a continuous sampling research program was conducted in Japan to demonstrate the seasonality of atmospheric PCBs and PCNs in three different seasons: spring 2008, summer 2008, and winter 2008/09 (Hogarh et al., 2013).

In India, a PUF-PAS monitoring campaign, sponsored by Zhang et al. (2008a), was conducted at 18 locations along the coastal length of India, from July 30 to September 26, 2006. Subsequently, a derivative project was implemented by Chakraborty et al. (2010). This study illustrated the contamination status and potential sources of selected OCPs in the atmosphere of major Indian cities, by adopting high spatial resolution of PUF-PAS deployment between December 2006 and March 2007. Additionally, Pozo et al. (2011) implemented a two-year monitoring project (2006/2007), deploying PUF-PAS at nine locations with a quarterly period, to evaluate seasonal and spatial trends of POPs in Indian agricultural regions.

In China, seasonal variations of OCPs and PAHs in the atmosphere of 37 Chinese cities and 3 background sites, was investigated by Liu et al. (2007, 2009) in 2005. The network plan is still in progress, and will be extended to Siberia and the Russian Far East (Zhang and Liu, 2009). Another national-scale program, the Chinese POPs Soil and Air Monitoring Program (SAMP), has also been implemented. In this project, PUF-PASs were deployed at 97 sites from mid-July to mid-October, 2005, and surface soil samples were collected in a subset of 51 sites during that same year (Zhang et al., 2008b). The SAMP reported the distribution of PCBs and Dechlorane Plus in the Chinese atmosphere and soil, and shed light on soil-air interactions and the ultimate fate of these chemicals (Ren et al., 2008; Zhang et al., 2008b). Additionally, a regional-scale survey was carried out in North China (Zhao et al., 2013). This project presented concentrations and spatial distributions of PBDEs, DecaBDE, and PCNs, based on gridded field observations of 90 sites from early June to early October 2011 (Lin et al., 2013; Zhao et al., 2013).

In other Asian nations, Wang et al. (2016) investigated spatial and seasonal variations of atmospheric POPs in Vietnam by deploying PUF-PAS at 15 sites for approximately 6 weeks during the summer and winter. Santiago and Cayetano (2007) measured the atmospheric concentration of PAHs in six residential areas of Philippines during four simultaneous sampling periods in 2005. In recent years, studies from Pakistan were also reported (Ali et al., 2015; Syed et al., 2013).

(iv) Passive air sampling in North and South America

Early research combining PAS with AAS sampling campaigns, relying on the Integrated Atmospheric Deposition Network (IADN), was conducted to explore the feasibility of using PUF-PAS in monitoring the seasonal and spatial distribution of various POPs in the Laurentian Great Lakes (Gouin et al., 2005). Additionally, Pozo et al. (2004) deployed PUF-PASs at 6 sites along a north-south transect in Chile to investigate the concentration and patterns of PCBs, OCPs, and PBDEs over a large latitudinal variation. Recently, Schuster et al. (2015) established a passive air sampling network to assess PCDDs and PCDFs in air across Latin American countries. The PUF-PASs were installed at 13 sites, including background, agricultural, rural, and urban sites, for four consecutive periods of 6 months from January 2011 to January 2013.

3.2.Special subject research on atmospheric POPs

(i) Influence of the monsoon on atmospheric transport of POPs

The atmosphere is regarded as the primary pathway for POPs migration from their source region to pristine areas, and the monsoon plays an important part in LRAT. Based on the analysis of seasonal characteristics of POPs, Ren et al. (2014) concluded the Indian Monsoon contributes to driving the LRAT of DDTs to the Tibetan Plateau. Qu et al. (2015) observed that the seasonal fluctuation of atmospheric DDTs, HCB, and Endosulfan at the Dajiuhu site, central China, are intimately related to the East Asian monsoon. And Wang et al. (2016) found a significant seasonal variability of DDTs in the atmosphere of Vietnam caused by the monsoon. These observations are clearly supported by a high-volume air sampler (Gong et al., 2010; Li et al., 2007).

(ii) Forest filter effect vs. Cold trapping effect

POPs are released by their primary sources, and are preferentially accumulated at the higher altitudes of mountains due to colder temperatures, called “Mountain Cold-Trapping”. Moreover, forests can play a key role in filtering and intercepting airborne POPs, namely the “Forest Filter Effect”. The PAS technique provides a possibility for the monitoring of atmospheric POPs in remote mountain areas. Many related research programs have been implemented to explore the main controlling factors in the altitudinal distribution of POPs in mountain air (Jaward et al., 2005a; Liu et al., 2014; Ren et al., 2014).

(iii) Study of urban–rural transects

POPs are usually introduced into the environment through anthropogenic activity, and thus their source and fate may show significant differences between urban and rural environments. One classic study was carried out to investigate the spatial trends of POPs along an urban-rural transect in the summer of 2002 (Harner et al., 2004), and subsequently, seasonal trends were assessed (Motelay-Massei et al., 2005). The study illustrated that the PUF-PAS is applicable to investigate POPs in urban and rural areas, and can provide insightful data. These results of the study indicated that strong urban-rural gradients exist in the concentrations of PAHs and PCBs, and a complex gradient change for OCPs was found, possibly caused by their physicochemical properties and urban use-history.

(iv) Investigation of POPs in the atmosphere of industrial regions

A series of studies on the source-receptor relationship of POPs in an industrial region have been implemented in the past ten years. Their results are important for verifying the feasibility and efficiency of the PUF-PAS in industrial source identification. For example, Baek et al. (2008) found the steel and petrochemical industries might act as the main sources of Coplanar PCBs, PCNs, and PBDEs in a multi-industry region of South Korea, however, they have little impact on the air of surrounding residential and rural areas. Aydin et al. (2014) concluded that iron/steel plants are significant sources of PAHs and PCBs in ambient air of an industrial region in Turkey.

(v) Estimations of health risk

The PUF-PAS have been shown as a reasonable and practical method in evaluating the hazardous risk of inhalation exposure to POPs in the atmosphere. Cheng et al. (2013) revealed that atmospheric PAHs in the overwhelming majority of sampling sites from three Indian cities exceeded the criterion of 1 ng/m^3 BaP$_{eq}$ (BaP toxic equivalent). Hogarh et al. (2012b) concluded that dioxin-like toxicity of PCNs in the atmosphere of Ghana with an estimated range of 0.49 to 5.6 fg TEQ (toxic equivalency)/m^3, and Xu et al. (2014) found that the total TEQ of atmospheric PCNs in India and Pakistan ranged from 0 to 3.0 fg/m^3 with an average of 0.09 fg/m^3. Moreover, Zhang et al. (2013) found that the potential carcinogenic risk from inhaling OCPs and PCBs for the residents of the Yangtze River Delta are almost negligible.

4. Perspective

A variety of PUF-PAS monitoring programs have been implemented successfully around the world, and these results can facilitate the understanding of geographical distribution, environmental fate, and health effects of atmospheric POPs. The following future research and applications of PUF-PAS are highlighted (Zhang and Liu, 2009):

4.1.The improved PUF-PAS

Researchers are continuing to develop the PUF-PAS sampling technology in order to overcome its deficiencies. For example, a PUF disk impregnated with XAD-4 powder was developed to expand the applicability of PUF disks to more volatile chemicals, which easily reach the saturation point of their adsorption capacity of the PUF disk (Shoeib et al., 2008). Additionally, a passive sampler combined with a PUF disk and a piece of glass fiber filter, was designed to individually collect gaseous and particulate phase PAHs in air (Tao et al., 2007). The improved PUF-PAS is suitable for particle-associated chemicals as well as volatile chemicals and should be developed in the future studies.

4.2.Evaluation of PUF-PAS performance

PAS techniques are generally thought to give an effective estimation of the “true concentration” of a target compound in air within a factor of 2-3 (Harner et al., 2006a). Through the comparative studies of the AAS and PUF-PAS, sampling rates for gas-phase chemicals have been shown to vary by about a factor of 2 with temperature and wind speed (Klánová et al., 2008). Research into PAS techniques has, and continues to be, undertaken, with the aim of improving the accuracy of measurements of atmospheric POP concentrations (Melymuk et al., 2014). Although the DC method provides the possibility for determining the site-specific R_s, more research is still necessary to illustrate the PUF-PAS performance under different conditions, especially understanding the influence of environmental parameters on particle-associated POPs.

4.3.The establishment of regular monitoring systems

The successful implementation of PUF-PAS monitoring campaigns, especially global and national programs, indicates that the sampling technology is feasible in investigating atmospheric POPs on a large scale. Some of these programs have considered the seasonal trend of atmospheric POPs by monitoring over the course of one year. Future research should concentrate on establishing regular monitoring systems on regional/national levels.

4.4.Studies on environmental behaviors and toxicology

The physical and chemical properties of POPs indicate that they could be globally circulated in all spheres of the earth surface system. The atmosphere plays an important role in the circulation of these substances in different sectors of the environment, including soil, water, sediment, and living organisms. Understanding the environmental behaviors of POPs between the atmosphere and other environment media will contributes to the understanding of their ultimate fate. Some research, such as studies of air-soil/water/snow/lichen exchange, and LART of POPs, continue to be explored (Cabrerizo et al., 2013; Qu et al., 2015; Ren et al., 2014). The health risk involved in site-specific POP exposure may also warrant further study.

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Section 3.2

Spatial and seasonal variations of atmospheric organochlorine pesticides along the plain-mountain transect in central China: regional source vs. long-range transport and air-soil exchange

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Spatial and seasonal variations of atmospheric organochlorine pesticides along the plain-mountain transect in central China: regional source vs. long-range transport and air-soil exchange

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Highlights:

- Variations in spatial and seasonal concentration of atmospheric OCPs were observed.
- Since 2005, levels of atmospheric legacy OCPs decreased while Endosulfan increases.
- The plains act as an OCP contaminant emitter to atmosphere.
- Seasonal fluctuation of atmospheric OCPs are linked to the East Asian monsoon.

Abstract: Polyurethane foam (PUF) disk passive air samplers (PAS) were deployed to measure spatiality and seasonality of atmospheric OCPs in Jianghan Plain (JHP) and Western Hubei Mountain (WHM), to make a preliminary explorative study of the source-sink relationship of organochlorine pesticides (OCPs) and their association with the monsoon. The concentrations of individual OCPs in the JHP were generally higher than those in the WHM. Significantly high levels of DDTs and Endosulfan were found in the spring and summer, HCB was found in autumn and winter, and HCHs displayed uniform distributions. Compared with the levels of 2005, a significant decrease of atmospheric HCHs, DDTs and HCB was observed, whereas an increase in Endosulfan was observed. The air-soil equilibrium status of OCPs suggested that Dajiuhu (DJH) soils are likely to be a sink for OCPs, and JHP soils are acting as the emitter, contaminating the atmosphere at certain monitoring stations. Backward air trajectory analysis demonstrated that the seasonal fluctuation of atmospheric DDTs, HCB and Endosulfan at the DJH site were closely associated with the variations of the East Asian monsoon.

Keywords: Organochlorine pesticides; Passive air sampling; Plain; Mountain; Air-soil exchange; East Asia monsoon

1. Introduction

For the last several decades, organochlorine pesticides (OCPs) have been introduced into the environment through anthropogenic activity. As typical semi-volatile organic compounds, OCPs can be released in tropical/subtropical environments and dispersed globally, and may eventually pose significant threats to human health and ecosystem safety (Liu et al., 2010; Nasir et al., 2014; Willett et al., 1998). Despite the use of DDTs and HCHs being prohibited for decades, the accumulation of these legacy pesticides has converted agricultural soil into an important reemission source (Qiu et al., 2005; Tao et al., 2008). In Particular, some plains areas have become severely OCP-contaminated zones due to intensive farming (Hu et al., 2014; Liu et al., 2009; Zhang et al., 2012). Mountain areas can be regarded as some of the more pristine ecosystems in relation to OCP contamination, due to their distance from the pesticide sources (Meire et al., 2012). Recently, however, detailed research has revealed that high mountains have gradually become sinks and important reservoirs for OCPs (Estellano et al., 2008; Meire et al., 2012; Sheng et al., 2013).

The primary pathway for the OCP migration from their source region to pristine areas is through the atmosphere. Research has suggested the Asian monsoon exerts a strong influence on long-range atmospheric transport (LRAT) of OCPs (Li et al., 2007). Thus, the understanding of the source-sink relationship of OCPs in Asia and this relationship to the Asian monsoon is of vital importance, contributing to the understanding of the dynamics and global budget of OCPs (Xu et al., 2013). Recently, numerous studies have confirmed that the South Asian monsoon plays a key role in driving atmospheric transport of OCPs from India to the Tibetan Plateau (TP), and influences the seasonal variations in the concentrations of atmospheric OCPs in the TP (Gong et al., 2010; Ren et al., 2014; Sheng et al., 2013). Similarly, China is also one of the largest consumers of OCPs, which has resulted in locally high environmental levels of the pesticides (Hu et al., 2014; Liu et al., 2009; Tieyu et al., 2005; Zhang et al., 2012). The climate in the central-eastern part of China is dominated by the East Asian monsoon (EAM). Recent research has shown that Chinese sources are the major contributors to OCP contamination in the TP, driven by the East Asian summer monsoon (Gong et al., 2010; Xu et al., 2013). However, targeted research regarding how the EAM affects atmospheric transport of OCPs from heavy polluted area of China to remote mountainous regions, especially the TP, still remains limited.

This paper presents the results of a study using polyurethane foam-based passive air samplers (PUF-PAS) to monitor the variations in concentration of atmospheric OCPs in a plain–mountain transect in central China, with the aim of clarifying the role of the plains as the primary emitter of OCPs, contaminating the mountains through the atmospheric transport with the EAM. The specific objectives of this study are to (I) clarify the spatial and seasonal variability of atmospheric OCPs; (II) identify potential sources of these contaminants and discuss their regional differences; (III) distinguish the potential role of plain and mountain (i.e. sink or source of OCPs), and (IV) explore the potential influence of the EAM on the atmospheric transport of OCPs and how they may contribute to the seasonal variations of atmospheric OCPs in the mountain.

2. Methodology

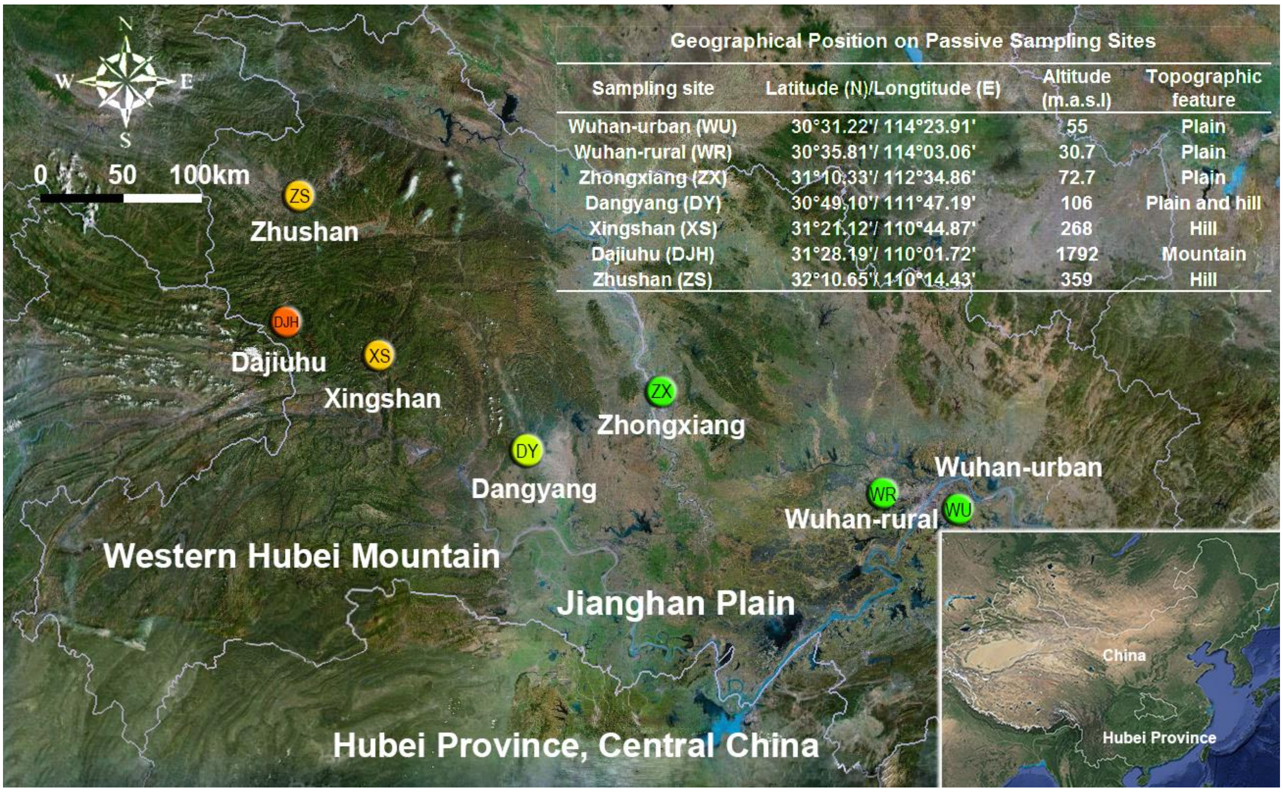
2.1.Study area

Hubei is a large agricultural province of central China with an annual pesticide use of up to ten thousand tons in the past 20 years (PSBH&HITNSB, 2012). Jianghan Plain (JHP), located in central Hubei, is a key national grain and cotton production base with an accordingly wide application of pesticides (Yuan et al., 2013). In recent years, the contamination of OCPs in topsoil, sediment and waters of the JHP has been subject of many detailed research projects (He et al., 2013; Hu et al., 2014; Yuan et al., 2013). These results confirmed the serious environmental pollution by pesticide residue in the JHP. The western regions of Hubei mainly comprise hills and mountains, the so-called "Western Hubei Mountain" (WHM). As the component of the WHM, Shennongjia Forest Region (SFR), known as the "Roof of Central China", is located at the eastern margin of the second topographic terrace of China, which extends from the Qinghai-Tibet Plateau to the north and east. The SFR is a primeval forest and is situated at the point of violent collision between East Asian summer and winter monsoons, and therefore an ideal place for investigating the EAM transport (LRAT) of OCPs.

2.2. Sampling programs

The sampling campaign was performed at seven monitoring stations distributed along the plain-mountain transect (Fig.1). The sampling sites were separated into those representing the JHP (the Wuhan Rural: WR; Wuhan Urban: WU; Zhongxiang: ZX, and Dangyang: DY sites) and WHM (the Xingshan: XS; Zhushan: ZS, and Dajiuhu; DJH sites). Wuhan, situated in the eastern part of the JHP, is a densely populated and highly industrialized metropolitan city. Dajiuhu (DJH), located at the western margin of SFR, is a relatively closed basin and original wetland, surrounded by high mountains. The sampling sites from the plains district will collect air samples from a rural area influenced by localized agricultural activities. The sampling campaign lasted from April 2012 to March 2013, for four seasons: spring (1st April - 1st July 2012), summer (1st July - 26th September 2012), autumn (26th September - 4th December 2012), and winter (4th December - 22nd March 2013). Information on sampling schedule and meteorological parameters have been presented in the supporting information (Table 1).

Samples were collected using polyurethane foam (PUF) passive air samplers, the details of which can be found elsewhere (Estellano et al., 2008; Pozo et al., 2006). PUF disks were prepared and analyzed at State Key Laboratory of Biogeology and Environmental Geology (BGEG), China. Before being deployed for sampling, all PUF disks were pre-cleaned in a Soxhlet extractor using dichloromethane (DCM) for 24h, and then dried in a clean desiccator and wrapped in double layers of aluminum foil, sealed in polyethylene zipped bags (Bohlin et al., 2008). After retrieval, PUF samples were transferred to BGEG and immediately stored at −20 °C until analysis.



Geographical Position on Passive Sampling Sites

Sampling site	Latitude (N)/Longtitude (E)	Altitude (m.a.s.l)	Topographic feature
Wuhan-urban (WU)	30°31.22'/ 114°23.91'	55	Plain
Wuhan-rural (WR)	30°35.81'/ 114°03.06'	30.7	Plain
Zhongxiang (ZX)	31°10.33'/ 112°34.86'	72.7	Plain
Dangyang (DY)	30°49.10'/ 111°47.19'	106	Plain and hill
Xingshan (XS)	31°21.12'/ 110°44.87'	268	Hill
Dajiuhu (DJH)	31°28.19'/ 110°01.72'	1792	Mountain
Zhushan (ZS)	32°10.65'/ 110°14.43'	359	Hill

Fig.1. Map showing the study area and geographical locations of passive air sampling sites.

Table 1. Geographical Position and Exposure Periods on Passive Sampling Sites.

Sampling site	Latitude (N)/ Longtitude (E)	Altitude (m.a.s.l.) [a]	Topographic feature	Period (days) [b] spring/summer/autumn/winter	Temperature (°C) [c] spring/summer/autumn/winter
Wuhan-urban (WU)	30°31.22'/ 114°23.91'	55	plain	91/87/68/109	22.5/27.8/14.9/5.63
Wuhan-rural (WR)	30°35.81'/ 114°03.06'	30.7	plain		
Zhongxiang (ZX)	31°10.33'/ 112°34.86'	72.7	plain		22.9/27.7/15.2/5.45
Dangyang (DY)	30°49.10'/ 111°47.19'	106	plain and hill		22.6/27.5/14.7/6.50
Xingshan (XS)	31°21.12'/ 110°44.87'	268	hill		21.4/26.4/14.7/8.39
Dajiuhu (DJH)	31°28.19'/ 110°01.72'	1792	mountain		17.8/24.2/10.8/3.30
Zhushan (ZS)	32°10.65'/ 110°14.43'	359	hill		21.2/26.0/13.3/6.08

[a] m.a.s.l. = meters above sea level.

[b] Sampling periods from April 2012 to March 2013: 1st April to 1st July 2012 (spring), 1st July to 26th September 2012 (summer), 26th September to 4th December 2012 (autumn), 4th December to 22nd March 2013 (winter).

[c] Meteorological data were provided by Hubei Meteorological Bureau.

2.3.Chemical analysis and quality control

The 16 OCPs targeted were identified and quantified for all samples. These compounds were divided into 5 chemical sub-groups including HCHs (α-, β-, γ-, and δ-HCH), DDTs (p,p'-DDE, p,p'-DDD, o,p'-DDT, and p,p'-DDT), HCB (Hexachlorobenzene), CHLs (Heptachlor, Heptachlor epoxide, trans-Chlordane, cis-Chlordane), and SULPHs (α-Endosulfan, β-Endosulfan, Endosulfan sulfate).

Detailed descriptions of analytical procedures and quality control are as following:

Reagents and glassware

Chemical reagents, pesticide grade dichloromethane (DCM) and n-hexane were purchased from Tedia Co. (Fairfield, Ohio, USA). HPLC grade acetone was purchased from Fisher Scientific (Waltham, Massachusetts, USA). Standards of 2,4,5,6-tetrachloro-m-xylene (TCMX), decachlorobiphenyl (PCB 209) and pentachloronitrobenzene (PCNB) were purchased from Ultra Scientific (North Kingstown, Rhode Island, USA). Standard mixtures of organochlorine pesticides including α-β-γ- and δ-HCH, p,p'-DDE, p,p'-DDD, o,p'-DDT, p,p'-DDT, Hexachlorobenzene, Heptachlor, Heptachlor epoxide, trans-Chlordane, cis-Chlordane,α-Endosulfan, β-Endosulfan and Endosulfan sulfate were purchased from Ultra Scientific, USA. Other chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). Silica gel and alumina gel (100–200 mesh) were activated at 180 °C and 240 °C for 12 h, respectively, deactivated with 3.0% purified water, and stored in desiccators. Anhydrous sodium sulfate was baked at 450 °C for 6 h before it was used. Anhydrous sodium sulfate was baked at 450 °C for 6 h before use. All glass apparatus were cleaned with detergent, $K_2Cr_2O_7$–H_2SO_4 solution, and tap water and deionized water, respectively and finally baked at 180 °C for 3.5 h before use.

Extraction and cleanup

Prior to their separate extraction, PUF disks were spiked with 20 ng mixture of surrogate standards containing TCmX and PCB209 to quality ensure the method performance during extraction and cleanup procedures. PUF disk samples were extracted in a Soxhlet apparatus for 48h using DCM. Activated copper granules were added to the collection flask to remove elemental sulfur. The OCPs extracts were concentrated and solvent-exchanged by hexane and further volume reduced to 2-3 mL by rotary evaporation. The hexane solution was further purified by an alumina/silica (v/v=1:2) gel column (48 h extraction with DCM, then 180 °C and 240 °C muffle drying for 12 h, both 3% deactivated with H2O) and OCPs were eluted with 30 mL of DCM/hexane (2/3,v/v). Then, the eluate was blown down to a final volume of 0.2 mL under a gentle pure nitrogen stream and spiked with PCNB as an internal standard for instrument analysis.

Instrumental analysis

The instrumental analysis of the target compounds were performed using an Agilent 7890A gas chromatograph with a 63Ni electron capture detector (GC-μECD) and a HP-5 MS capillary column (30 m length, 0.32 mm i.d., 0.25 μm film thickness). High-purity nitrogen was used as carrier gas at 2.5 mL/min under the constant-flow mode. The temperature program was as follows: injector temperature 250 °C; detector temperature 300 °C; oven temperature initially began at 100 °C (equilibrium time 1 min), raised to 200 °C at 10 °C/min, and then increased to 230 °C at 1 °C/min, up to 290 °C at a rate of 10 °C/min, and held for 20 min. 2.0 μL of each sample was injected in the splitless mode. The individual OCPs was identified by comparison of their retention times (previously confirmed with GC-MS) and quantified by a six-point internal standard calibration curve. An Agilent 6890GC-5975MSD system was employed. The chromatographic conditions were the same as described above. The MS was operated using electron impact (EI) ionization at 70 Ev and in the selected ion monitoring (SIM) mode.

Quality assurance/quality control

All analytical procedures were monitored using strict quality assurance and control measures. A standard OCPs solution (100μg/L) was analyzed for daily instrument correction of the calibration, and the deviation was less than ±15 percent. To check for laboratory and field contamination, laboratory blanks and field blanks were routinely processed in the same manner as samples. There was no significant difference between concentrations of analytes in the laboratory and field blanks, indicating negligible contamination during transport, storage and analysis. The instrumental detection limits (IDLs) were determined by the lowest standard in calibration, extrapolating to the corresponding amount of analyte that gave a signal-to-noise ratio (S/N) of 3:1. The method detection limits (MDLs) were calculated as the average values of blanks plus three standard deviations (SD) of blank values. When the target compounds were not detected in the blanks, a standard of 3 times the IDLs was used for calculating the MDLs. Concentrations below the MDLs were considered as zero in further calculations. The surrogate recoveries (mean+standard deviation) were 69.8±9.2% and 85.7±15.7% for TCmX and PCB209, respectively. Reported values were corrected by the surrogate recoveries and field blanks.

2.4.Backward air trajectories

To evaluate the aerial transport of OCPs from potential source regions, 5-day backward trajectories were calculated for each seasonal period using NOAA's HYSPLIT model, arriving at DJH (http://www.arl.noaa.gov/ready/hysplit4.html). Meteorological data were obtained from the NCEP/NCAR Global Reanalysis data. Backward trajectories at 500 m above ground level, which represents a well-mixed convective boundary layer for regional transport investigation (Jin et al., 2013), were calculated once a day at 00:00 UTC. Subsequently, standard HYSPLIT cluster analysis was used to elucidate different patterns of air mass origin.

2.5.Calculation of air concentrations

Passive air samplers only represent information on the absolute quality of the chemical sequestered (pg/PAS). The average amounts of chemicals collected per day (pg/day/PAS) can be used to demonstrate spatial and temporal differences between regions. To further compare air concentration with previous studies, the amount of chemical sequestered in the PAS (pg/PAS) must be converted into a volumetric air concentration (pg/m^3). Air concentrations can be derived from the following equation (Baek et al., 2008):

$$C_{\mathrm{air}} = C_{\mathrm{PAS}}/R_S D_S$$

where C_{air} is the concentration of chemical in ambient air (pg/m^3), CPAS is the quantity of chemical in a PAS (pg/PAS), RS is the sampling rate (m^3/day), and DS is the sampling period (day).

The sampling rate of the PUF disk, however, is liable to be changed by meteorological conditions (such as wind speed, wind direction and air temperature), therefore, it is not sensible for us to calculate the volumetric concentration of air (pg/m) in all sampling sites only by using of the same sampling rate. During the sampling period, the sampling rate is considered to be relatively constant due to low wind speed (m/s) between sampling sites (Tuduri et al., 2006). In previous studies (Baek et al., 2008; Choi et al., 2012; Liu et al., 2009; Zhang et al., 2013), which were focused on understanding the seasonal and spatial trends of atmospheric POPs, an average sampling rate of 3.5 m^3/day has been widely used in calculation of air concentrations. Therefore, we suggest that R, 3.5 m^3/day as an estimate was acceptable to make a rough comparison between air concentrations from this study and previous observations.

2.6.Air-soil exchange

Fugacity is an effective method for evaluating the air-soil equilibrium status by measuring the escaping tendency of a chemical from a particular medium (Mackay, 2001). In this study, the equilibrium status of OCPs between two interacting phases was assessed for all sampling sites where soil data sets were collected in the same period, respectively (Guo, 2014).

Fugacity of OCPs in air (f_a) and in soil (f_s) and the fugacity fraction (ff) were calculated using the following equations from Harner et al. (2001):

$$f_s = C_s RT/0.411\varphi_{om} K_{oa}$$

$$f_a = C_a RT$$

$$ff = f_s/(f_s + f_a)$$

where C_s and C_a are concentration of OCPs in soil and air (mol/m^3), R is the gas constant (8.314 Pa m^3/mol/K), T is the absolute temperature (K), φ_{om} is the fraction of organic matter in the soil (1.7 times the soil organic carbon fraction), K_{oa} is the octanol/air partition coefficient of the compound. Factor 0.411 improves the correlation between air-soil partition coefficient and K_{oa}.

Mathematically, the ff ~0.5 represents no net gas exchange, ff >0.5 indicates net volatilization from soil to air and, ff <0.5 represents net gaseous deposition to soil. Due to uncertainty of ff calculation, the values of ff between 0.15 and 0.85 are considered to represent air-soil equilibrium (Daly et al., 2007).

3. Results and Discussion

3.1.General comments on air concentration

The atmospheric concentrations (pg/day/PAS) of OCPs at the JHP and WHM are summarized in Fig.2 and also listed in Table.2. To make a rough comparison with previous studies, an average sampling rate of 3.5 m^3/day was used to convert the quantity of chemical sequestered per day (pg/day/PAS) into a volumetric air concentration (pg/m^3) (Liu et al., 2009).

The concentration of individual OCPs fluctuated in both regions, with much higher coefficients of variation (range: 32.0-204%), which reflected the significant difference in spatial and seasonal variations of atmospheric OCPs (Fig.2). Significant geography-related differences (Mann-Whitney U test, P<0.05) in the concentrations of HCHs, and DDTs were observed in the comparison between JHP and WHW, and there was a significant seasonal variability (Kruskal-Wallis test, P<0.05) in atmospheric concentration of HCB and SULPHs (Table.3).

The ∑OCPs concentrations at the JHP (2210 pg/day/PAS) were more than twice as high as at the WHM (919 pg/day/PAS). In terms of the JHP, the atmospheric levels of individual OCPs were (in sequence of concentration) SULPHs > HCB > DDTs > HCHs > CHLs. Atmospheric concentration of HCHs, DDTs, and SULPHs observed here were similar to those recorded for agricultural areas from Punjab (Nasir et al., 2014) and Ghana (Hogarh et al., 2013), and were both significantly lower than those measured in India (Pozo et al., 2011) (Table. 4).

At the WHM, the atmospheric concentrations measured were HCB > SULPHs > CHLs > DDTs > HCHs. Atmospheric concentrations of HCHs, DDTs, CHLs at the DJH site were comparable to those reported from the Brazilian mountains (Meire et al., 2012), Sygera mountain (Ren et al., 2014) and Bolivian Andes (Estellano et al., 2008), conversely, the SULPHs concentrations were much lower than those in the Bolivian Andes (Estellano et al., 2008) and Brazilian mountains (Meire et al., 2012) (Table. 4). The spatial distribution pattern of these target OCPs were consistent with the results from the Global Atmospheric Passive Sampling (GAPS) study (Pozo et al., 2009; Pozo et al., 2006) which displayed a similar trend between China and South American countries.

Of particular note was that atmospheric concentration of HCHs at the WU site during the entire sampling campaign (42.3 pg/m^3) (Table. 4), which was decreased by one order of magnitude compared with its recorded concentration in 2005 (683 pg/m^3) (Liu et al., 2009). If we use Hangzhou as a proxy representing the Yangtze River Delta (YRD), a similar decreasing trend was also observed in Jun 2010-Jun 2011 (18.8 pg/m^3) (Zhang et al., 2013) and 2005 (618.1 pg/m^3) (Liu et al., 2009). Moreover, atmospheric DDTs and HCB levels at the WU and YRD sites also displayed a decreasing trend compared with that of 2005 (Liu et al., 2009; Zhang et al., 2013). Conversely, the concentration of Endosulfan has been increased by approximately 300% compared to 2005 levels (Liu et al., 2009). This can be interpreted as the result of changing patterns in pesticide use with the phasing out of HCHs and DDTs and the increase in the use of Endosulfan.

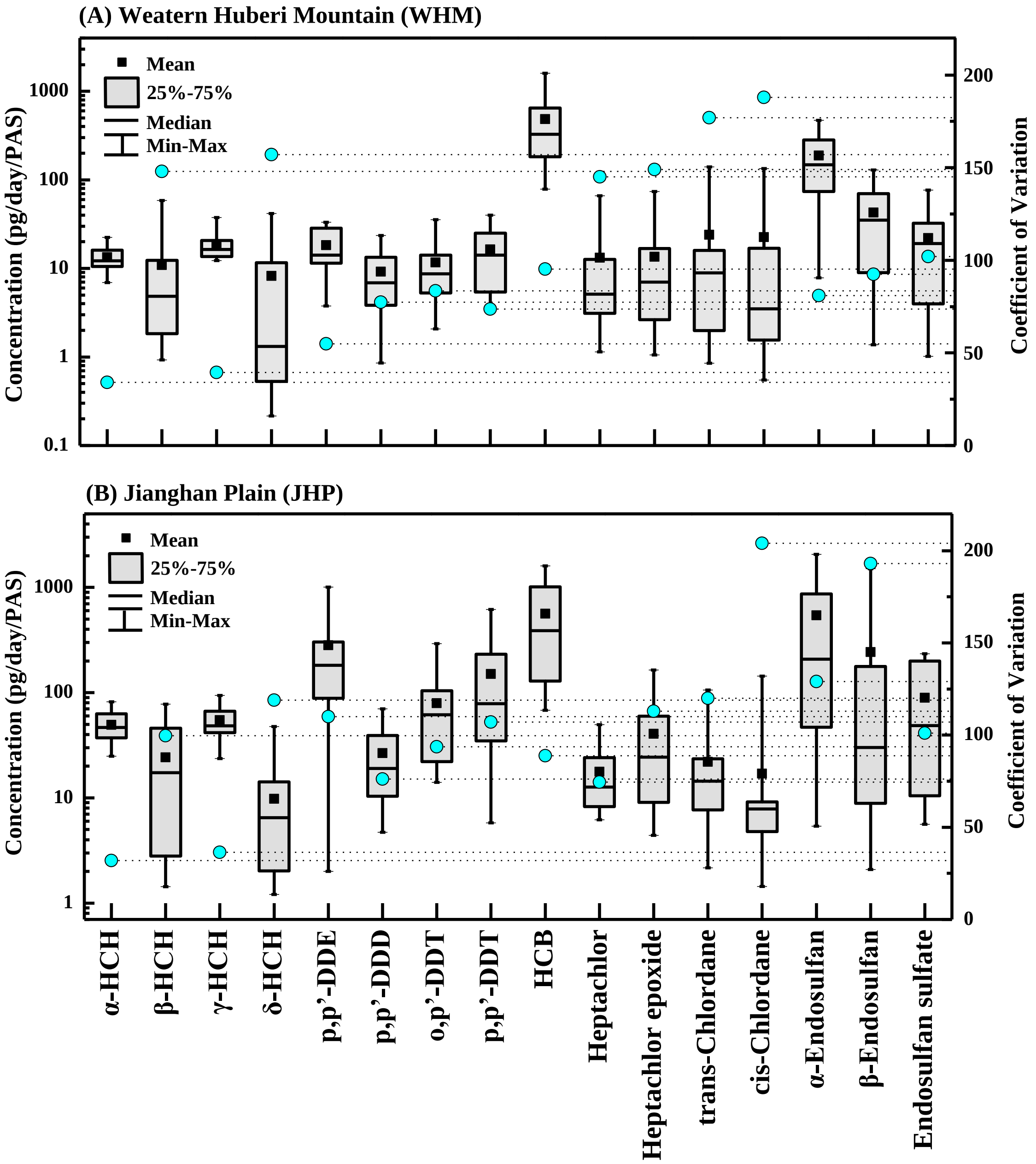


Fig.2. Box-and-whisker plots of atmospheric concentrations of individual OCPs and their coefficient of variation in (A) Western Hubei Mountain. (WHM) and (B) Jianghan Plain (JHP).

Table 2. Air concentrations (pg/day/PAS) of OCPs in Western Hubei Mountain (WHM) and Jianghan Plain (JHP) during April 2012 and March 2013.

		α-HCH	β-HCH	γ-HCH	δ-HCH	p,p’-DDE	p,p’-DDD	o,p’-DDT	p,p’-DDT	HCB	HEPT	HEPX	TC	CC	α-ESLF	β-ESLF	ESLF SUL
	MDLs	0.82	0.74	1.02	0.65	1.55	1.74	1.34	2.18	0.90	1.12	0.94	1.96	1.38	1.44	1.21	2.52
Spring	Wuhan-urban (WU)	81.9	1.44	59.9	13.4	161	25.4	69.2	70.4	107	49.7	121	25.3	9.18	295	34.6	195
	Wuhan-rural (WR)	65.1	49.7	41.8	47.7	234	34.1	119	219	195	15.9	16.7	13.7	9.10	623	97.7	28.8
	Zhongxiang (ZX)	24.9	9.89	23.7	1.31	128	70.2	161	160	68.1	10.9	59.3	106	144	9.67	2.09	45.8
	Dangyang (DY)	48.0	1.65	41.7	6.64	203	17.7	89.6	139	96.5	10.3	29.4	62.5	34.0	522	95.4	51.3
	Xingshan (XS)	6.91	58.6	16.2	41.7	27.6	10.4	15.1	30.3	225	3.37	8.45	3.01	3.01	136	37.2	27.9
	Dajiuhu (DJH)	16.8	18.9	27.1	24.3	10.7	3.68	13.2	8.70	88.7	3.04	2.19	9.11	3.98	160	17.3	12.4
	Zhushan (ZS)	12.5	12.1	17.8	0.96	31.0	3.45	7.49	27.0	238	5.51	18.3	14.9	5.91	187	71.7	76.6
Summer	Wuhan-urban (WU)	42.9	44.6	58.9	10.7	258	17.1	54.3	245	151	6.37	20.9	8.07	9.13	1111	257	209
	Wuhan-rural (WR)	46.7	26.9	87.0	15.2	1005	31.3	73.7	347	85.8	13.9	27.8	8.51	8.74	1396	512	235
	Zhongxiang (ZX)	46.1	3.56	50.4	2.74	593	55.2	293	617	150	11.5	31.8	15.3	5.75	1929	1505	204
	Dangyang (DY)	50.9	56.0	72.8	6.88	348	55.8	157	261	165	6.71	73.4	21.9	7.54	2057	1256	226
	Xingshan (XS)	15.5	6.42	20.4	1.25	33.2	23.6	9.94	40.0	78.5	66.0	21.3	140	134	308	87.0	25.8
	Dajiuhu (DJH)	11.5	0.93	37.6	n.d.	13.8	11.0	25.1	17.7	164	3.18	5.97	2.38	1.68	470	68.0	29.9
	Zhushan (ZS)	22.4	3.27	21.1	n.d.	23.7	15.8	10.9	23.2	1598	36.4	73.9	10.1	5.08	445	129	35.0
Autumn	Wuhan-urban (WU)	71.2	24.9	80.2	15.0	2.01	6.47	14.0	5.78	737	39.6	10.5	19.1	12.5	5.83	4.94	6.18
	Wuhan-rural (WR)	60.7	47.2	94.1	17.8	50.8	44.4	81.3	86.3	1154	7.65	4.41	15.2	5.80	17.4	12.3	7.50
	Zhongxiang (ZX)	46.5	7.51	32.5	1.43	202	4.70	50.1	62.0	767	32.6	60.5	9.80	3.60	5.38	3.23	104
	Dangyang (DY)	40.7	28.2	43.7	6.32	104	8.38	17.1	27.4	581	6.18	6.18	6.53	3.32	229	41.5	8.53
	Xingshan (XS)	13.1	10.3	12.8	0.74	14.4	3.97	7.35	3.53	200	12.7	3.09	78.8	84.3	56.4	7.62	n.d.
	Dajiuhu (DJH)	20.0	1.92	14.3	n.d.	12.2	5.72	4.14	10.6	419	1.14	1.32	1.60	1.44	7.84	1.37	4.08
	Zhushan (ZS)	12.0	12.5	14.6	1.38	13.4	8.03	6.42	4.40	817	2.60	8.08	8.70	2.68	91.3	10.4	3.86
Winter	Wuhan-urban (WU)	33.8	5.41	46.4	2.02	60.7	16.2	22.7	36.2	985	17.5	5.41	26.1	8.15	115	9.45	66.6
	Wuhan-rural (WR)	66.9	77.7	60.6	0.91	968	20.3	21.6	64.6	1600	30.7	164	4.94	5.24	187	25.6	12.5
	Zhongxiang (ZX)	32.6	2.04	40.4	6.07	117	5.82	25.1	33.3	1122	8.89	7.64	2.16	1.44	81.0	8.27	5.60
	Dangyang (DY)	32.9	1.56	43.6	2.02	72.7	12.4	20.2	33.2	1044	15.5	10.8	7.34	4.31	76.4	11.9	25.4
	Xingshan (XS)	11.7	2.40	16.6	9.91	29.5	18.8	35.6	21.5	436	12.6	3.84	17.1	27.8	111	33.0	41.5
	Dajiuhu (DJH)	8.62	1.56	12.9	4.16	3.76	n.d.	2.07	3.47	475	4.76	1.06	n.d.	n.d.	34.4	4.15	n.d.
	Zhushan (ZS)	9.54	1.74	12.3	13.3	6.97	4.77	3.30	6.42	1096	7.07	15.2	n.d.	n.d.	256	45.8	5.32

Note: HEPT (Heptachlor), HEPX (Heptachlor epoxide), CC (cis-Chlordane), TC (trans-Chlordane), α-ESLF (α-Endosulfan), β-ESLF (β-Endosulfan), ESLF SUL (Endosulfan sulfate).

Table 3. Multiple-statistical analysis of atmospheric OCPs concentration (pg/day/PAS) in Western Hubei Mountain (WHM) and Jianghan Plain (JHP) during April 2012 and March 2013.

Compound	P^a	P^b
α-HCH	<0.001	
β-HCH		
γ-HCH	<0.001	
δ-HCH		
HCHs	<0.001	
p,p'-DDE	0.001	
p,p'-DDD	0.004	
o,p'-DDT	<0.001	
p,p'-DDT	<0.001	
DDTs	<0.001	
HCB		0.002
Heptachlor epoxide	0.029	
HEPX	0.017	
trans-Chlordane		
cis-Chlordane		
CHLs		
α-Endosulfan		0.001
β-Endosulfan		0.001
Endosulfan sulfate	0.023	0.006
SULPHs		<0.001

[a] values result from the comparison between Jianghan Plain and Western Hubei Mountain (Mann-Whitney U test).

[b] values result from the comparison between spring, summer, autumn and winter (Kruskal-Wallis test).

Table 4. Comparison of the average concentrations of selected OCPs in PUF passive samples in the present study and other regions (pg/m^3).

	Sampling date	**α-HCH**	**β-HCH**	**γ-HCH**	**δ-HCH**	**HCHs**	**p,p'-DDE**	**p,p'-DDD**	**o,p'-DDT**	**p,p'-DDT**	**DDTs**	**Reference**
Agriculture area												
Jianghan Plain	Apr 2012-Mar 2013	14	7	16	3	40	80	8	23	43	154	This study
Indian agricultural regions	2006	443	-	1553	-	1996	273			377		(Pozo et al., 2011)
	2007	95	-	377	-	472	141			NA		(Pozo et al., 2011)
Punjab, Pakistan	Jan-Mar 2011	19	16	20	-	55	79	35	30	34	178	(Nasir et al., 2014)
Ghana	May-Jul 2010	2	4	82	1	89	83	33	70	95	281	(Hogarh et al., 2014)
Mountain area												
Western Hubei Mountain	Apr 2012-Mar 2013	4	3	5	2	15	5	3	3	5	16	This study
Dajiuhu	Apr 2012-Mar 2013	4	2	7	2	14	3	1	3	3	10	This study
NPSO/ NPSJ, Brazilian	2007-2008	7	-	10	-	17						(Meire et al., 2012)
Sygera Mountain	2008-2011	5		2			5		12	7		(Ren et al., 2014)
Bolivian Andes Mountains	Feb 2005- Jan 2006	7		15						BDL-119		(Estellano et al., 2008)
Other areas												
Wuhan-urban (WU)	Apr 2012-Mar 2013	16	5	18	3	42	34	5	11	26	76	This study
Wuhan	2005	115	60	508	-	683	139	-	229	78	447	(Liu et al., 2009)
Yangtze River Delta	Jun 2010- Jun 2011					19					168	(Zhang et al., 2013)
Hangzhou	2005	58	96	464	-	618	114	-	159	75	348	(Liu et al., 2009)

	Sampling date	**HCB**	**HEPT**	**HEPX**	**TC**	**CC**	**CHLs**	**α-ESLF**	**β-ESLF**	**ESLF-SUL**	**SULPHs**	**Reference**
Agriculture area												
Jianghan Plain	Apr 2012-Mar 2013	161	5	12	6	5	28	155	69	26	249	This study
Indian agricultural regions	2006						15				6156	(Pozo et al., 2011)
	2007						6				2786	(Pozo et al., 2011)
Punjab, Pakistan	Jan-Mar 2011	33			47	48		22	11			(Nasir et al., 2014)
Ghana	May-Jul 2010	22	17	1	16	5	39	132	41	4	177	(Hogarh et al., 2014)
Mountain area												
Western Hubei Mountain	Apr 2012-Mar 2013	139	4	4	7	6		54	12	6	72	This study
Dajiuhu	Apr 2012-Mar 2013	82	1	1	1	1		48	6	3	58	This study
NPSO/ NPSJ, Brazilian	2007-2008							603	102	32	737	(Meire et al., 2012)
Sygera Mountain	2008-2011											(Ren et al., 2014)
Bolivian Andes Mountains	Feb 2005- Jan 2006		BDL-0.5	BDL-276	BDL-1.6	BDL-2.4		382	16	14	412	(Estellano et al., 2008)
Other areas												
Wuhan-urban (WU)	Apr 2012-Mar 2013	141	8	11	6	3		109	22	34	165	This study
Wuhan	2005	354	12	-	29	390		34	7	-		(Liu et al., 2009)
Yangtze River Delta	Jun 2010- Jun 2011	151					110					(Zhang et al., 2013)
Hangzhou	2005	448	57		161	286		24	7	-		(Liu et al., 2009)

Note: HEPT (Heptachlor), HEPX (Heptachlor epoxide), CC (cis-Chlordane), TC (trans-Chlordane), α-ESLF (α-Endosulfan), β-ESLF (β-Endosulfan), ESLF SUL (Endosulfan sulfate).

3.2.Spatial and seasonal variations

3.2.1. HCHs

Significant spatial variability ($p<0.01$) for α-HCH and γ-HCH was observed (Table.3). The concentration (pg/day/PAS) of ∑HCH (sum of α, γ isomers) at the JHP was calculated as between 48.5 and 155 (average=104) whereas, at the WHM, it ranged from 21.5 to 49.1 (average=32.0) (Fig.2). Higher concentrations of HCHs at the JHP were observed in Wuhan, and more specifically, HCHs concentrations in Wuhan were elevated in proximity to agricultural activity (WR) relative to urban site (WU) (Fig.3). The average fraction of HCH isomers at the JHP was 39.7% γ-HCH, 35.8% α-HCH, 17.5% β-HCH, and 7.10% δ-HCH. In agricultural soils polluted by historic technical HCH, the levels of β-HCH are expected to be dominant over the levels of other individual HCH isomers (Qu et al., 2015). The difference in the molecular composition of HCHs in the atmosphere and soil can be attributed to the relatively higher air-water partitioning coefficient of α, γ isomers, which results in these two isomers being more easily incorporated into LRAT (Liu et al., 2010). Despite the absence of identifiable local emission sources within the area of the DJH site, a relative abundance of β-HCH is 1.85%, 5.24% and 5.72% for summer, autumn and winter, respectively, and higher fraction of α, γ isomers were observed (Fig.4). This supports the hypothesis that LRAT is responsible for the supply of HCHs to the DJH site. The concentrations of HCHs did not demonstrate seasonal variations ($p>0.05$) (Table.3) with a ratio of the highest to lowest values of 3.68 and 4.54 for the JHP and WHM, respectively. This reflected that HCHs displayed particularly uniform distributions at the JHP and WHM.

A significant correlation (Spearman's test, $p<0.01$, $R_s=0.86$) (Table. 5) was observed between α-HCH and γ-HCH. The α/γ-HCH ratio can be used to ascertain HCH sources (i.e. historic technical HCH vs. lindane) and as an indicator of LRAT (Zhang et al., 2008). High α/γ-HCH ratio (>4) is recognized as a marker of recent use of technical HCH, whereas a ratio close to or below unity means fresh inputs or atmospheric transport of lindane from neighboring regions (Willett et al., 1998). The α/γ-HCH ratios along the transect ranged from 0.31 to 1.56 (average=0.88) (Fig.4A), which were lower than those in technical HCH formulations (4-7) (Li and Macdonald, 2005). The low α/γ-HCH ratio probably signifies the ongoing local usage and/or re-emission of lindane. The observation agrees with the GAPS study (Shunthirasingham et al., 2010b), which affirmed lindane as the prevailing source of HCH in the global atmosphere. A series of recent surveys have been demonstrated that low α/γ-HCH ratios found in topsoil, sediment and water of the JHP might be associated with the usage of lindane (He et al., 2013; Hu et al., 2014; Yuan et al., 2013).

Table 5. Spearman’s coefficient matrix for individual OCPs along the plain-mountain transect in central China.

OCPs	α-HCH	β-HCH	γ-HCH	δ-HCH	p,p’-DDE	p,p’-DDD	o,p’-DDT	p,p’-DDT	HCB	HEPT	HEPX	TC	CC	α-ESLF	β-ESLF
β-HCH	0.32	1.00													
γ-HCH	0.86[b]	0.36	1.00												
δ-HCH	0.30	0.36	0.36	1.00											
p,p’-DDE	0.65[b]	0.31	0.64[b]	0.13	1.00										
p,p’-DDD	0.54[b]	0.24	0.60[b]	0.20	0.68[b]	1.00									
o,p’-DDT	0.63[b]	0.19	0.68[b]	0.32	0.79[b]	0.80[b]	1.00								
p,p’-DDT	0.64[b]	0.31	0.67[b]	0.26	0.92[b]	0.81[b]	0.87[b]	1.00							
HCB	-0.02	0.01	-0.04	-0.16	-0.24	-0.31	-0.36	-0.36	1.00						
HEPX	0.54[b]	-0.04	0.37	-0.02	0.35	0.38[a]	0.26	0.32	0.07	1.00					
HEPX	0.52[b]	0.15	0.40[a]	-0.07	0.66[b]	0.53[b]	0.48[a]	0.64[b]	-0.15	0.54[b]	1.00				
TC	0.35	0.09	0.22	-0.01	0.24	0.47[a]	0.40[a]	0.33	-0.42[a]	0.53[b]	0.31	1.00			
CC	0.41[a]	0.19	0.31	0.10	0.37	0.54[b]	0.46[a]	0.42[a]	-0.50[b]	0.57[b]	0.34	0.88[b]	1.00		
α-ESLF	0.19	0.12	0.31	0.17	0.51[b]	0.47[a]	0.39[a]	0.53[b]	-0.40[a]	0.04	0.46[a]	0.08	0.17	1.00	
β-ESLF	0.17	0.20	0.32	0.22	0.47[a]	0.46[a]	0.37	0.52[b]	-0.33	0.07	0.47[a]	0.11	0.20	0.95[b]	1.00
ESLF SUL	0.39[a]	0.11	0.49[b]	0.13	0.70[b]	0.56[b]	0.70[b]	0.76[b]	-0.46[a]	0.29	0.64[b]	0.39[a]	0.44[a]	0.58[b]	0.59[b]

Note: HEPT (Heptachlor), HEPX (Heptachlor epoxide), CC (cis-Chlordane), TC (trans-Chlordane), α-ESLF (α-Endosulfan), β-ESLF (β-Endosulfan), ESLF SUL (Endosulfan sulfate).

[a] Correlation is significant at the 0.05 level (2-tailed).

[b] Correlation is significant at the 0.01 level (2-tailed).

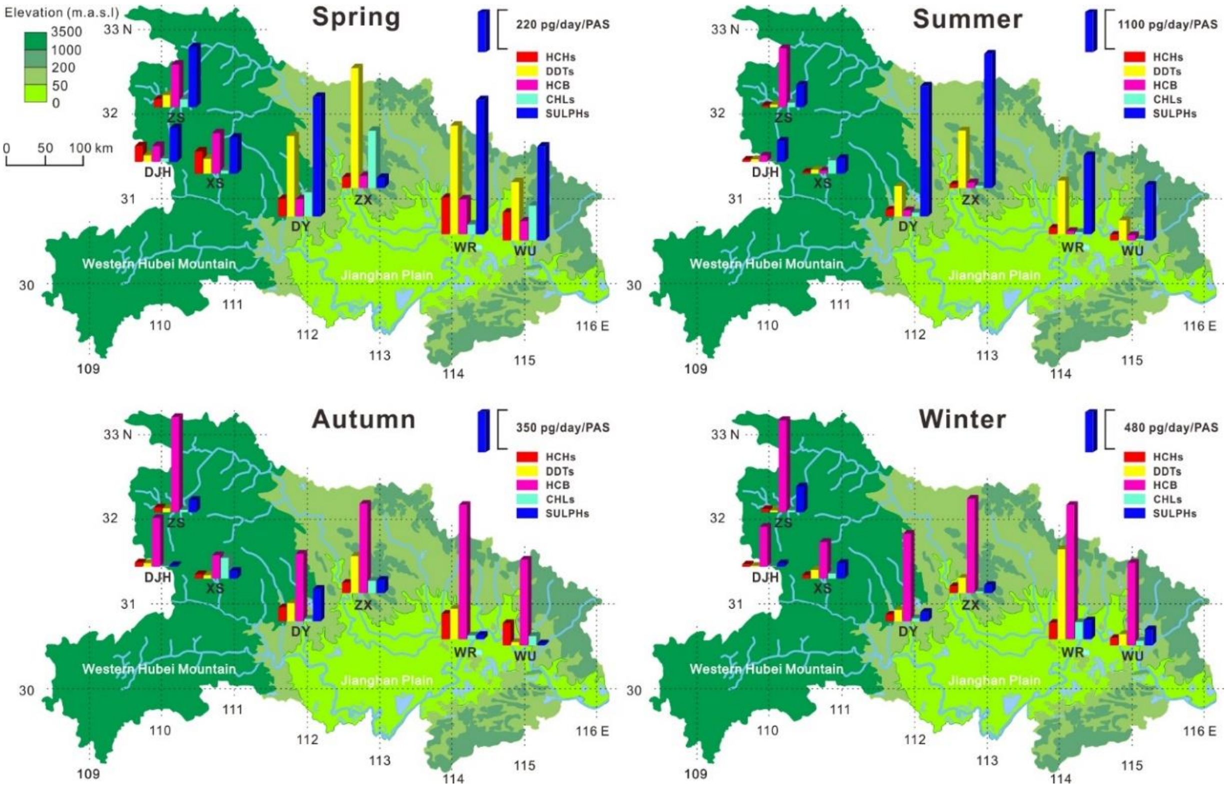


Fig.3. Diagram of the spatial and temporal variations of atmospheric OCPs along the plain-mountain transect in central China.

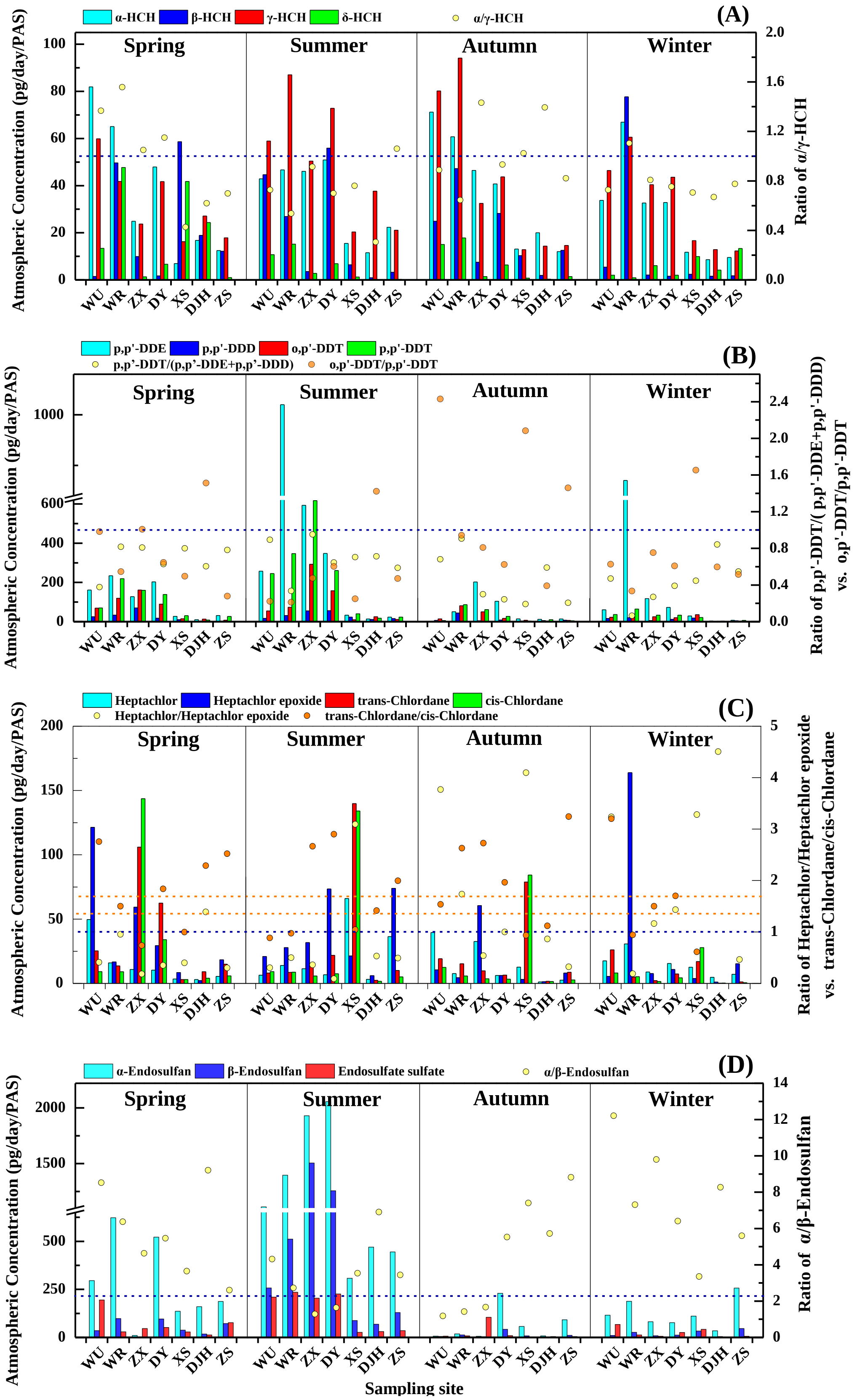


Fig.4. Compositions and sources of HCHs, DDTs, CHLs and SULPHs at the sampling sites.

3.2.2. DDTs

There was a significant difference ($p<0.01$) in the concentrations of the individual DDT chemicals between JHP and WHM, but they were without seasonal variations ($p>0.05$). The concentration (pg/day/PAS) of DDTs in the JHP (average=538) was higher than the value observed for the WHM (average=55.6) (Fig.2). Summer concentrations of DDTs were higher than those of any other season of the year (Fig.3). There was a significant positive correlation ($p<0.01$) between the parent compounds and their metabolites, especially for p,p'-DDE vs. p,p'-DDT ($R_s=0.92$) and o,p'-DDT vs. p,p'-DDT ($R_s=0.87$) (Table. 5). In the JHP, the average fraction of DDT compounds decreased in the following order: 52% p,p'-DDE, 28% p,p'-DDT, 15% o,p'-DDT, and 5% p,p'-DDD. This finding is completely contrary to the trend in Indian agricultural regions where the abundance of parent compounds were attributed to the ongoing use of DDT (Pozo et al., 2011). Moreover, significantly higher p,p'-DDE concentration was also reported by Shunthirasingham et al. (2010a), who concluded that the volatilization of p,p'-DDE is the dominant loss process from arid subtropical soils by analyzing a multimedia fate model.

The p,p'-DDT/(p,p'-DDE+p,p'-DDD) ratio has been used successfully to distinguish between recent application (if ratio>1) or historical signatures (if ratio<1) (Nasir et al., 2014; Zhang et al., 2008; Zhang et al., 2013). The p,p'-DDT/(p,p'-DDE+p,p'-DDD) ratios at the JHP and WHM were all less than unity (Fig.4B), and therefore indicated the prevalence of aged technical DDT in the atmosphere. Moreover, the o,p'-DDT/p,p'-DDT ratio can be employed as a marker of technical DDT from "dicofol-type DDT" (Qiu et al., 2005). The o,p'-DDT/p,p'-DDT ratio ranged from 0.21 to 2.43 (average=0.82) which was quite close the calculated ratio of 0.74-0.96 for technical DDT and far below ~28 for dicofol-type DDT in the air (Liu et al., 2009). Consequently, our results excluded the possibility of the "dicofol-type DDT" pollution at the regional scale, and indicated the addition of aged technical DDT emission to the atmosphere. This fact further demonstrated that the atmospheric DDTs in China originated mostly from technical DDT (Liu et al., 2009). Additionally, our findings seem to have underpinned the observation which the elevated concentrations of DDTs, as observed in high temperature seasons, were likely influenced by temperature-driven evaporation from previously DDT-contaminated soils (Zhang et al., 2013).

3.2.3. Hexachlorobenzene (HCB)

The concentration (pg/day/PAS) of HCB at the JHP was measured between 68.1 and 1600 (average=563.1) whereas, at the WHM, it ranged from 78.5 to 1598 (average=486) (Fig.2). As shown in Table 4, the average HCB concentrations at the JHP and WHM were both comparable to those reported at YRD, but apparently higher than those in Punjab, Ghana and the atmosphere of northern hemisphere (~50 pg/m^3) (Barber et al., 2005). Due to its higher volatility, HCB is potentially more mobile and subject to LRAT and, as a result, tends to be distributed globally (Liu et al., 2010). Indeed, the HCB concentrations showed statistically significant seasonal differences ($p<0.01$), however no regional variations ($p>0.05$) (Table.3). The concentrations of HCB in autumn and winter were higher than those observed in other seasons, except for ZS (Fig.3). Unlike the relatively uniform distributions of HCB in western China, Europe and the Arctic (Jaward et al., 2004; Liu et al., 2010; Su et al., 2006), when only considering the elevated concentrations of HCB in autumn and winter, the spatial patterns of HCB during cold seasons displayed distinctive regional variations ($p<0.05$) (Fig.3). This may imply that the elevated HCB concentrations were largely associated with regional sources and transfer processes.

Globally, HCB chiefly originates from three source categories, namely it's use as a fungicide, as a precursor in the manufacture of pentachlorophenol (PCP) and Na-PCP, and being released as a byproduct of chlorination processes (i.e. pesticide production, fuel combustion and waste incineration) (Chakraborty et al., 2010; Liu et al., 2009). In this study, the higher HCB concentrations in colder seasons were consistent with the finding of three year atmospheric monitoring study in Tibetan Plateau (Sheng et al., 2013) that concluded biomass combustion for heating to be an important local source. Additionally, recent research by Wang and Zhang (2008) found that the peak time for the open-air burning of crop residues occurred in October in South China. Therefore, perhaps the elevated HCB concentrations in autumn can also be traced to biomass combustion. HCB has never been registered as pesticide for agricultural purposes in China, however, about 66 thousand tons of HCB was produced for PCP/Na-PCP from 1988 to 2003 (Liu et al., 2009). The JHP is the location of the most serious incident rates of schistosomiasis, perhaps as a result of the suitability of the growth of the aquatic gastropod mollusk *schistosoma japonicum* (namely *oncomelania hupensis*). The usage of PCP/Na-PCP for schistosome control, and chlorothalonil containing HCB residue may become an important source. Indeed, recent studies have confirmed that HCB is frequently detected in surface water, groundwater, soil and sediment from Jianghan Plain (Hu et al., 2014; Zhou et al., 2011). Therefore, current sources for air concentration of HCB are mostly likely caused by the integrated influence of the three source categories described above.

3.2.4. Chlordane-related compounds

Technical Chlordane has been widely used as a chemical barrier to prevent destructive damage of building foundations by termites in China (Zhang et al., 2012). Approximately 9,000 tons of Chlordane have been produced for application in China, with 834 tons and 363 tons being produced in 1998 and 2004, respectively (Jin et al., 2013; Zhang et al., 2012). Neither seasonality nor spatiality for trans-Chlordane (TC) and cis-Chlordane (CC) was displayed. However, extremely high concentrations (pg/day/PAS) of TC and CC were observed at the ZX (spring: 250), DY (spring: 96.5) and XS sites (summer: 274, autumn: 163 and winter 44.9) (Fig.4C). The main components of technical Chlordane are 13% TC, 11% CC, 5% Heptachlor and 5% trans-Nonachlor (Zhang et al., 2012). TC/CC ratio of the technical chlordane is 1.17 (Chakraborty et al., 2010). Nevertheless, one would expect the TC/CC ratio in air arising from vaporization of technical chlordane or from soil to be 1.63 and 1.95 at 20 and 25 °C, respectively (Park et al., 2011). As illustrated in Fig.4C, relatively high values of TC/CC (above 1.95) were observed in the atmosphere of the study areas, suggesting the ongoing use of technical Chlordane.

Heptachlor (HEPT), as a chlorinated cyclodiene insecticide, was isolated from technical Chlordane in 1946 (Zhang et al., 2012). It is degraded via photolysis or epoxidation in soils, plants and animals to heptachlor epoxide (HEPX), which is more stable in air (Nasir et al., 2014). This reflects that HEPT/HEPX ratio was generally below unity (Fig.4C). Atmospheric levels of HEPT together with HPEX were the lowest of all targeted OCPs, only contributing an average of 2.64% and 2.92% to the ∑OCPs at the JHP and WHM, respectively. Presumably this is caused by the relatively short half-life of HEPT in environmental media compared with that of other OCPs (Baek et al., 2013). Importantly, the total consumption amount of HEPT was only approximately 17 tons from 1948 to 1982 in China, and additionally, there has been no production of HEPT at all in recent years (Wei et al., 2007). Statistically significant correlations (Spearman's test, $p<0.01$) were observed between HEPT and HEPX ($R_s=0.54$), HEPT and CC ($R_s=0.53$), HEPT and TC ($R_s=0.57$), CC and TC ($R_s=0.88$) (Table. 5). This implies that Heptachlor in the atmosphere most likely originates from local application of technical Chlordane.

3.2.5. Endosulfan

Endosulfan is extensively applied in China to control various insects and mites, and the total usage from 1994 to 2004 was estimated to be approximately 25,700 tons (Jia et al., 2010). The Chinese government has implemented the amendment of Stockholm Convention on POPs designed to prohibit the production, trade, use, import and export of Endosulfan from 26th March 2014, however, there are specific exemptions for the purposes of insect control in the cotton and tobacco industries (MEP, 2014). Hubei province with nearly 5 million hectares planted in cotton is subject to intensive farming practices with extensive use of Endosulfan (PSBH&HITNSB, 2012). He et al. (2013) reported that SULPHs could be detected in all topsoil samples of central JHP with an average concentration of 1.67 ng/g.

The concentrations (pg/day/PAS) of SULPHs ranged from 13.3 to 609 (average = 253), and from 17.0 to 3638 (average = 873) for WHM and JHP, respectively (Fig.2). We observed significant seasonal variability ($p<0.01$) in SULPHs concentrations (Table 3). The peak concentration of SULPHs occurred in the JHP during the summer (Fig.3). The summer concentrations at the ZX and DY sites (3638 and 3538 pg/day/PAS, respectively) were about six times higher than those observed at the DJH site (568 pg/day/PAS). The summer sampling campaign is contemporaneous with high agricultural activity, therefore, it is unsurprising that the elevated levels of atmosphere SULPHs in the JHP could be attributed to its application during the growing season for cotton. The same conclusion was drawn by Meire et al. (2012) and Sofuoglu et al. (2013), who also observed the elevated summer concentrations of Endosulfan, and attributed this to the result of the seasonal application of certain agricultural activities.

The annual mean concentrations (pg/day/PAS) of α-Endosulfan, β-Endosulfan and Endosulfan sulfate were 390±558, 157±362 and 60.5±76.9, respectively. α-Endosulfan tended to have the highest concentration, which is more consistent with results of previous measurements, as reported by the GAPS study (Shunthirasingham et al., 2010b). Previous research indicates that Endosulfan sulfate present in the atmosphere mainly originates from the release of the degradation of Endosulfan in soil by microorganisms (Pozo et al., 2009; Pozo et al., 2006). Based on this, one could expect the relatively lower atmospheric concentrations of Endosulfan sulfate recorded in this study, as it is similar to previous research (Meire et al., 2012; Pozo et al., 2009). The lower relative abundance of Endosulfan sulfate at the DJH site, relative to the JHP (Fig.4D), is further proof of the LRAT of Endosulfan to DJH area. The atmospheric concentrations of β-Endosulfan follow a similar seasonal pattern to α-Endosulfan, with increasing concentrations corresponding to increasing agricultural activities in the summer.

Technical formulation of Endosulfan mainly consists of α- and β-Endosulfan in a ratio of about 7:3 (Chakraborty et al., 2010). β-Endosulfan is more reactive in the atmosphere and converts to α-Endosulfan after it is applied. (Nasir et al., 2014). Therefore, higher α/β-Endosulfan ratio indicates the presence of an aged signature or the influence of LRAT, whereas the ratio closer to the staring technical mixture (about 2.3) suggests the recent usage of technical Endosulfan (Pozo et al., 2011; Shunthirasingham et al., 2010b). As shown in Fig.4D, the α/β-Endosulfan ratios were found to be 1.18 to 12.2 (average=5.32), indicated a combination of fresh applications (lower ratios) and an aged signature (higher ratios). The seasonal variation of this ratio was observed at the JHP (P=0.012), but not at the WHM (Kruskal-Wallis test, p>0.05). Higher level of SULPHs and lower value for α/β-Endosulfan in summer may be largely attributed to the results of ongoing usage of technical Endosulfan. One notable exception was the elevated α/β-Endosulfan ratios (average=7.53) at the DJH, where, in the absence of agricultural activity, reflects that the DJH area was most likely influenced by LRAT from surrounding regions.

3.3.Air-soil exchange

We assessed air-soil equilibrium through fugacity modelling to clarify the potential role of the plains and mountains as OCP sources or sinks (RůŽičková et al., 2008). Detailed calculation of the fugacity fraction (*ff*) can be found in Harner et al. (2001). Due to uncertainty of *ff* calculation, the *ff* values between 0.15 and 0.85 are considered to represent air-soil equilibrium, *ff*<0.15 represents net gaseous deposition to soil, and *ff*>0.85 represents net volatilization from soil to air (Daly et al., 2007).

The *ff* values for the individual compounds displayed a wide variation ranging 0 to 0.99 (Fig. 5). Within the uncertainty of *ff* values (0.15-0.85), this means that air-soil exchange cannot be addressed by using only a single chemical flux direction representing all chemicals. Similar trends showing wide ranges of *ff* were recorded in the soil of Pakistan (Syed et al., 2013), Mexico (Wong et al., 2010), USA and Europe (RůŽičková et al., 2008). Generally speaking, α-HCH, γ-HCH and HCB are largely in a situation of net volatilization from soil due to their greater volatility. o,p'-DDT, p,p'-DDT, trans-Chlordane, cis-Chlordane are most likely at air–soil equilibrium, and p,p'-DDE, p,p'-DDD, α-Endosulfan show net deposition to soil. The average *ff* values of the JHP were slightly elevated compared to the *ff* values of the individual OCPs in the WHM, and the *ff* values for most selected OCPs are greater in summer than the corresponding values in other seasons (Fig. 5A&B).

The *ff* values of all selected OCPs were below 0.85 for DJH, except HCB in summer (Fig. 5A). This result demonstrated that soil in DJH is likely to be a sink for OCPs, especially DDTs, Chlordane and Endosulfan. The *ff* of α-HCH, γ-HCH, p,p’-DDE, p,p’-DDT and HCB at the DJH site is slightly lower than those recorded in the TP (Wang et al., 2012). DJH is a subalpine peat-swamp wetland, with a cold climate and high levels of organic matter in the soil. The cold climate can enhance the deposition of chemicals, and higher quantity of organic matter in the soil increases the ability of DJH soil to retain the chemicals. These factors undoubtedly contribute to net deposition of gas-phase OCPs at the DJH site.

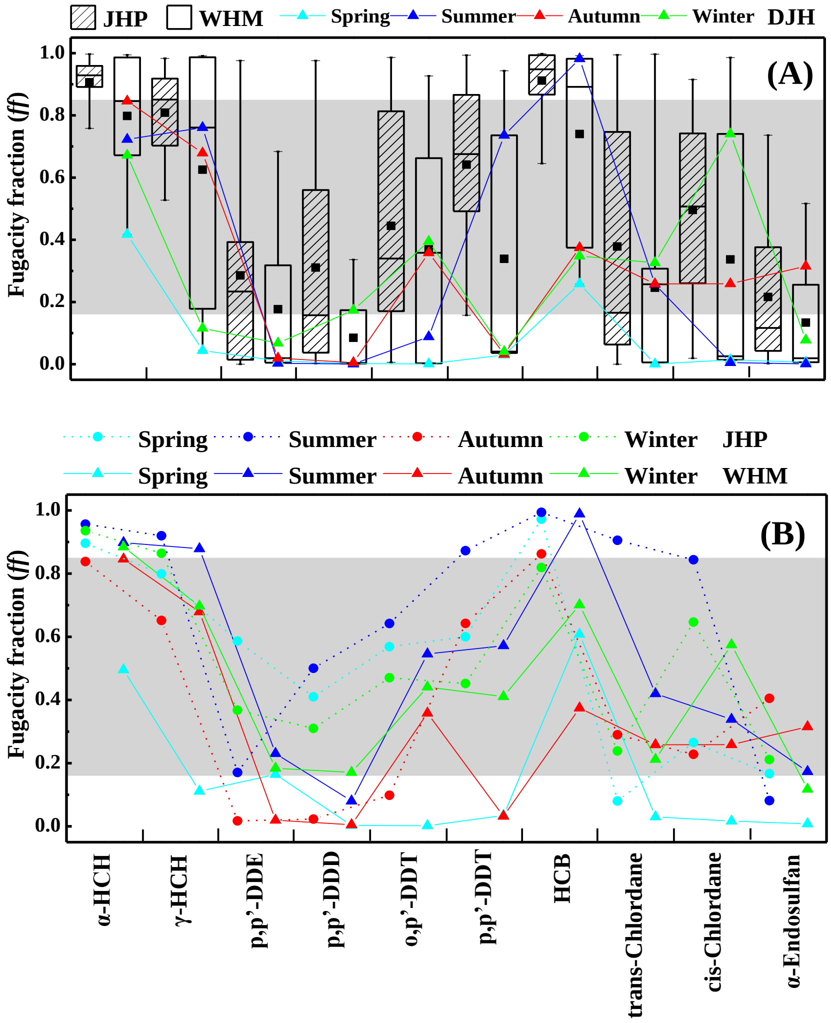


Fig.5. (a) Box-and-whisker plots showing the variation in air-soil fugacity fraction (*ff*) of individual OCPs for the combined sites representing the JHP (WU, WR, ZX, and DY) and WHM (XS, DJH, ZS), overlain by the seasonal variation in *ff* of individual OCPs from the DJH site. (b) Seasonal variation of the air-soil fugacity fraction for the combined sites representing the JHP and WHM.

Interestingly, low values of *ff* for α-Endosulfan were observed (Fig. 5A), which reflects a net trend of atmospheric deposition to the soil. The use of high-capacity spraying techniques means the efficiency of pesticide-spraying in Chinese agriculture is still only about 10% to 30%, and the majority of agrochemicals are dispersed into the atmosphere during the spraying process (Sun et al., 2009). Thus, the low *ff* values for α-Endosulfan at the JHP might be associated with farming activities, suggesting the inefficient pesticide-spraying method may be an important pathway to introduce current-use pesticides into the atmosphere. This is supported by the lowest *ff* values for α-Endosulfan in the JHP being recorded in the summer (Fig. 5B). Our results were consistent with the findings of studies in Mexico and Pakistan (Syed et al., 2013; Wong et al., 2010). However, the low *ff* values recorded in the WHM, in particular the DJH site, suggests that α-Endosulfan originates from an Endosulfan hotspot, which may act as the potential source, controlling the air-soil exchange in the area.

3.4.Impact of air mass transport

Influenced by the variability of EAM, the long-range transport pattern of air masses arriving at DJH exhibited significant seasonality. The results of the trajectory simulation illustrated that atmospheric transport and deposition of OCPs at the DJH site were greatly influenced by the southeast monsoon during summer and spring, whereas the northeast monsoon was the dominant influence in the autumn and winter. The backward trajectories of air masses to DJH during the sampling period are categorized in Fig. 6.

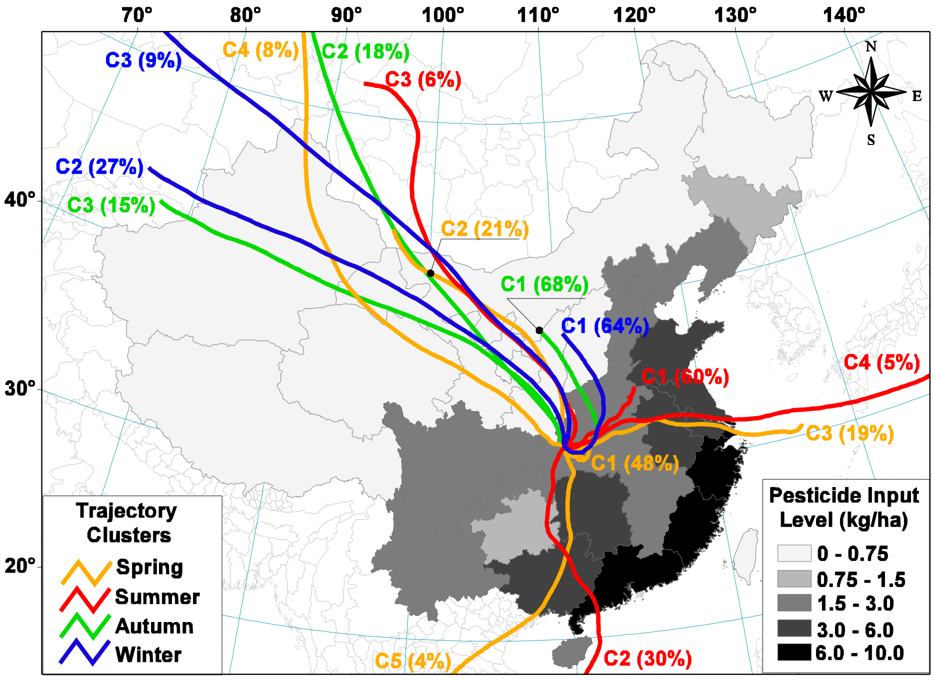


Fig.6. 5-day backward trajectory clusters plotted on a map of the distribution pesticide application in different areas of China in 1996 (Tieyu et al., 2005).

Under the influence of the southeast monsoon, some trajectories (C2) during the summer originated in the South China Sea, and subsequently passed through Southern China (Fig. 6). China is the only country that has reported the use of a paint mix using approximately 5% DDT in a marine anti-fouling paint, leading to an estimated release to the environment of 250 tons of DDT per annum (SEPA GEF Project., 2015). The importance of DDT-containing antifouling paint was highlighted in a study of the sediments of fishing harbors by Lin et al. (2009). Our summer sampling campaign completely overlapped the fishing suspension period in northern South China Sea, (July-August) (Wang et al., 2007). The use of DDT antifouling paints for maintenance purposes during the suspension period may result in high atmospheric concentrations of technical DDT along the coastal regions of China (Zhang et al., 2007). DJH exhibited similar technical DDT signatures, suggesting that DDTs transported by the EAM from Southern China. Similarly, Gong et al. (2010) observed that air mass transport from Southeastern China pathway may contribute to the elevated atmospheric DDTs concentrations in August of Lhasa due to the influence of EAM. Furthermore, the ratios of o,p'-DDT/p,p'-DDT in summer (1.42) and spring (1.51) were both higher than those in autumn (0.39) and winter (0.60) (Fig.4B). In summer, the flow patterns of C1 displayed a relative short-range transport from northeast, and these trajectories circulated through the middle southern region. In spring, the trajectories in clusters 1, 3 and 5 passed over the polluted areas, considered the most intensive region concerning the consumption of dicofol in China (Qiu et al., 2005). Importantly, the air-mass trajectories generally travelled over the regions with fewer potential contamination sources in autumn and winter, which is reflected in the seasonal fluctuations. This enforces that the levels of atmospheric DDTs at the DJH site, is most likely attributed to the transport of EAM, from the region of higher usage of technical DDT or/and DDT-containing products, particularly in the warmer months.

Atmospheric ESULPHs recorded the highest concentrations in summer, with the most frequent trajectory (C1) coming from the northeasterly airflow that circulated in the region of Hubei and Henan provinces, where higher Endosulfan usage had been observed (Jia et al., 2009). Therefore, this observation also supports a seasonal agricultural input of Endosulfan through the atmospheric transportation of the EAM. The abundance of α-Endosulfan relative to β-Endosulfan in these four seasons (summer: 6.91, autumn: 5.72 vs. spring: 9.21, winter 8.27) of the DJH site descend with the application of Endosulfan in the JHP (Fig.3D), which could also be the evidence of LRAT as Endosulfan has a characteristically high travel distance as a result of its volatility and long half-life in air (Meire et al., 2012).

Airflow is most frequently from a northerly direction during the winter and autumn seasons, with 68% of simulated trajectories in the autumn and 64% in the winter. Air masses originated from the northwest, passing through Inner Mongolia in 18% of autumn and 9% of winter simulations and from through the northern region of Xinjang in 15% of autumn and 27% of winter simulations. Previously, Jaward et al. (2005) observed an increasing trend in the level of airborne HCB from southwest to northeast China and suggested the primary emission during HCB production to be an important source in North China. In autumn, the trajectory clusters were very similar to those in winter. Consequently, considering the apparent lack of local HCB emission sources, the presence of HCB in the study area, might be a result of LRAT of HCB from the neighboring Northern Provinces.

4. Implications

This study is a pioneering investigation of atmospheric transport of OCPs from plain to mountain to understand the source-sink relationship of OCPs and roughly estimate the impact of the EAM. To be specific, this study has explained the level of contamination of OCPs in the atmospheres of the JHP and WHM. The DJH soils are likely to be a sink for OCPs, and JHP soils are acting as the emitter to contaminate atmosphere at certain monitoring stations. Based on backward trajectory analysis, and the absence of local potential sources, the seasonal fluctuation of atmospheric DDTs, HCB and Endosulfan at the DJH site are closely associated with the variation in the EAM and the LRAT of these compounds from neighboring areas. The shortest cluster (C1) was the most frequent in all seasons, and passed through the JHP before arriving at DJH, indicating that the JHP may be recognized as a potential source of these chemicals to the WHM.

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Conflicts of interest

The authors declare that they have no conflict of interests.

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Chapter 4: Dustfall

Polycyclic aromatic hydrocarbons (PAHs) in atmospheric dustfall from the industrial corridor in Hubei province, central China

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Polycyclic aromatic hydrocarbons (PAHs) in atmospheric dustfall from the industrial corridor in Hubei Province, Central China

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Abstract: Thirty atmospheric dustfall samples collected from an industrial corridor in Hubei Province, central China, were analyzed for 16 USEPA priority polycyclic aromatic hydrocarbons (PAHs) to investigate their concentrations, spatial distributions, sources, and health risks. Total PAH concentrations (ΣPAHs) ranged from 1.72 to 13.17 μg/g and averaged 4.91 μg/g. High molecular weight (4–5 rings) PAHs averaged 59.67 % of the ΣPAHs. Individual PAH concentrations were not significantly correlated with total organic carbon, possibly due to the semi-continuous inputs from anthropogenic sources. Source identification studies suggest that the PAHs were mainly from motor vehicles and biomass/coal combustion. The incremental lifetime cancer risks associated with exposure to PAHs in the dustfall ranged from 10^{-4} to 10^{-6}; these indicate potentially serious carcinogenic risks for exposed populations in the industrial corridor.

Keywords: Polycyclic aromatic hydrocarbons (PAHs), Dustfall, Industrial corridor, Source apportionment, Health risk assessment

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are neutral, nonpolar, organic compounds composed of two or more fused aromatic rings, and 16 PAHs have been placed on a priority control list by the US Environmental Protection Agency (US-EPA) because of their carcinogenic and mutagenic properties (Yang et al. 2013; Kwon and Choi 2014). PAHs in the environment mainly originate from anthropogenic activities, especially the burning of organic materials (e.g., fossil fuels, wood, and straw), many industrial processes (Peng et al. 2011), and motor vehicle emissions (Lee and Dong 2010) although smaller amounts are produced by forest fires and volcanic eruptions (Ravindra et al. 2008).

Polycyclic aromatic hydrocarbons are ubiquitous environmental contaminants, and they have been found in a variety of media, including, soils, sediments, and surface dust (Khairy and Lohmann 2013; Xing et al. 2011; Wang et al. 2011). Atmospheric processes are largely responsible for the transport and deposition of PAHs (Fang et al. 2004), and these aromatic hydrocarbons adhere to both atmospheric aerosols and dustfall. Indeed, dustfall has been regarded as an important carrier of PAHs (Lian et al. 2008; Wu et al. 2005), and the deposition of airborne particulate matter leads to the transfer of PAHs from the air to the earth’s surface. In urban and industrial areas, some toxic compounds carried by dustfall can be transferred to surface structures including buildings and streets, and this poses a threat to human health (Lian et al. 2008).

With the rapid development of industrialization and urbanization in China, the problems of environmental pollution caused by PAHs have become increasingly serious, and the high concentrations of these substances have serious implications for human health, ecological systems, and the environment (Yang et al. 2013; Xing et al. 2011; Peng et al. 2011). Hubei Province, located in central China, is an important base for traffic, agriculture, and industry. The area we studied is mainly composed of three small- to medium-scale industrial cities (Ezhou, Huangshi, and Daye) which form a metal-working corridor in the southeastern part of the province that exacerbates the problems associated with environmental pollution. Studies of PAHs in the industrial corridor will make it possible to evaluate the contributions of the heavy industries and transportation to the atmospheric burdens of PAHs. Furthermore, it is equally important to evaluate the human health risks associated with exposure to PAHs in the region. Therefore, the objectives of the present study were as follows: (a) to investigate the concentrations and distribution of 16 priority PAHs in atmospheric dustfall from the industrial corridor; (b) to determine the potential sources for the PAHs; and (c) to evaluate the potential cancer risks of PAHs using the incremental lifetime cancer risk approach.

2. Methodology

2.1.Sampling

The locations of the sampling stations for the study are shown in Fig. 1. Thirty atmospheric dustfall samples were collected from the famous industrial corridor of Hubei Province during May 2012. The dustfall samples were collected 1.2–1.5 m above the floor from various surfaces (shelves, window sills, etc.), using a brush and a dust pan on sunny, windless days. Samples were put into small sealable plastic bags and later air-dried in the laboratory. They were then processed with a 100-μm sieve to remove coarse debris and small stones.

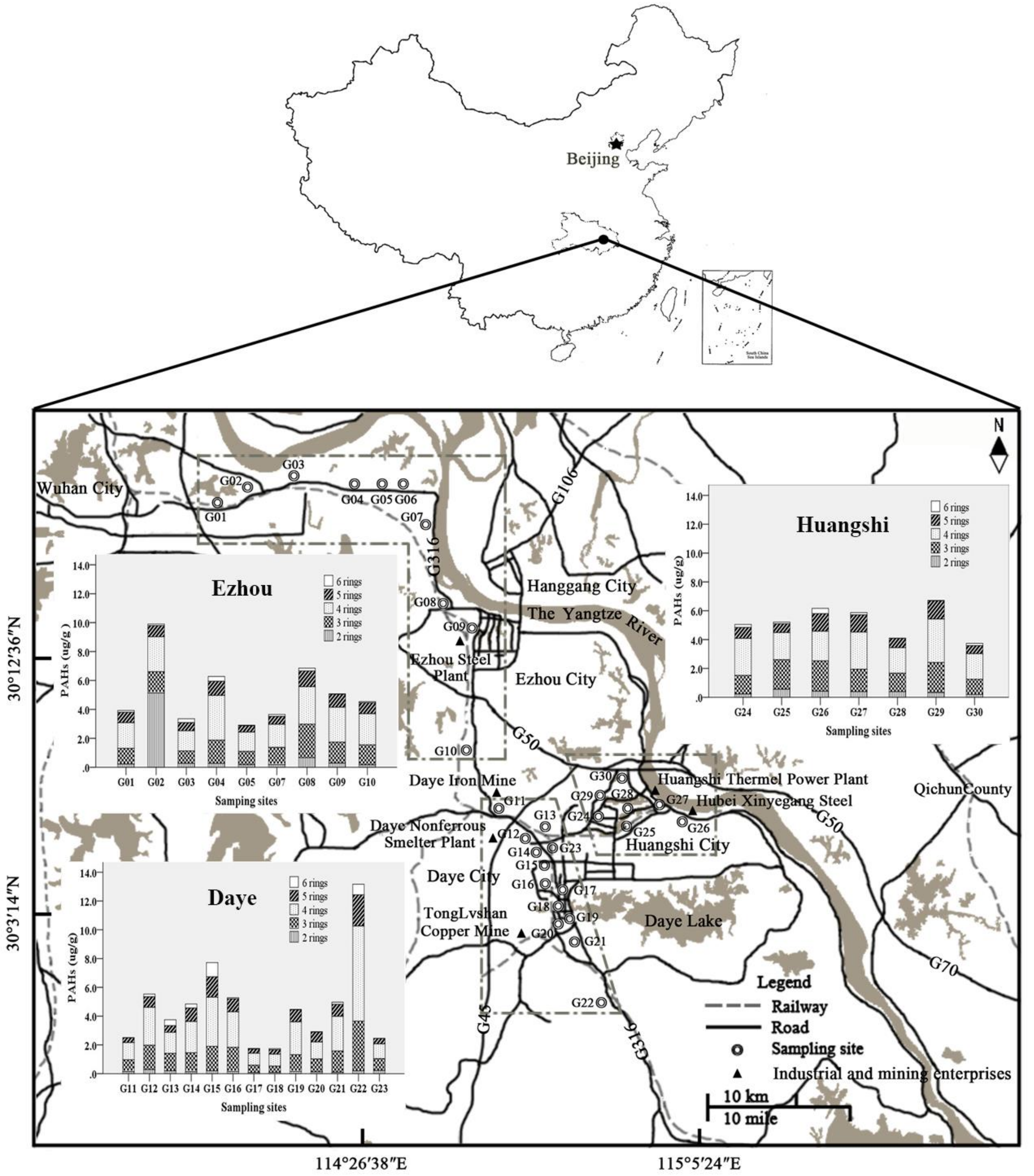

Fig. 1 sampling sites for the atmospheric dustfall samples

2.2.Analysis of PAHs

The compounds measured were 16 USEPA priority PAHs: naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IcdP), dibenzo[a,h]anthracene (DBA), and benzo[g,h,i]perylene (BghiP).

After sieving, 10 g of each soil sample was spiked with 5 μL (200 µg/mL) mixed-recovery surrogates (naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12 and perylene-d12), and the spiked sample was then extracted with dichloromethane (DCM) using soxhlet apparatus for 24 h. Elemental sulfur was removed by adding activated copper granules to the collection flasks. The sample extract was concentrated and the solvent exchanged with hexane and further reduced to 2–3 mL with the use of a rotary evaporator (Heidolph4000, Germany). A 1:2 (v/v) alumina/silica gel column (48-h extraction with DCM, then 180 and 240 °C muffle drying for 12 h, both deactivated 3 % with H_2O before use) was used to clean-up the extract; then the PAHs were eluted with 30 mL of DCM/hexane (2:3). The eluate was concentrated to 0.2 mL under a gentle nitrogen stream. Prior to analysis, a known quantity (1,000 ng) of hexamethylbenzene was added to the eluates as an internal standard.

PAHs were analyzed with the use of a gas chromatograph-mass spectrometer (GC–MS, 7890A/5975MSD, Agilent Technologies, Santa Clara, CA, USA) equipped with a DB-5 capillary column (30 m × 0.25 mm i.d × 0.25 µm film thickness). The instrument was operated using electron impact (EI) ionization at 70 Ev and in the selected ion monitoring (SIM) mode. The chromatographic conditions were as follows: injector temperature 270 °C and detector temperature 280 °C. The oven temperature program was kept at 60 °C for 5 min and increased to 290 °C at a rate of 5 °C/min and kept at 290 °C for 20 min. The high-purity He carrier gas was delivered at a constant flow rate of 1.0 mL/min.

2.3.Quality assurance and quality control

Procedural blanks, spiked blanks, and sample duplicates (analyzed at a rate of 20 % of the total samples) were analyzed to evaluate the precision of the analyses. The PAHs found in the field blanks were generally below the limits of detection (LOD), which were defined as the amount of an analyte that would generate a signal-to-noise ratio of 3:1. No target PAHs were detected in any of the procedural blanks. The variations in PAH concentrations in duplicate samples were <15 %. Minimum detection limits (MDLs) for the 16 PAHs were in the range of 0.27–0.78 ng/g dry weight. Representative average percentage recoveries (arithmetic mean ± SD) were 58 ± 6, 82 ± 9, 108 ± 10, 112 ± 13, and 118 ± 11 % for naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12, and perylene-d12, respectively.

2.4.Determination of total organic carbon

The samples were pretreated with 10 % HCl to remove carbonates. After each acid-pretreatment step, the residues were centrifuged and rinsed with deionized water. The retentates from the final pre-treatment step were dried in an oven at 50 °C for 6 h for total carbon analysis. A 5 mg subsample was placed into a tin capsule, which was folded and compressed with tweezers for CHN analysis (ELEMENTAR Vario EL Hanau, Germany). Samples were analyzed in duplicate, and the average percentages of total organic carbon (TOC) were calculated.

2.5.Risk assessment

Incremental lifetime cancer risks (ILCR) were calculated as a means of quantitatively evaluating the integrated lifetime risks of exposure to PAHs in atmospheric dustfall from the industrial corridor. The ILCRs for exposure by ingestion, dermal contact, and inhalation were calculated as probabilities from the following equations, which were adapted from the USEPA standard models (Peng et al. 2011; Chen and Liao 2006; USEPA 1991):

$$\mathrm{ILCRs_{Ingestion}} = \frac{\mathrm{CS}\times(\mathrm{CSF_{Igestion}}\times\sqrt[3]{(\mathrm{BW}/70)})\times\mathrm{IR_{Igestion}}\times\mathrm{EF}\times\mathrm{ED}}{\mathrm{BW}\times\mathrm{AT}\times10^{6}} \tag{1}$$

$$\mathrm{ILCRs_{Dermal}} = \frac{\mathrm{CS}\times(\mathrm{CSF_{Dermal}}\times\sqrt[3]{(\mathrm{BW}/70)})\times\mathrm{SA}\times\mathrm{AF}\times\mathrm{ABS}\times\mathrm{EF}\times\mathrm{ED}}{\mathrm{BW}\times\mathrm{AT}\times10^{6}} \tag{2}$$

$$\mathrm{ILCRs_{Inhalation}} = \frac{\mathrm{CS}\times(\mathrm{CSF_{Inhalation}}\times\sqrt[3]{(\mathrm{BW}/70)})\times\mathrm{IR_{Inhalation}}\times\mathrm{EF}\times\mathrm{ED}}{\mathrm{BW}\times\mathrm{AT}\times\mathrm{PEF}} \tag{3}$$

In these equations, CS is the sum of BaP equivalent concentration (BaPeq in µg/kg), BaPeq is the product of the concentration of individual PAH compound and its corresponding toxic equivalence factor (TEF) (Table 1); CSF is the carcinogenic slope factor (1/(mg/kg/d)); BW is the average body weight (kg); AT is the average life span (d); EF is the exposure frequency (d/yr); ED is the exposure duration (yr); $\mathrm{IR_{ingestion}}$ is the ingestion rate of soil (mg/d); $\mathrm{IR_{Inhalation}}$ is the inhalation rate (m^3/d); SA is the surface area of the skin that contacts the soil (cm^2/d); AF is the skin adherence factor for soil (mg/cm^2); ABS is the dermal absorption factor (chemical specific); and PEF is the particle emission factor (m^3/kg).

Carcinogenic slope factors (SCF) based on the cancer-causing ability of BaP were parameterized as 7.3, 25 and 3.85 (1/(mg/kg/d)) for ingestion, dermal contact and inhalation, respectively (Peng et al. 2011). Cancer risks were estimated for three age groups: childhood (0−10 yr), adolescence (11−18 yr), and adulthood (19−70 yr). Moreover, the cancer risks for males and females were calculated separately. Details of the values of the exposure parameters used to derive the ILCRs are shown in Table 2. Total risks were estimated as the sum of the individual risks for the three exposure routes.

Table 1 PAHs concentrations (µg/g) in atmospheric dustfall from the industrial corridor of Hubei Province.

Compound	Abbreviation	Aromatic rings	TEF	Minimum	Maximum	Mean	Median	Standard deviation
Naphthalene	Nap	2	0.001	0.07	5.14	0.41	0.21	0.90
Acenaphthylene	Acy	3	0.001	0.02	0.52	0.09	0.08	0.09
Acenaphthene	Ace	3	0.001	0.01	0.15	0.04	0.03	0.03
Fluorene	Flu	3	0.001	0.04	0.32	0.14	0.13	0.07
Phenanthrene	Phe	3	0.001	0.32	2.44	1.03	0.97	0.44
Anthracene	Ant	3	0.01	0.02	0.17	0.08	0.07	0.04
Fluoranthene	Fla	4	0.001	0.35	3.11	1.04	0.99	0.53
Pyrene	Pyr	4	0.001	0.02	2.20	0.64	0.57	0.39
Benzo[a]anthracene	BaA	4	0.1	0.04	0.65	0.21	0.20	0.12
Chrysene	Chr	4	0.01	0.09	0.65	0.25	0.22	0.14
Benzo[b]fluoranthene	BbF	5	0.1	0.08	0.86	0.31	0.29	0.18
Benzo[k]fluoranthene	BkF	5	0.1	0.06	0.58	0.20	0.19	0.10
Benzo[a]pyrene	BaP	5	1	0.08	0.69	0.26	0.24	0.13
Indeno[1,2,3-cd]pyrene	IcdP	6	0.1	0.01	0.53	0.09	0.04	0.12
Dibenzo[a,h]anthrancene	DBA	5	1	N.D. [a]	0.17	0.02	0.01	0.03
Benzo[g,h,i]perylene	BghiP	6	0.01	N.D.	0.49	0.09	0.05	0.13
	LMW PAHs[b]			0.52	6.60	1.80	1.54	1.14
	HMW PAHs[c]			1.00	8.78	2.93	3.01	1.47
	ΣPAHs[d]			1.72	13.17	4.91	4.69	2.41

[a]N.D. stands for not detected; [b]Low molecular weight 2-3 ring PAHs; [c]High molecular weight 4-5 ring PAHs; [d]Total concentrations of 16 individual PAHs

Table 2 Parameters used for the estimation of the incremental lifetime cancer risks (ILCRs).

Exposure parameters	Unit	Childhood		Adolescence		Adulthood		References
		Male	Female	Male	Female	Male	Female	
Body weight (BW)[a]	kg	14.3	13.6	48.1	45.4	62.8	54.7	MHC, 2007
Ingestion rate ($IR_{ingestion}$)	mg/d	200	200	100	100	100	100	USDOE,
Exposure frequency (EF)	d/yr	350	350	350	350	350	350	USDOE,
Exposure duration (ED)	yr	6	6	14	14	30	30	Wang, 2007
Average life span (AT)	d	LT×365	LT×365	LT×365	LT×365	LT×365	LT×365	USDOE,
Lifetime (LT)	yr	72	72	72	72	72	72	WHO,2006
Surface area (SA)	cm^2/d	2800	2800	2800	2800	5700	5700	USDOE,
Dermal surface factor (AF)	mg/cm	0.2	0.2	0.2	0.2	0.07	0.07	USDOE,
Dermal absorption factor	unitles	0.13	0.13	0.13	0.13	0.13	0.13	USEPA,
Inhalation rate ($IR_{Inhalation}$)	m^3/d	10.9	10.9	17.7	17.7	17.5	17.5	Wang, 2007
Particle emission factor	m^3/kg	1.36×10	1.36×10	1.36×10	1.36×10	1.36×10	1.36×10	USDOE,

[a] Values based on the 2002 National nutrition and health survey.

2.6.Statistical analysis

Correlation analyses, principal component analyses (PCA), and other statistical procedures were applied to the geochemical data using SPSS 18.0 and Origin 8.0. The correlation analyses were used investigate relationships among individual PAHs and between the PAHs and TOC. The PCA analyses were used to identify presumptive sources for the PAHs.

3. Results and discussion

3.1.Concentrations of PAHs

The statistical data for the individual PAHs and total PAHs in atmospheric dustfall from the industrial corridor are summarized in Table 1. The total concentrations of 16 individual PAHs (ΣPAHs) exhibited a rather moderate level of variability, ranging over roughly one order-of-magnitude from 1.72 (at G05) to 13.17 ug/g (at G22) with an arithmetic mean of 4.91 μg/g. The mean concentrations (μg/g) of individual PAHs increased in the following order: DBA (0.02) < Ace (0.04) < Ant (0.08) < IcdP (0.09) < Acy (0.09) < BghiP (0.09) < Flu (0.14) < BkF (0.20) < BaA (0.21) < Chr (0.25) < BaP (0.26) < BbF (0.31) < Nap (0.41) < Pyr (0.64) < Phe (1.03) < Fla (1.04). The three most abundant PAHs, Fla, Phe, and Pyr, accounted for 21.18%, 20.98% and 13.03% of the ΣPAHs, respectively, on average. With reference to the number of aromatic rings, 2-, 3-, 4-, 5- and 6-ring PAHs contributed averages of 8.27%, 28.30%, 43.62%, 16.10% and 3.70% to the ΣPAHs, respectively.

The concentrations of low-molecular weight PAHs (LMW PAHs: those with two or three aromatic rings) in the dustfall samples varied from 0.52 to 6.60 μg/g and had a mean of 1.80 μg/g. In comparison, the concentrations of high-molecular weight PAHs (HMW PAHs: those with four or five aromatic rings) varied from 1.00 to 8.78 μg/g with a mean of 2.93 μg/g. In general, the HMW PAHs made greater contributions to the total PAH concentrations than the LMW PAHs; indeed, the HMW PAHs contributed an average of 59.67% to the ΣPAHs. The LMW PAHs are more volatile than the HMW PAHs (Agarwal et al. 2009), and losses from the particles may have decreased the LMW PAH concentrations in the dustfall samples. In addition, the HMW PAHs have more emission sources compared with the LMW PAHs; these include domestic heating, industrial emissions and agriculture-related activities (Xing et al. 2011). Therefore, our observations concerning the relative abundances of LMW and HMW PAHs may be explained by the differences between the two groups in terms of their physicochemical properties and the emission sources.

3.2.Spatial distributions

To investigate the patterns in the spatial distributions of PAHs in the dustfall samples, the study area was separated into three regions: Ezhou, Daye and Huangshi. The sampling sites G11 to G15 and G23, which are actually in the city of Huangshi, were assigned to Daye because they located along the No. 316 national highway. This highway (shown in Fig. 1) is an important transportation route, and it passes through the central urban regions of Ezhou and Daye.

The mean concentrations of ΣPAHs in Ezhou were similar to those in Daye, and these two regions both had lower PAH concentrations than Huangshi. Compared with Huangshi, stronger gradients in PAH concentrations were observed in the dustfall samples from Daye and Ezhou. The strengths of the gradients are manifest in the coefficients of variation for the PAHs, which followed the order Daye (65.36%) > Ezhou (46.08%) > Huangshi (20.59%). Industrial and vehicle emissions increase the concentrations of ΣPAHs in urban surface dust (Wang et al. 2011), and therefore, the heavy traffic in Ezhou and Daye presumably contributed to their greater variability in PAHs.

The levels of PAHs in atmospheric dustfall varied greatly among the different sampling sites in the three regions. As shown in Fig. 1. The highest concentration of ΣPAHs was measured at G20 in Daye City. That site is located in an industrial area surrounded by a small smelter and an ore dressing plant where the high ΣPAHs concentrations presumably combined with PAHs from industrial releases and motor vehicle emissions. In contrast to the essentially uncontrolled emissions from these sources, a large factory in the region has established a systematic program for controlling and monitoring production activities. The sites near this large factory (G09, G11, G12 and G20) did not exhibit the same high levels of PAHs seen at G20.

3.3.Correlations among individual PAHs and between PAHs and TOC

Correlations among the individual PAHs were calculated and examined as a means of assessing whether specific compounds were likely to have originated from the same sources (Yang et al. 2012). A matrix of correlation coefficients among the individual PAHs (Table 3) showed that most of the compounds, especially the LMW PAHs, were significantly positively correlated with one another. In contrast, some of the HMW PAHs, including IcdP, DBA and BghiP, were not significant correlated with these compounds or with other members of the HMW group. This is an indication that these two groups of PAHs originated from the different sources. The vapor pressures of semi-volatile organic compounds, including organochlorine pesticides (OCPs) and PAHs, are critical determinants of their vapor-particle partitioning. This means that vapor pressure will affect the propensity for these compounds to be mobilized by long-range atmospheric transport and eventually to be transferred to soils, both directly and indirectly (Agarwal et al. 2009). As LMW PAHs exhibit higher vapor pressures and hence greater atmospheric mobility than the heavier compounds, they are more easily distributed by atmospheric transportation processes (Chung et al. 2007).

Table 3 Correlation coefficient matrix for individual PAHs and total organic carbon (TOC).

PAH	Nap	Acy	Ace	Flu	Phe	Ant	Fla	Pyr	BaA	Chr	BbF	BkF	BaP	IcdP	DBA	Bghi	LMW	HMW	ΣPAH
Nap	1																		
Acy	0.35	1																	
Ace	0.75*	0.62*	1																
Flu	0.80*	0.66*	0.91*	1															
Phe	0.52*	0.67*	0.67*	0.79*	1														
Ant	0.72*	0.69*	0.88*	0.93*	0.66*	1													
Fla	0.38*	0.71*	0.55*	0.65*	0.91*	0.54*	1												
Pyr	0.29	0.58*	0.47*	0.54*	0.79*	0.45*	0.90*	1											
BaA	0.50*	0.75*	0.73*	0.77*	0.68*	0.86*	0.69*	0.64*	1										
Chr	0.47*	0.35	0.58*	0.49*	0.29	0.56*	0.31	0.35	0.49*	1									
BbF	0.27	0.81*	0.49*	0.58*	0.83*	0.57*	0.86*	0.79*	0.72*	0.33	1								
BkF	0.49*	0.66*	0.59*	0.61*	0.55*	0.64*	0.64*	0.50*	0.72*	0.58*	0.58*	1							
BaP	0.38*	0.79*	0.59*	0.65*	0.75*	0.69*	0.83*	0.74*	0.86*	0.32	0.84*	0.79*	1						
IcdP	-0.04	0.18	-0.02	0.12	0.43*	0.08	0.47*	0.39*	0.19	-0.05	0.44*	0.27	0.34	1					
DBA	0.10	0.52*	0.19	0.27	0.47*	0.31	0.51*	0.39*	0.46*	0.09	0.62*	0.43*	0.55*	0.58*	1				
BghiP	0.20	0.01	0.15	0.23	0.49*	0.11	0.42*	0.45*	0.23	0.11	0.31	0.30	0.31	0.55*	0.43*	1			
LMW	0.72*	0.72*	0.80*	0.91*	0.91*	0.78*	0.83*	0.72*	0.75*	0.44*	0.73*	0.64*	0.73*	0.23	0.44*	0.41*	1		
HMW	0.47*	0.71*	0.63*	0.71*	0.86*	0.65*	0.94*	0.91*	0.79*	0.47*	0.88*	0.71*	0.89*	0.41*	0.49*	0.43*	0.83**	1	
ΣPAHs	0.61*	0.73*	0.71*	0.82*	0.91*	0.72*	0.92*	0.84*	0.81*	0.45*	0.83*	0.71*	0.85*	0.34	0.51*	0.47*	0.95**	0.94**	1
TOC	0.41*	0.13	0.31	0.26	0.20	0.21	0.07	-0.11	0.05	0.23	0.11	0.19	0.04	-0.26	-0.25	-0.24	0.20	0.08	0.12

*Correlation is significant at the 0.05 level (2-tailed); **Correlation is significant at the 0.01 level (2-tailed)

TOC has been shown to be important for the sorption, sequestration, and fate of PAHs (Jiang et al. 2009; Agarwal et al. 2009). The TOC concentrations in our study varied between 1.97% and 14.77%, with a mean value of 5.64%. As shown in Table 3, no significant correlations were found between the individual PAHs and TOC, except for a relatively weak correlation (correlation coefficient, r = 0.41) between TOC and Nap. Some researchers have previously reported that no significant correlations were observed between TOC and PAHs in soil and dustfall samples (Wang et al. 2013; Jiang et al. 2009; Zhang et al. 2006; Wu et al. 2005). The lack of correlation between TOC and PAHs might be a result of non-steady state partitioning (Wang et al. 2013; Jiang et al. 2009); that is, a semi-continuous input of fresh contaminants would prevent sorption-desorption processes from reaching a steady-state (Katsoyiannis 2006). In summary, the lack of correlations in our study suggests that the dustfall samplers were greatly affected by the inputs of anthropogenic PAHs, especially those from traffic emissions and biomass/coal combustion, and that steady-state partitioning was not reached.

3.4.Source identification

We used compositional pattern analysis, molecular composition analysis, and principal component analysis to identify the possible source for PAHs in atmospheric dustfall of the study area. The identification of likely sources for PAHs is important not only for understanding the patterns in the data from this study but also for developing scenarios of what might be expected as emissions change in the future.

3.4.1. Composition pattern analysis

Two of the main anthropogenic sources of PAHs are combustion processes and the incomplete combustion of petroleum products (Xing et al. 2011). Of the PAHs released by combustion, LMW PAHs are produced primarily at low- to moderate temperatures while HMW PAHs are generated at higher temperatures (Wang et al. 2006). Therefore, large relative abundances of LHM PAHs indicate that more of the PAHs originated from petrogenic sources while in contrast, high relative abundances of HMW PAHs can be explained by greater impacts from pyrogenic sources. In our study, the average LHM/HMW PAH ratios at all sites (except G02 and G25) were above unity, suggesting that combustion was a greater influence on the PAH contaminants than petrogenic emissions.

3.4.2. Molecular composition analysis

Molecular indices based on ratios of individual PAH congeners have been used to discriminate between petrogenic and pyrolytic sources. In particular, the ratios of Ant/(Ant+Phe), Fla/(Fla+Pyr), IcdP/(IcdP+BghiP) and BaA/(BaA+Chr) have been used for this purpose (Kwon and Choi 2013; Yang et al. 2012; Xing et al. 2011; Wang et al. 2011). Scatterplots of the ratios of selected PAH congeners were drawn based on the principle of molecular indices (Xing et al. 2011; Wang et al. 2011), and these PAH congener-pair relationships were employed to evaluate the PAH sources.

The scatterplot for Ant/(Ant+Phe) and Fla/(Fla+Pyr) (Fig 2A) shows that the data for twenty seven of the sampling sites (all except G01, G09 an G20) were influenced by petroleum and coal/biomass combustion, and this finding suggests that the PAHs mainly originated from motor vehicular emissions and biomass/coal combustion. This result is in agreement with the conclusions from studies in Guangzhou and Shanghai that vehicular emissions and biomass/coal combustion were the main contributors to PAHs in urban surface dusts (Wang et al. 2011; Liu et al. 2007). The ratios of BaA/(BaA+Chr) in our study ranged from 0.22−0.65 (Fig. 2B), suggesting that the PAHs were derived from the combustion of petroleum and biomass. However, the ratios of IcdP/(IcdP+BghiP) were concentrated in two areas of the plots, and this is consistent with mixtures of petrochemicals and coal/biomass burning products (Fig. 2B)

From the patterns in the congener-pair ratios, we can conclude that the PAHs in the dustfall were not dominated by a single source. Local human activities undoubtedly are the greatest influence on pollutant concentrations and overall a major influence on the environmental chemistry of the study area. For instance, several large factories, including the Ezhou Steel Plant and Daye Nonferrous Smelter Plant, consume large amounts of energy and release substantial levels of pollutants. In addition, the No. 316 national highway, as the lifeline of the industrial corridor, bears a heavy burden of transportation. Recent statistics reported by National Bureau of Statistics of China show that coal remains the predominant energy source, accounting for ~76.7 percent of China's energy consumption (NBSC, 2009). In any case, the sources of PAHs clearly are complex and their concentrations are affected by many factors, including industrial activity, transportation, day-to-day human routines, and so on.

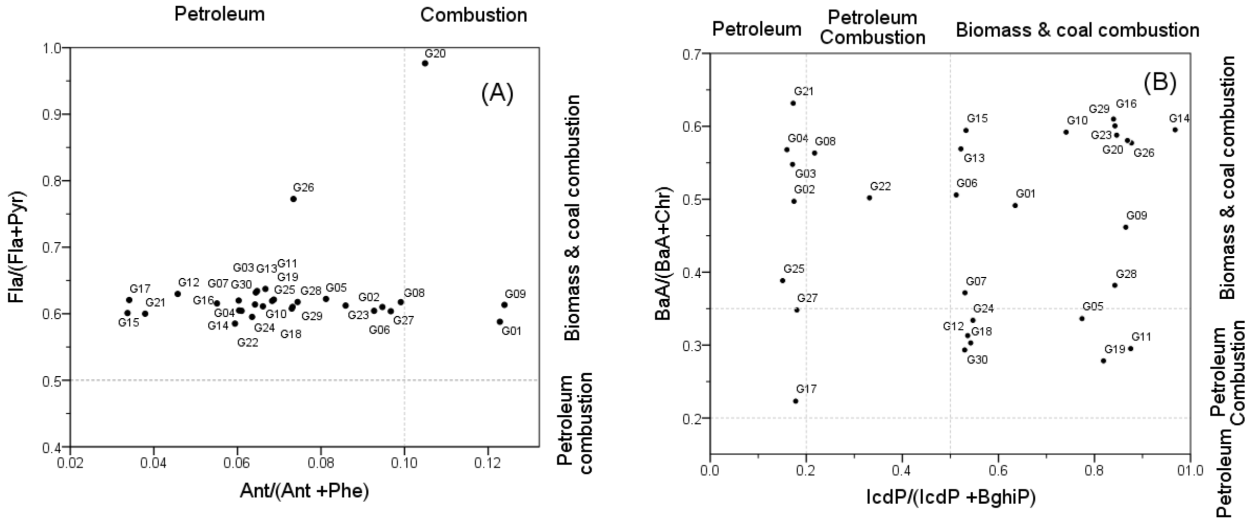

Fig. 2. Scatterplot of molecular indices used to identify PAH sources: (A) Fla/(Fla+Pyr) versus Ant(Ant + Phe) and (B) BaA/(BaA + Chr) versus Icdp(Icdp + BghiP).

3.4.3. Principal component analysis

Three principal components (PC1, PC2 and PC3) with the eigenvalues > 1 were extracted, and they collectively accounted for the majority (79.46%) of the total variance in the ΣPAH concentration data (Table 4). PC1 explained 45.96% of the total variance, and it had strong loadings of Acy, Phe, Fla, Pyr, BaA, BbF, BkF, BaP and BghiP and moderate loadings of Chr. Of these Fla, Pyr, BaA, BaP and Chr are the typical markers for coal combustion (Larsen and Baker 2003; Simcik et al. 1999) while BkF and BbF are components of fossil fuels and thus associated with their combustion products (Kavouras et al. 2001). BaA and Chr often originate from the combustion of both diesel fuels and natural gas (Khalili et al. 1995), and BghiP is associated with traffic emission (Fraser et al. 1997). Therefore, PC1 apparently represents mixed sources of petroleum and coal combustion.

PC2 accounted for 22.98% of the total variance in the data: it was mainly loaded with Ace, Flu and Ant, and had moderate loadings of Nap. Two of these PAHs, Flu and Ant, have been used as the indicators of emissions from coke ovens (Yunker et al. 2002; Simcik et al. 1999). Furthermore, all four of these compounds are LMW PAHs, and so they presumably have significant contributions from low-temperature pyrogenic processes (Yang et al. 2012; Jenkins et al. 1996). Nap is one of the LMW PAHs that accounted for the majority of the PAH mass in a study conducted in Chicago, USA of emissions from coke ovens, a highway tunnel, and gasoline engines (Khalili et al. 1995). Thus, PC2 apparently represents low-temperature combustion sources.

The last principal component extracted, PC3, accounted for 10.51% of the total variance, and it had high loadings of IcdP and DBA. This factor probably represents road traffic because these two PAHs previously have been linked to motor vehicle emissions (Simcik et al. 1999; Fraser et al. 1997).

Table 4 Principal components for the individual PAHs (factor loadings greater than 0.5 are shown in bold).

Variable	Principal Component		
	PC1	PC2	PC3
Nap	-0.07	0.42	-0.05
Acy	**0.81**	0.30	0.08
Ace	0.25	**0.88**	0.05
Flu	0.38	**0.84**	0.16
Phe	**0.79**	0.43	0.27
Ant	0.43	**0.87**	0.07
Fla	**0.94**	0.17	0.19
Pyr	**0.96**	0.09	0.01
BaA	**0.78**	0.57	-0.05
Chr	**0.56**	0.40	-0.41
BbF	**0.84**	0.17	0.23
BkF	**0.79**	0.41	0.10
BaP	**0.87**	0.33	0.22
IcdP	0.48	-0.26	**0.73**
DBA	0.13	0.26	**0.82**
BghiP	**0.79**	**-0.17**	0.17
Eigenvalue	7.35	3.68	1.68
% of Variance	45.96	22.98	10.51
Cumulative %	45.96	68.95	79.46
Probable sources	Diesel and coal combustion	Low temperature combustion	Traffic emission

3.5.Health risk assessments

We calculated the incremental life cancer risks (ILCRs) associated with the contaminated dustfall with the aim of estimating the potential health risks to humans caused by PAH exposure through ingestion, dermal contact and inhalation. The ILCRs calculated for the three exposures routes and the total ILCRs for each of the sampling sites are presented in Fig. 3. The cancer risks for PAHs for the different routes of exposure decreased in the following order: dermal contact > ingestion > inhalation (Fig. 3A). In fact, the cancer risks calculated for the inhalation of PAHs on resuspended particles ranged from 10^{-9} to 10^{-11}, approximately 10^{-3} to 10^{-6} times lower than those for ingestion or dermal contact. Therefore, the cancer risks calculated for the inhalation of resuspended particles contaminated with PAHs would be vanishingly small in comparison with those for the other exposure routes. The differences between the ILCRs stratified by gender for persons of the same age group were not significant. On the other hand, the ILCRs for children or adulthood were higher than for adolescence, suggesting that adolescents have the lowest health risks of three age groups. Hu et al. (2013) similarly observed that the cancer risk for youths exposed to OCP contaminated soils were less than for children or adults.

In terms of regulatory concerns, minimal risks are indicated by an ILCR of 10^{-6} or less while an ILCR between 10^{-6} and 10^{-4} signifies potential human health risks; higher risks have been connected to ILCRs larger than 10^{-4} (Chen and Liao 2006). In this study, the total ILCRs for the three age groups fluctuated from 10^{-6} to 10^{-4}, indicating a potential carcinogenic risk for the residents who are exposed to the atmospheric dustfall, especially by contact. As shown in Fig. 3B, the total ILCRs for the regions with the high PAH concentrations tend to have more serious cancer risks. Nonetheless, it is important to point out that the sampling site (G02) with the second-highest ΣPAH concentration did not have particularly high total ILCRs; this can be explained by the high proportion of LMW PAHs at the site, which tend to be less harmful. As to the toxicity of individual PAHs (BaPeq), BaP accounted for the largest fraction of the total PAH BaPeq (range = 54.14% to 78.08%; mean = 71.60%), and therefore BaP made the greatest contribution to the overall ILCRs. BaP has been used a tracer for vehicular emissions (Khairy and Lohmann 2013), and therefore, one can infer that PAHs emitted from motor vehicles play a significant role relative to cancer risks. This finding has important implications the formulation of effective environmental health protection policies.

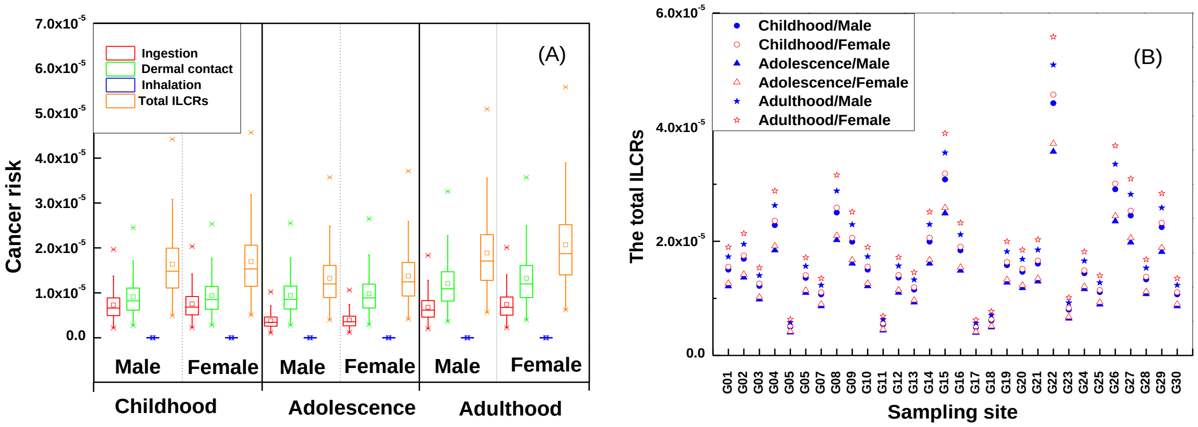

Fig. 3. Incremental lifetime cancer risks (ILCRs) calculated for atmospheric dustfall: (A) ILCRs for three exposures routes and (B) total ILCRs stratified by age group and gender at the sampling sites.

4. Summary and Conclusions

Sixteen priority PAHs in atmospheric dustfall from the industrial corridor of Hubei Province were analyzed to investigate their spatial distributions, possible sources and health risks. The total concentrations of 16 PAHs ranged from 1.72 to 13.17 μg/g with a mean of 4.91 μg/g. The highest concentrations of PAHs were found in an industrial area surrounded by small smelter and ore dressing plant. However, other sites near the factory did not have especially high ΣPAH concentrations. The dustfall samples showed a common pattern in terms of PAH composition; that is, the HMW PAHs averaged 59.67% of the ΣPAHs and thus heavier compounds were more abundant than the LMW PAHs.

Source identification studies indicated that motor vehicle emissions and biomass/coal combustion were the major sources for PAHs in dustfall from the industrial corridor. The individual PAH concentrations were not significantly correlated with TOC, and therefore TOC cannot be used as an indicator of the levels of PAHs in the industrial corridor. Incremental life cancer risks (ILCRs) were calculated to evaluate the potential risks associated with exposure PAHs in dustfall from the area. The ILCRs fluctuated within the range of 10^{-6} to 10^{-4}, and this is strong evidence that there are potentially serious carcinogenic risks for exposed populations in the industrial corridor.

The ILCRs indicate that the exposure to PAHs from the inhalation of contaminated particles presented a much smaller risk than either ingestion of the PAHs or exposure through dermal contact, which had the highest ILCRs. It should be noted, however, that the ILCRs were calculated for only for the PAHs in dustfall, and the risks from exposure to the vapor-phase fractions of the PAHs were not considered. The first implication of this limitation is that the combined cancer risks from exposure to the particle-bound and vapor-phase PAHs will be higher than those calculated here, and the second is that the relative risks of the three routes of exposure may change. The partitioning of PAHs between the particulate- and vapor phases also will vary with temperature (Lang et al. 1999), and so in addition to seasonal changes in PAH sources and sinks, weather and climate also will play a role in exposure and the effects of PAHs on human health.

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Chapter 5: Dissolved phase, suspended particle matter, and surface sediment samples

Contamination characteristics of organochlorine pesticides in multimatrix sampling of the Hanjiang river basin, southeast China

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Contamination Characteristics of Organochlorine Pesticides in Multimatrix Sampling of the Hanjiang River Basin, Southeast China

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Highlights:

- Dissolved phase, SPM, and surface sediment in Hanjiang River Basin were analyzed for OCPs.
- K_d was used to determine the partition between SPM and water on horizontal profile.
- Transport was predicted based on fugacity model.

Abstract: Hanjiang River, the second largest river in Guangdong Province, Southern China, is the primary source of drinking water for the cities of Chaozhou and Shantou. Our previous studies indicated that soils from an upstream catchment area of the Hanjiang River are moderately contaminated with organochlorine pesticides (OCPs), which can easily enter the river system via soil runoff. Therefore, OCPs, especially downstream drinking water sources, may pose harmful health and environmental risks. On the basis of this hypothesis, we measured the OCP concentrations in dissolved phase (DP), suspended particle matter (SPM), and surface sediment (SS) samples collected along the Hanjiang River Basin in Fujian and Guangdong provinces. OCP residue levels were quantified through electron capture detector gas chromatography to identify the OCP sources and deposits. The concentration ranges of OCPs in DP, SPM, and SS, respectively, were 2.11–12.04 (ng/L), 6.60–64.77 (ng/g), and 0.60–4.71 (ng/g) for hexachlorocyclohexanes (HCHs), and 2.49–4.77 (ng/L), 6.75–80.19 (ng/g), and 0.89–252.27 (ng/g) for dichloro-diphenyl-trichloroethanes (DDTs). Results revealed that DDTs represent an ecotoxicological risk to the Hanjiang River Basin, as indicated by international sediment guidelines. This study serves as a basis for the future management of OCP concentrations in the Hanjiang River Basin, and exemplifies a pattern of OCP movement (like OCP partition among multimedia) from upstream to downstream. This pattern may be observed in similar rivers in China.

Keywords: Hanjiang River Basin; Organochlorine pesticide; Partition coefficient; Sediment–water exchange; Risk assessment

1. Introduction

Organochlorine pesticides (OCPs) are typical persistent organic pollutants (POPs), which are internationally controlled by the 2004 Stockholm Convention. OCPs have attracted global attention because of their resistance to environmental degradation, toxicity, and potential to bioaccumulation (UNEP, 2008). On the basis of these properties, OCPs were banned because of their adverse human health effects, including cancer, reproductive defects, endocrine, and immunological toxicities (Mrema et al., 2013). Because of their high pesticide efficiency and low cost, OCPs were widely used in agriculture, industry, and for disease prevention. Similar to dichloro-diphenyl-trichloroethanes (DDTs), hexachlorocyclohexanes (HCHs) were commonly used OCPs in China. Approximately 4.5 million tons of technical HCHs and 0.27 million tons of DDTs were produced in China after 1952 until being banned in 1983.

OCPs can enter the aquatic environment through different pathways, such as industrial discharge, runoff from agriculture farmland, and deposition (dry or wet). Given their relatively high lipophilicity, as reflected by elevated n-octanol/water partition coefficients (log KOW values: 3.7–6.95), and low water solubility (0.096–17 ppm) (Willett et al., 1998; Shen and Wania, 2005), OCPs can be easily adsorbed on to suspended particulate matter (SPM) as sediments (Montuori et al., 2014). SPM can then precipitate in sediments and eventually lower the OCP concentrations in water. Under favorable conditions (e.g., turbulence from ship movement or by flooding), sediments can be resuspended, release previously adsorbed OCPs back into the water phase, and reinitiate another cycle of environmental contamination (Feng et al., 2011; Zhou et al., 2014) Otherwise, when OCPs enter water, they can transfer into food chain by accumulating in aquatic organisms. Subsequently, OCPs may reach to humans by consuming contaminated water and marine food (Zhou et al., 2008). Increased research has focused on OCP pollution in Chinese estuaries and rivers (Luo et al., 2004; Tang et al., 2008; Wang et al., 2010; Wei et al., 2014)

The Hanjiang River is the second largest river in Guangdong Province, with a basin area of 30,112 km2, holding approximately 200 million inhabitants. This river is also the mother river for Chaoshan region, consisting of the cities of Chaozhou (an old town with a large historic and cultural value), Shantou (is a port on the South China Sea, and one of China’s special economic zones), and Jieyang. There is scant research on the environmental impact of OCPs on this river and its important basin.

Our earlier preliminary study on soil OCP pollution (sampling conducted in 2009) in Fujian Province revealed that Shanghang and Yongding counties (along the Hanjiang River) suffered from OCP pollution issues. Because OCPs can dissociate (by desorption) from OCP-contaminated soil to mobile OCPs in the soil–water interface (Hu et al., 2010), it is possible that HCHs and DDTs enter the Hanjiang River system (by soil runoff). This possibility causes public health concerns, because the Hanjiang River is the only source providing drinking water for 139 million inhabitants (in 2010) of the

Chaoshan region.

In this study, we examined the hypothesis that upstream soil pollution can affect downstream water and sediments following runoff and ultimately threaten public as well as environmental health in this region. To test this possibility, we quantified the distribution of OCPs in the dissolved phase (DP), suspended particle matter (SPM), and surface sediment (SS) in samples from the Hanjiang River Basin. We then analyzed the relationship among these different media, considering upstream and downstream locations, and identified possible OCP sources. Finally, toxicological risks are assessed with respect to human health and the nontarget ecological receptors inhabiting this study area.

2. Materials and methods

2.1.Chemicals and reagents

All chemical standards, HCHs (α-HCH, β-HCH, γ-HCH, and δ-HCH; purity ≥ 98.9%), DDTs (p,p'-DDE, p,p'-DDD, o,p'-DDT, and p,p'-DDT; purity ≥ 97%), surrogate standards 2,4,5,6-tetrachoro-m-xylene (TCmX), decachlorobiphenyl (PCB 209), and the internal standard pentachloronitrobenzene (PCNB) were purchased from Anpel Scientific Instrument Co. Ltd (Shanghai, China). Dichloromethane (DCM) and n-hexane were of chromatographic grade purchased from Tedia Chemicals (Fairfield, OH, USA). Silica gel (100–200 mesh) and alumina (100–200 mesh) were extracted by DCM in the Soxhlet apparatus for 48 h, activated at 180°C and 240°C for 12 h, respectively. The silica gel and alumina were then inactivated by adding 3% (w/w) deionized water. Anhydrous sodium sulfate was baked in a retort furnace at 450°C for 4 h. Glassware was washed with $K_2Cr_2O_7$ H_2SO_4, rinsed with deionized water before drying at 105°C for 4 h. All reagents were of analytical grade or higher.

2.2.Sample collection

The main body of the Hanjiang River has a length of up to 470 km. It originates from Fujian Province and passes through Dapu and Fengshun counties, to arrive at Chaozhou, and finally empties into the East China Sea. The sampling sites of this study are shown in Figure 1. A total of 17 sampling sites along the entire Hanjiang River were selected. Among these sites, H2 is located at Sanhe Dam (a boundary of upstream to midstream), whereas H11 is located in Guangji Bridge (a boundary of midstream to downstream). SS and water samples were collected at the same sites. A total of 11 SS samples (H1–H5, H7–H9, H12, H13, and H17 sampled at 0–20 cm depth) were collected beside the riverine; eight water samples (H2, H4, H5, and H7–H11) were collected along the mainstream (at 0–20 cm depth); and nine water samples (H1, H3, H6, and H12–H17) were collected from the tributaries (at 0–20 cm depth). All samples were collected in April 2013. The water samples were brought to the laboratory and were immediately filtered through fluorine ethylene filters (50 mm × 0.45 μm; Millipore, USA) to separate the DP and SPM phases. The weight of SPM was measured. The sediment, soil (not reported in this study), and SPM-loaded filters were initially wrapped in aluminum foil. Filters loaded with SPM were placed on the contaminated sides facing each other to prevent the transfer of residues to the aluminium foil. The wrapped aluminum foil was then placed and sealed in polythene bags, and freeze-dried at −20°C before analysis. The filtered water samples were stored at 4°C in precleaned glass bottles before analysis. Each water sample was associated with two or three SPM filters, the latter being regarded as one SPM sample. All water and sediment samples were analyzed in 2013.

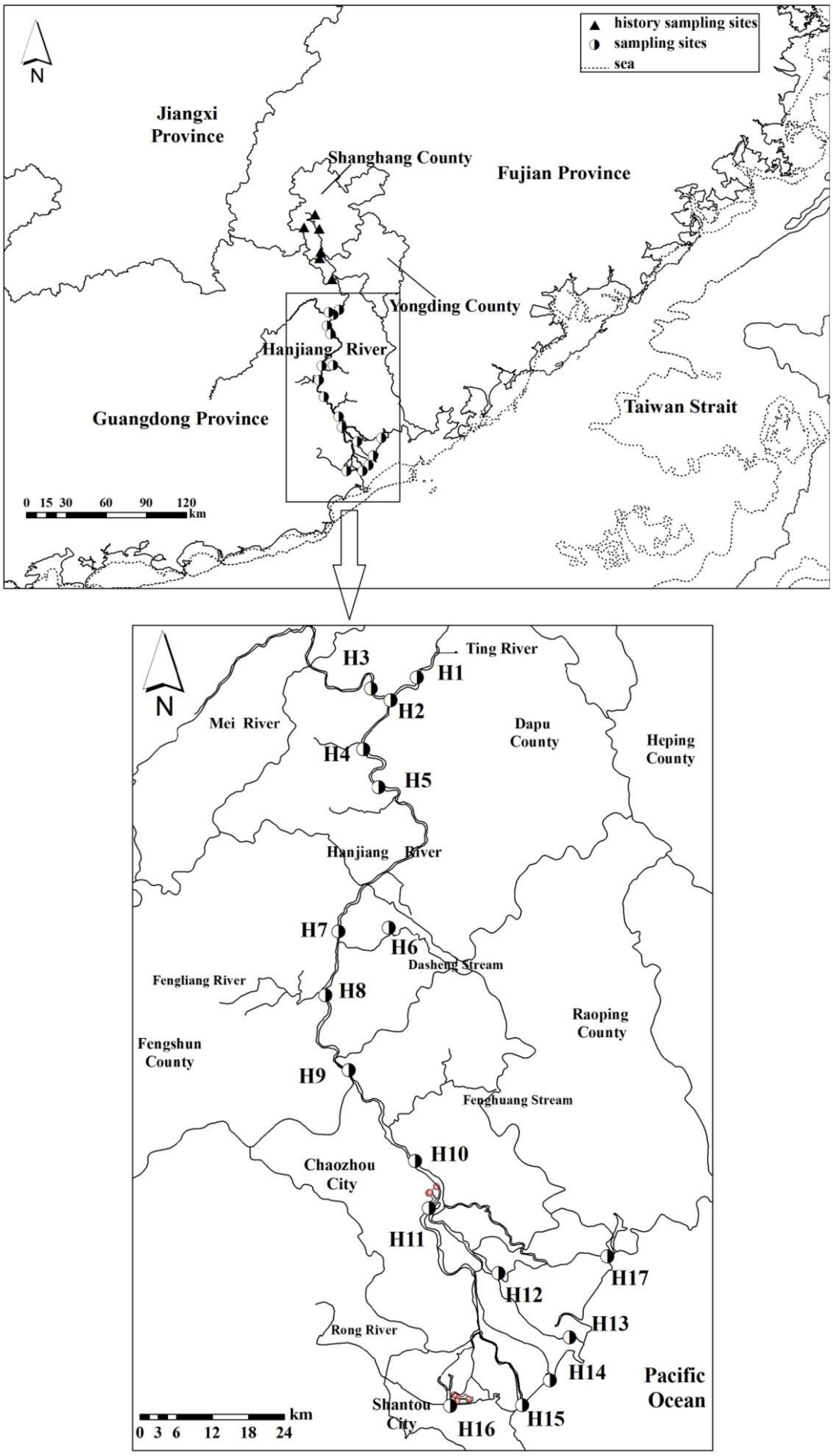

Fig. 1. Study sampling sites of Hanjiang River Basin. Upper panel shows a sketchy orientation of sampling sites located in southeast China. The lower panel shows specific sampling sites, H1eH17.

H2 is a boundary of upstream to midstream, whereas H11 is a boundary of midstream to downstream. Circle denotes the samples collected in 2013 and triangle denotes history sampling in 2009.

2.3.Environmental sample extraction and analyses

Samples were extracted and analyzed according to published methods (Yang et al., 2013; Qu et al., 2015). Briefly, air-dried sediment samples were passed through a 100-mesh sieve. Approximately 0.2 g of the pulverized sediment sample was treated with 0.1 M HCl to remove inorganic carbon until no bubbles remained. The acidified sample was then oven-dried for 4–5 h at 105°C. Total organic carbon (TOC) was analyzed using the LiquiTOC system (Elementar, Germany). The SPM-loaded filters and dried sediments were extracted using the Soxhlet procedure. The samples (~10 g) were extracted for 24 h with a spike of 20 ng mixed recovery surrogates (TCmX + PCB209), copper granules (removing elemental sulfur), and 120–140 mL of DCM in a water bath maintained at 45°C. The filtered water samples (1 L) were spiked with 20 ng of recovery surrogate in a separatory funnel. The water samples were extracted thrice with 25 mL of DCM. The extract was reduced to 5 mL using a rotary evaporator and added twice with 2–3 mL of n-hexane for replacement. The concentrated extract was passed through an alumina–silica (1:2, v/v) gel column packed with 1 cm of anhydrous sodium sulfate at the top to remove water. The eluent was mixed with 30 mL of DCM: hexane (2:3, v/v), concentrated to 0.2 mL under dry nitrogen, and then spiked with 20 ng of internal standard PCNB, until later analysis.

OCP analysis was performed using an Agilent 7890A gas chromatograph with a 63Ni electron capture detector (GC-ECD) and DB-5 (30 m × 0.32 mm × 0.25 μm) chromatography column. The injector and detector were maintained at temperatures of 290 and 300°C, respectively. Nitrogen served as the carrier gas with a constant flow rate of 2.5 mL/min. The oven temperature program was started at 100°C for 1 min and then increased to 200°C at 4°C/min, then to 230°C at 2°C/min, and finally to 280°C at 8°C/min lasting for 15 min. Sample volumes of 2 μL were injected into the GC–ECD together with the predetermined volume of internal standard.

2.4.Quality assurance

A total of 12 field samples were analyzed as a batch experiment, which included one blank sample and one duplicate sample. No HCHs and DDTs were detected in the blank samples. The method detection limits (MDLs) compared to the signal-to-noise ratio (S/N) was 3:1. The injected recovery surrogates ranged from 70% to 102%.

2.5.Data and statistical analyses

The SPM water partition coefficient K_d (kg SPM or sediment/L water) is calculated as follows:

$$K_d = C_S / C_W, \qquad [1]$$

where C_S (mg OCP/kg SPM or sediment) and C_W (mg OCP/L water) are the OCP concentrations in solid and aqueous phases, respectively.

Organic carbon normalized partition coefficient (K_{OC}) is an empirical value under simulated steady-state environmental conditions in the laboratory, which can be predicted by using K_{OW} (n-octanol/water partition coefficient) (Seth et al., 1999):

$$K_{OC} = 1.03\ \log K_{OW} - 0.61. \qquad [2]$$

K_{OC}^* is modified organic carbon normalized partition coefficient found in the field, which can be calculated as

$$K_{OC}^* = (C_S/C_W)/f_{OC} = K_d/f_{OC}, \qquad [3]$$

where f_{OC} is the mass fraction of organic carbon (based on measured TOC) in the sediment. The fugacity of contamination in sediment and water were calculated as follows (Wang et al., 2011):

$$f_S = C_S \rho_S H/f_{OC}\ K_{OW} \qquad [4]$$

$$f_W = C_W\ H, \qquad [5]$$

where f_S and f_W are the fugacities in sediment and water, respectively, and ρ_S is the density of the solid sediment (1.5×10^3 kg/m^3 for all calculations) (Mackay, 2001).

Spearman's bivariate correlation analyses were conducted using the SPSS Statistics version 17.0 Values software. Data are expressed as mean ± standard deviation (SD), unless otherwise stated.

3. Results and discussion

3.1.OCPs in the DP, SPM, and SS

Results indicated that surface water collected from the Hanjiang River contained residues of HCH (sum of α-HCH, β-HCH, γ-HCH, and δ-HCH) and DDT (p,p'-DDE, p,p'-DDD, o,p'-DDT, and p,p'-DDT) isomers. Table 1 summarizes the results of the water and sediment sample analyses. The concentration ranges (ng/L) of HCHs and DDTs in DP were 2.11–12.04 (mean ± SD, 5.65 ± 2.33) and 2.49–4.77 (3.76 ± 0.84), respectively. The dominant HCH was β-HCH (2.65 ± 1.11), followed by α-HCH (2.08 ± 0.70). As known, β-HCH had a lower solubility in water, and dissolved organic matter (DOM) can absorb on this compound, which may increase the concentration in water. The ratio of β-HCH in the HCHs was high and suggests that these pollutants were probably aged in the environment (Wang et al., 2013), rather than following a recent environmental release. Among the metabolites of DDTs, p,p'-DDE (1.92 ± 0.16) had the highest mean concentration, followed by p,p'-DDT (1.17 ± 0.08).

The HCH concentration range (ng/g) in SPM was 6.60–64.77, with a mean of 18.97 ± 13.85 (Table 1). The highest HCH concentration was observed at site H16 (Fig. 2b and Table 3), which is an estuary near the Shantou dockyard, and is easily influenced by artificial factors (e.g., industrial sewage). The DDT concentration (ng/g) ranged between 6.75 and 80.19, with a mean of 20.12 ± 16.65 (Table 1). The highest DDT level was recorded at site H15 (Fig. 2b), which is situated near a large fishery. High residue levels of DDTs in water samples were likely related to resuspended sediments releasing OCPs, like the high water turbulence by fish movement. A high variability was observed in the concentrations of HCHs or DDTs among the different study sites. Because this section of the river does not flow in a steady and independent manner, variations caused by water dilution and point source pollution would be expected (Tang et al., 2008; Li et al., 2014).

The HCH concentration (ng/g) in SS ranged from 0.60 to 4.71 (1.74 ± 1.14); the concentrations of HCHs were in the following order: α-HCH > γ-HCH > δ-HCH > β-HCH. The low concentration of β-HCH suggests a new and recent release of HCHs. The highest concentration of sediment HCHs was found in site H1 located on a paddy field, which is an upstream tributary of the Hanjiang River. The DDT concentration range was 0.89–252.27 (29.24 ± 75.52). Two sites (H13 and H17) downstream were two orders of magnitude higher than the other study sites (Table 5). Sites H13 and H17 are located at the North and Yilong ports, respectively, and are highly affected by human activity (e.g., sewage). The average HCH concentration in upstream was higher than that in the downstream (Table 5), whereas the DDT concentration showed the opposite trend.

Table 1. Concentration of OCPs in surface water and sediment samples of Hanjiang River Basin

Pesticides	DP (ng/L, *n* = 17)		SPM (ng/g, *n* = 17)		SS (ng/g dry weight, *n* = 11)	
	Range	Mean ± SD[a]	Range	Mean ± SD	Range	Mean ± SD
α-HCH	nd[b]–3.71	2.08 ± 0.70	5.07–44.77	12.40 ± 9.17	0.19–1.31	0.48 ± 0.34
β-HCH	1.32–6.22	2.65 ± 1.11	nd–7.24	3.55 ± 1.78	0.09–1.43	0.41 ± 0.37
γ-HCH	nd–2.11	1.47 ± 0.37	nd–20.00	4.43 ± 4.92	0.11–0.98	0.43 ± 0.23
δ-HCH	nd–0.58	0.04 ± 0.16	nd.	nd	nd–0.99	0.42 ± 0.24
p,p'-DDE	nd–2.31	1.92 ± 0.16	1.17–11.90	6.33 ± 2.33	0.16–7.14	1.36 ± 2.20
p,p'-DDD	0.2 5–0.71	0.32 ± 0.11	0.57–8.79	1.49 ± 1.91	nd–28.67	3.98 ± 8.75
o,p'-DDT	nd–1.17	1.08 ± 0.07	0.24–7.83	3.81 ± 1.83	nd–35.37	4.59 ± 11.58
p,p'-DDT	nd–1.33	1.17 ± 0.08	1.63–52.98	8.49 ± 11.82	0.51–184.32	20.14 ± 55.23
∑HCH	2.11–12.04	5.65 ± 2.33	6.60–64.77	18.97 ± 13.85	0.60–4.71	1.74 ± 1.14
∑DDT	2.49–4.77	3.76 ± 0.84	6.75–80.19	20.12 ± 16.65	0.89–252.27	29.24 ± 75.52

[a] Arithmetic mean ± standard deviation (SD). [b] nd : Not detectable

Table 2. OCP concentration (ng/L) in dissolved phase

Sample sites	α-HCH	β-HCH	γ-HCH	δ-HCH	*p,p'*-DDE	*p,p'*-DDD	*o,p'*-DDT	*p,p'*-DDT	∑ HCH	∑ DDT
H1	1.51	1.71	1.00	0.00	1.60	0.25	0.91	0.97	4.22	3.73
H2	1.94	2.77	1.33	0.00	Nd	0.27	1.08	1.16	6.04	2.50
H3	3.71	6.22	2.11	0.00	2.31	0.32	nd	nd	12.04	2.63
H4	2.62	3.44	1.91	0.00	2.07	0.31	1.17	1.21	7.97	4.77
H5	1.24	1.32	0.87	0.00	Nd	0.25	1.06	1.17	3.43	2.49
H6	2.69	2.88	1.76	0.00	2.03	0.30	1.13	1.17	7.33	4.63
H7	1.50	2.48	1.41	nd	1.78	0.26	1.03	1.24	5.38	4.31
H8	2.42	2.87	1.68	0.00	1.87	0.27	nd	1.14	6.96	3.28
H9	1.44	1.98	1.21	0.00	1.90	0.28	1.07	1.26	4.63	4.51
H10	nd	3.61	nd	0.58	1.89	0.71	nd	1.20	4.20	3.80
H11	2.98	3.12	1.85	0.00	1.88	0.40	1.14	1.33	7.95	4.75
H12	1.59	2.07	nd	nd	1.94	0.27	nd	1.11	3.66	3.32
H13	1.61	2.07	1.23	0.00	Nd	0.29	1.15	1.27	4.91	2.70
H14	nd	2.11	nd	0.00	1.84	0.33	1.05	1.13	2.11	4.34
H15	2.48	1.77	1.53	0.00	1.99	0.29	1.09	1.13	5.78	4.50
H16	1.72	2.56	1.23	nd	1.97	0.30	1.07	1.11	5.52	4.45
H17	1.74	2.10	nd	0.00	1.83	0.27	nd	1.10	3.84	3.20
Average	2.08	2.65	1.47	0.04	1.92	0.32	1.08	1.17	5.65	3.76

nd: Not detectable

Table 3. OCP concentration (ng/g) in SPM.

Sample sites	α-HCH	β-HCH	γ-HCH	δ-HCH	*p,p'*-DDE	*p,p'*-DDD	*o,p'*-DDT	*p,p'*-DDT	∑HCH	∑DDT
H1	8.50	3.48	3.21	0.00	6.30	1.56	3.29	5.08	15.19	16.24
H2	14.73	4.74	3.05	0.00	6.78	0.82	6.12	7.82	22.52	21.53
H3	18.54	5.43	8.98	nd	5.84	1.15	2.94	3.64	32.95	13.56
H4	10.26	2.08	1.88	0.00	6.05	0.82	2.95	3.93	14.23	13.76
H5	10.31	1.85	1.52	nd	4.08	0.79	1.82	1.63	13.68	8.31
H6	8.77	2.60	nd	nd	6.83	0.95	3.88	4.18	11.37	15.84
H7	7.15	2.12	nd	nd	5.56	0.77	3.16	3.41	9.26	12.90
H8	7.29	3.68	2.48	0.00	6.01	1.16	3.02	3.89	13.45	14.08
H9	16.01	5.34	5.80	0.00	11.90	1.57	5.67	13.15	27.15	32.29
H10	7.44	nd	2.08	0.00	5.00	0.78	2.35	3.30	9.52	11.42
H11	11.13	4.26	2.66	0.00	5.65	0.65	4.15	6.90	18.06	17.35
H12	7.10	3.24	1.68	0.00	5.49	0.91	2.81	3.95	12.02	13.16
H13	6.99	3.39	nd	nd	6.14	1.37	3.61	7.49	10.38	18.61
H14	5.07	0.29	1.23	nd	1.17	0.57	0.24	4.78	6.60	6.75
H15	10.99	nd	3.45	nd	10.59	8.79	7.83	52.98	14.45	80.19
H16	44.77	nd	20.00	0.00	6.80	1.23	5.23	8.68	64.77	21.94
H17	15.65	7.24	4.03	0.00	7.41	1.36	5.74	9.60	26.92	24.11
Average	12.40	3.55	4.43	0.00	6.33	1.49	3.81	8.49	18.97	20.12

nd: Not detectable

Table 4. OCP (ng/L) concentration in SPM.

Sample sites	α-HCH	β-HCH	γ-HCH	δ-HCH	*p,p'*-DDE	*p,p'*-DDD	*o,p'*-DDT	*p,p'*-DDT	∑HCH	∑DDT
H1	3.28	1.34	1.24	0.00	2.43	0.60	1.27	1.96	5.86	6.27
H2	6.29	2.02	1.30	0.00	2.90	0.35	2.61	3.34	9.61	9.19
H3	7.99	2.34	3.87	nd	2.52	0.49	1.27	1.57	14.20	5.84
H4	3.78	0.77	0.69	0.00	2.23	0.30	1.09	1.45	5.24	5.06
H5	7.65	1.37	1.13	nd	3.03	0.58	1.35	1.21	10.15	6.17
H6	4.46	1.76	1.15	0.00	2.70	0.64	1.25	3.17	7.37	7.76
H7	3.35	0.99	nd	nd	2.61	0.36	1.48	1.60	4.34	6.05
H8	2.54	1.28	0.86	0.00	2.09	0.40	1.05	1.35	4.68	4.90
H9	3.41	1.14	1.23	0.00	2.53	0.34	1.21	2.80	5.78	6.88
H10	3.04	nd	0.85	0.00	2.04	0.32	0.96	1.35	3.88	4.66
H11	5.16	1.98	1.24	0.00	2.62	0.30	1.93	3.20	8.38	8.05
H12	2.74	1.25	0.65	0.00	2.12	0.35	1.09	1.53	4.64	5.08
H13	2.60	1.26	nd	nd	2.28	0.51	1.34	2.79	3.86	6.92
H14	1.71	0.10	0.42	nd	0.39	0.19	0.08	1.61	2.22	2.28
H15	4.27	nd	1.34	nd	4.11	3.41	3.04	20.56	5.61	31.12
H16	15.80	nd	7.06	0.00	2.40	0.43	1.85	3.07	22.87	7.75
H17	4.98	2.30	1.28	0.00	2.36	0.43	1.83	3.05	8.56	7.67
Average	4.89	1.42	1.62	0.00	2.43	0.59	1.45	3.27	7.49	7.74

nd: Not detectable

Table 5. OCP concentration (ng/g) and TOC value (%) in surface sediment.

Sample sites	α-HCH	β-HCH	γ-HCH	δ-HCH	*p,p'*-DDE	*p,p'*-DDD	*o,p'*-DDT	*p,p'*-DDT	∑HCH	∑DDT	TOC
H1	1.31	1.43	0.98	0.99	0.81	1.31	0.47	0.81	4.71	3.40	1.370
H2	0.78	0.41	0.54	0.41	0.94	1.26	0.38	0.59	2.14	3.17	1.025
H3	0.38	0.30	0.42	0.42	0.23	0.25	0.34	0.51	1.52	1.33	0.285
H4	0.74	0.62	0.54	0.52	0.67	0.45	0.43	0.72	2.42	2.27	0.809
H5	0.42	0.35	0.52	0.55	0.27	0.27	0.39	0.62	1.84	1.54	0.154
H7	0.21	0.09	0.18	0.26	0.16	Nd	nd	0.73	0.74	0.88	0.442
H8	0.33	0.24	0.36	0.38	0.24	0.25	nd	0.52	1.32	1.00	0.303
H9	0.45	0.34	0.49	0.50	0.35	0.36	0.40	0.58	1.79	1.68	0.436
H12	0.26	0.21	0.32	0.31	0.31	0.26	0.42	0.63	1.10	1.61	0.605
H13	0.22	0.19	0.27	0.28	3.92	28.67	35.37	184.32	0.95	252.27	0.630
H17	0.19	0.29	0.11	nd	7.14	10.71	3.15	31.47	0.60	52.46	0.618
Average	0.48	0.41	0.43	0.46	1.37	4.38	4.59	20.14	1.74	29.24	0.61

nd: Not detectable

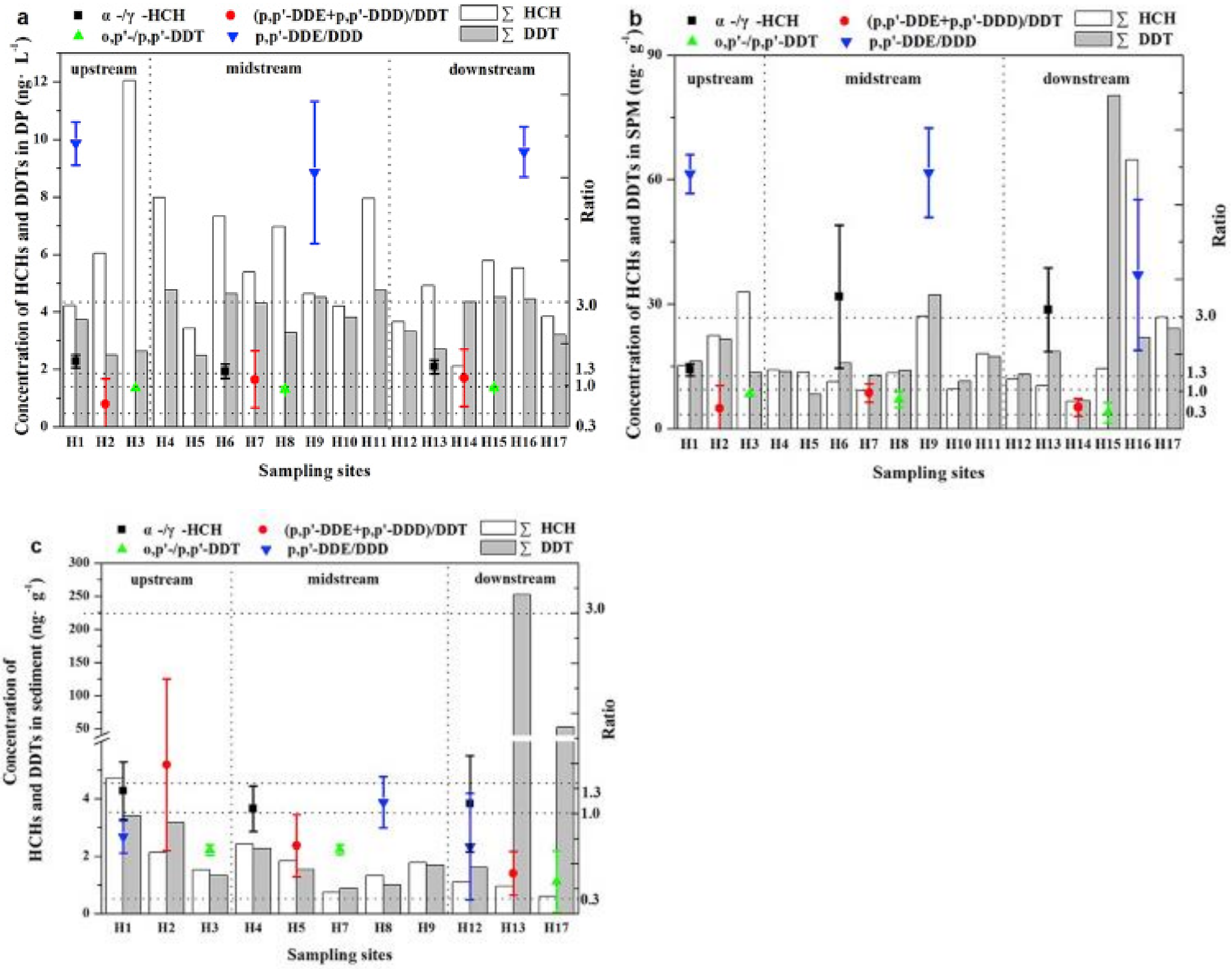

Fig. 2. Concentration, distribution, and ratio of OCPs in dissolved phase, DP (a), suspended particulate matter, SPM (b), and surface sediment, SS (c) at study sites (H1eH17) in Hanjiang River Basin. Symbols denoting the different OCP isomers are indicated above each panel.

3.2.Potential sources of OCP contamination and correlation

Technical HCH, which contains α-HCH (60–70%), β-HCH (5–12%), γ-HCH (10–12%), and δ-HCH (6–10%), started to be officially banned in China in the mid-1980s (Willett et al., 1998). Lindane (> 99% γ-HCH) was used as a substitute for technical HCH until the 1990s (Li et al., 2001). Previous studies suggest that α-/γ-HCH ratio between 3 and 7 usually indicates the presence of technical HCH, whereas a value of <3 indicates the use of lindane (Toan et al., 2009). The α-/γ-HCH ratios in DP and SS samples were reported to be <3 in this study (Figs. 2a and 2c), indicating that lindane was the major source of HCH. It is also interesting to note that SPM samples from upstream had this ratio <3(indicating lindane source) while the midstream and downstream in SPM samples showed values >3(indicating technical HCH source) (Fig. 2b).

Technical DDT contains p,p’-DDT (80–85%) and o,p’-DDT (15–20%) (Metcalf, 1973). The low ratio (<1) of p,p’-(DDE+DDD)/DDT indicates a fresh DDT input; otherwise the ratios > 1 indicate that the main source is from aged DDT (Hu et al., 2009; Ouyang et al., 2014). Dicofol contains approximately 11.4% o,p'-DDT and 1.7% p,p'-DDT as impurities (Qiu et al., 2005), of which the former is more unstable than the latter (Li et al., 2008). For example, the o,p'-DDT/p,p'-DDT ratio varies from 0.2 to 0.3 for technical DDT and from 1.3 to 9.3 or higher for dicofol (Qiu et al., 2005). In general, DDE/DDD ratio was used for identifying the environmental degradation conditions, according to different degradation pathways (Hitch and Day, 1992; Li et al., 2014). Thus, the data showed that the DDE/DDD ratio was >1 under aerobic conditions, otherwise <1.

Combining the ratio values (Fig. 2) and principal component analysis (PCA, Table 6), it is more reasonable to find further possible sources and degradation behaviors of target contaminants. It was under aerobic conditions in DP, and mixed DDT (technical DDT and dicofol) was the major contaminant. A freshly mixed DDT input remained in the upstream. For DP, PC 1 (40.0%) was associated with α-HCH, β-HCH, p,p'-DDE, and p,p'-DDT. γ-HCH, p,p'-DDD, and o,p'-DDT were loaded on PC 2 (29.2%). Considering that p,p'-DDT can easily degrade into p,p'-DDE under aerobic conditions, suggesting PC 1 could be the aerobic degradation pathway. In SPM, it was also under aerobic conditions and was composed of fresh mixed DDT input. PC1 (47.9%) was highly associated with the DDT group, and possibly could be the DDT source. PC2 (27.1%) was correlated with α-HCH and γ-HCH, both of which exhibited similar physicochemical properties, such as a relatively higher volatility than those of other contaminants. PC2 could be the HCH source. β-HCH was loaded on PC3 (19.4%). The data showed that the upstream contained a mixed aged DDT input under anaerobic conditions in SS. The midstream consisted of a mixed fresh DDT input under aerobic conditions. Similarly, the downstream contained a mixed fresh DDT input under anaerobic conditions. Two principal components, namely DDT and HCH groups, were loaded on PC1 (59.1%) and PC2 (30.2%), respectively.

Table 6. PCA on DP, SPM, and SS.

Compounds	DP		SPM			SS	
	PC 1	PC 2	PC 1	PC 2	PC 3	PC 1	PC 2
α-HCH	0.788	0.509	0.083	0.991	0.019	0.951	-0.167
β-HCH	0.882	-0.260	-0.070	-0.068	0.960	0.945	-0.049
γ-HCH	0.621	0.686	0.068	0.982	-0.048	0.967	-0.209
δ-HCH	-	-	-	-	-	0.937	-0.228
p,p'-DDE	0.499	-0.369	0.790	0.210	0.448	-0.292	0.659
p,p'-DDD	0.007	-0.726	0.936	-0.061	-0.276	-0.148	0.989
o,p'-DDT	-0.359	0.745	0.830	0.315	0.366	-0.075	0.957
p,p'-DDT	-0.800	0.176	0.961	-0.009	-0.218	-0.115	0.972

Table 7 summarizes the results of Spearman's bivariate correlation analyses of the multimedia samples from upstream to downstream. Upstream, midstream, and downstream were significantly and positively correlated with one another in the same media, such as DP and SPM. Compared with SS, DP and SPM can be more easily transported by water. The SPM upstream was significantly and positively correlated with DP from upstream, midstream, and downstream. This phenomenon can be attributed to the equilibrium among different media and can be visually illustrated by Kd (detailed in Section 3.4).

Table 7. Correlation of HCH and DDT concentrations among DP, SPM, and sediment samples of Hanjiang River Basin

Media	DP-up	DP-mid	DP-down	SPM-up	SPM-mid	SPM-down	SD-up	SD-mid	SD-down
DP-up	1.000								
DP-mid	1.000^{**}	1.000							
DP-down	0.976^{**}	0.976^{**}	1.000						
SPM-up	0.738^{*}	0.738^{*}	0.714^{*}	1.000					
SPM-mid	0.643	0.643	0.619	0.905^{**}	1.000				
SPM-down	0.571	0.571	0.524	0.952^{**}	0.905^{**}	1.000			
SD-up	0.429	0.429	0.381	0.286	0.143	0.119	1.000		
SD-mid	−0.333	−0.333	−0.405	0.167	0.119	0.357	−0.500	1.000	
SD-down	−0.619	−0.619	−0.524	−0.286	−0.143	−0.119	−0.286	0.143	1.000

* *Correlation is significant at $p < 0.01$ (two-tailed)

3.3.Comparison with OCP concentrations from other regions

Table 8 reveals the HCH and DDT concentrations among multimatrix samples compared with published studies of other sampling locations in different sample seasons and sample preparation methodologies. Like the Hanjiang River, the Yangtze and Huaihe rivers (flowing through major cities such as Wuhan and Xinyang, respectively) are important sources of drinking water for millions of residents.

The concentrations of HCH and DDT in DP and SPM samples found in this study of the Hanjiang River were different from those found in Wuhan on the Yangtze River, which might be due to the seasonal fluctuations. For example, the residual levels of HCHs in DP were a little higher in Hanjiang River than that in Yangtze River (during the flood season) and Huaihe River. Whereas the levels of DDTs in DP samples of the Hanjiang River are a little higher than that of Yangtze River in Wuhan, but less than that of Huaihe River. There were also methodological differences in sample preparation between studies. For example, a 0.7-μm pore size filters were used for the Huaihe River (Feng et al., 2011) and Deep Bay (Qui et al., 2009) studies, whereas 0.45-μm-sized filters were used for this study and the Yangtze River catchment of Wuhan study (Tang et al., 2008). These differences may explain some of the variations in the literature, in that the OCP concentrations in the filtrate can differ depending on filter size. It is possible that OCPs bound to DOM (Carter and Suffet, 1982) can pass through the filter, resulting in detectable and perhaps variable levels of residual OCP in the DP sample. The HCH and DDT levels in the Hanjiang River were moderate (using a 0.45-μm filter membrane) compared with the levels reported in the other regions (Table 8).

Hanjiang River, Deep Bay, Quanzhou Bay, Yangtze Estuary, and Liaodong Bay either impinge upon, or are located along the coast from South China to the Bohai Sea. The first four water bodies are considered subtropical, whereas the last one (Liaodong Bay) is within a warm temperate zone. The mean annual temperature of the subtropical zone is higher than that of the warm temperate zone. One expects high soil runoff, leaching, as well as atmospheric deposition in rivers within the subtropical rain belt, resulting in accelerated release of OCPs from contaminated soil (Qiu et al., 2009) (Wu et al., 2015). Accordingly, Liaodong Bay had less DDT residues in both DP and SPM fractions than those found in the Yangtze Estuary, Deep Bay, Quanzhou Bay, and Hanjiang River (Table 8). Lake Small Baiyangdian and Lake Chaohu are inland lakes in China, which have relatively less flow dynamics than the aforementioned rivers. This would explain why the DDT residual levels in SPM are one or two orders of magnitude higher than those in rivers and estuaries (e.g., Huaihe River, Sarno River and Estuary, Campo Mare, Yangtze Estuary, Hanjiang River, Quanzhou Bay, and Deep Bay).

Table 8. Comparison of HCH and DDT concentrations in multimatrix sampling studies of different rivers, lakes, and estuaries in China

Sample location	Dissolved phase (DP, ng/L)		Suspended Particulate Matter (SPM , ng/g)		Surface Sediment (SS, ng/g)		Reference
	HCH	DDT	HCH	DDT	HCH	DDT	
Yangze estuary[a]			6.2–14.8 (12.3)	3.4–25.7 (16.4)	0.5–17.5 (6.0)	0.9–33.1 (8.2)	(Liu et al., 2008)
Yangze River catchment of Wuhan[a]	1.42–4.70 (2.64)f 5.5–10.13 (6.91)d	nd–1.10 (0.45)[f] nd [d]					(Tang et al., 2008)
Deep Bay[a]	0.31–1.83 (0.71)	0.66–3.81(1.96)	0.05–6.40(2.54)	1.15–288.20 (36.65)	0.22–1.07(0.5)	2.92–82.27(20.23)	(Qiu et al., 2009)
Liaodong Bay [b]	3.4–23.8 (10.2)	0.02–5.24 (1.7)	2.5–13.7 (6.5)	0.4–5.5 (2.1)	1.1–8.5 (4.2)	0.3–12.6 (3.8)	(Tan et al., 2009)
Huaihe River[a]	0.85–12.77 (4.29)	3.54–33.59 (12.5)	1.01–25.22 (10.74)	nd–4.74 (1.80)			(Feng et al., 2011)
Lake Small Baiyangdian[b]	0.53–6.81 (1.59)	nd.	nd–104.35 (25.42)	60.49–319.95 (158.79)	0.15–3.11 (0.86)	0.03–1.41 (0.46)	(Wang et al., 2013a)
Quanzhou Bay[a]	10.92–17.28 (14.0)	2.56–4.97 (3.56)	0.93–14.24 (5.37)	22.9–32.8 (26.0)	0.36–1.88 (0.92)	0.21–7.83 (4.73)	(Yang et al., 2013)
Lake Chaohu[b]	0.4–14.7 (2.0)	0.5–18.4 (5.9)	2.3–47.6 (13.1)	12.9–657 (121.2)	0.2–1.9 (0.8)	0.3–31 (4.4)	(Liu et al., 2013)
Campo Mare[d]	15.7	0.2	25.8	4.9	0.9	0.1	(Ballesteros et al., 2014)
Sarno River and Estuary,Italy[c]	0.006–0.85 (0.24)	0.23–1.18	0.02–1.22 (0.23)	0.04–1.17	0.018–1.47 (0.61)	0.027–2.09	(Montuori et al., 2014)
Hanjiang River basin [a]	2.11–12.04 (5.65)	2.49–4.77 (3.76)	6.60–64.77 (18.97)	6.75–80.19 (20.12)	0.60–4.71 (1.74)	0.89–252.27 (29.24)	Present study

[a] *p,p′*-DDE + *p,p′*-DDD + *o,p′*-DDT + *p,p′*-DDT

[b] *o,p′*-DDT + *p,p′*-DDT + *o,p′*-DDD + *p,p′*-DDD + *o,p′*-DDE + *p,p′*-DDE

[c] *p,p′*-DDD + *p,p′*-DDE + *p,p′*-DDT

[d] *p,p′*-DDT + *p,p′*-DDE.

nd: not detectable

( ): the values in parenthesis represent the mean concentration.

f indicates flood season and d indicates dry season

3.4.Exchange of HCHs and DDTs among multimatrix compartments

Upon mixing with water, hydrophobic organic pollutants can adsorb onto natural organic matter (NOM) with time. Nevertheless, the mechanism is a very complicated process, including intermolecular physical and chemical interactions, that is, Van der Waals forces, covalent bonds, dipole–dipole ion, hydrogen bonds, and ion exchange. The SPM water partition coefficient (K_d) is an important parameter that reflects whether sorption of a chemical to SPM is favored, compared to dissolution in the aqueous environment. On the basis of equation [1] using measured concentrations of OCPs in sediment SPM and DP samples, the following log K_d profile was calculated with fluctuation: α-HCH > γ-HCH > β-HCH (Fig. 3a). The log Kd values of p,p'-DDE, p,p'-DDD, o,p'-DDT, and p,p'-DDT were 2.8–3.8, 3.01–4.48, 2.35–3.75, and 3.14–4.67, respectively (Fig. 3b). As might be expected even on the same site, Kd values varied, because of different water solubilities (α-HCH, 17 ppm; β-HCH, 10 ppm; and γ-HCH, 5 ppm) and log KOW values (from 3.7 to 3.9) (Willett et al., 1998). Sorption on natural solids is an underlying process affecting the transportation, degradation, and biological activity of organic compounds in the environment. Kd exhibits a strong affinity to organic matter (OM) content. When particle size decreases, particle organic matter (POM), specific surface area, and composition (aromatic and aliphatic C, O-alkyl C) could change, indicating particle size could directly affect the sorptive sites and sorption capacity (Benoit et al., 2008). Experimental method is another influential factor. OM removal also depends on selected extractants, such as 2% HCl, ether, ethanol, and hot water (Wahid and Sethunathan, 1978; Delle Site, 2001). DP may contain soluble OM that can bind to OCPs, such as DOM (Carter and Suffet, 1982). OM is an organic colloid, whose diameter varies from 1 nm to 10 μm in water and can also aggregate quickly (Lead and Wilkinson, 2006). The separation of DOM and POM in water is commonly performed using filter membranes, which are characterized by pore sizes ranging from 0.22 to 0.7 μm (Akkanen et al., 2012). Filter membranes can also be used to determine the "cutoff" or passing rate of a colloid through a filter with different pore sizes. DOM can be transformed into POM with the cavitation of dissolved gases during filtration (Zsolnay, 2003). Clay content and free iron oxide can also affect the sorption of hydrophobic organic compounds when OM content is low (Wahid and Sethunathan, 1978). Temperature can affect sorption isotherms and thus lead to variations in CW in sediment–water partitioning (CS/CW ratios). Furthermore, moisture content affects the adsorption on mineral fraction, because water molecules can compete with nonpolar organic compounds for sorption sites on mineral surfaces (Li et al., 2003). "Salting out" phenomenon affects the activity of solute and OM and clay surface energy distribution; as a result, charges are altered (Means, 1995; Liling et al., 2014).

Diffusion of dissolved contamination between sediment and water column is one of the main processes in sediment–water exchange (Wang et al., 2011). Compared with the KOC, the KOC* (Eq. [3]) predicts whether the contaminants have reached equilibrium between sediment and water in the field. The values of log KOC* of HCHs varied from 2.06 to 3.26, which was <log KOC (α-HCH, β-HCH) = 3.40, and log KOC (γ-HCH) = 3.20, except for γ-HCH at site H5. On the contrary, log KOC* of p,p'-DDE, p,p'-DDD, and p,p'-DDT ranged from 2.35 to 3.86, 3.54 to 5.26, and 2.70 to 5.38,

respectively, which are less than the predicted equilibrium log KOC values of 6.55, 5.78, and 5.86, respectively. It indicates that HCHs and DDTs in sediment–water exchange did not reach equilibrium.

The fugacity approach is used to achieve equilibrium and to understand the sediment–water diffusion of OCPs. Preliminary studies assessed the sediment–water equilibrium by calculating the fugacity fraction (ffsw) in sediment and water for samples with quantifiable residues in both compartments. At equilibrium, ffsw was calculated as fs/(fs + fw). Using Eqs. (4), and (5), ffsw was found to be <0.5, which indicated HCH and DDT sorption from water to sediment. “Hysteresis” can also influence the transport model. Hydrophobic organic chemicals can rapidly bind to a liquid film under a concentration gradient when they enter the water column. As liquid flows, chemicals can spread on the solid surface by entering intraparticle pores and a penetrable solid phase. This phenomenon is accompanied by film diffusion, pore diffusion, and matrix diffusion (Pignatello and Xing, 1995).

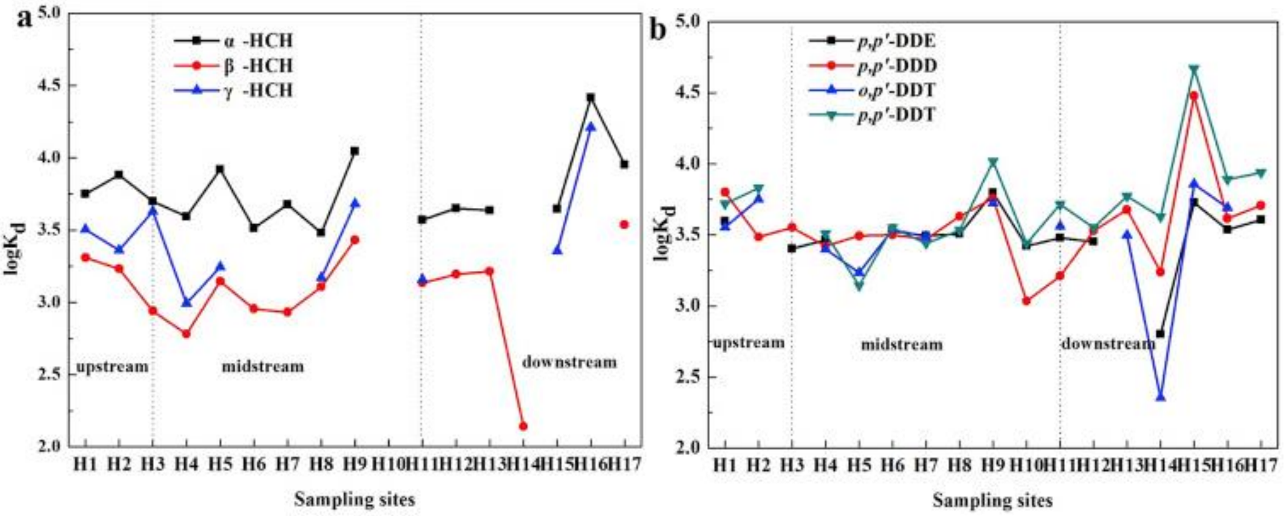

Fig. 3. Partition coefficient (logK$_d$) of HCHs (a) and DDTs (b) from upstream to downstream sites (H1-H17) along Hanjiang River. Symbols denoting the different OCP isomers are indicated within each panel.

3.5.Preliminary environmental risk assessment

As the Hanjiang River is the major source of drinking water for Chaozhou and Shantou cities, we also considered the standards for surface water of Chinese guideline (GB3838–2002) for permissible concentrations of HCHs and DDTs. According to this standard, the maximum allowable concentrations (ng/L) of lindane and DDTs are 2000 and 1000, respectively. Compared with environmental quality standard (EQS) in the water policy of the European Union (EU) (http://ec.europa.eu/environment/water/water-framework/index_en.html), the maximum allowable concentration is 20 ng/L for HCHs and 25 ng/L for DDTs, which are more conservative than the Chinese standards. Similarly, according to the United States Environmental Protection Agency (US EPA), the maximum level of contaminant (lindane) in drinking water is 200 ng/L (http://water.epa.gov/drink/contaminants/#Organic).

In this study, the OCP concentrations (ng/L) in the prefractionated water samples (i.e., SPM + DP fractions, Table 4) ranged from 4.34 to 28.38 for HCH, and from 6.62 to 35.62 for DDT. These values conform to the Chinese and American regulations. Sites H16 and H15 exceeded the allowable HCH and DDT concentrations set by the EU, respectively. Therefore, there is no anticipated risk to human health, based on the measured HCH and DDT levels in the surface water of the Hanjiang River.

We also analyzed whether an ecotoxicological risk exists. On the basis of the analysis results, one can identify the probability of toxicity to ecological receptors, using samples and predicting the incidence based on published sediment quality guidelines (SQGs) (Macdonald et al., 1996; Long et al., 1998; EC MDEPQ, 2007). These values are based on data from benthic toxicity bioassays, and are expressed using toxicological effect concentrations, ECx values (e.g., LC50 or LD50 values for lethality). The effect range level (ERL), and the effect range median (ERM) are not used as a sediment standard per se, but can be used to determine whether there is a possibility of sediment toxicity. For example, ERL indicates the 10th percentile ranked data, whereas the ERM refers to the 50th percentile ranked data. Analogous to the ERL, the threshold effect level (TEL) is identified as concentration causing adverse effects at an incidence of 25% or less. The incidence of adverse effects at 50% or higher is defined as the probable effects level (PEL). Environmental concentrations less than the ERL and PEL are indicative of a low frequency of adverse effects. By contrast, concentrations are greater than the ERM and PEL levels, which indicate a high possibility of adverse effects.

Table 9. Potential ecotoxicological risk assessment of OPCs in surface sediments of Hanjiang River Basin

Compounds	Range (ng/g)	ERL	ERM	% <ERL	%ERL − ERM	% > ERM	TEL	PEL	% < TEL	% TEL − PEL	% > PEL
DDT[a]	0.52–219.69	1	7	45	36	19	1.19	4.77	73	9	18
p,p'-DDD	nd–28.67	2	20	82	9	9	1.22	7.81	64	18	18
p,p'-DDE	0.6–7.14	2.2	27	82	18	0	2.07	374	82	18	0
∑DDT	0.88–252.27	1.58	46.1	36	45	19	3.87	51.7	82	0	18
γ-HCH	0.11–0.98	—	—				0.32	0.99	27	73	0

[a] *o,p'*-DDT and *p,p'*-DDT; ERL: effect range level; EMR: effect range median; TEL: threshold effect level; PEL: probable effects level

In the following analysis, we examined the ecotoxicological risks using a comparison of sites, as well as on an individual chemical basis. Results were calculated using concentrations at the study sites, and were compared with the ERM, ERL, PEL, and TEL values. Ratio exceedance values were then determined. In order to assess whether exposure to a given chemical represents the greatest ecotoxicological risk, we compared the environmental concentration of each chemical with the ERM, ERL, PEL, and TEL values. The 20th percentile site was calculated and compared with the value of ERM and PEL. Chemical concentrations exceeding the ERM and the PEL values indicate that adverse effects may occur frequently at these sites (or at least at 20% of the sites). Table 9 suggested that frequent and adverse effects may be caused by o,p'-DDT, p,p'-DDT, p,p'-DDD, and g-HCH. Future higher-tier ecotoxicological risk assessment studies using the standard ecotoxicity bioassays should be conducted to characterize the ecological receptors at risk by exposure to the identified OCPs at the study sites. On the basis of EQS, the influence of moderate OCP pollution from upstream to downstream water and sediment was limited. However, this finding is in contrast to our initial hypothesis. Hence, this phenomenon should be further investigated.

4. Conclusions

This field study examined the distribution of different HCH- and DDT-related compounds in multimatrix samples taken from various sites along a major Chinese river. The ratio and PCA results indicated that a fresh input of DDT was detected. Technical HCH was considered the major HCH pollutant in these sampling sites. The horizontal profiles of OCPs and their partitions between DP and SPM fractions were quite variable among the sites, which were associated with OM, particle size, moisture content, and salinity. The fugacity model also revealed that the equilibrium between sediment and water was not reached because HCHs and DDTs were transported from water to sediment. On the basis of EQS, the HCH and DDT concentrations on the surface water posed less health risk to humans than to nontarget ecological receptors. The major OCPs that may adversely affect benthic organisms include o,p’-DDT, p,p’-DDT, p,p’-DDD, and γ-HCH.

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Appendix A

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Currently used organochlorine pesticides in Mianzhu–Aba prefecture transect, eastern of the Tibetan Plateau, western China

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ABSTRACT

Mianzhu–Aba prefecture transect, eastern of the Tibetan Plateau, was selected to study the occurrence of currently used organochlorine pesticides (OCPs) along an altitudinal gradient. Soil mean concentrations (ng g^{-1}, dw) in winter (March) and summer (July) changed as follows: 0.24 and 0.27 for hexachlorobenzene (HCB), 0.15 and 0.12 for heptachlor (HEPT), 0.43 and 0.04 for heptachlor epoxide (HEPX), 0.53 and 0.11 for chlordane, 0.10 and 0.10 for nonachlor, 0.10 and 0.35 for endosulfan, respectively. Soil OCP concentrations in this transect were slightly higher than those in other mountainous regions. Analysis of some compound ratios showed that the OCPs in this transect might be partly attributed to the long-range atmospheric transport and also suggested current chlordane and endosulfan inputs. The total OCPs in winter soil (1.55 ng g^{-1}) were slightly higher than those in summer soil (0.99 ng g^{-1}), in full agreement with seasonal distribution pattern with input of new substance in winter and loss of unstable organic substance in summer. Different spatial distribution for different OCPs was observed along the transect. Individual linear regression analyses between OCP concentrations and some available variables showed that OCPs distribution along this transect were influenced by many factors, not solely a variable. A primary fugacity analysis on OCPs soil–air exchange in summer indicated that this transect may be a sink for *cis*-chlordane, and a secondary source for HCB and HEPT. As with *trans*-chlordane, α-endosulfan and β-endosulfan, this transect may be both a sink and a secondary source.

1. Introduction

Organochlorine pesticides (OCPs) are persistent semivolatile compounds, which are ubiquitously detected at the global scale. They are subject to long-range atmospheric transport and are deposited in remote areas including polar and high-altitude regions (Blais et al., 1998; Daly and Wania, 2005; Kallenborn, 2006). Although various studies on the transport and fate of OCPs in high-altitude regions were performed (Borghinia et al., 2005; Daly et al., 2007c; Holoubek et al., 2009; Tremolada et al., 2008; Turgut et al., 2011), few studies focus on the distribution of OCPs along a presumed long-range transport path, from low-altitude regions (sources) to high-altitude regions (sinks).

In Sichuan province of western China, a steep altitudinal transect separates the highly populated and intensively cultivated Chengdu plain from the Tibetan Plateau. Xing et al. (2009) had concluded that Chengdu plain was an obvious basin source of OCPs. Although there had been a number of investigations for OCP contamination in the Tibetan Plateau (Gong et al., 2010; Tao et al., 2011; Wang et al., 2012; Yang et al., 2010; Yang et al., 2012; Zheng et al., 2009), few studies were conducted on the potential for contaminant transport and accumulation in this transition area between Chengdu plain and the Tibetan Plateau. Studies had been carried out on OCP concentrations from Chengdu plain to Wenchuan county (Liu et al., 2010), Balangshan region (Chen et al., 2008) and Jiuzhaigou Natural Scenic Area (Xing et al., 2010), which are all high-altitude regions on the east margin of the Tibetan Plateau. The results had confirmed that many contaminants in above high-altitude regions were attributed to the long-range atmospheric transport, which was mostly likely from Chengdu plain.

Compared with dichlorodiphenyltrichloroethanes (DDTs) and hexachlorocyclohexanes (HCHs), studies on other OCPs are even less in such transition area. Hexachlorobenzene (HCB) was observed in soil (Chen et al., 2008; Tao et al., 2011; Wang et al., 2010b), air (Liu et al., 2010; Wang et al., 2010a), vegetation (Wang et al., 2007; Yang et al., 2008) and fish (Yang et al., 2012) of the transition area. Endosulfan was detected in grass (Wang et al., 2007) and air (Gong et al., 2010; Liu et al., 2010; Wang et al., 2010a; Xiao et al., 2010) of the transition area. Chlordane, heptachlor (HEPT), heptachlor epoxide (HEPX) and nonachlor were found in air (Li et al., 2008; Xiao et al., 2010) and snow (Kang et al., 2009) of the transition area. Although the detectable ratios and concentrations of other OCPs were comparatively low, many studies had shown that they can deposit in the high-altitude areas during the progress of long-distance transport. What's more noteworthy was that some

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pesticides were still in use, such as endosulfan and chlordane. Endosulfan was currently in use in many countries including China, Europe, Canada, and India (Barrett and Jaward, 2012; Jia et al., 2009; Weber et al., 2010). Chlordane was on China's 5 year exemption list and phased out in 2009 under the Stockholm Convention. In China, technical chlordane was still being extensively used against termites in buildings, with an estimated amount of over 200 t year^{-1} in recent years (Xu et al., 2004). And some pesticides were produced as raw materials or intermediate products, such as HCB (Barber et al., 2005; Kengara et al., 2013). Therefore, it is much important on discussion of other OCPs around the transition area between Chengdu plain and the Tibetan Plateau.

Mianzhu—Aba Tibet and Qiang Minority Autonomy (Aba prefecture) transect was selected to study the residues of other OCPs. The sampling location and basic situation of study areas were listed in Fig. 1 and Table 1, respectively. Mianzhu city is in the northwest of Chengdu plain which is located in the east margin of the Tibetan Plateau, and adjacent to Maoxian, northwest of Aba prefecture. And it is one of the most developed industrial and agricultural areas in Sichuan Province. As a typical region for the use of OCPs, Mianzhu city has higher OCPs residues (Xing et al., 2009). Aba prefecture is on the southeast margin of the Tibetan Plateau, close to Chengdu plain. Aba prefecture is under the influence of westerlies during winter (from November to April) and a southeast monsoon during summer (from May to October). Maoxian and Heishui county stand in hilly areas, as essential channel for the transmission of OCPs to the plateau. Hongyuan and Aba county are situated in the plateau region, which lie by mountains and streams with very steep and awkward terrain. Especially in winter, most of the plateau region along the transect were covered with snow. Thus, Mianzhu—Aba prefecture transect creates a better example for understanding the long-range transport phenomenon and distribution of OCPs from the possible source areas to the remote high-altitude areas. The objectives of this study were to investigate the residual levels of OCPs in soils from Mianzhu—Aba prefecture transect and to analyze the influencing factors on temporal and spatial distribution of such contaminants along the transect, and also to discuss OCPs soil–air equilibrium status with the aid of fugacity concept in this transect.

2. Sampling and experiment

2.1. Sampling

As a consequence of the meteorological variations, vegetation cover changes with elevation in this transect, such as deciduous woods, coniferous woods, alpine bush and meadow. The soil layer at the profile is shallow, rocky and patchy. So the total organic carbon (TOC) in the profile varies strongly, evenly between replicate samples (Chen et al., 2008; Xing et al., 2010). Soil samples were collected from all the 11 sampling sites, represented different topography (Table 1), at intervals of about 25 km. The sampling was carried out in March (winter) and July (summer), 2011. A total of 22 surface (0–10 cm) soil samples were collected from all the 11 sampling sites with one sample per area, respectively. At each site, four sub samples were collected from a 10 m × 10 m plot, and thoroughly mixed to form a composite sample in order to represent the sampling site adequately and uniformly. Each sample was collected by a pre-cleaned stainless steel scoop. About 1 kg of a soil sample was packed into polyethylene plastic bag. All soil samples were immediately stored at −4 °C until stored in freezer (−20 °C). Polyurethane foam-passive air sampling method (PUF-PAS) was employed for collecting air samples. A total of 22 air samples were collected at the same sites in the same year with soil samples. Details of the sampling program and air concentrations of OCPs in the transect have been reported (Liu et al., 2013). In this study, comparison of coupled soil and air concentrations will provide interactions and fate of OCPs in the transect.

2.2. Extraction and cleanup

The soil samples were spiked with 2,4,5,6-tetrachloro-m-xylene (TCmX) and decachlorobiphenyl (PCB-209) as surrogates, Soxhlet-extracted with dichloromethane (DCM) for 24 h. The extract was concentrated by a rotary evaporator after addition of anhydrous sodium sulfate, and purified by passing through a column (8 mm in inner diameter) consisting of, from bottom to top, 6 cm neutral alumina (deactivated with 3% deionized water) and 10 cm neutral silica gel (deactivated with 3% deionized water). Before using, neutral alumina, neutral silica gel, and anhydrous sodium sulfate were Soxhlet-extracted for 48 h with DCM, and baked for 12 h at 250 °C, 180 °C, and 450 °C, respectively. The column was eluted with 30 ml of DCM/hexane (2:3, *v:v*) to obtain OCP fractions. The fractions were concentrated to 0.2 ml under a gentle pure nitrogen stream. Pentachloronitrobenzene (PCNB) was added as an internal standard prior to analysis.

2.3. Instrumental analysis

A HP 6890 gas chromatograph equipped with a ^{63}Ni electron capture detector (GC-ECD) was used for detecting the OCP concentrations,

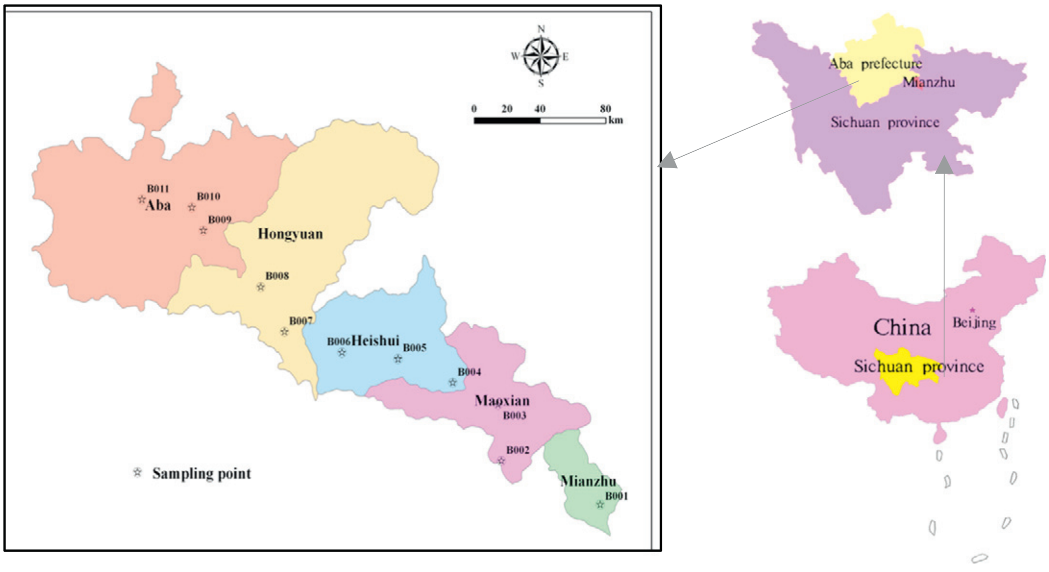

Fig. 1. Sampling location of Mianzhu—Aba prefecture transect, eastern of the Tibetan Plateau, western China.

Table 1
Basic situation of sampling sites from Mianzhu—Aba prefecture transect, eastern of the Tibetan Plateau, western China.

Area	Site no.	Altitude/m	Topography	Geographic information	Average air temperature/°C	
					Winter (March)	Summer (July)
Mianzhu city	B001	588	Basin	E:104°13′25.4″N:31°18′31.6″	16.5	28.0
Maoxian of Aba Prefecture	B002	1410	Hilly area	E:103°40′59.8″N:31°32′12.6″	8.0	23.0
Maoxian of Aba Prefecture	B003	1710	Hilly area	E:103°39′53.9″N:31°49′47.3″	10.0	25.5
Heishui of Aba Prefecture	B004	1840	Hilly area	E:103°25′02.9″N:31°56′39.9″	8.0	24.0
Heishui of Aba Prefecture	B005	2190	Hilly area	E:103°07′01.4″N:32°04′08.9″	6.0	22.4
Heishui of Aba Prefecture	B006	2690	Hilly area	E:102°48′39.3″N:32°06′05.6″	−3.4	16.0
Hongyuan of Aba Prefecture	B007	3620	Plateau	E:102°29′45.1″N:32°12′37.8″	6.8	20.0
Hongyuan of Aba Prefecture	B008	3578	Plateau	E:102°21′57.5″N:32°26′45.2″	−6.0	17.0
Aba county of Aba Prefecture	B009	3320	Plateau	E:102°03′09.4″N:32°44′26.1″	6.0	24.4
Aba county of Aba Prefecture	B010	3490	Plateau	E:101°59′24.2″N:32°51′42.3″	−8.2	16.5
Aba county of Aba prefecture	B011	3320	Plateau	E:101°43′01.1″N:32°54′07.9″	−3.8	20.0

including HCB, HEPT, HEPX, *cis*-chlordane (CC) and *trans*-chlordane (TC), *cis*-nonachlor (CN) and *trans*-nonachlor (TN), α-endosulfan (α-ES) and β-endosulfan (β-ES). The capillary column used for the analysis was a HP-5 (30 m length × 0.32 mm inner diameter × 0.25 μm film thickness). Nitrogen was used as a carrier gas at 2.5 ml min^{-1}. 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 °C min^{-1} to 200 °C, at 2 °C min^{-1} to 230 °C, and at last at 8 °C min^{-1} to 280 °C, with a final holding time of 15 min. A 2 μl sample was injected into the GC-ECD for analysis. A six-point calibration curve was established to quantify the target analytes.

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

A mixture of OCP standards was purchased from Ultra Scientific, Inc (USA). For each sample, the procedural blanks, spiked blanks, sample duplicates were run to check for interference and cross-contamination. The OCP concentrations were quantitatively determined by comparing the peak area of each compound with the peak area of PCNB. The resulting correlation coefficients for the calibration curves of OCPs were all greater than 0.99. The limits of detection for OCPs were based on a signal-to-noise ratio (S/N) of 3. The detection limits were 0.01–0.05 ng g^{-1}, and the recoveries of OCPs were 75%–111%.

3. Results and discussion

3.1. OCP concentrations in the soil of the transect

As a mixture of 147 relevant compounds, the main components of industrial chlordane are CC (11%) and TC (13%), HEPT (5%), TN (5%) (Jiang et al., 2009; Martinez et al., 2012). In this study, chlordanes (sum of TC, CC, HEPT, HEPX, TN and CN) were found to be the most abundant compounds in winter soil and accounted for about 78% of total OCPs, followed by HCB (15%) and endosulfan (7%) (Table 2). While in summer soil, OCPs in this transect were in the order chlordanes (39%) > endosulfan (35%) > HCB (27%) (Table 2).

Compared with DDTs and HCHs in the soils of this transect (Table 2), the concentrations of 9 OCPs in this study were one or two orders of magnitude lower than those. Comparison of 9 OCP concentrations in this study with various industrial/agricultural sites was also conducted. Chlordanes were much lower than those of industrial/agricultural sites in southeastern Romania (53 ng g^{-1}; Antoaneta et al., 2012), Cedar Rapids, USA (130 ng g^{-1}; Martinez et al., 2012) and Zhejiang (3.9 ng g^{-1}; Zhang et al., 2012), and Shanghai (2.47 ng g^{-1}; Jiang, et al., 2009), China. Endosulfan was also lower than some agricultural sites in Uganda (16.4 ng g^{-1}; Ssebugere et al., 2010), Greece (2.7 ng g^{-1}; Chrysikou et al., 2008) and Zhejiang, China (7.9 ng g^{-1}; Zhang et al., 2012). HCB was much lower than those reported in industrial/agricultural areas of Germany (100–1300 ng g^{-1}; Wilken et al., 1994), Poland (0.19–30 ng g^{-1}; Falandysz et al., 2001) and the Czech Republic (0.60–16.60 ng g^{-1}; Holoubek et al., 2009). Therefore, the low OCP values in the soils of the transect reflected the less of local pollution sources near the sampling sites (Lv et al., 2010) and were consistent with the lower use of OCPs in the high-altitude regions (Borghinia et al., 2005)

3.1.1. Chlordane, HEPT, HEPX and nonachlor

Compared with previous studies on different mountainous regions (Table 3), chlordane (sum of TC and CC) concentration in winter soil was higher than Revelstoke, Yoho, Observation in western Canada, Italian Alps, Peruvian Andes, and Turkish Taurus Mountains. The concentration of chlordane in summer soil was higher than Observation in western Canada, Italian Alps, Peruvian Andes and Turkish Taurus Mountains, and just comparable to Revelstoke, Yoho in western Canada. The ratio of industrial TC/CC is 1.56 (Bidleman et al., 2002) and 1.20 (Harner et al., 1999), which is commonly used to show the source of chlordane. TC has a higher volatility than CC and tends to degrade in the environment, and the high TC/CC ratio suggests new chlordane sources (Martinez et al., 2012). In winter soil, the concentration of TC was higher than that of CC in most sites with high ratio of TC/CC (Fig. 2), which may indicate fresh source of chlordane (Li et al., 2008). On the contrary, the concentration of TC was lower than that of CC in most sites with low ratio of TC/CC in summer soil (Fig. 2), which may indicate local residue of chlordane. However, there was no plausible reason for the high TC/CC ratios at the sites B008 (4.94) and B011 (2.65) in winter soil, and at the sites B002 (3.07), B010 (4.21) and B011 (3.35) in summer soil (Fig. 2). It may be caused by a potential input of chlordane from an unknown source signifying high TC/CC ratio (such as technical HEPT), or from the use of technical chlordane with different formulas (Li et al., 2007).

Table 2
OCP concentrations in soil samples from Mianzhu—Aba prefecture profile, eastern of the Tibetan Plateau, western China.

OCP	Winter (March)		Summer (July)	
	Mean and range (ng g^{-1})	Detectable ratio (%)	Mean and range (ng g^{-1})	Detectable ratio (%)
TC	0.33 (N.D.[a] –2.89)	64	0.07 (N.D.[a] –0.66)	82
CC	0.20 (N.D.[a] –2.14)	46	0.04 (N.D.[a] –0.20)	91
HEPT	0.15 (N.D.[a] –1.41)	64	0.12 (0.02–0.26)	100
HEPX	0.43 (N.D.[a] –1.20)	82	0.04 (N.D.[a] –0.36)	18
TN	0.10 (N.D.[a] –1.01)	36	0.04 (0.01–0.08)	100
CN	N.D.[a]	0	0.06 (N.D.[a] –0.42)	73
α-ES	0.04 (N.D.[a] –0.47)	9	0.23 (0.01–2.00)	100
β-ES	0.06 (N.D.[a] –0.35)	36	0.12 (N.D.[a] –0.89)	100
HCB	0.24 (0.10–0.77)	100	0.27 (0.07–1.39)	100
DDTs	22.49 (0.37–179.16)	100	7.09 (0.32–42.57)	100
HCHs	1.53 (0.14–10.76)	100	7.73 (0.55–32.71)	100

[a] Not detected.

Table 3
OCP mean concentrations in surface soils from different mountainous regions (ng g^{-1}).

Mountainous region	Chlordane [a]	Endosulfan	HCB	HEPT	HEPX	Nonachlor	References
Revelstoke, western Canada	0.12	0.20	0.12	N.D.[c]	0.14	0.25 [d]	Daly et al., 2007c
Yoho, western Canada	0.13	0.61	0.05	N.D.[c]	N.D.[c]	0.11 [d]	Daly et al., 2007c
Observation, western Canada	0.005	0.03	0.01	N.D.[c]	N.D.[c]	0.03 [d]	Daly et al., 2007c
Alps, Italy	0.02	–[b]	0.24	–[b]	–[b]	–[b]	Tremolada et al., 2008
Andes, Peru	< 0.001	–[b]	0.02	–[b]	–[b]	–[b]	Tremolada et al., 2008
Taurus Mountains, Turkey	0.04	0.12	0.30	0.001	0.05	–[b]	Turgut et al., 2011
Costa Rica, Central America	–[b]	0.09	–[b]	–[b]	–[b]	–[b]	Daly et al., 2007b
the Andean, Chile	–[b]	–[b]	0.07	–[b]	–[b]	–[b]	Borghinia et al., 2005
mountains, the Czech Republic	–[b]	–[b]	1.57	–[b]	–[b]	–[b]	Holoubek et al., 2009
the Tibetan Plateau, China	–[b]	–[b]	0.08	–[b]	–[b]	–[b]	Wang et al., 2012
Balang Mountain, China	–[b]	–[b]	0.25	–[b]	–[b]	–[b]	Chen et al., 2008
Wolong Natural Reserve, China	–[b]	–[b]	0.11	–[b]	–[b]	–[b]	Zheng et al., 2009
Mianzhu—Aba Prefecture profile, China	0.53	0.10	0.24	0.15	0.43	0.10	This study in winter
Mianzhu—Aba Prefecture profile, China	0.11	0.35	0.27	0.12	0.04	0.11	This study in summer

[a] This referred to the sum of CC and TC.
[b] No available data.
[c] Not detected.
[d] This referred to the concentration of TN.

Technical HEPT which contains 20–22% TC was used as a treatment drug for soil and seed, and also used for killing termites and household insects (Bidleman et al., 1998). HEPT can be metabolized in the soil through epoxidation, hydrolysis and dechlorination, while as a primary metabolite, HEPX is more stable and durable than HEPT (Murano et al., 2009; Xiao et al., 2011). In this study, HEPT concentrations in both winter and summer soil were higher than Turkish Taurus Mountains (Table 3). HEPX concentration in winter soil was higher than Revelstoke in western Canada and Turkish Taurus Mountains, but lower than such mountainous regions in summer soil (Table 3). The study on the relationship between chlordane concentration and the sum concentration of HEPT and HEPX in both seasons indicated that there was significantly correlation (Fig. 3). It suggested that the residues of chlordane in this transect were mainly from local existence of HEPT. In winter soil, HEPT concentration was lower than that of HEPX in most sites, suggesting historical usage of chlordane or HEPT (Table 2, Fig. 2). While in summer soil, HEPT concentration was higher than that of HEPX in most sites (Table 2, Fig. 2), indicating new source of chlordane or HEPT (Jiang, et al., 2009). Therefore, combining the above analyses for chlordane, it can be deduced that HEPT could be widely used in this transect, or come from long-range atmospheric transportion by summer monsoon.

The mean concentration of TN was 0.10 ng g^{-1} in winter soil and 0.04 ng g^{-1} in summer soil (Table 2), which were all lower than Revelstoke, but higher than Observation, and just comparable to Yoho in western Canada (Table 3). It was no detectable for CN in all sampling sites in winter soil. But CN was detected in most sites in summer soil, with a mean concentration of 0.06 ng g^{-1} (Table 2).

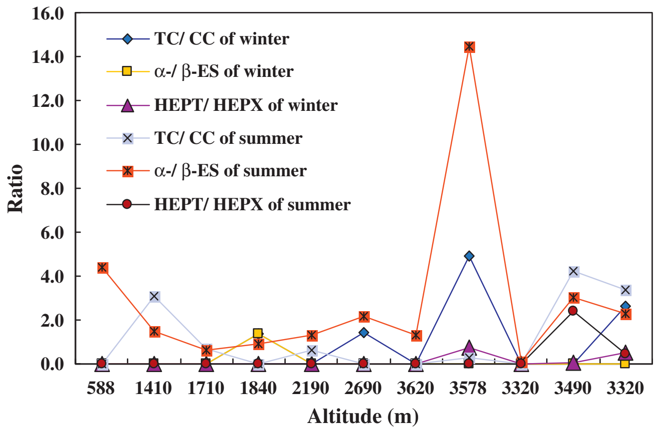

Fig. 2. Relationship between altitude with compound ratio of TC/CC, α-/β-ES and HEPT/HEPX in winter and summer soil.

3.1.2. Endosulfan

The endosulfan concentration in winter soil was lower than Revelstoke, Yoho in western Canada and Turkish Taurus Mountains, but higher than Observation in western Canada and Costa Rica in Central America. The endosulfan in summer soil was higher than Revelstoke, Observation in western Canada, Turkish Taurus Mountains and Costa Rica in Central America, but lower than Yoho in western Canada (Table 3).

Commercial endosulfan contains more than 95% of α-ES and β-ES (the ratio of α-/β-ES is 7:3), with α-ES having a higher volatility, toxicity, and rapid degradation compared with β-ES (Gong et al., 2010; Mukherjee, 2012). In this study, there was much low detectable ratio of endosulfan in winter soil with no available ratio of α-/β-ES (Table 2, Fig. 2). In summer soil, the α-ES concentration was observed to be higher than that of β-ES in most sampling sites, with much higher ratio of α-/β-ES above the technical formula ratio (Fig. 2). It implied new input of endosulfan in this transect, and possible long-distance transport processes by monsoon in summer (Gong et al., 2010; Tuduri et al., 2006).

3.1.3. HCB

Although HCB production has been ceased in most countries, it is still being generated as a by-product or impurity in several chemical processes, such as the manufacture of chlorinated solvents, chlorinated

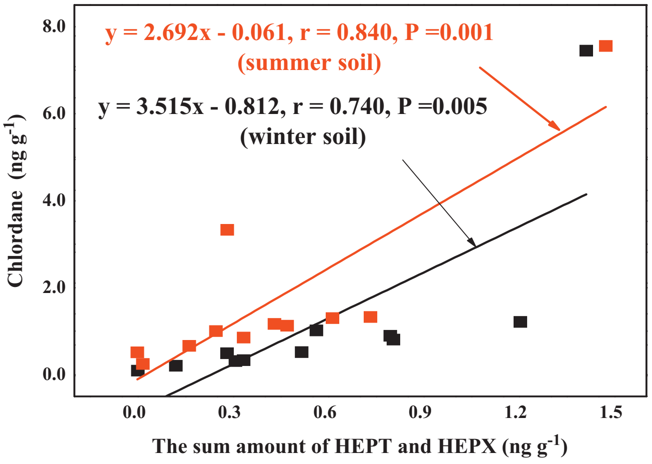

Fig. 3. Significant relationship between chlordane concentration and the sum of HEPT and HEPX in winter and summer soil.

aromatics and pesticides (Holoubek et al., 2009; Li et al., 2008). And it is also released to the environment by incomplete combustion, and released from old dump sites (Tremolada et al., 2008). It is worthy to note that HCB has never been registered as a pesticide in China. The total production of HCB from 1988 to 2003 was about 66 000 t in China (Zhang et al., 2009).

In this study, HCB widely occurred in winter and summer soil, and the detectable rates of both seasons were 100% (Table 2). The mean concentration of HCB was 0.24 ng g^{-1} in winter soil and 0.27 ng g^{-1} in summer soil, which were all higher than Revelstoke, Yoho, Observation in western Canada, Peruvian Andes, Chile Andean and the Tibetan Plateau, Wolong Natural Reserve, China, but lower than Turkish Taurus Mountains and mountains in Czech Republic, and just comparable to Italian Alps and Balang Mountain, China (Table 3). The HCB levels in this transect were appreciably lower than the mean global background level of 0.68 ng g^{-1} (Meijer et al., 2003). As Mianzhu and Aba prefecture are both cities with limited industrial activities, the major source of HCB in this transect could be incomplete combustion (Li et al., 2008; Li et al.,

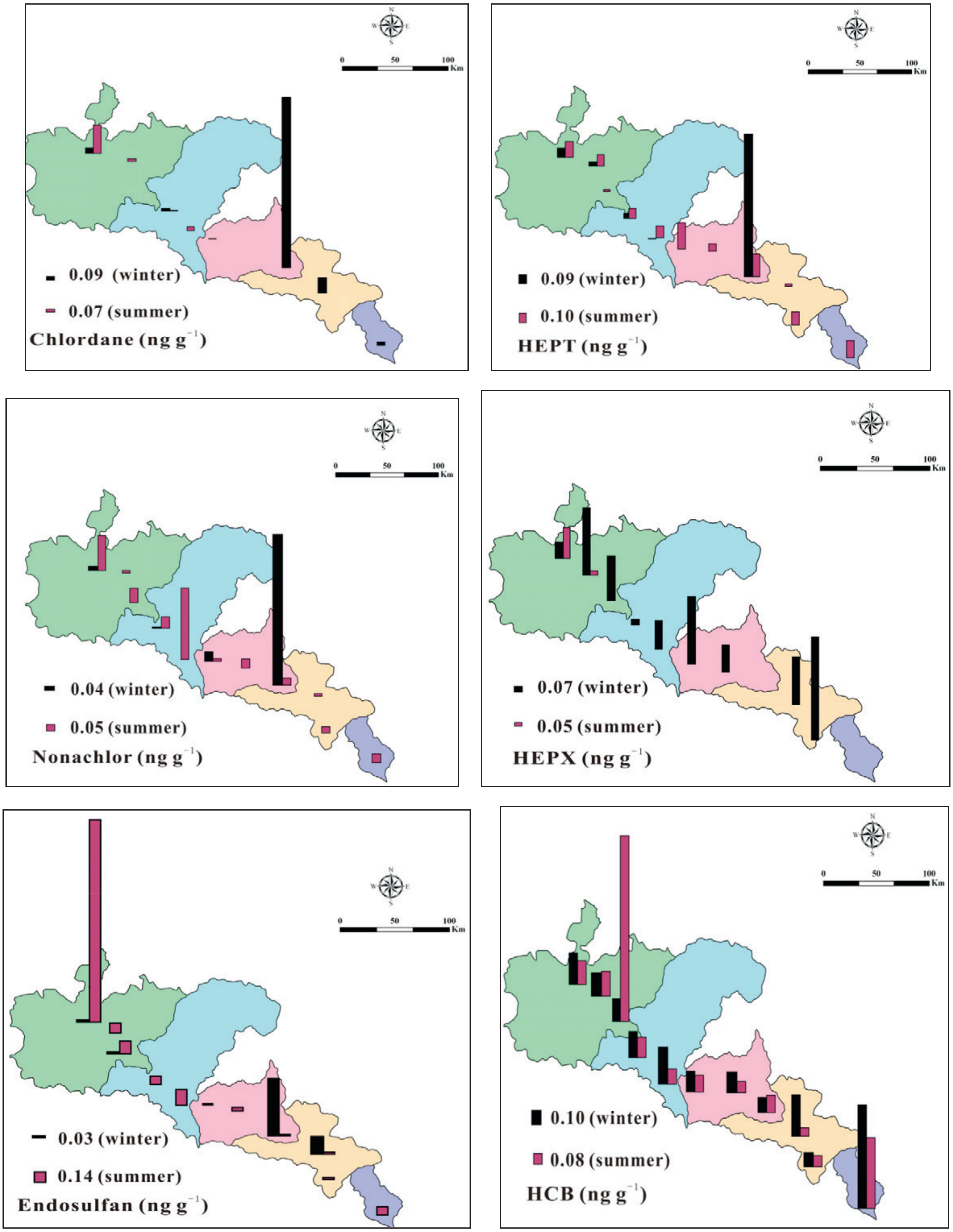

Fig. 4. Temporal and spatial distribution of chlordane, HEPT, nonachlor, HEPX, endosulfan and HCB in the soils of Mianzhu–Aba prefecture transect, eastern of the Tibetan Plateau, western China.

2012; Wang et al., 2010a) and possible long-distance transport processes (Zhang et al., 2009).

3.2. Temporal and spatial distribution of soil OCP concentrations in the transect

Fig. 4 presented the temporal and spatial distribution of chlordane, HEPT, nonachlor, HEPX, endosulfan and HCB in the soils of Mianzhu—Aba prefecture transect. There were three different patterns for the temporal distribution observed for those compounds: the pattern of higher winter soil concentrations exhibited for chlordane and HEPX, the pattern of higher summer soil concentration exhibited for endosulfan, and the pattern of comparable mean concentration in winter soil and summer soil exhibited for HCB, HEPT and nonachlor. Accordingly, the detectable ratios for HCB in both seasons were 100%, but the detectable ratios for HEPT (46%) and nonachlor (36%) in winter soil were all lower than that in summer soil (100%) (Table 2). Generally speaking, the total OCP concentrations in winter soil (1.55 ng g^{-1}) were slightly higher than those in summer soil (0.99 ng g^{-1}), in full agreement with seasonal distribution pattern with the input of new substance in winter and the loss of unstable organic substance in summer (Chen et al., 2008; Daly and Wania, 2005; Tremolada et al., 2011).

The highest levels of chlordane, HEPT and nonachlor in winter soil were all found at the site B004. The ratio of TC/CC was 1.35 at the site B004 in winter soil, suggesting not direct chlordane input but currently new HEPT source at the site. The highest level of chlordane, HEPT and nonachlor in summer soil was at the site B011, B006 and B007, respectively. There was no HEPX being detected at the site B001 in both seasons. The HEPX concentration in winter soil showed very little changes along the transect, while HEPX in summer soil was only observed at the sites B010 and B011. In winter soil, endosulfan was only detected at the sites B003, B004, B009 and B011, with the highest level at the site B004. Higher levels of endosulfan occurred in the high-altitudes in summer soil, such as the sites B007, B008, B009, B010 and B011, and the highest level was observed at the site B011. The highest level of HCB existed at the site B001 in winter soil, and at the site B009 in summer soil, respectively. Various concentration distribution could be described for the different analyzed compounds along the transect. It is not surprising to find a variety of soil concentration trends in high-altitude regions, as they are determined by many factors, such as the properties of the chemicals, geographical characteristics and climatic condition of the sampling sites (Daly and Wania, 2005; Kallenborn, 2006; Kirchner et al., 2009; Tremolada et al., 2008).

3.3. Influencing factors on the distribution of soil OCP concentrations in the transect

So what were the major factors influencing the distribution of OCPs along the transect? Individual linear regression analysis between OCP concentration and some available variable was performed to determine the major variables that correlated with the distribution of OCPs (Table 4). Single variables included: total organic carbon (TOC) of the soil, annual air temperature (T) during sampling dates, altitude (H) and longitude (L)

3.3.1. TOC

Linear regression analysis was performed between OCP concentration and %TOC, which were all natural log-transformed. Regressions for HEPT in winter and summer soil were weak significant ($P < 0.100$) (Table 4). TOC alone could explain up to 49% and 42% HEPT concentration variability in winter soil and summer soil, respectively. Nonachlor concentration in summer soil showed a weak correlation, with P-level < 0.100 (Table 4). Similar result had been observed by Daly et al. (2007c), with significant correlation for noachlor against soil organic matter in Yoho ($r = 0.92$, $P = 0.008$) and Observation ($r = 0.94$, $P = 0.001$), western Canada. This implied that TOC was an important variable that determined the distribution of soil HEPT and nonachlor concentrations in this transect.

However, chlordane, HEPX, endosulfan and HCB did not show significant correlations with TOC (Table 4), which mean other competing processes confound any influence of TOC. Soil Organic matter is a key parameter in the accumulation of hydrophobic organic contaminants in soils (Borghinia et al., 2005; Daly et al., 2007c; Tremolada et al., 2008). But in several cases, it can be partially or totally hidden by other elements being more important in determining the contamination levels in soil, e.g., distance from contamination sources, altitude or latitude (Holoubek et al., 2009; Tremolada et al., 2009; Wang et al., 2012).

3.3.2. Temperature

Mountain cold-trapping refers to the relative enrichment of some semivolatile organic compounds at high altitudes as a result of temperature controlled environmental partitioning processes (Daly et al., 2007c; Wania and Westgate, 2008). In the absence of significant local pollution sources, temperature was the primary factor to determine OCP accumulation in high-altitude regions (Daly and Wania, 2005; Kirchner et al., 2009; Tremolada et al., 2008).

When regressing against temperature, HCB concentration in winter soil showed a significant correlation, with P-level <0.050. The concentration of HCB in winter soil displayed a positive correlation versus temperature ($r = 0.53$) (Table 4). From the above spatial distribution of HCB, this transect, dominated by westerlies in winter and having relatively high temperature, showed higher HCB concentrations. The same results for HCB had been reported by various studies (Borghinia et al., 2005; Tremolada et al., 2009; Wang et al., 2012). The concentrations of chlordane, HEPT, HEPX, nonachlor and endosulfan did not show significant correlations (Table 4). This suggested that trapping of OCPs in this transect must be influenced by a complex integral of

Table 4

Correlation coefficients for variable linear regressions (r, P).

	Winter soil				Summer soil			
	Log TOC	T/K	H/m	L/m	Log TOC	T/K	H/m	L/m
Chlordane	0.21, 0.263	0.17, 0.312	−0.24, 0.238	0.21, 0.270	0.25, 0.234	−0.24, 0.241	0.37, 0.131	**−0.54, 0.045**
HEPT	**0.49, 0.065**	0.14, 0.341	−0.18, 0.297	0.18, 0.299	**0.42, 0.100**	−0.27, 0.211	−0.20, 0.277	0.04, 0.457
Nonachlor	–[a]	–[a]	–[a]	–[a]	**0.48, 0.097**	−0.12, 0.360	**0.46, 0.076**	−0.30, 0.183
HEPX	0.34, 0.154	−0.16, 0.316	−0.01, 0.492	−0.17, 0.307	–[a]	–[a]	–[a]	–[a]
Endosulfan	–[a]	–[a]	–[a]	–[a]	0.05, 0.442	−0.14, 0.344	0.30, 0.186	**−0.52, 0.050**
HCB	0.04, 0.450	**0.53, 0.046**	**−0.50, 0.060**	**0.49, 0.065**	0.10, 0.389	0.35, 0.143	0.11, 0.371	−0.01, 0.485

[a] Not calculated.

many factors, not solely temperature (Daly et al., 2007c; Shen et al., 2009; Wang et al., 2012).

3.3.3. Altitude

The HCB concentration in winter soil showed a weak correlation with altitude ($P < 0.100$), displaying a negative correlation ($r = -0.50$) (Table 4). Influenced by westerlies in winter, the air temperature in this transect showed decreasing trend with increasing altitude. As discussed above, the HCB concentration in winter soil displayed a positive correlation versus temperature. So HCB concentration in winter soil showed decreasing trend with increasing altitude. The result was contrary to previous studies that the HCB concentration had little changes (Barra et al., 2005; Daly et al., 2007c) or increasing trends along altitudinal gradient (Wang et al., 2012). Nonachlor concentration in winter soil was observed a weak correlation against altitude ($P < 0.100$), with a positive correlation ($r = 0.46$). But chlordane, HEPT, HEPX and endosulfan did not show significant correlations against altitudes (Table 4).

3.3.4. Longitude (distance from probable sources)

When regressing against longitude, the HCB concentration in winter soil was weak correlation ($P < 0.100$), displaying a positive correlation ($r = 0.49$) (Table 4). It indicated that higher HCB concentration occurred at the low-altitude regions where were probable sources or in the vincity of the probable sources (Fig. 4). The same result had been reported by Wang et al. (2012). The concentrations of chlordane and endosulfan in summer soil were significant correlation ($P < 0.050$) against longitude, with negative correlations (Table 4). It implied that the higher concentrations of such contaminants were observed far away probable source in summer soil (Fig. 4).

To sum up, there were no significant correlations between most soil OCP concentrations and various single variables in this study. This suggested that distribution of OCPs in this transect must be influenced by a complex integral of many factors. Similar results had been studied in various high-altitude regions, which may cause different variations at different mountainous regions. Turgut et al. (2011) found that OCPs in Taurus Mountains were not subject to the altitudinal gradient and soil physico-chemical property. Tremolada et al. (2008) showed that HCB and chlordane concentrations in Italian Alps mountain had a significant relationship with altitudinal gradient; while in Peruvian Andes, only DDT concentrations had some relevance with altitude. Daly et al. (2007c) detected that there was no significant correlation between the OCPs concentrations with altitude at Yoho in Canada; while in the soil of Revelstoke, there was a clear correlation between the concentrations of α-ES and β-ES with altitude. Ultimately, only model calculations would be able to provide a full understanding of how the interplay among such influencing factors determines the variability of contaminant in high-altitude regions (Daly et al., 2007a).

3.4. Soil–air exchange of OCPs in the transect

Soil–air exchange is a dynamic process resulting from the fugacity differences between the compounds. Fugacity model is used in many studies to monitor the migration direction of contaminants (Bozlaker et al., 2009; Cabrerizo et al., 2011; Wang et al., 2012). Table 5 listed relevant parameters and model equation for soil–air exchange fugacity models.

According to OCP concentrations in the soil and air at the same site in this transect, fugacity was calculated in winter and summer. Because of the low detectable ratios in soil, f_s and f_a calculations for some OCPs were unavailable. So this study only discussed the soil–air exchange status of CC, TC, α-ES, β-ES, HCB and HEPT in summer. The contour maps of f_s / f_a for such contaminants were shown in Fig. 5. The area shown from yellow to red referred to net volatilization from the soil to air, with $f_s / f_a > 1$; while the area shown below green referred to net deposition from air to soil with $f_s / f_a < 1$.

Except for the site B011, the f_s / f_a ratio of CC was less than 1 in all studied sites, suggesting evident net deposition from air to soil. The proportion of $f_s / f_a < 1$ for TC was 64%, indicating obvious deposition to soil at most sites; while the low-altitude areas (B002, B003 and B004) and the high-altitude area (B011) indicated obvious volatilization from soil to air.

The proportion of $f_s / f_a > 1$ for α-ES was 55%, indicating evident volatilization to air mainly at the sites (B001, B005, B007, B008, B010 and B011). Similarly, the proportion of $f_s / f_a > 1$ for β-ES was 55%, suggesting evident volatilization to air, mainly at the sites (B003, B004, B007, B009, B010 and B011).

In addition to the site B001, the f_s / f_a ratio of HCB was greater than 1 in all studied sites, with volatilization tendency to air, which was particularly evident in the high-altitude Hongyuan County and Aba County. As with HEPT, with the exception of the site B008, the f_s / f_a ratio was greater than 1 in all studied sites, all with volatilization tendency to air, which was particularly evident in the low-altitude Maoxian and the high-altitude Aba County.

In a word, Mianzhu—Aba prefecture transect may be a sink for CC, experiencing net deposition from air to soil. While this transect may be not only a sink, but also a secondary source for TC, α-ES and β-ES. As with HCB and HEPT, this transect may be a secondary source, experiencing net volatilization from the soil to air.

4. Conclusions

A total of 9 OCPs, including HCB, HEPT, HEPX, CC and TC, TN and CN, α-ES and β-ES were analyzed in Mianzhu—Aba prefecture transect, eastern of the Tibetan Plateau. Soil OCP concentrations in this transect were lower than those of some industrial/agricultural sites in various countries, which reflected the less of local pollution sources near the sampling sites and were consistent with the lower use of OCPs in high-altitude regions. The concentrations of OCPs in surface soils were slightly higher than those in other mountains, which might be partly attributed to the long-range atmospheric transport and also suggest current chlordane and endosulfan inputs. The temporal distribution observed for those compounds showed that chlordane exhibited higher winter soil concentration and HEPX exhibited higher summer soil concentration. And comparable mean concentrations in winter soil and summer soil were observed for HCB, HEPT and nonachlor. Different

Table 5
Fugacity model equation between soil and air (Wong et al., 2010).

Fugacity equation	Fugacity/Pa	Concentration/mol m^{-3}	Temperature/ K	Other parameters
$f_s = C_sRT/0.411\Phi_{om}K_{oa}$ $f_a = C_aRT$	f_s: fugacity in soil f_a: fugacity in air	C_s: soil concentration[a] C_a: air concentration	T: the average soil temperature T: the average air temperature	R: 8.31 $Pa\ m^3/(mol\ K)$; Φ_{om}: 1.7 times TOC[b]; K_{oa}: the octanol–air partition coefficient.
f_s / f_a	The $f_s / f_a > 1$ indicates net volatilization from the soil to air. The $f_s / f_a < 1$ indicates net deposition from air to soil. The $f_s / f_a \sim 1$ indicates equilibrium.			

[a] C_s is translated from ng g^{-1} to mol m^{-3} by water content in soil, molar mass and soil density ρ, which is 2650 kg m^{-3}.

[b] TOC in winter soil and summer soil are cited form the reports of Xing et al. (2010) and Xing et al. (2009).

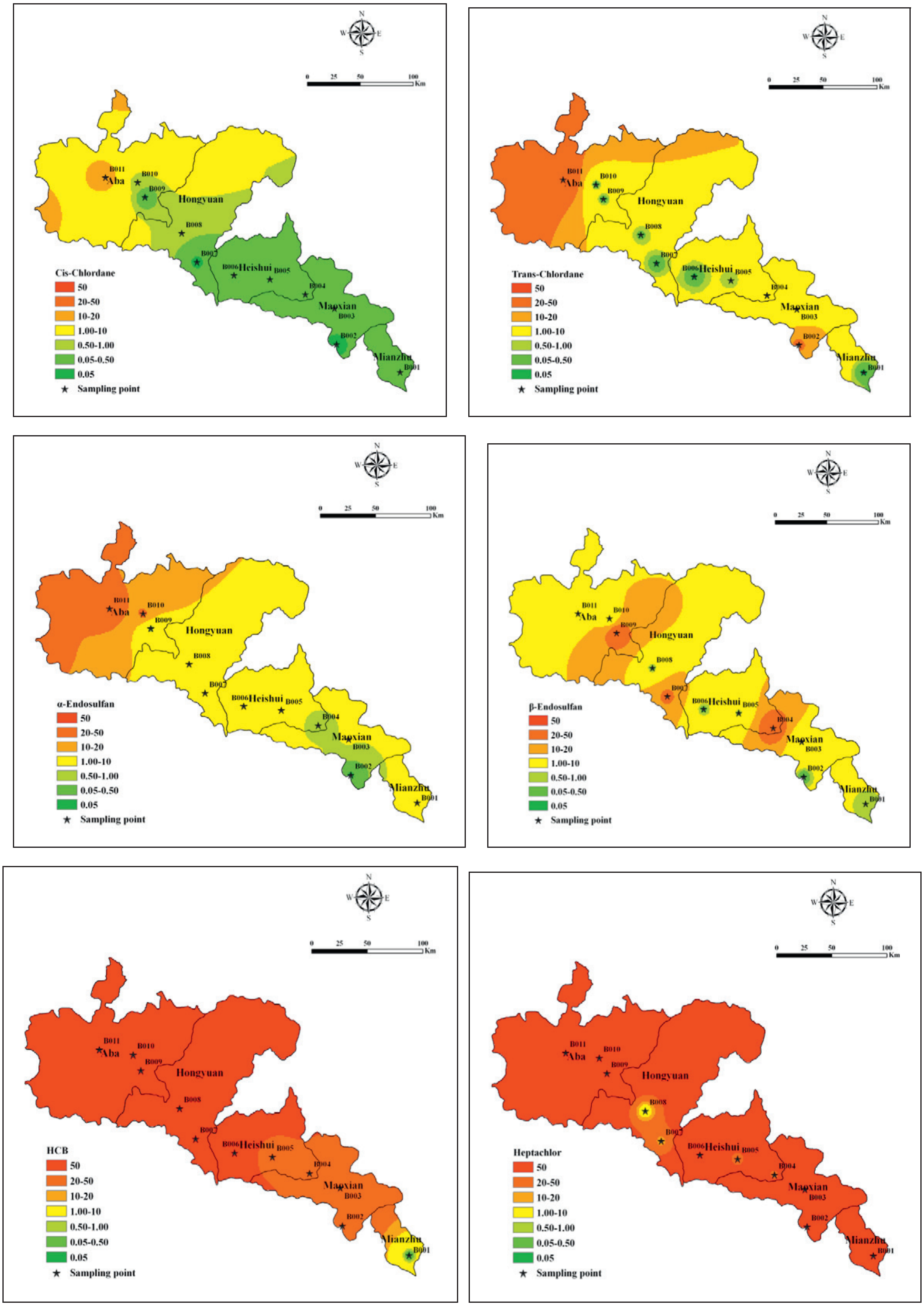

Fig. 5. The contour maps of f_s/f_a for CC, TC, α-ES, β-ES, HCB, HEPT in summer at Mianzhu—Aba prefecture transect, eastern of the Tibetan Plateau, western China.

distribution pattern for different OCPs along the transect. Individual linear regression analyses between OCP concentrations and some available variables showed that OCP distribution along this transect was influenced by many factors, not solely a variable. A primary fugacity analysis on OCP soil–air exchange indicated that this transect may be a sink for CC, and a secondary source for HCB and HEPT. While this transect may be not only a sink, but also a secondary source for TC, α-ES and β-ES.

This study made a preliminary analysis on the currently used OCPs in Mianzhu—Aba prefecture transect. The occurrence and distribution of OCPs in this transect further illustrated that various factors could determine the OCPs fate in the high-altitude regions. There are still many work needed to be done along this transect in the future. Climatic conditions should be considered (Daly and Wania, 2005; Kirchner et al., 2009; Tremolada et al., 2011), such as wind speed and direction, dry and wet precipitation, rain and snow, and so on. Various soil kinds including different vegetation and organisms should be analyzed (Daly et al., 2007c; Murano et al., 2009; Yang et al., 2008; Zheng et al., 2009). For OCPs, high-altitude water resources are considered to be valuable indicators for ecotoxicological risk assessment of these remote environments (Kallenborn, 2006; Yang et al., 2010). So water and aquatic lives should be monitored along this transect, considering that Aba prefecture is crisscrossed by more than 530 rivers.

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Appendix B

Hongxia Liu, Ying Hu, Shihua Qi, Xinli Xing, Yuan Zhang, Dan Yang and Chengkai Qu, 2015. Organochlorine Pesticide Residues in Surface Water from Sichuan Basin to Aba Prefecture Profile, East of the Tibetan Plateau. Frontiers of Earth Science, 9(2): 248-258.

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RESEARCH ARTICLE

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 $ng \cdot L^{-1}$. 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

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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.

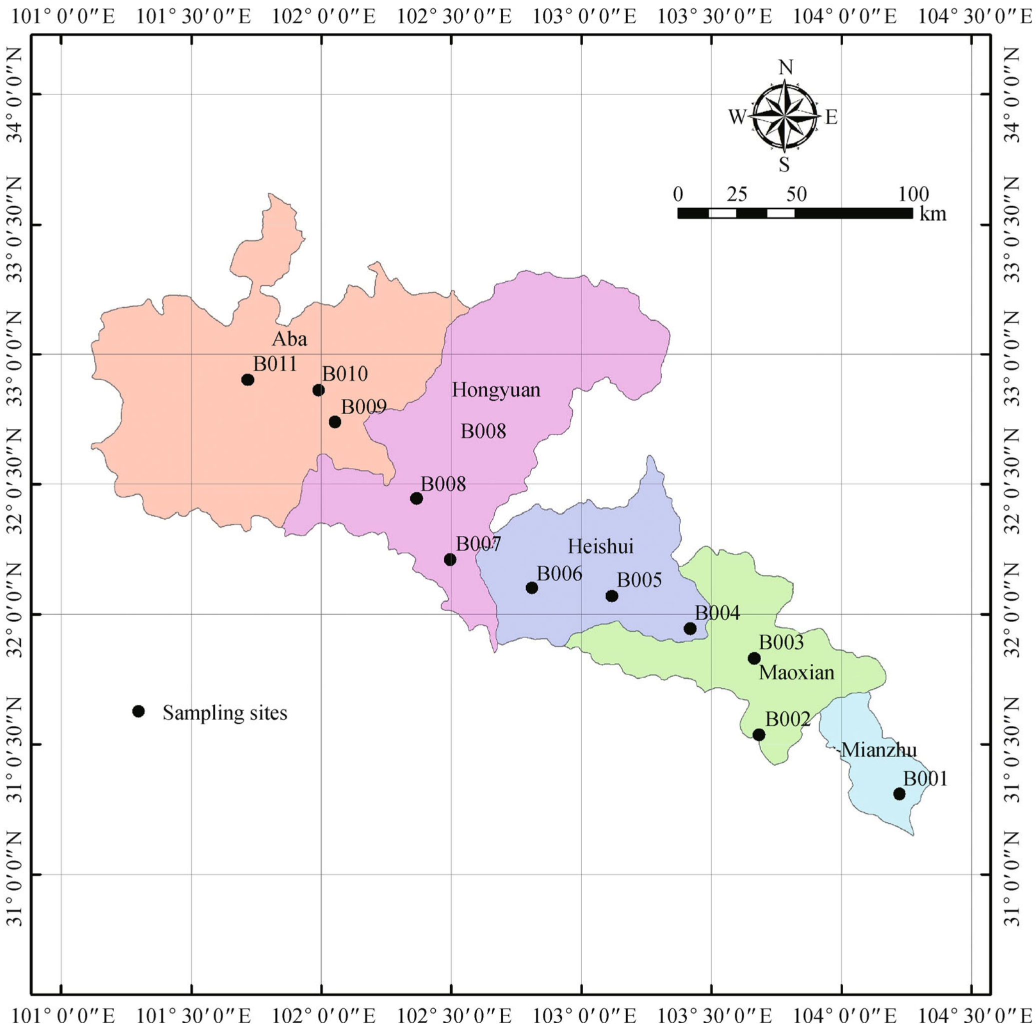


Fig. 1 Sampling sites along the Aba profile, Sichuan Province, China.

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*-*c*hlordane (TC), *trans*-nonachlor (TN) and *cis*-nonachlor (CN), *α*-endosulfan (*α*-ES) and *β*-endosulfan (*β*-ES). Silica gel (75–150 μm) 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 × 0.32 mm inner diameter × 0.25 μm 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°C/min to 200°C, at 2°C/min to 230°C, and lastly, at 8°C/min to 280°C, with a final holding time of 15 min. A 2 μL 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±10% and 76±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 $\mathrm{ng \cdot L^{-1}}$.

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:

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

$$R = CDI \times SF, \tag{2}$$

where CDI = chronic daily intake ($\mathrm{mg \cdot kg^{-1} \cdot day^{-1}}$), C = chemical concentration in water ($\mathrm{mg \cdot L^{-1}}$), IR = water ingestion rate ($\mathrm{l\ day^{-1}}$) (for children: $IR = 1.0$, for adults: $IR = 2.0$), EF = exposure frequency ($\mathrm{365\ days \cdot year^{-1}}$), 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 ($\mathrm{kg \cdot day^{-1} \cdot mg^{-1}}$).

To estimate non-carcinogenic risk, hazard quotient (HQ) was calculated using the following equation:

$$HQ = \frac{CDI}{RfD}, \tag{3}$$

where RfD ($\mathrm{mg \cdot kg^{-1} \cdot day^{-1}}$) 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 $\mathrm{ng \cdot L^{-1}}$. *β*-HCH, *o,p′*-DDT, HEPX, CN, *α*-ES, and *β*-ES were not detected in all samples. Mean concentrations ($\mathrm{ng \cdot L^{-1}}$) 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* /$(\mathrm{mg \cdot kg^{-1} \cdot day^{-1}})^{-1}$	*RfD* /$(\mathrm{mg \cdot kg^{-1} \cdot day^{-1}})$	Parameters	*SF* /$(\mathrm{mg \cdot kg^{-1} \cdot day^{-1}})^{-1}$	*RfD* /$(\mathrm{mg \cdot kg^{-1} \cdot day^{-1}})$
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
p,p'-DDT	N.D–28.39	5.55	6/11
p,p'-DDD	N.D–6.12	0.56	1/11
p,p'-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.

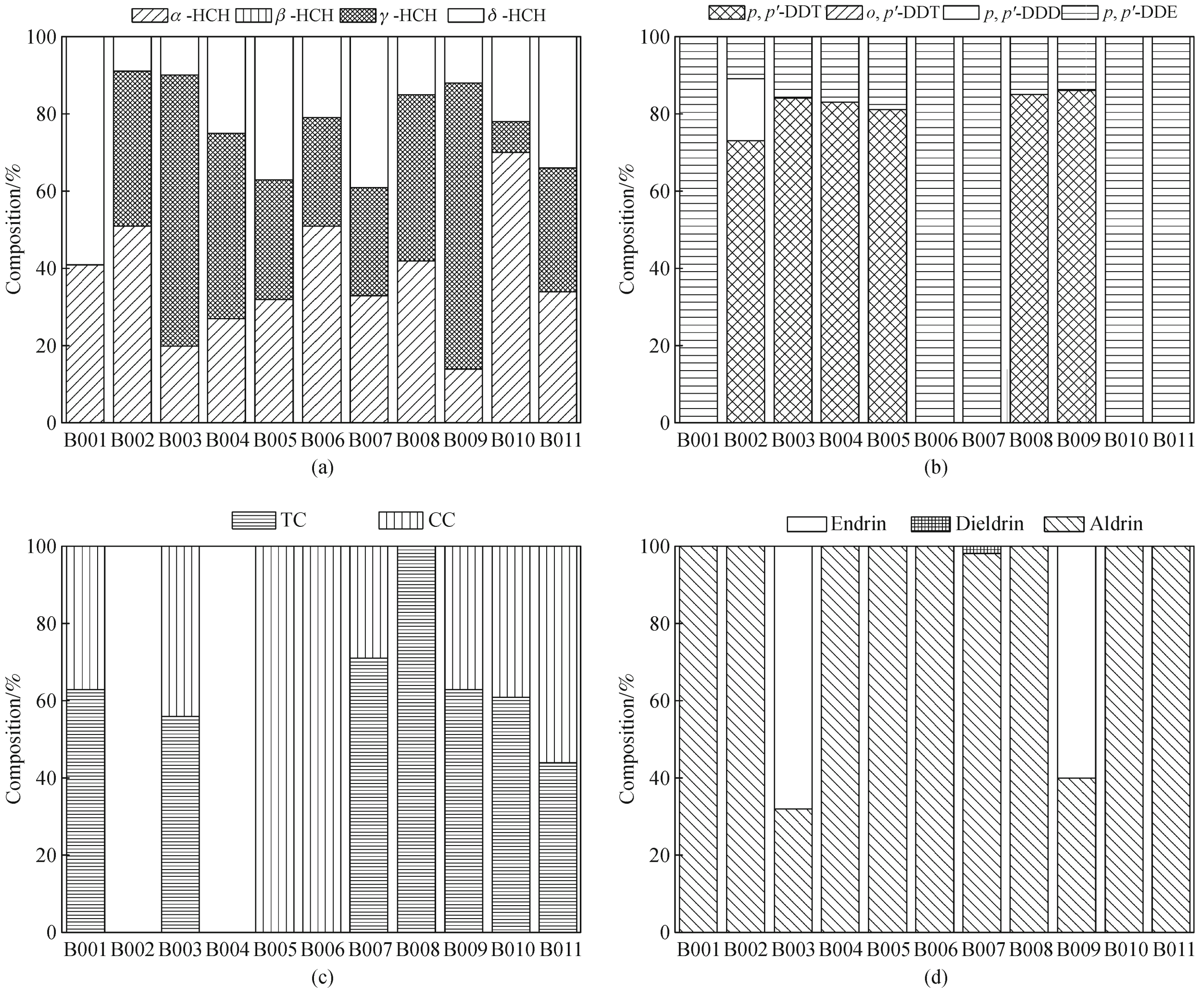
3.2 Potential sources of OCPs

In an aquatic system, HCB is more hydrophobic (logK_{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.



(a) (b)

(c) (d)

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 $\mathrm{t \cdot year^{-1}}$ 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-distance transport from neighboring countries (Jiang et al., 2009; Zhang et al., 2012).

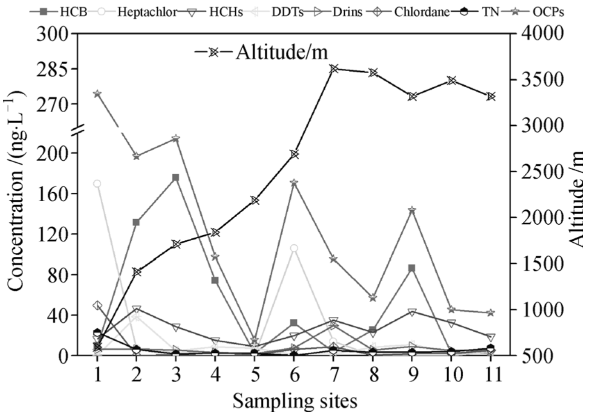


Fig. 3 Organochlorine pesticides in water samples along an altitudinal gradient in the Aba profile.

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

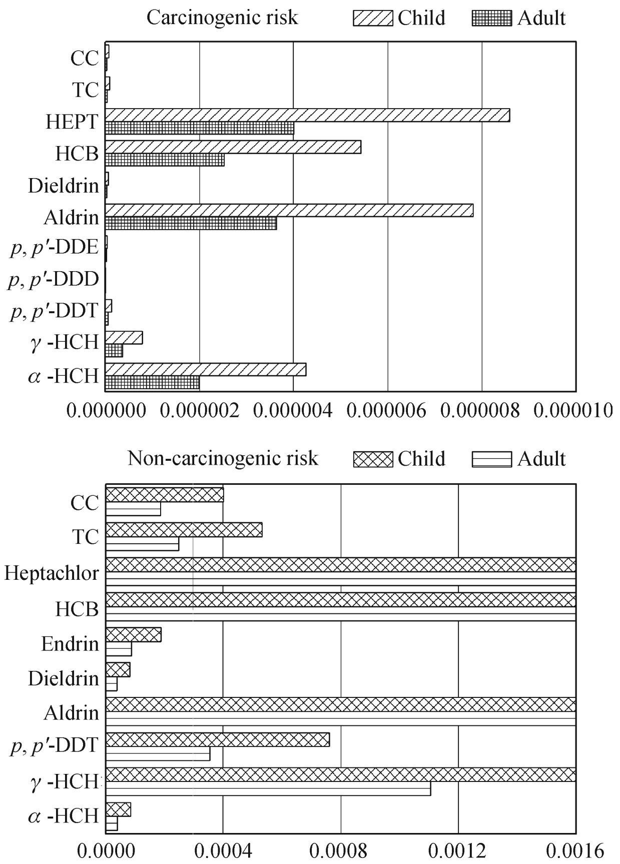


Fig. 4 Health risk assessment of organochlorine pesticides for individuals through drinking water in the Aba profile.

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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Appendix C

Dan Yang, Shihua Qi, Yuan Zhang, Xinli Xing, Hongxia Liu, Chengkai Qu, Jia Liu and Feng Li, 2013. Levels, Sources and Potential Risks of Polycyclic Aromatic Hydrocarbons (Pahs) in Multimedia Environment Along the Jinjiang River Mainstream to Quanzhou Bay, China. Marine pollution bulletin, 76: 298-306.

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Levels, sources and potential risks of polycyclic aromatic hydrocarbons (PAHs) in multimedia environment along the Jinjiang River mainstream to Quanzhou Bay, China

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ABSTRACT

This study investigated the levels, sources and potential risks of polycyclic aromatic hydrocarbons (PAHs) in soil, water (dissolved phase, suspended particulate matter) and sediment along the Jinjiang River mainstream to Quanzhou Bay. The distribution coefficient of ΣPAHs varied disorderly along the Jinjiang River, indicating the non-equilibrium status for the partition. The various distribution features of ΣPAHs in the sediments of the north and south coast of Quanzhou Bay were probably due to the flow motions in the bay. High correlations of PAHs were found between different media, suggesting the approximately same source of PAHs. Furthermore, three source factors and their contributions were extracted using the positive matrix factorization model. Toxicity and biological risk were assessed using toxic equivalent quantity and sediment quality guideline quotient. The contamination of PAHs in the soil and sediments may turn to unconspicuous risks for the environment and humans except very few sites with moderate pollution.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are widespread contaminants listed by international environmental protection agencies as priority pollutants due to their carcinogenic, mutagenic, and toxic effects (Carmichael et al., 1997). PAHs are originated mainly from anthropogenic sources such as the direct release of fossil oil and its products, and the combustion of fossil fuels, wood and other organic substances (Readman et al., 2002; Simpson et al., 1996; Yunker et al., 2002). In recent years, the environmental behavior of PAHs in estuarine and bay systems obtains increasing attentions, since these areas act as transition zones in which land-based pollutants caused by numerous human activities are transmitted to ocean via river (Tian et al., 2013; Pozo et al., 2011; Wang et al., 2013a).

Quanzhou Bay, located in the southeast coast of China, is an important bay in Fujian Province with its mouth opening towards Taiwan Straits. It is a semi-enclosed bay that receives industrial and municipal wastewaters from the watershed of the Jinjiang River and the Luoyang River. The Jinjiang River, the third largest river with most sand in Fujian Province, has much higher capacity of contaminants than the Luoyang River to Quanzhou Bay, because PAHs are hydrophobic and tend to associate with particulate matter, and then finally deposite to the underlying sediments of the estuary and bay (Tolosa et al., 2004). Moreover, Quanzhou Bay is rich in biodiversity with an important fishery port nearing the mouth of the Jinjiang River Estuary, hence the distribution of PAHs in the environment and potential risk to biota and human health need to be the focus of much attention. However, few studies have been reported to discuss the PAHs in Quanzhou Bay and the Jinjiang River area, especially the simultaneous and multimedia studies. Therefore, present study aims: (a) to assess the distributions and characteristics of PAH contamination along the Jinjiang River mainstream to Quanzhou Bay, focusing on the main phases in which pollutants may transport and accumulate in soil, water, suspended particles and sediment, (b) to identify possible sources of PAHs by composite pattern, isomeric ratios, relationships of PAHs between different environmental media and PMF model, and (c) to evaluate the potential toxicological and biological impacts on humans and environment using toxic equivalent quantity (TEQ) and sediment quality guideline quotient (SQGQ).

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2. Materials and methods

2.1. Sample collection

Sampling station locations are shown in Fig. 1. The surface soil (0–20 cm) (S1–18), water (J1–5) and sediment (Q1–8) sampling campaign were conducted during August 2011. Site S1 through S8 were located in the watershed of the Jinjiang River (JRW), while site S9 through S18 were located along the coast of Quanzhou Bay (QBC). Five water samples were collected along the mainstreams (lower reach) of the Jinjiang River from near surface (0–20 cm depth). These sites could reflect the transport of PAHs in the Jinjiang River mainstream, and PAHs inputs to Quanzhou Bay via river runoff. Each sample was mixed with both sides of the river water at one transect. After collection, the water samples were transported back to the field station immediately for filtration through fluorine ethylene filters (50 mm × 0.45 μm, Millipore, USA) to obtain dissolved phase (DP) samples (J1–5) and suspended particulate matter (SPM) samples (J1s–5s) for PAH analysis. Sixteen sediment samples were taken from intertidal mud flats along coastal areas nearing Quanzhou Bay, while eight surface (0–20 cm) and corresponding subsurface (20–40 cm) layers were sampled respectively. The soil, sediment and SPM samples wrapped with aluminum foil were stored in sealed polythene bags and freeze dried at −20 °C before extraction. Water samples were taken using pre-cleaned glass bottles and kept at −4 °C until further analysis.

2.2. Sample extraction

The sediment (10 g), soil (10 g) or filters samples were weighed and injected with PAH surrogates (naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12 and perylene-d12), and Soxhlet-extracted with dichloromethane (DCM) for 48 h. Water samples were spiked with the PAH surrogates mentioned above and extracted three times with 25 mL DCM each time. The extracts were treated with activated copper granules to remove elemental sulfur, concentrated and solvent-exchanged to *n*-hexane and further reduced to 2–3 mL by a rotary evaporator (Heidolph 4000, Germany). A 1:2 (v/v) alumina/silica gel column (48 h extraction with DCM, then 180 °C and 240 °C muffle drying for 12 h, both 3% deactivated with H_2O before using) was used to clean up the extracts and PAHs were eluted with 70 mL of DCM/hexane (2:3). The eluate was then reduced to 0.2 mL under a gentle stream of nitrogen. A known quantity of hexamethylbenzene was added as an internal standard for PAHs analysis prior to instrumental quantitation for the PAHs.

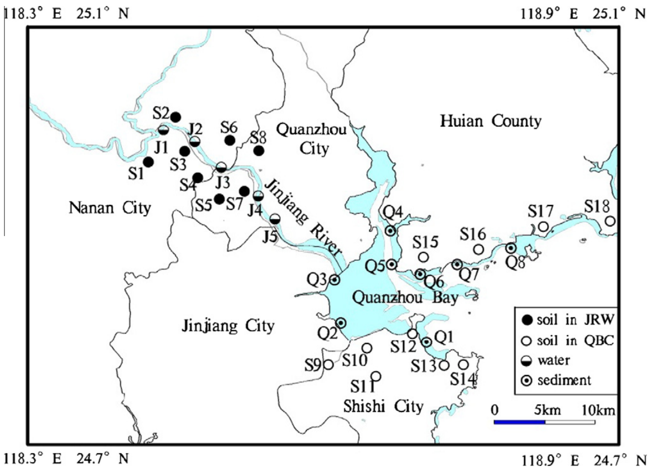

Fig. 1. Location of the sampling sites.

2.3. Analysis

PAHs were analyzed using GC-MS (Agilent 6890N/5975 MSD) coupled with a HP-5972 mass selective detector operated in the electron impact mode (70 eV) installed with a DB-5 capillary column (30 m × 0.25 mm diameter, 0.25 μm film thickness). Helium (99.999%) was used as the GC carrier gas at a constant flow of 1.5 $\mathrm{mL\,min^{-1}}$. An 1 μL concentrated sample was injected with splitless mode. The chromatographic conditions were as follows: injector temperature 270 °C; detector temperature 280 °C; oven temperature initially at 60 °C for 5 min, increased to 290 °C at 3 $\mathrm{°C\,min^{-1}}$, and held for 40 min. Chromatographic peaks of samples were identified by mass spectra and retention time. In this study, target analytes were 16 EPA priority PAH compounds: naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Fla), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]-pyrene (BaP), indeno[1,2,3-cd]pyrene (InP), dibenzo[a,h]anthrancene (DahA), and benzo[g,h,i]perylene (BghiP).

2.4. Quality assurance/quality control

Sixteen PAHs in a mixture and PAH surrogates were obtained from Ultra Scientific Inc. (North Kingston, RI, USA). Hexamethylbenzene were purchased from Aldrich Chemical (Gillingham, Dorset, USA). Chemical reagents, DCM and *n*-hexane were purchased from Tedia Co., USA.

In the QA/QC program, the instruments were calibrated weekly against reference materials. Method blanks, spiked blanks and sample duplicates were routinely analyzed with field samples in this study. No target compounds were detected in these blanks. In addition, surrogate standards were spiked to all the samples to correct procedural performance and matrix effects. Mean surrogate recoveries of naphthalene-d8, acenaphthene-d10, phenanthrene-d10, chrysene-d12 and perylene-d12 ranged from 77.0 ± 9.5% to 109 ± 8.8% in soil samples, from 83.2 ± 13.5% to 107 ± 7.9% in water samples, and from 85.4 ± 17.5% to 110 ± 10.2% in sediment samples, respectively. The variation of PAHs concentrations in duplicates was under 15%. The detection limit was calculated as three times of the signal-to-noise (S/N) level in blank samples. Detection limits for 16 PAHs were in the range of 0.12–0.47 $\mathrm{ng\,g^{-1}}$ dw, 0.09–0.52 $\mathrm{ng\,g^{-1}}$ dw, 0.24–0.56 $\mathrm{ng\,L^{-1}}$ and 0.09–0.52 $\mathrm{ng\,L^{-1}}$ for the soil, sediment, SPM and DP samples, respectively. Reported concentrations were corrected by surrogate recoveries. The PAHs concentrations in soil and sediment were expressed on dry weight (dw) basis.

2.5. Statistical analysis

Correlation analysis was performed using SPSS 18.0 software.

2.6. Data analysis by the positive matrix factorization (PMF) method

PMF is a powerful and useful factorization method that can calculate source profile and contribution of organic pollutants in the environment. PMF was widely used for source identification in atmosphere, and a few studies have applied it to determine source apportionment in soil and sediments (Tian et al., 2013; Yang et al., 2013). The PMF model is a receptor model with non-negative constraints that defines the concentration matrix of chemical species measured at receptor sites as the product of source composition and contribution factor matrices matrix with a residue matrix:

$$X_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \tag{1}$$

where X_{ij} is the concentration of species i measured in the sample j; f_{kj} is the contribution of the source k to the sample j; g_{ik} is the concentration of the species i from the source k; and e_{ij} is the residual for each sample/species. The task of PMF is to minimize the sum of squares Q by the residual matrix elements (e_{ij}) along with uncertainty (U_{ij}) estimates defined as:

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} (e_{ij}/U_{ij})^2 \tag{2}$$

The robust Q value reduces the impact of outliers in the fitting of the model. The theoretical Q value should be approximately equal to the number of data entries in the concentration file for a model. The uncertainties for each sample were calculated using measurement uncertainties (MU%) and method detection limits (MDL). If the concentration ⩽MDL, the uncertainty U_{ij} is calculated as:

$$U_{ij} = \frac{5}{6} \times \mathrm{MDL} \tag{3}$$

when the concentration >MDL, U_{ij} is calculated as:

$$U_{ij} = \sqrt{(\mathrm{MU} \times \mathrm{concentration})^2 + (\mathrm{MDL})^2} \tag{4}$$

More details about PMF can be found in reference (Paatero, 2007). The US EPA version of PMF (PMF 3.0) was used in the present study.

3. Results and discussion

3.1. PAH distributions in soil, water and sediment

3.1.1. PAHs in soil

The concentrations of the 16 PAHs, summed as ΣPAHs (Table 1), determined in the soils ranged from 19.03 to 179.35 ng g^{-1} with a mean value of 108.72 ± 61.31 ng g^{-1} in the watershed of the Jinjiang River (JRW) and from 63.22 to 281.48 ng g^{-1} with a mean value of 119.88 ± 73.18 ng g^{-1} in the coast of Quanzhou Bay (QBC) (Table 1), respectively. The ΣPAHs concentrations were found almost at the same level in JRW and QBC. The highest concentrations of ΣPAHs were observed at site S2 in JRW and S9 in QBC, while lowest at site S7 in JRW and S12 in QBC, respectively. Spatial variation of PAHs at different sites could be explained in terms of site environmental characteristics. Highest ΣPAHs concentrations were detected at site S9 (281.48 ng g^{-1}) in QBC, while compare with other present study sites. Possibly, it might be attributed from vehicular emission where passenger transport station was situated. Additionally, lower vehicular speed and frequent gear changing contributed higher PAH emissions (Wilcke, 2000). Lowest ΣPAHs concentrations were detected at site S7 (19.03 ng g^{-1}) in JRW, which is far from the urban, industrial and residential areas. In comparison with soils in Huanghuai Plain (China) (Yang et al., 2013), Shanghai (China) (Wang et al., 2013b), Viseu (Portugal) (Cachada et al., 2012), Bergenin (Norway) (Haugland et al., 2008) and Delhi (India) (Agarwal et al., 2009), the ΣPAHs concentrations in both JRW and QBC were relatively low (Table 4). Moreover, the pollutant levels suggested by Baumard et al. (1998) can be used to classify the relative contamination level. The four categories or groups were classified: (a) low, 0–100 ng g^{-1}; (b) moderate, 100–1000 ng g^{-1}; (c) high, 1000–5000 ng g^{-1}; and (d) very high, >5000 ng g^{-1}. Soils from JRW and QBC can be characterized as lowly to moderately PAHs pollution: (a) Sites S1, S4, S7, S8 in JRW, and S10–14, S17 in QBC (low); and (b) Sites S2–3, S5–6 in JRW and S9, S15–16, S18 in QBC (moderate).

The total concentration of seven PAHs (ΣC-PAHs, including BaA, Chr, BbF, BkF, BaP, InP, and DahA) are considered to be carcinogens (Sprovieri et al., 2007). ΣC-PAHs accounted for 0 (S7) to 73.06% (S3) of ΣPAHs in JRW, and 55.12% (S12) to 69.95% (S16) of ΣPAHs in QBC. S3 is near the trunk road, which is important for heavy trucks transporting and it is an important contributor for ΣC-PAHs. S16 is about 50 m away from a coal yard, the emission might be the reason for high ΣC-PAHs. ΣC-PAHs were not observed in S7, which has been mentioned above and considered to be the relatively clean site.

3.1.2. PAHs in surface water

Table 2 lists the PAHs concentration in dissolved phase (DP) and suspended particulate matter (SPM) of the surface water of the Jinjiang River. The ΣPAHs varied from 42.02 to 63.00 ng L^{-1}, with a mean concentration of 53.23 ± 7.69 ng L^{-1} in DP and from 144.00 to 217.24 ng L^{-1}, with a mean concentration of 173.99 ± 29.23 ng L^{-1} in SPM, respectively. The ΣPAHs in the Jinjiang River can be characterized as lower PAHs pollution while compared with other studies (Table 4). The ΣC-PAHs accounted for

Table 1
Concentrations of PAHs (ng g^{-1} dw) in surface soil of JRW and QBC.

Compound	JRW (*n* = 8)		QBC (*n* = 10)	
	Mean ± SD[a]	Range	Mean ± SD	Range
Nap	4.89 ± 3.55	ND[b]–12.20	3.60 ± 2.05	2.33–9.02
Acy	0.64 ± 0.40	ND–1.41	1.02 ± 1.12	0.30–4.11
Ace	1.00 ± 2.07	ND–6.11	0.53 ± 0.30	0.31–1.18
Flu	1.91 ± 1.99	ND–6.56	2.07 ± 1.18	0.85–4.94
Phe	9.62 ± 3.09	6.01–14.59	9.45 ± 4.34	5.29–20.65
Ant	1.59 ± 2.71	0.26–8.24	0.74 ± 1.05	0.24–3.67
Fla	5.38 ± 3.12	0.96–9.59	7.21 ± 6.13	2.83–20.28
Pyr	4.50 ± 2.32	1.97–7.62	6.51 ± 6.18	2.26–19.85
BaA	1.92 ± 1.46	ND–3.52	3.03 ± 3.35	0.76–9.40
Chr	20.25 ± 12.47	ND–36.07	19.91 ± 9.09	10.44–38.48
BbF	11.68 ± 8.63	ND–21.01	12.59 ± 7.39	4.88–26.06
BkF	8.05 ± 5.95	ND–14.36	10.79 ± 8.67	3.74–30.91
BaP	14.60 ± 10.64	ND–26.19	16.43 ± 9.30	6.68–30.70
InP	9.91 ± 7.14	ND–19.50	11.07 ± 5.95	4.85–21.25
DahA	1.70 ± 1.35	ND–3.49	3.18 ± 5.22	0.71–17.55
BghiP	11.08 ± 8.61	ND–25.69	11.78 ± 8.09	4.28–26.67
ΣC-PAHs	68.11 ± 46.99	ND–120.10	76.99 ± 45.99	34.84–173.00
ΣPAHs	108.72 ± 61.31	19.03–179.35	119.88 ± 73.18	63.22–281.48
ΣC-PAHs/ΣPAHs	53.83 ± 23.70%	0–73.06%	64.03 ± 5.26%	55.12–69.95%

[a] Arithmetic mean ± standard deviations.
[b] ND represents not detected.

Table 2
Concentrations of PAHs (ng L^{-1}) in DP and SPM of surface water in the Jinjiang River.

Compound	DP (n = 5)		SPM (n = 5)	
	Mean ± SD[a]	Range	Mean ± SD	Range
Nap	11.45 ± 4.37	7.23–18.78	14.84 ± 2.56	11.83–18.11
Acy	2.85 ± 1.27	1.93–5.00	8.05 ± 3.41	3.04–12.06
Ace	2.15 ± 1.97	0.72–5.58	14.36 ± 3.56	11.71–20.25
Flu	4.95 ± 0.78	3.88–5.85	13.45 ± 1.91	10.98–15.67
Phe	13.07 ± 1.99	10.66–15.43	32.13 ± 34.70	14.94–94.11
Ant	0.68 ± 1.18	ND[b]–2.76	1.98 ± 0.61	1.31–2.83
Fla	6.14 ± 1.17	4.79–7.67	16.34 ± 2.38	13.75–20.10
Pyr	2.97 ± 0.40	2.54–3.59	16.89 ± 5.18	1.20–22.50
BaA	0.42 ± 0.13	0.28–0.60	8.62 ± 2.11	5.99–10.66
Chr	5.65 ± 3.17	0.66–9.18	12.99 ± 1.35	10.86–14.44
BbF	0.54 ± 0.48	ND–1.14	6.60 ± 1.90	4.12–8.78
BkF	0.72 ± 0.51	ND–1.36	16.00 ± 9.25	3.40–27.70
BaP	1.67 ± 3.09	ND–7.12	5.28 ± 1.89	3.18–8.09
InP	ND	ND	3.50 ± 1.02	2.31–4.88
DahA	ND	ND	2.97 ± 2.04	1.13–6.29
BghiP	ND	ND	ND	ND
ΣC-PAHs	9.00 ± 6.04	2.72–18.57	55.96 ± 14.31	35.91–74.90
ΣPAHs	53.23 ± 7.69	42.02–63.00	173.99 ± 29.23	144.00–217.24
ΣC-PAHs/ΣPAHs	16.35 ± 8.94%	4.93–29.48%	33.18 ± 10.00%	16.53–41.65%

[a] Arithmetic mean ± standard deviations.

[b] ND represents not detected.

16.35 ± 8.94% in DP and 33.18 ± 10.00% in SPM of the ΣPAHs concentration. These ratios were much lower than that in the soil samples, which might be due to the characteristic of PAHs, dilution and precipitation during river transport. Obviously, the concentrations of PAH compounds were all much higher in SPM than in DP which agrees with that PAHs tend to associate with particulate matter due to their hydrophobic nature. However, the distribution coefficient (K_P) (defined as the ratio of the concentration of PAHs with SPM to that in DP) of ΣPAHs varied (from 2.29 to 4.30) irregularly along the Jinjiang River, and the highest ΣPAHs in SPM and DP were found in J5 (217.24 ng L^{-1}) and J2 (63.00 ng L^{-1}), respectively. In addition, there was no correlation between K_P and dissolved organic carbon (DOC), or conductance. This is similar to the reports on the Yangtze Estuary where no correlation between K_P and DOC, or salinity of seawater was found (Luo et al., 2008). Therefore, the possible reason for this behavior may be that the particulate organic carbon and heterogeneous mixtures of particulate soot carbon could influence the PAH partition (Wu et al., 2011), thus partitioning is probably in the non-equilibrium status for the partition.

3.1.3. PAHs in sediment

Concentrations of individual PAHs, ΣC-PAHs and ΣPAHs in surface sediments (SS) (0–20 cm) and subsurface sediment (SSS) (20–40 cm) along coastal areas nearing Quanzhou Bay were shown in Table 3. The status of ΣPAHs contamination were found at the same low level in SS (39.63 ± 30.28 ng g^{-1}) and SSS (38.14 ± 27.29 ng g^{-1}), comparing with other bays and estuaries in the world. The highest ΣPAHs were recorded at Q3 (108.35 ng g^{-1} for SS and 85.61 ng g^{-1} for SSS). Site Q3 is located in the downstream of the Jinjiang River running into Quanzhou Bay where heavy pollution from land-based sources via river runoff might occur at Q3. Moreover, only site Q3 can be characterized as moderate PAHs pollution according to the classification suggested by Baumard et al. (1998), while other sites were of the low PAHs pollution with the ΣPAHs concentration much lower than 100 ng g^{-1}. Q4 is also located in the river mouth of the Luoyang River, but the ΣPAHs concentration (45.40 ng g^{-1} for SS and 41.09 ng g^{-1} for SSS) were not that high as Q3, which might because the Luoyang River has less runoff and carries less sand and pollutants.

It is interesting to find that the concentration of ΣPAHs in SS (9.48–25.10 ng g^{-1}) were all lower than that in SSS (11.48–78.77 ng g^{-1}) in the sites Q5–8, which are in the north coast of Quanzhou Bay, whereas ΣPAHs were found higher in SS (34.68–59.99 ng g^{-1}) than in SSS (19.91–29.93 ng g^{-1}) in site Q1–2 located in the south coast of the bay. This was probably due to the flow motions in the bay, which play a major role in transporting substances and in redistributing particles and related contaminants in the environment (Ko and Baker, 1995). The sand tend to accumulate in the north of Quanzhou bay accompanying the river and ocean current running into it, while south channel is the main way for sand to flow off the bay (Li et al., 2008). So, the sand with pollutants had enough time to settle down, move downwards and accumulate in the SSS in the north of Quanzhou bay. But for Q1–2, the river runoff moved faster and the pollutants were washed away before moving downwards to the south of the bay.

Additionally, ΣC-PAHs in the SS (22.39 ± 21.12 ng g^{-1}) and SSS (19.71 ± 19.10 ng g^{-1}) were at the same level, and accounted for 41.06 ± 17.26% and 41.57 ± 17.08% of the ΣPAHs in SS and SSS, respectively. These ratios were a little lower than those in the soil in JRW and QBC, but much higher than surface water of the Jinjiang River in the present study.

3.2. Source identification

3.2.1. Composition pattern of PAHs

PAHs composition pattern conveys the important information on different sources that contribute PAHs to environmental samples (Cao et al., 2005). The high molecular weight PAHs (HPAHs) (4- to 6-ring) are mainly from the high-temperature combustion process (*i.e.* vehicular exhaust, anthropogenic combustion or pyrogenic sources), while the light molecular weight PAHs (LPAHs) (2- to 3-ring) are chiefly originated from low- or moderate-temperature combustion process (*i.e.* coal burning) (Harrison et al., 1996; Mai et al., 2003). The PAH composition characteristics varied in different phases and sites in this study (Fig. 2). HPAHs were dominant in soil, SPM and sediment samples except S7 (clean site), J5s and Q7–8, indicating a prevalence of high temperature pyrogenic contamination processes over petrogenic sources. This predominance may also be due to the higher persistence of these high molecular weight compounds in soils, SPM and sediment, and the tendency of HPAHs to accumulate in solid phase which has higher organic

Table 3
Concentrations of PAHs (ng g^{-1} dw) in surface (0–20 cm) and subsurface (20–40 cm) layers of sediment along nearby coastal areas of Quanzhou Bay.

Compound	SS ($n = 8$)		SSS ($n = 8$)	
	Mean ± SD[a]	Range	Mean ± SD	Range
Nap	3.23 ± 1.41	1.08–5.74	3.11 ± 0.96	1.69–4.62
Acy	0.36 ± 0.22	0.07–0.69	0.32 ± 0.14	0.08–0.51
Ace	0.34 ± 0.11	0.17–0.50	0.37 ± 0.10	0.17–0.49
Flu	1.19 ± 0.71	0.41–2.37	1.16 ± 0.61	0.57–2.01
Phe	6.66 ± 2.44	3.59–10.74	6.16 ± 2.52	3.97–10.41
Ant	0.34 ± 0.29	0.00–0.92	0.34 ± 0.22	0.10–0.72
Fla	2.90 ± 1.99	0.97–7.28	2.68 ± 1.78	1.11–5.80
Pyr	2.33 ± 1.64	0.67–5.72	2.11 ± 1.51	0.70–4.70
BaA	0.72 ± 0.75	0.07–2.46	0.71 ± 0.73	0.07–2.01
Chr	8.49 ± 7.82	0.92–26.80	7.67 ± 6.17	1.66–19.04
BbF	3.30 ± 3.69	0.04–12.24	3.07 ± 3.08	0.14–8.24
BkF	1.76 ± 2.28	0.06–6.98	1.90 ± 2.14	ND[b]–6.09
BaP	4.04 ± 4.16	0.10–13.11	4.06 ± 4.27	0.06–12.16
InP	1.81 ± 2.21	ND–6.60	1.94 ± 2.29	ND–5.97
DahA	0.26 ± 0.43	ND–1.07	0.35 ± 0.60	ND–1.60
BghiP	1.89 ± 2.21	ND–6.86	2.19 ± 2.58	ND–7.09
ΣC-PAHs	22.39 ± 21.12	1.22–69.27	19.71 ± 19.10	1.93–51.35
ΣPAHs	39.63 ± 30.28	9.48–108.35	38.14 ± 27.29	11.48–85.61
ΣC-PAHs/ΣPAHs	41.06 ± 17.26%	12.85–63.93%	41.57 ± 17.08%	16.82–64.78%

[a] Arithmetic mean ± standard deviations.
[b] ND represents not detected.

matter (Chung et al., 2007). However, the dominance of HPAHs in SPM were relatively weak and LPAHs were found dominant in DP in the study (Fig. 2), showing the partition may influence the PAHs distribution in SPM and DP in the water. So, the PAHs in water are likely derived from petroleum and its products.

3.2.2. Isomeric ratios of PAHs

Several PAH congener ratios have been selected as indicators for the best potential to elucidate pyrolytic and petrogenic sources. PAH isomer pairs ratios, such as Ant/(Phe + Ant) and Fla/(Fla + Pyr) have been widely used to distinguish the possible source categories of PAHs in the environment, for their relative stable feature (Yunker et al., 2002; Wu et al., 2011; Magi et al., 2002). The Phe is thermodynamically more stable than Ant, and the Ant/(Phe + Ant) ratio of 0.1 is generally used to differentiate between pyrolytic (*i.e.* combustion of organic matter, anthropogenic industrial activities, or natural fire) and petrogenic origins (crude oil and its refined products). Petroleum product usually exhibits a quite low Ant/(Phe + Ant) ratio, whereas it reveals that the environment is mainly contaminated by petrogenic inputs with Ant/(Phe + Ant) > 0.1 (Yunker et al., 2002). Moreover, the Fla/(Fla + Pyr) ratio is another useful indicator in analyzing the attribution of PAH pollution (Magi et al., 2002). When Fla/(Fla + Pyr) is less than 0.4, PAHs are mainly from typical petroleum contamination. If the ratios are between 0.4 and 0.5, PAHs are originated from combustion of petroleum. Typical biomass combustion (grass, wood, or coal

Table 4
Total PAHs in different locations.

Medium	Locations	n[a]	ΣPAHs (ng g^{-1}, ng L^{-1})[b]		References
			Mean	Range	
Soil	Huanghuai Plain, China	15	128	14–1246	Yang et al. (2013)
	Shanghai, China	16	1970	83.3–7220	Wang et al. (2013b)
	Viseu, Portugal	16	169	6.0–790	Cachada et al. (2012)
	Bergenin, Norway	16	6780	1600–9500	Haugland et al. (2008)
	Delhi, India	16	1910	830–3880	Agarwal et al. (2009)
	Jinjiang River Watershed, China	16	108.72	19.03–179.35	This study
	Quanzhou BayCoast, China	16	119.88	63.22–281.48	This study
DP	Daliao River Estuary, China	16	486.39	139.16–1717.87	Men et al. (2009)
	Yellow River Delta, China	16	121.3	64.8–334.6	Wang et al. (2009a,b)
	River Tiber, Italy	6	43.4	23.9–72.0	Patrolecco et al. (2010)
	New York Estuary, USA	27	31.9	6.0–72.2	Gigliotti et al. (2002)
	Jinjiang River, China	16	53.23	42.02–63.00	This study
SPM	Daliao River Estuary, China	16	466.84	226.57–1404.85	Men et al. (2009)
	Yellow River Delta, China	16	209.1	65.6–675.4	Wang et al. (2009b)
	Hugli Estuary, India	19	270.5	25–1081	Guzzella et al. (2005)
	Sarno River Estimate, Italy	16	254.9	6.1–778.9	Montuori and Triassi (2012)
	Jinjiang River, China	16	173.99	144.00–217.24	This study
Sediment	Liaodong Bay, China	16	743.03	276.26–1606.89	Men et al. (2009)
	Jiaozhou Bay, China	16	559.1	16–2164	Wang et al. (2006)
	Gulf of Gela, Italy	16	103.91	2.4–434	Orecchio et al. (2010)
	Lenga Estuary, Chile	16	2025	290–6118	Pozo et al. (2011)
	Pearl River Estuary, China	18	362	189.1–636.7	Luo et al. (2006)
	Quanzhou Bay, China	16	39.63	9.48–108.35	This study

[a] n is the number of PAH compounds analyzed in each study.
[b] Concentration of DP and SPM in ng L^{-1}; concentration of soil and sediment in ng g^{-1} dw.

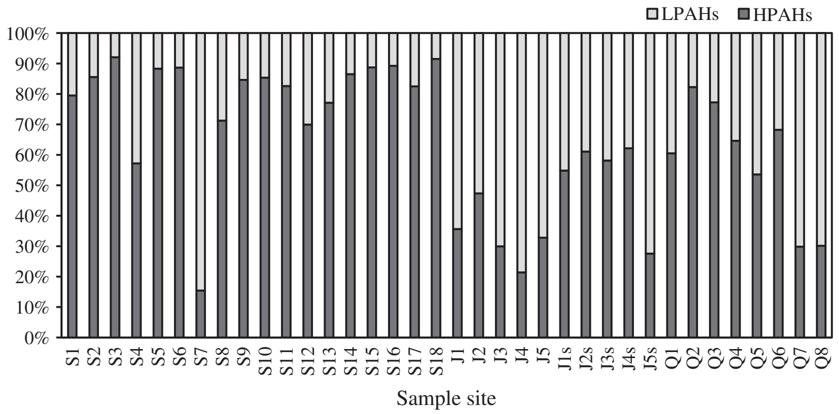

Fig. 2. Percentage level of LPAHs (2- to 3-ring) and HPAHs (4- to 6-ring) at sampling stations. J1–5 represent DP in surface water of the Jinjiang River, while J1s–5s are the corresponding SPM samples for site J1–5. Q1–8 present SS along nearby coastal areas of Quanzhou Bay.

combustion) would cause the increase of PAHs when this ratio is higher than 0.5.

As showed in Fig. 3, the ratios of Ant/(Phe + Ant) at most sites were lower than 0.1, indicating that the main PAH source was petroleum products. Stations J5, J1s, S7 and S9 were higher than 0.1, which implies that the PAH source could be combustion activities. For Fla/(Fla + Pyr), the ratios of most sites (especially the soil and sediment sites) <0.4 suggested that PAHs were mainly from petroleum contamination. These ratios in site S8, S13, S17, J2s, J3s and Q8 were between 0.4 and 0.5, suggesting the combustion of petroleum was the cause of PAHs, while the ratio of some sites (e.g. S4, S12, J1–5, J5s, Q7) > 0.5 indicated that PAHs were mainly from biomass combustion. It can be concluded that a mixed pattern of PAH sources was found in the soil, DP, SPM and sediment in the study area, while this is a simplified interpretation and the varying combinations of PAH sources (combustion of fossil fuels and vehicle traffic) may contribute to the isomer ratios observed.

3.2.3. *Relationships of PAHs between different environmental media*

Moreover, in order to make a further study of the source identification of PAHs, in this section, the relationships of ΣPAHs and ΣC-PAHs between different environmental media were investigated (Tables 5 and 6), respectively, which can give the information to study the transport and relationships of PAHs in these different environment media. The distributions of ΣPAHs and ΣC-PAHs in the soil of NJR and QBC, as well as the sediment of Quanzhou Bay showed high correlation ($p < 0.01$, detailed in Tables 5 and 6), suggesting a possible same source of PAHs in the soil and sediment in these areas. The ΣPAHs in SPM, considered to be the important source of sediment, had low correlation with that in sediment ($r = 0.488$ for SPM and SS, $r = 0.456$ for SPM and SSS), and for ΣC-PAHs, the correlation was much lower ($r = 0.389$ for SPM and SS, $r = 0.385$ for SPM and SSS). Conversely, the ΣPAHs

Table 5
Correlations of ΣPAHs between different environmental media.

Media	NJR	QBC	DP	SPM	SS	SSS
NJR	1.000					
QBC	0.982**	1.000				
DP	0.095	0.000	1.000			
SPM	0.020	0.002	0.792**	1.000		
SS	0.823**	0.761**	0.584*	0.488	1.000	
SSS	0.848**	0.790**	0.568*	0.456	0.977**	1.000

* Correlation is significant at the 0.05 level (2-tailed).
** Correlation is significant at the 0.01 level (2-tailed).

Table 6
Correlations of ΣC-PAHs between different environmental media.

Media	NJR	QBC	DP	SPM	SS	SSS
NJR	1.000					
QBC	0.991**	1.000				
DP	0.800**	0.753**	1.000			
SPM	0.296	0.325	0.491	1.000		
SS	0.940**	0.901**	0.947**	0.389	1.000	
SSS	0.955**	0.923**	0.938**	0.385	0.998**	1.000

** Correlation is significant at the 0.01 level (2-tailed).

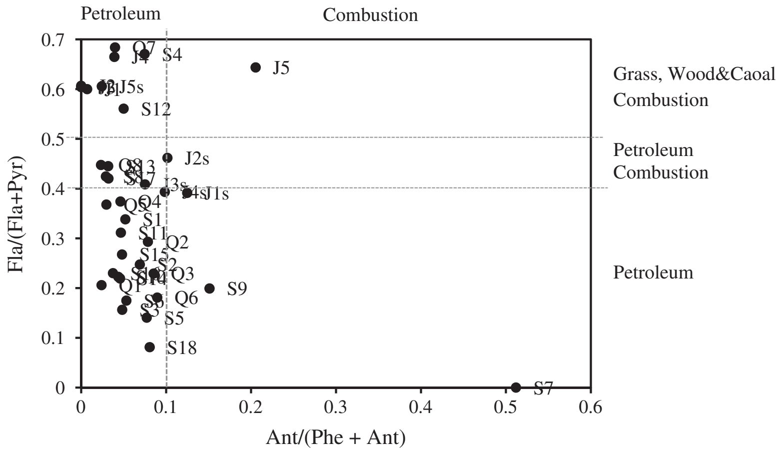

Fig. 3. PAHs cross plots for the ratios of Fla/(Fla + Pyr) and Ant/(Phe + Ant) in the study region.

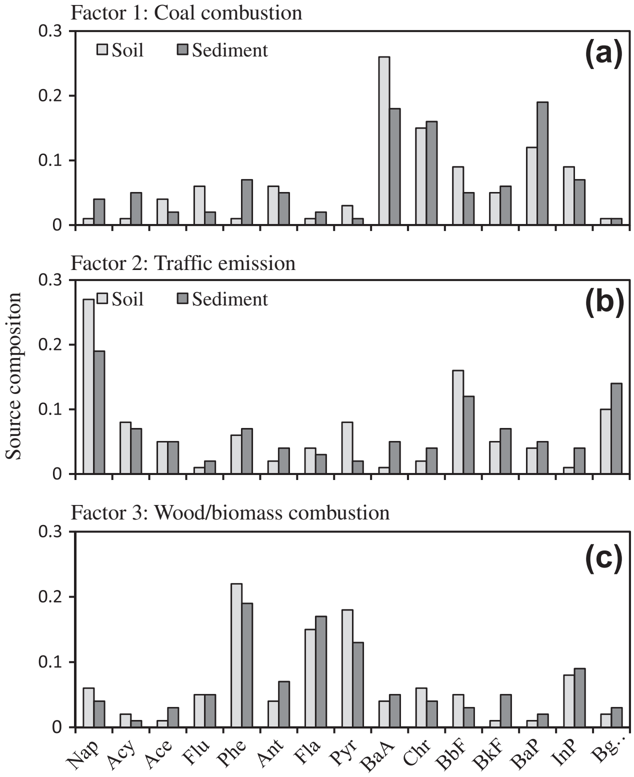

Fig. 4. Source profiles of the PAHs obtained from the PMF model in soil and sediment of the study area.

especially ΣC-PAHs in DP showed high correlation with that in sediment ($r = 0.584$, $p < 0.05$ for ΣPAHs in DP and SS, $r = 0.568$, $p < 0.05$ for ΣPAHs in DP and SSS, $r = 0.947$, $p < 0.01$ for ΣC-PAHs in DP and SS, $r = 0.938$, $p < 0.01$ for ΣC-PAHs in DP and SSS). The possible reason may be that the Jinjiang River is rich in SPM, and SPM usually increase in the summer sampling time, then concentration of colloid organic matters increase, which caused the increase of dissolved PAHs (Schrap et al., 1995), especially for ΣC-PAHs with high molecular weight. So, the PAHs in DP performed to have the similar source with that in sediment. The relatively high correlations of ΣPAHs ($r = 0.792$, $p < 0.01$) and low correlations of ΣC-PAHs ($r = 0.491$) between DP and SPM in the surface water, respectively, might imply the ΣC-PAHs had different partition in DP and SPM by their features, such as high hydrophobicity, or other controlling factors unknown to influence the occurrence of PAHs in the environment (Desaules et al., 2008).

3.2.4. Positive matrix factorization (PMF)

The foregoing source analysis had provided the qualitative identification, and implied that the PAHs in soil and sediment might have similar source. Therefore, PMF was applied to identify the possible sources and their contributions of PAHs in the soil and sediments in this work, respectively. Considering DahA with low detectable ratio in both soil and sediment and ΣC-PAHs with low detectable ratios in Q7–8, the PMF analysis were applied using 15 PAHs from 18 soil samples (matrix: 18 × 15) and 12 sediment samples (sum of SS and SSS in sites Q1–6) (matrix: 12 × 15), separately. The PMF model was run requesting 3–6 factors, and each run was initialized with different starting points *i.e.* changing the seed value from 1 to 20. This was done to better understand the stability of the solution. The model was run in the robust mode to keep outliers from unduly influencing the results. Different runs were performed to improve results by down weighting species with low S/N ratio from "strong" to "weak". In this way, only Acy was considered as "weak" and the other 14 variables as "strong". The *Q* values were not significantly different from each other, which was approximately equivalent to the theoretical *Q*, so we could consider that the PMF calculation reached a global minimum point in this work. The robust *Q* was found to be 3302 and the true *Q* was 3425. The "optimal" solution was considered as a stable solution that did not depend on the initial seed and had a robust *Q* value near the theoretical *Q* value. In addition, the factor number was determined by considering whether the decrease of *Q* is significantly higher than double of the sum of variables and samples numbers when increasing factor number by one.

Consequently, three source factors were extracted by the PMF model in the soil and sediment, respectively (Fig. 4). It can be distributed that the first factor showed high loading for BaA, Chr and BaP, indicating a coal combustion source (Simcik et al., 1999). The second factor correlated strongly with the PAH species including Nap, BbF and BghiP, which were consistent with sources related to traffic emission sources (Wang et al., 2009a). The third factor was predominated by Phe, Fla and Pyr, which were linked with wood/biomass combustion sources (Yang et al., 2013). The source contributions to ΣPAHs of the three factors were also estimated by the PMF model. The coal combustion source (Factor 1), traffic emission sources (Factor 2) and wood/biomass combustion sources (Factor 3) represented 39.6%, 27.3% and 33.1% of the PAHs for soil and 34.5%, 29.2% and 36.3% of the PAHs for sediment, respectively.

3.3. Toxicity and risk assessment

3.3.1. Toxic equivalent quantity

Soils and sediment with high organic matter were considered to be the important reservoirs for the PAHs in the environment, as well as pose persistent potential toxicological and biological impacts to biota and even human beings through bioaccumulation in food chains (Pozo et al., 2011). Therefore, we focus on the potential toxicological and biological impacts of soil and sediment on humans and the environment in this section.

The assessment of soil and sediment toxicity in this study was performed based on the benzo[a]pyrene toxic equivalency factors (TEFs). Among PAHs, ΣC-PAHs are of high concern due to their potentially carcinogenic toxicities. In order to estimate the toxicity of PAHs, toxic equivalent quantity (TEQ) was calculated by multiplying the concentration of ΣC-PAHs by the corresponding TEF (USEPA, 2012). According to USEPA (2012), TEFs for BaA, Chr, BbF, BkF, BaP, InP, and DahA were 0.1, 0.01, 1, 0.1, 0.1, 0.1 and 1, respectively. The TEQ for all ΣC-PAHs in each site was calculated using the following equation:

$$TEQ_{PAHs} = \sum TEF_i \times C_{PAHi} \quad (5)$$

where, C_{PAHi} is the carcinogenic PAHs concentration (ng g^{-1} dw); TEF_i is the toxic factor of each ΣC-PAHs relative to benzo[a]pyrene. In this study, the total TEQ_{PAHs} calculated for the soil of JRW and QBC varied from 0 to 33.71 ng TEQ g^{-1} dw, with a mean of 18.75 ng TEQ g^{-1} dw and from 9.09 to 54.14 ng TEQ g^{-1} dw, with a mean of 22.41 ng TEQ g^{-1} dw, respectively. Among all soil samples, the maximum value of TEQ_{PAHs} was found at S9 which was located near a passenger transport station, suggesting the great influence of vehicular sources. The risk-based soil criterion for protection of human health from Canada, based on PAH carcinogenic effect (CCME, 2010), indicates a safe level of 600 ng TEQ g^{-1} dw. All the soil samples showed values below this guideline.

The total TEQ_{PAHs} ranged from 0.12 to 16.41 ng TEQ g^{-1} dw, with an average of 4.91 ng TEQ g^{-1} dw in the sediment along coastal areas nearing Quanzhou Bay, and they were much lower than in sediment from Fenhe watershed, China (145.39 ng TEQ g^{-1} dw)

(Tian et al., 2013), Meiliang Bay, China (94–845 ng TEQ g^{-1} dw) (Qiao et al., 2006), and Barents Sea (Kola Bay), Russia (71–583 ng TEQ g^{-1} dw) (Savinov et al., 2003). The BaP played the dominant role for total TEQ_{PAHs} of JRW sites (72.73–79.57%), QBC sites (56.71–83.20%) and all the surface sediment sites (78.12–89.25%).

3.3.2. Potential biological effects

Sediment Quality Guidelines (SQG) of the US National Oceanic and Atmospheric Administration provide a scientifically justifiable basis for evaluating the potential effects of sediment-associated contaminants on aquatic organisms except for the TEQ. The sediment quality guideline quotient (SQGQ) was developed to assess the potential biological effects at each site affected by contaminant mixtures (Long and MacDonald, 1998). The probable effects level (PEL) quotient for each contaminant was based on the published guideline values for sediments (Macdonald et al., 2004), and the SQGQ for each site was calculated according to the formula below (Long and MacDonald, 1998):

$$SQGQ = \frac{1}{n}\sum_{i=1}^{n}\frac{c_i}{PEL_i} \tag{6}$$

where, C_i is the measured concentration of the contaminant i and PEL_i is the corresponding guideline value for the same contaminant, n is the total number of analyzed contaminants whose sediment quality guidelines are available. Three degree of potential adverse biological effects by sediment contamination with different ranges of SQGQ was given by MacDonald et al. (2004): unimpacted ($SQGQ < 0.1$); moderately impacted ($0.1 \leqslant SQGQ < 1$); highly impacted ($SQGQ \geqslant 1$).

The result of calculated SQGQ for all the surface sediment showed that only the SQGQ for Q3 were $\geqslant 0.1$ but <1, indicating that the PAHs would cause moderately adverse biological effects at this site. While at the other sites, these contaminants would cause no adverse effects. The highest SQGQ occurred at Q3, which located in the downstream of the Jinjiang River running into the Quanzhou Bay, where the PAHs need more attention for controlling adverse biological effects of the sediment, especially for the fishery port which was nearby the site Q3.

In general, contamination of PAHs in the soil and coastal marine sediments of the study area may pose unconspicuous risks for the environment and humans through food chains except very few of the moderately polluted sites.

4. Conclusions

This study provided important data on priority hazardous PAH occurrence in soil, water, suspended particulate matter and sediment along the Jinjiang River mainstream to Quanzhou Bay. The levels of PAH concentrations in the study area were low in comparison with other locations, though several sites of soil and sediment were characterized as moderate PAHs pollution. The partition coefficient analysis is helpful to predict the PAHs distributions in the DP and SPM, but the particulate organic carbon and heterogeneous mixtures of particulate soot carbon could influence the PAH partition. Analysis of the possible source of PAHs suggests a complicated and combined PAH source in the area of interest. Three source factors and their contributions were extracted by the PMF model. Toxic equivalent quantity (TEQ) and sediment quality guideline quotient (SQGQ) of PAHs were calculated, which revealed unconspicuous risks existed in the soil and sediments in the study region.

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Appendix D

Chen Wenwen, Zhang Jianxin, Abass Olusegun-kazeem, Wen Xinyu, Huang Huanfang, Qu Chengkai and Qi Shihua, 2016. Distribution Characteristics, Concentrations, and Sources of Cd and Pb in Laoxiawan Channel Sediments from Zhuzhou, China. Bulletin of Environmental Contamination and Toxicology, 96, 797-803.

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Distribution Characteristics, Concentrations, and Sources of Cd and Pb in Laoxiawan Channel Sediments from Zhuzhou, China

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Abstract Twenty sediment cores encompassing surface (0–20 cm) and deeper (50–60 cm) sediment layers were retrieved from the 3000 m-long Laoxiawan Channel, which receives industrial effluents from Zhuzhou City (China). Analytical results showed that cadmium (Cd) concentrations ranged between 115.7–1126.7 and 108.8–2059.3 mg/kg while lead (Pb) values ranged between 234–3000 and 145–4292 mg/kg in the surface and bottom sediments, respectively. The results also indicated that high levels of Cd and Pb were present in the vicinity of the channel mouth and confluence area. Indices for potential ecological risk and geo-accumulation were used to evaluate the environmental effects and intensity of heavy metal pollution over time. High concentrations of Cd and Pb in the bottom sediments of Laoxiawan Channel were mainly associated with wastewater discharge (10^6 m^3/year). Thus, the Laoxiawan Channel may be an important metal contaminant source for the Xiang River.

Keywords Cd · Pb · Laoxiawan Channel sediments · Potential ecological risk index · Geo-accumulation index

Heavy metals are classed as environmental pollutants because of their toxicity, persistence, and non-degradability (Senthil Kumar et al. 2008). Currently, sediment pollution by toxic metals is a major problem in fluvial and marine ecosystems as a result of industrial and urban activities (Abdallah and Mohamed 2014). These sediments have become the main sink and source of toxic metals in river environments. Metals, such as Cd, zinc (Zn), copper (Cu), and Pb can be adsorbed onto sedimentary grains and then released under certain conditions (Wu et al. 2015). It is reported that toxic metals in sediments can act as an archive of natural and anthropogenic sources of elements to the environment (Miller et al. 2014).

The Xiang River is the largest tributary of the Yangtze River in Hunan Province, China. The sediments in the lower reach of this river are extremely enriched in Cd and contain significantly high concentrations of Pb, Zn, tin (Sn), and antimony (Sb) (Peng et al. 2011). The high heavy metal concentrations are the result of the exploitation and use (e.g., mining, smelting, and refining) of Pb–Zn ore mineral resources in the river's upper reaches (Rodríguez et al. 2009). The Qingshuitang area is one of the most famous industrial bases in Zhuzhou. To date, over 10 million cubic meters of industrial wastewater from the Qingshuitang, containing a large amount of heavy metals (Pb and Zn) from metallurgy industries, are discharged into the Xiang River each year. This wastewater has passed through the Laoxiawan Channel since the 1950s (Li 2007). Laoxiawan has a catchment area of 4.5 km^2. The main channel is 3000 m long and hosts more than six metallurgical plants in its basin before finally flowing into the Xiang River. There is also a branch channel (2000 m long) that originates from Yingfeng Lake, which is polluted by wastewater, smelting waste, and non-point discharges from

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industrial activities. However, to the best of our knowledge, no historical data of toxic heavy metal levels are available for the Laoxiawan Channel.

Based on previous studies of toxic metal contamination in Xiang River sediments (Mao et al. 2013; Peng et al. 2011; Sun et al. 2012; Zhang et al. 1989), a more thorough understanding of the mechanisms governing the distribution and prevalence of heavy metals in the tributary regions is required to fully illuminate the pollution status. Therefore, in this study, we (1) investigate the levels and distribution characteristics of Cd and Pb in the Laoxiawan Channel, (2) identify the potential sources of Cd and Pb, and (3) assess the ecological risk.

Materials and Methods

Sample collection was based on a pilot study of possible pollution sources and channel morphology. Significant sites (1–20) for toxic metal pollution were determined and the channel system was divided into two zones: the main channel and the branch channel, depending on sources and other factors, such as river proximity (Fig. 1).

In the Laoxiawan Channel, 20 sediment cores (60 cm length), covering the key nodes of the estuary and the confluence of the main and branch channels, were sampled in November 2011 (Fig. 1) using a polypropylene coring device (6 cm internal diameter). Material from the surface (0–20 cm) and deeper (50–60 cm; hereafter, "bottom") sediment layers were examined, providing information on the relationship of the sedimentary profile and toxic metal input. The samples were air-dried, crushed with a pestle and mortar, homogenized, sieved over 75-µm mesh, and then stored at 4°C until analysis.

All standard chemicals used in the laboratory were purchased from CNW Technologies GmbH (Dusseldorf, Germany), and certified as analytical grade. High-purity water produced by the Heal Force water purification system (Cannex Analytic Instrument, Shanghai, China) was used for all analyses. All glassware and sample bottles were soaked for 24 h in 10 % nitric acid, then washed and rinsed with ultrapure water. An aliquot (0.1 g) of a dry sample was digested with HNO_3–$HClO_4$–HF (*v*:*v*, 2:1:1) (Tessier et al. 1979). The digest was diluted to 20 mL with ultrapure water and stored in polyethylene containers at 4°C. The residue was filtered and Cd and Pb were determined by graphite furnace atomic absorption spectrometry and flame atomic absorption spectrometry, respectively, using a Hitachi Z2000 tandem spectrophotometer (Tokyo, Japan). These measurements are routine analyses performed by the Zhuzhou Environmental Monitoring Central Station. Quality assurance and quality control were performed with trip and analytical blanks, duplicate sample runs, and standard reference materials (GSS-1, Sediment Sample, Standard Substances Center, China). Trip blanks, consisting of ultrapure water, were taken into the field, returned to the laboratory and analyzed as field samples. Acid blanks were used to determine contamination from the acids and deionized water. Blank subtraction was less than 5 % for Cd and Pb. The relative standard deviations (RSD) for Pb and Cd were less than 5.0 % and 9.7 %, respectively. The accuracy was examined by comparison with standard reference materials, which had 94 %–103 % recovery. The detection limits of Cd and Pb were

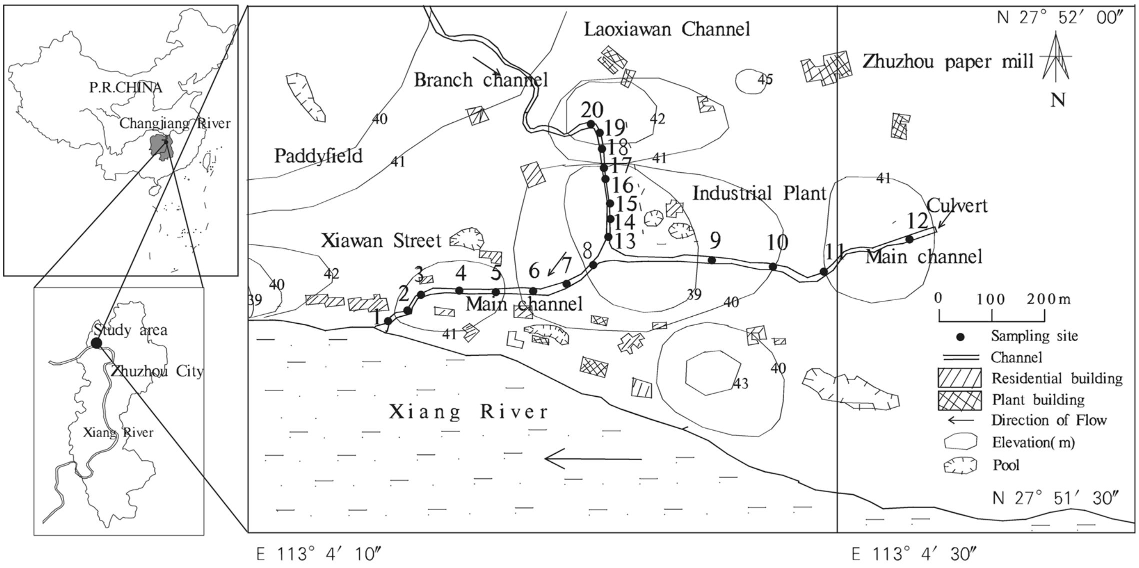

Fig. 1 Location of sediment sampling sites in the Laoxiawan Channel

established as three times the RSD in blank samples with values of 0.03 and 2 mg/kg, respectively.

Statistical analyses were performed using IBM SPSS 19.0. Concentrations of Cd and Pb were analyzed with one-way ANOVA to determine the significant differences between surface and bottom sediments. A probability level of $p < 0.05$ was considered significant. A Pearson correlation matrix was applied to identify any relationship between the metals. Cluster analysis based on the between-groups linkage method was performed to quantitatively identify specific areas of contamination using dendrograms. Based on results obtained from the 20 sampling sites, contour maps integrated into a geographical information system (GIS) were used to obtain the spatial distribution of Cd and Pb.

Results and Discussion

Table 1 provides the summary statistics of Cd and Pb sedimentary concentrations from the Laoxiawan Channel. The concentrations of Cd ranged between 115.7–1126.7 (surface) and 108.80–2059.3 (bottom) mg/kg while Pb values were between 234–3000 (surface) and 145–4292 (bottom) mg/kg. Usually, high variability in metal concentrations between samples may suggest an anthropogenic influence and/or natural factors (Zhang et al. 2010). Notably, all values in the Laoxiawan Channel had high standard deviations, indicating high variability in metal concentrations between samples. These temporal and spatial variations are likely caused by the sources of pollution. The Probable Effects Level (PEL), established by the Canadian Council of Ministers of the Environment (CCME 1999) and China Marine Sediment Quality Standards (GB18668-2002) (CSBTS 2002) were compared to sediment concentrations from the present study to assess the sediment quality (Table 2). The Chinese Marine Sediment Quality Standards use three criteria with which to predict marine sediment quality and assess resulting effects. The primary criterion is the protection of habitats for marine life, including natural, rare, and endangered species, as well as places for human recreation and sports. The secondary criterion regulates general industrial use and coastal tourism, and the tertiary criterion defines harbors and special uses for ocean exploration. It has been reported that sediment samples were predicted to be toxic if the metal concentration was higher than the PEL (MacDonald et al. 2000). Compared with the PEL, the concentrations of Cd and Pb were above it in 100 % of investigated sample locations, which reflects very poor sediment quality. Pb concentrations were 1–46 times higher than the PEL, while Cd concentrations were 28–570 times higher than the PEL. This was interpreted to produce severe adverse biological effects in the Laoxiawan Channel. Similarly, compared with the tertiary standard criterion of GB18668-2002, the concentrations of Pb were 0.6–17 times higher, while Cd was 22–411 times higher. The high frequency of guideline exceedance of Cd indicated that serious pollution is present in the Laoxiawan Channel sediments. Under natural conditions, Cd is usually associated with Pb–Zn and Cu–Pb–Zn ore; thus, Cd in the channel likely originates from smelting (Rodríguez et al. 2009). Industrial discharge from minerals refining over decades is likely responsible for the introduction of large quantities of Cd.

Compared with other regions of the world (Table 2), concentrations of Cd in the Laoxiawan Channel sediments were two- to 2000-fold higher than those reported from other channels and rivers. Concentrations of Pb in the study area were much lower to Tisa drainage basin (Bird et al. 2003), but similar than that from high anthropogenic impact areas, such as Xiawan Channel in China (Chen et al. 2007; Zhu et al. 2012). They were up to tenfold higher than those from less affected areas, such as Haihe River (Kamala-Kannan et al. 2008; Mao et al. 2013; Wu et al. 2015; Yang et al. 2009). Cd and Pb concentrations in the surface sediments of the Xiang River, close to the mouth of Laoxiawan Channel, were 4.8 and 35.2 mg/kg, respectively. However, after the Xiang River passes through the Qingshuitang area, the Cd and Pb concentrations were much higher (81.79 and 198.0 mg/kg, respectively) (Mao et al. 2013). Because the Laoxiawan Channel flows into the Xiang River, this is likely a source of the increased concentration of Cd and Pb in the Xiang River.

Figure 2 summarizes the concentrations of Cd and Pb from three sections of the Laoxiawan Channel. Contour maps were plotted using the concentrations of Cd and Pb in

Table 1 Sedimentary concentration of Cd and Pb

Site	Max (mg/kg)	Min (mg/kg)	Median (mg/kg)	Mean (mg/kg)	SD	Skew	CV (%)
Cd[a]	1126.7	115.7	184.0	260.1	221.87	3.43	86.30
Cd[b]	2059.3	108.8	181.0	344.3	446.45	3.34	130.77
Pb[a]	3000.0	234.0	579.6	871.9	676.66	1.78	74.92
Pb[b]	4292.5	145.4	809.3	1082.2	1054.23	2.05	95.44

[a] Samples from surface sediments (0–20 cm depth)

[b] Samples from bottom sediments (50–60 cm depth)

Table 2 Cd and Pb concentrations (mg/kg, mean) in sediments from different regions of the world

Site	Cd	Pb	Site	Cd	Pb
Laoxiawan Channel, China	260.10	871.86	Xiang River, China (Mao et al. 2013)	14.97	71.10
Tisa drainage basin channel, Romania and Hungary (Bird et al. 2003)	95.00	21,100	Haihe River, China (Wu et al. 2015)	2.92	91.25
Kaohsiung Harbor, Taiwan (Chen et al. 2007)	0.1–6.8	9.5–470	PEL(CCME 1999)	3.5	91.3
Pulicat, India (Kamala-Kannan et al. 2008)	64.21	8.32	Standard of marine sediment quality (CSBTS 2002)		
Yangtze River, China (Yang et al. 2009)	1.53	45.18	Primary standard	0.5	60
			Secondary standard	1.5	130
Xiawan Channel, China (Zhu et al. 2012)	70.00	502	Tertiary standard	5	250

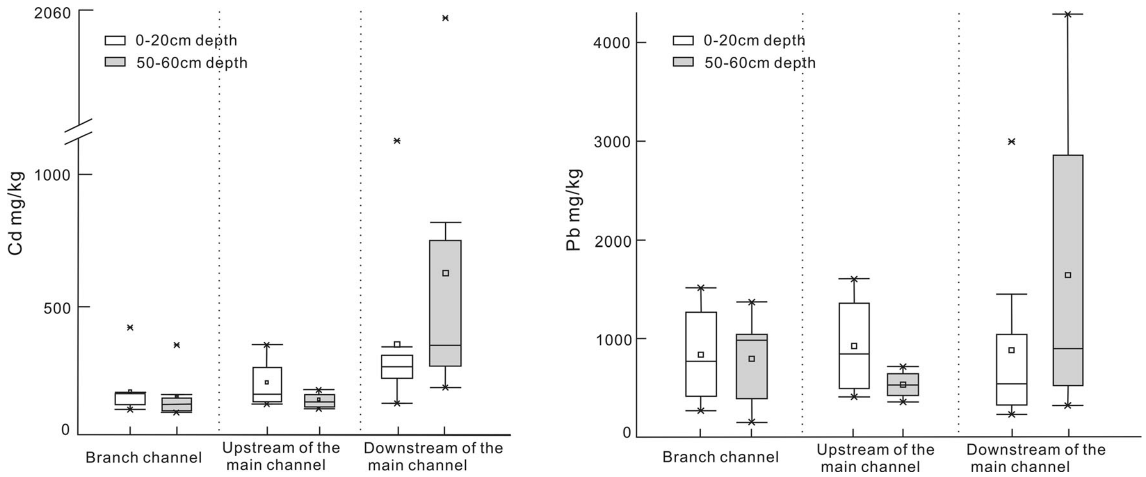

Fig. 2 Cd and Pb concentrations of surface and bottom sediments from different sections of the Laoxiawan Channel

the surface and bottom sediments (Fig. 3). Along the branch channel, the distribution patterns of Cd and Pb in the two different sediment layers showed a decreasing trend from sites 20 to 13 (Fig. 3). No significant differences between Cd and Pb at the different layers were observed (F = 0.245, $p = 0.628$ for Cd and F = 0.033, $p = 0.858$ for Pb), implying a consistent input of Cd and Pb from wastewater discharge. No significant spatial correlation between Cd and Pb was found, likely because of their different chemical behavior in sediments. The strong positive correlations for Cd ($r = 0.965$, $p < 0.01$) and Pb ($r = 0.\ 796$, $p < 0.05$) concentrations between different layers indicated that the metals at the bottom are associated with the surface and share a common anthropogenic source. Thus, heavy metals in the branch channel may originate from industrial wastewater discharge.

Upstream of the main channel, Cd and Pb concentrations in the surface sediments showed an increasing trend from sites 12 to 9 (Fig. 3). Higher concentrations were particularly found at site 9. In the bottom sediments, heavy metal concentrations from sites 12 to 9 were generally consistent. This suggested a Cd and Pb contribution from surrounding metallurgical slag upstream. A smelting waste disposal site has been situated in the upper reaches of the Laoxiawan Channel in recent years (sites 12–9; Fig. 1). The metallurgical slag could release small quantities of Cd and Pb into the channel water, which would subsequently be deposited into sediments. However, the concentration differences between the two layers were not significant (F = 1.360, $p = 0.288$ for Cd and F = 1.921, $p = 0.215$ for Pb). The correlation matrix revealed that there were no significant correlations between Cd and Pb at different sediment intervals, indicating that Cd and Pb upstream may have originated from different sources. Laoxiawan Channel has a long history of contamination from the Zhuzhou Smelting Factory. Therefore, high concentrations of Cd and Pb in the bottom sediments were mainly associated with wastewater discharge (Li 2007), whereas Cd and Pb in the surface sediments might be associated with the recent input of metallurgical slag.

Downstream of the main channel, the mean concentrations of Cd slightly increased to 260 mg/kg in the surface

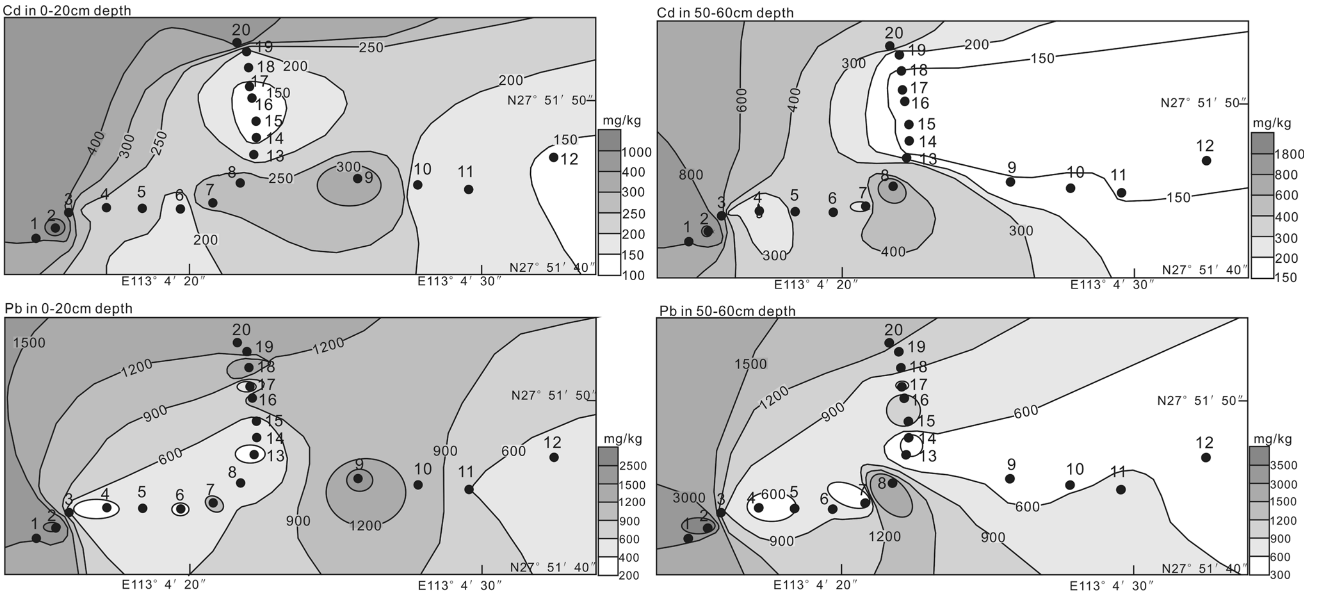

Fig. 3 Distribution of Cd and Pb concentrations in the surface and bottom sediments

sediments, coincident with discharge from the branch. In contrast, concentrations of Pb decreased. In the bottom sediments, the spatial distribution of Cd and Pb highlighted a substantial increase in concentration. A decrease in heavy metal concentrations toward the top of a sediment core commonly indicated a decreasing rate of heavy metal input in recent years (Zheng et al. 2008). No significant differences were found between the different layers ($F = 1.158$, $p = 0.3$ for Cd and $F = 1.515$, $p = 0.239$ for Pb).

Downstream of the main channel appeared to have much higher concentrations of metals in the bottom sediments. Because there is no direct metal contaminant source in the surrounding area except what is discharged from upstream, we deduce that metals originated from upstream, migrated downstream, and accumulated in the sediment, resulting in increased concentrations in the bottom layer. Site 8, situated beneath the confluence area of channels, had high concentrations of Cd and Pb in the bottom sediments, while low concentrations were found at surface. Cd and Pb concentrations in both surface and bottom layers at sites 1 and 2, located in the vicinity of the channel mouths, were significantly higher than those at sites 3–7. This observation is consistent with other studies (e.g., Chen et al. 2007) that suggested that stations situated in the vicinity of river mouths had higher concentrations of heavy metals. A significant correlation of Cd between the top and bottom layers downstream ($r = 0.948$, $p < 0.01$) and the Pb in surface and bottom layers ($r = 0.835$, $p < 0.01$), as well as between Cd and Pb in the surface sediments ($r = 0.950$, $p < 0\ 0.01$) and bottom sediments ($r = 0.910$, $p < 0.01$), suggests these might be attributed to the contribution of heavy metals from upstream to downstream.

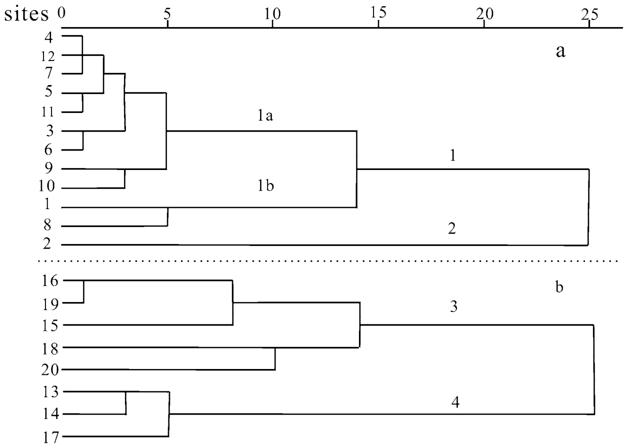

Fig. 4 Cluster analysis dendrogram indicating relatedness of sites with heavy metal contamination in sediments. **a** Represents the main channel, and **b** the branch channel

We used cluster analysis to identify specific areas of contamination through dendrograms to summarize samples obtained from the channel (Fig. 4). Two major clusters in the main channel were noted, 1b and 2, which represent highly contaminated sites where ecotoxicological damage might be occurring. These clusters were located at the confluence of the main and branch channels, and the mouth of the Laoxiawan Channel (Fig. 4a). The other clusters represented sites of moderately toxic metal levels. Site 2 appeared to be from a different source compared with sites 1 and 8. In the branch channel, we identified two major clusters (Fig. 4b). Cluster 4 represented relatively less contaminated sites (sites 13, 14, and 17).

The potential ecological risk index (PERI) (Hakanson 1980) and geo-accumulation index (I_{geo}) (Müller 1979) were applied to assess the risk and intensity of toxic metal pollution over time in the Laoxiawan Channel. Detailed descriptions of the calculations and the appraisal indices can be found in a previous study (Hou et al. 2013). The toxic metal concentrations of sediments in the Xiang River catchment (Cd = 0.5 mg/kg, Pb = 25 mg/kg) were used as the regional background value (HRAES 1985). The order of single-risk indices (E_r^i) of Cd and Pb in sediment samples was Cd (50–60 cm depth) > Cd (0–20 cm depth) > Pb (50–60 cm depth) > Pb (0–20 cm depth). The average E_r^i of Cd and Pb in the surface sediments were 15,605.7 and 173, respectively, indicating that Cd poses an exceptionally high risk to the local ecosystem, while for Pb, the E_r^i indicated it poses a risk to the surroundings. The PERI values of the surface sediments ranged from 7162.6 to 68 202, with an average value of 15 780. High PERI values correspond to high Cd contents. Following the I_{geo} classification, sediments at the Laoxiawan Channel sites with values between 7 and 11 were very strongly polluted by Cd. Accordingly, the sediments were moderately to very strongly polluted by Pb. A slight difference in results was obtained by use of either PERI or I_{geo}. The I_{geo} value of Cd was much higher than Pb; suggesting Cd has greater biological toxicity and magnitude. Thus, the results presented in this work suggest that the sites, sediment quality, and resulting pollution were more likely to be affected by Cd than Pb.

This study showed that channel sediments in Laoxiawan are severely contaminated with Cd and Pb, and may be a metal contaminant source to the Xiang River. The highest Cd and Pb concentrations were observed in the downstream bottom sediments. High concentrations of Cd and Pb in the Laoxiawan Channel were mainly associated with industrial wastewater and metallurgical slag discharged in the upstream portion of the channel. Different distribution patterns of Cd and Pb were found between the branch channel and the main channel. Geo-accumulation and potential ecological risk indices showed that Cd poses an exceptionally high risk to the local ecosystem, while Pb poses a high risk to the surroundings.

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