ORGANOCHLORINE COMPOUNDS IN AIR AT THE YELLOW SEA - MEASUREMENTS IN QINGDAO, CHINA, AND GOSAN, JEJU ISLAND, KOREA

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Introduction

Eastern China's economy is developing extremely rapidly which has created significant pressure to the environment, even on a regional scale. [1-3]

Despite the suspected significance of China as a source area, measurements of organic pollutants in the atmospheric environment are almost not existent: [2] In south China cities 350-700 pg m^{-3} of polychlorinated biphenyls (PCBs), 4-116 pg m^{-3} of 1,1,1-trichloro-2,2-bis(chlorophenyl) ethanes and transformation products thereof (DDTs) and 22 pg m^{-3} of endrin were measured. [2] The observations in various media show that much more PCBs had been released into the environment in China than anticipated based on usage data. [4,5]

The purpose of this study was to investigate the levels of organochlorines in eastern China and to address the regional transport of these pollutants in the Yellow and East China Seas region through simultaneous sampling at a coastal and an island site.

Materials and Methods

The measurements were performed 6-22 June 2003 at a coastal site, Qingdao, eastern China, and an island site, Gosan, on Jeju (Fig. 1, Table 1). The distance between the sites is about 500 km. The large-scale weather situation was characterized by a cyclone which moved from NW China (Heilongjiang) to the Yellow Sea and stayed there, and anti-cyclones over the Takla Makan desert / Tibetan plateau, moving N to the Gobi desert, and over the South China Sea. During the entire campaign Qingdao was influenced by the cyclone while Jeju was under its influence from 11-17 June, until a typhoon approached from the S. Advection above the boundary layer (in 700 hPa) at the sites was from W-SW over Qingdao during the entire campaign and over Jeju first from S-SW (9-12 June), then from W (13-17 June) and finally again from S (17-21 June).

Samples fromQingdaowereanalysed for hexachlorobenzene (HCB), hexachlorocyclohexanes (HCHs, i.e. the*a-, b-, g-, d-*, and *e*-isomers), PCB congeners #28, 52, 101, 153, 180, DDTs, namely*o,p'*- and *p,p'*-DDD, -DDE and -DDT), drins (aldrin, dieldrin, endrin). Samples from Gosan were analysed for HCHs (a-, b-, g-isomers) and the PCB congeners #28, 52, 77, 81, 101, 114, 118, 123, 126, 138, 153, 156, 167, 169, 170, 180 and 189 using similar methods (Table 1).

Fig. 1: Map of coastal and island sites, Qingdao and Gosan

Table 1: Sampling and analysis characteristics at Qingdao and Gosan

Site	Qingdao, China	Gosan, Korea
Location	36° 05' N, 120° 20' E 78 m asl, 500 from coast	33° 17' N, 126° 10' E 70 m asl, on cliff, western shore
Site type	urban (7 million inhabitants in the wider area)	Rural (0.5 mn inhabitants on the island)
Sampling period	9-21 June 2003, 6 day-time samples lacking	6-22 June 2003 2 24-h samples lacking
Number of samples	9 (4 day-time, 5 night-time)	15 or 5[a]
Sampling time	1-4 11-hour intervals combined	1 or 3[a] 23-hour intervals combined
Gas sampling	PUF (5 cm high, 2-4 in series), 26 ± 3 m^3 h^{-1}	PUF (5 cm high), 42 m^3 h^{-1}
Particulate matter sampling	quartz filter (Munktell, 79 cm^2), no upper size cut-off, 26 ± 3 m^3 h^{-1}	quartz filter (Whatman QM-A, 516 cm^2), no upper size cut-off, 42 m^3 h^{-1}
Sample preparation	Extraction (acetone), fractions separation (silica-alumina column)	Extraction (dichloromethaneortoluene)[a], fractionsseparation (silica-alumina-activatedcarboncolumn)
Analysis	GC-EPD (column DB5)	GC-m-ECD or HRGC/HRMS[a]
Determination limit (d.l.)	0.2-5 ng per PUF sample and 0.2-10 ng per filter membrane corresponding to 1-120 (typically 10-20) pg m^{-3} per sampling train for individual substances	corresponding to 0.1-1 or 0.01-0.1 pg m^{-3}[a] per sampling train for individual substances

[a] The second for PCBs, the first for all other

Results and Discussion

Mean concentrations and derived ratios thereof are listed in Table 2.

Table 2: Organochlorines' and selected elemental concentrations and concentration ratios (day/night). Data are given in the form time-weightedmean (μ), minimum and maximum (min-max) in pg m^{-3} (ng m^{-3} for Ca, Pb) For values < d.l. half of the d.l. was used for the calculation of the mean value.

	Qingdao, China			Gosan, Korea	
Species	μ	min-max	μ_{night}/μ_{day}	μ	min-max
HCB	123	73-217	1.4	32	2.6-76
a-HCH	145	10-277	2.2	20	6-34
b-HCH	72	< 3-400		96	21-223
g-HCH	68	< 13-132	2.0	21	6-60
d-HCH	19	< 2-62			
e-HCH	109	< 36-345			
PCB-28	113	< 10-248	4.5	1.7	0.6-3.7
PCB-52	25	< 7-59		0.9	0.4-1.4
PCB-101	27	< 6-81		0.28	0.15-0.37
PCB-153	47	< 6-207	0.9	0.16	0.09-0.21
PCB-180	98	< 6-448	0.7	0.06	0.02-0.12
o,p'-DDT	45	< 1-101	1.5	16	< 0.5-49
p,p'-DDT				98	28-308
o,p'-DDE	16	< 1-32	1.9		
p,p'-DDE	32	< 2-72	0.7	7.5	< 0.5-15

o,p'-DDD	14	< 6-33			
p,p'-DDD	70	26-163	1.9	424	88-1022
aldrin	1.2	< 0.6-12		24	< 0.5-50
dieldrin		< 5.4		< 0.5	
endrin	33	< 5-366		5.6	< 0.5-22
a-,b-,g-HCHs	*286*	*< 25-401*	*3.4*	*138*	*55-271*
total PCBs	*310*	*66-567*	*1.6*	*3.0*	*1.3-5.8*
total DDTs	*176*[a]	*86-285*[a]	*1.5*	*547*	*176-1365*
total drins	*37*	*< 11-369*		*30*	*6-55*
a-/g-HCH	*2.1*	*1.7- > 8.5*	-	*1.2*	*0.5-2.7*
DDT/totDDTs[b]	*0.44*	*<0.03-0.86*	*1.7*	*0.35*	*0.22-0.51*
Ca	830	500–2410	1.4	87	37-122
Pb	102	28-215	2.6	13	2-34

[a] one main species, *p,p'*-DDT, not measured

[b] note that these encompass different substances for the two sites, *o,p*-DDTs for Qingdao and *p,p'*-DDTs for Gosan

The concentrations retained by filter membranes as well as by polyurethane foams (PUFs) placed downstream were below detection limits in many cases. The particulate fraction of organochlorines, according to the amount found in the filter vs. found in the PUFs, was negligible in most cases with some exceptions for drins and DDTs.

Many organochlorines including persistent organic pollutants (POPs) were found at significant to high concentration levels in air at the coastal urban site (Table 2). At the same time some other air pollutants, e.g. heavy metals, were elevated, too. [6] Air pollution was highest in samples collected at least partly during advection from W and N. This points to local sources within the urban area: Many industries are located along the Jiaozhou Bay shore (cf. Fig. 1). By average, night-time concentrations exceeded day-time concentrations ($\mu_{night}/\mu_{day} > 1$) for most of the trace substances, while no significant deviation from 1 was found for the heavier PCBs (one penta- and one hexa-chloro congener; Table 2). $\mu_{night}/\mu_{day} > 1$ points to local sources at the ground, while $\mu_{night}/\mu_{day} £ 1$ may indicate advection of pollutants (regional-scale pollution or long-range atmospheric transport) or local emissions which are stronger during day-time.

In general lower concentration levels of HCHs and PCBs were found at the island site confirming the background character. [7] The concentration gradient between the sites was > 5 for a-HCH and endrin and > 30 for the PCBs, i.e. similar to the concentration gradients found for heavy metals measured in parallel. [6] However, the gradient is smaller (£ 3) for *b*-HCH, *g*-HCH, DDTs and aldrin. In combination with the findings of night vs. day levels (above) it can be concluded that regional distribution or long-range atmospheric transport, possibly in combination with secondary sources (re-emission) are indicated for *b*-HCH, *g*-HCH, DDTs and aldrin. This would be in line with the perception of the fate of persistent substances. Rather high DDT/total-DDTs ratios point to recent DDT usage, though. DDT was banned in China in 1983. In contrast, the east China coastal region seems to be an active source region of *a*-HCH, endrin and, in particular, PCBs. The heavier ones may be subject to significantly stronger emissions during day-time, which could be caused by the diurnal temperature variation.

With respect to PCBs and DDTs, the observed atmospheric concentrations are comparable with earlier results reported for cities of south China a few years ago. [2] Rather high values of a-/g-HCH are surprising as technical HCH, the source of a-HCH in the environment, was phase out in China in the 1980s We are not aware of any measurements of HCHs in China to compare our findings with.

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