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Upper Yellow River air concentrations of organochlorine pesticides estimated from tree bark, and their relationship with socioeconomic indices

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ABSTRACT

Organochlorine pesticide (OCP) concentrations in tree bark from the upper Yellow River region were determined. Total OCP concentrations ranged from 2.7 to 82 ng/g dw, with a mean of 20 ng/g dw. Concentrations of total (Σ) DDTs (0.49–37 ng/g dw), HCHs (0.55–4.5 ng/g dw), and HCB (0.1–1.0 ng/g dw) were much higher than the other OCPs and accounted for 89% of the ΣOCP concentrations. *p,p′*-DDT was the dominant member of the DDT pesticide group and β-HCH was the dominant HCH isomer. The *p,p′*-DDT/*p,p′*-DDE and α-HCH/γ-HCH ratios suggested that there were recent DDT and γ-HCH releases. OCP concentrations in the air were estimated from the tree bark, and the estimated median ΣDDTs, ΣHCHs, and HCB concentrations in the air were 0.09, 0.14, and 0.024 pg/m^3, respectively. The relationship between total OCP concentrations and socioeconomic and natural environment indices were assessed using multiple linear regression analysis, and a regression equation including all these factors was obtained. Population density and tertiary industry were the two dominant factors that appeared to affect OCP concentrations in the upper Yellow River region.

Introduction

Organochlorine pesticides (OCPs) are persistent organic pollutants (POPs) that have been put under controls around the world because of their low biodegradability, high toxicity, and ability to bio-concentrate and undergo long-range atmospheric transport (Norstrom et al., 1988). The semi-volatility of OCPs allows them to migrate around the world through global distillation and the "grasshopper effect", and they can be found in areas where they have not been used (Ribes et al., 2002). In May 2001, the Stockholm Convention on Persistent Organic Pollutants, in which an agreement was reached that actions would be taken to reduce and eventually eliminate the production and emission of 12 POPs, was signed by a number of countries. Nine of the 12 POPs first put on the controlled list were OCPs, including aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, toxaphene, hexachlorobenzene (HCB), and mirex (Mohammed et al., 2011). Hexachlorocyclohexane (HCH) has recently been included as a new POP (Vijgen et al., 2011). Between the 1950s and 1980s OCPs were widely used in China because of their high efficiency, low price, and low acute toxicity to humans. Although China has gradually banned the use of OCPs since 1983, OCP residues in the environment are still considerable because of their persistence (Feng et al., 2011a).

Concentrations of POPs in the atmosphere are important indicators for air quality assessment, and there are two methods for monitoring their concentrations in air, active sampling and passive sampling. Active sampling is more direct and simple to interpret, but has disadvantages, including being labor intensive, incurring high costs, and posing practical difficulties in remote areas. Passive sampling (such as measuring concentrations in tree bark) does not suffer from these disadvantages. Tree bark is a good natural passive sampler because it contains more lipids than many other types of vegetation and is exposed to

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the air throughout the year (Simonich and Hites, 1997). Bark is also cheap and convenient to sample and has been considered as a passive bio-sampler for the determination of polybrominated diphenyl ethers (PBDEs) (Zhu and Hites, 2006), OCPs (Àngels et al., 2012), polychlorinated biphenyls (PCBs) (Hermanson and Hites, 1990; Meredith and Hites, 1987), polychlorinated dibenzodioxins and furans (PCDD/Fs) (Di Lella et al., 2006), and dechlorane plus (DP) (Qiu and Hites, 2007).

The upper Yellow River region, including the Ningxia Hui Autonomous Region, the Inner Mongolia Autonomous Region, Gansu Province, and Qinghai Province, has the highest population density in North-West China, and has a number of minority nationalities. However, until now, only Liu et al. (2012) have reported OCP concentrations in soil in this area, and there have been no studies of OCP concentrations in air.

The main aims of this study were to use OCP concentrations in bark to estimate OCP concentrations in the atmosphere in the upper Yellow River region, and to study the relationship between OCP concentrations and socioeconomic and natural environment indices.

1 Materials and methods

1.1 Chemicals

The chemicals used were acetone, *n*-hexane, and dichloromethane (all pesticide grade; J.T. Baker, Phillipsburg, USA), ultra-pure water (Millipore, Billerica, USA), high purity nitrogen gas, anhydrous sodium sulfate (analytical grade, baked for 5 hr at 450°C), silica gel (100–200 mesh Merck, Germany), and neutral alumina (60 mesh Alfa Aesar, USA). Silica gel and alumina were extracted with dichloromethane, activated at 105°C and 130°C for 12 hr, respectively, then cooled and deactivated with 3% deionized water.

OCP standards (aldrin, *cis*-chlordane, *trans*-chlordane, *p,p′*-DDD, *o,p′*-DDD, *p,p′*-DDE, *o,p′*-DDE, *p,p′*-DDT, *o,p′*-DDT, dieldrin, endosulfan I, endosulfan II, endrin, heptachlor, heptachlor epoxide A, heptachlor epoxide B, hexachlorobenzene, α-HCH, β-HCH, γ-HCH, δ-HCH, isodrin, methoxychlor, mirex, and oxychlordane) were purchased from AccuStandard (New Haven, CT, USA). Internal standards ($^{13}C_{12}$-*p,p′*-DDE, $^{13}C_{10}$-dieldrin, $^{13}C_6$-HCB, $^{13}C_6$-β-HCH, $^{13}C_6$-γ-HCH, $^{13}C_{10}$-mirex, and $^{13}C_{10}$-*t*-nonachlor) were purchased from Cambridge Isotope Laboratories (Andover, MA, USA).

1.2 Sample information

Fifteen willow tree bark samples were collected in August 2011. The sampling site distribution is shown in **Fig. 1** and the sampling site information is shown in **Table 1**. There were 10 rural sampling sites (#1, #2, #3, #5, #6, #7, #9, #10, #12, #13), where willows grew on the Yellow River bank, and five urban sampling sites (#4, #8, #11, #14, #15) taken from cities near the Yellow River. All bark samples were chiseled from around 1.5 m height from three willows less than 50 m apart with similar trunk diameters (around 35 cm), to ensure the tree bark had fully absorbed pollutants from the air. The samples were wrapped in aluminum foil, sealed in plastic bags, and stored at 5°C for transport to the laboratory, where they were frozen and stored at –20°C until analysis.

1.3 Sample preparation

Each raw bark sample (10.0 g) was cut into small pieces (< 1 cm) and covered with 20.0 g anhydrous sodium sulfate in a Soxhlet apparatus, spiked with 2 ng OCP internal standards, and extracted with 200 mL of a hexane:acetone mixture (1:1, *V/V*) for 24 hr. Each extract was concentrated

Table 1 Tree bark sample information

No.	Sampling site	Province	Latitude (°N)	Longitude (°E)	Type
1	Sanhu Estuary	Inner Mongolia	40.61	108.77	Rural
2	Dengkou		40.28	107.02	Rural
3	Dusitu River	Ningxia	39.08	106.89	Rural
4	Yinchuan		38.48	106.26	Urban
5	Yingu Highway Bridge		38.29	106.23	Rural
6	Qingtongxia		37.95	105.99	Rural
7	Jinsha Bay		37.83	105.94	Rural
8	Zhongning		37.49	105.67	Urban
9	Shapotou		37.45	104.98	Rural
10	Wufo Temple		37.46	104.99	Rural
11	Baiyin	Gansu	36.55	104.14	Urban
12	Qingcheng Bridge		36.36	104.22	Rural
13	Shichuan Bridge		36.15	103.99	Rural
14	Lanzhou		36.05	103.86	Urban
15	Xining	Qinghai	36.62	101.77	Urban