DDTs, chlordanes and hexachlorobenzene in the atmosphere of Chinese cities

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Abstract
Passive air samplers (PAS) were therefore utilized to obtain seasonal data from 37 Chinese cities in 2005. Concentrations and spatial and seasonal distribution of dichlorodiphenyltrichloroethanes (DDTs), chlordanes (CHLs) and hexachlorobenzene (HCB) are presented in this paper, and their potential sources are discussed based on the dataset. The authors suggested that approximately 95% of DDTs in the Chinese cities was still technical DDT, for which DDT application for public health control and DDT activated antifouling paint for fishing ships may be the major sources. A low TC/CC ratio was observed across China in the winter to spring, maybe related to the secondary emission from past use of chlordanes for house protection. The data showed that China is an important global source for HCB, and combustion may be an important HCB source.

Introduction
From a global perspective, recent attention on potential source areas for the 'old generation' organochlorine pesticides (OCPs) has focused on developing countries in tropical and sub-tropical regions. Recent developments in passive air samplers (PAS) have made it possible to conduct large-scale spatial surveys of POPs distributions in the atmosphere, with the purpose of building up information on compound distribution and sources[3] . This paper presents for DDTs, chlordanes, HCB and endosulfan during the four seasons of 2005, from 37 cities. The data are shown here and used to explore source information about the chemicals.

Materials and Methods
Thirty seven cities (provincial capitals and major regional centres). The PUF disk PAS apparatus has been used and described previously (e.g.[4]). All the PUF disks including 116 samples, 54 field blanks and 12 lab blanks were pre-extracted with dichloromethane (DCM) and acetone at Guangzhou Institute of Geochemistry and transferred by express mail service to sampling sites in glass jars. Four separate deployments of 8 weeks were made in 2005: winter (Feb 1 to Mar 28), spring (Apr 1 to May 28), summer (Jul 5 to Aug 30) and autumn (Sep 15 to Nov 11), respectively.

Analytical method and QA/QC
Briefly, after adding surrogates, the PUF disks were Soxhlet extracted with DCM. Clean-ups were done by column chromatography, and the measurement was conducted using an Agilent 5975N GC-MSD. All reported values were corrected by the field blanks and surrogate recoveries.

Results and Discussion
Introductory remarks on the dataset.
Table 1 presents summary data for concentrations and isomer ratios of OCPs obtained by PAS in the Chinese cities (pg·day^{-1} per disk) for the winter, spring, summer and autumn of 2005. The concentrations of DDTs, chlordanes and HCB in the Chinese cities were much higher than in those in Europe and North America[4,5], and also higher than other parts of Asia previously reported[3,6]. By contrast, endosulfans occurred at relatively low concentrations compared to North America and Europe[3].

Table 1. Summary data of DDTs, chlordanes, Endosulfans and HCB in the atmosphere of 37 Chinese cities ($pg\cdot d^{-1}$)

Season	Winter				Spring				Summer				Autumn			
	min	**max**	**Mean**	**Std**	**min**	**max**	**Mean**	**Std**	**min**	**max**	**Mean**	**Std**	**min**	**max**	**Mean**	**Std**
o,p′-DDT	97	2200	315	426	33	5080	833	1170	n.d.	6620	1390		25	4050	761	1070
p,p′-DDT	31	1050	210	211	11	1600	474	491	n.d.	2730	515		20	2370	464	626
p,p′-DDE	47	568	169	140	5.9	3340	453	625	24	3650	712		n.d.	3110	423	635
Hep	n.d.	1240	120	235	n.d.	2220	174	396	n.d.	788	144		n.d.	422	114	128
TC	43	733	182	176	24	5620	322	995	35	3690	586		34	4290	688	936
CC	20	4720	1270	1020	25	4760	839	895	35	3940	909		90	5300	1250	1240
TN	12	137	47	34	8.9	1140	70	201	9.2	1000	143		10	1240	170	262
CN	n.d.	107	21	21	n.d.	1100	49	199	n.d.	147	31		n.d.	165	24	37
α-Endo	54	1190	197	215	3	224	64	46	n.d.	170	40		9.5	592	98	115
β-Endo	5.3	422	49	86	1.8	328	41	62	n.d.	404	63		n.d.	126	20	28
HCB	123	6510	2080	1410	207	5450	1280	1230	48	3790	1180		490	4300	1380	936
TC/CC	0.04	5.7	0.45	1.1	0.04	3.8	0.38	0.68	0.07	1.6	0.59		0.05	2.1	0.59	0.53
op′/pp′-DDT	0.21	14	2	2.6	0.16	7.1	2	1.7	n.d.	5.4	2.6		0.37	3.6	1.7	0.75
p,p′-DDT/*p,p′*-DDE	0.18	7.1	1.7	1.5	0.04	23	2.2	4.1	n.d.	7.4	1.1		0.38	5.2	1.2	0.99

n.d.: Not detected.

Sources of DDT in Chinese cities. Ratios of DDT isomers can provide useful source information. Taking isomer fractionation during the air-soil exchange processes into consideration, the average *p,p′*-DDT/*p,p′*-DDE in soil, which is more comparable to industrial products than that in the air, was calculated to be 11.8, 14.9, 7.7 and 8 for winter, spring, summer and autumn, respectively. These high ratios obviously suggest a fresh DDT input.

The ratios of *o,p′*-DDT/*p,p′*-DDT can be used to distinguish technical DDT from “dicofol- type DDT”. The *o,p′/p,p′*-DDT ratios were 2.01±2.59, 2±1.69, 2.64±1.42 and 1.66±0.75 in the winter, spring, summer and autumn, respectively (Table 1). Based on a correction by subcooled liquid vapor pressures, we estimated that the current DDT sources in the Chinese cities was composed of ~95% of technical DDT and ~5% of dicofol-type DDT.

Technical DDT may be introduced to the atmosphere of the Chinese cities *via* (i) direct use in cities for killing mosquito and health control programs. (ii) emission from DDT producing factories (e.g. in Tianjin) and (iii) release from DDT-activated anti-fouling paints.

Chlordanes. Table 1 shows the chlordane patterns and spatial distribution in the Chinese cities for the 4 sampling seasons. The total chlordane levels were 1640±1320, 1450±2100, 1810±1670 and 2500±2390 $pg\cdot d^{-1}$ for winter, spring, summer and autumn, respectively. The TC/CC ratios in the Chinese cities displayed a significant seasonality, lower in winter (mean 0.25±0.33) and spring (0.38±0.68) and higher in summer and autumn (0.61±0.53). This result is similar to the recent PAS campaign conducted in the Pear River Delta of South China (0.27 ± 0.04 and 0.79± 0.13 in winter and summer, respectively)[7]. We suggested that this maybe related to the secondary emission from past use of chlordanes for house protection, dominant when fresh chlordane use is absence in winter and springtime.

HCB. Figure 1 presents the HCB distributions in the atmosphere of Chinese cities. The HCB concentrations in the Chinese cities were in the range of 48.4-6510 $pg\cdot d^{-1}$, up to 2 orders of magnitude higher than those reported in Europe and North America[5,10]. It seems that China is an important current global source region for HCB. The observed HCB levels were linearly correlated with the average air temperatures of the cities in winter and spring, for which more fuel combustion and less combustion efficiency in colder cities in winter and spring was suggested to be responsible.

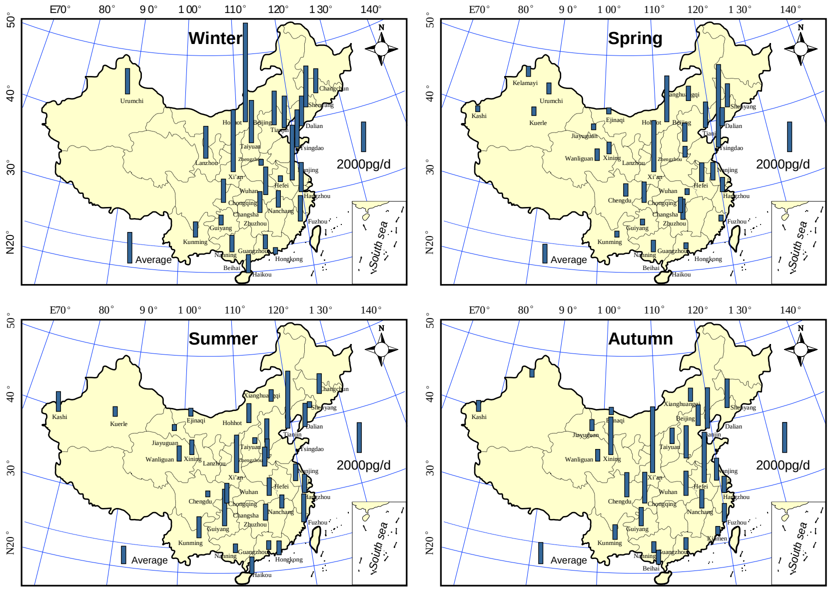

Figure 1. Spatial-temporal distributions of HCB in the atmosphere of 37 Chinese cities in the year of 2005

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