

PCDD/Fs in sodium pentachlorophenate (Na - PCP) and human blood, milk and sediment samples from Chinese schistosomiasis areas

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Abstract—Sodium pentachlorophenate (Na - PCP) has been used as molluscicide in China for about 30 years. The results of an analysis of Chinese Na - PCP for PCDDs and PCDFs revealed that the content of total PCDDs was significantly higher than that of PCDFs. This paper also reported the PCDD/Fs levels in human blood, milk and sediment samples from schistosomiasis areas, which were markedly higher than those of other regions. It suggested a possible relationship between the elevated levels of PCDDs in human body or environment and the use of Na - PCP.

Keywords: sodium pentachlorophenate; PCDD/Fs; molluscicide.

1 Introduction

Schistosomiasis is one of the main epidemiologic diseases caused by parasite, it once created severe harmful effects to the health of many peasants who lived in the middle and lower valleys of Yangtze River. Since 1949, most of the patients have been cured under the schistosomiasis prophylactic of Chinese government. Moreover, fruitful preventive measures have been taken. Schistosomiasis is no longer the main disease in some areas. Killing off oncomelania is the key link of the precaution against schistosomiasis. In view of the facts that sodium pentachlorophenate (Na - PCP) is powerful in killing off oncomelania with its cheapness on price, a large amount of Na - PCP has been spread over vast areas since 1960's in China. However, due to their potential harmful effects on ecological environment, Chinese government has worked out a plan to replace Na - PCP with a new molluscicide by the support of World Bank in recent years. Although the use of dioxin - containing products has been significantly reduced in many industrialized countries, China produces about 6000 tons of Na - PCP annually. Being by - products of technical Na - PCP, dioxins may enter the environment and contribute to human exposure.

Our laboratory has been engaged in investigation to evaluate the potential environmental hazard and human health effects caused by Na - PCP which has been used for as long as 30 years in some areas. In order to provide a basis for risk evaluations, an analysis of Chinese Na - PCP for PCDD/Fs was carried out. [^{13}C]2,3,7,8-TCDD was spiked into the sample as internal standard prior to extraction/back extraction, the extract was subjected to chromatographic separation on

columns of basic alumina. The fraction containing PCDD/Fs was collected and concentrated for the quantitative analysis using HRGC/HRMS.

In addition, the quantitative results of total PCDD/Fs measured in the human blood and milk and sediment samples from schistosomiasis areas were reported.

2 Experimental

2.1 Materials

Sodium pentachlorophenate was made in Dagu Chemical Factory in Tianjin. In this department of the factory, non- γ isomers of hexachlorocyclohexane are processed into Na-PCP. Trace level PCDDs and PCDFs have been detected (Cheng, 1990; Ding, 1990; Jiang, 1990). This sample was obtained in 1991.

The human blood and milk samples were collected from the residents who lived in the middle valleys of Yangtze River where Na-PCP has been used as molluscicide for over 30 years. The control samples were collected from individuals who live 300 km away from schistosomiasis areas (no Na-PCP was sprayed). Pooled specimens were analyzed. We chose 50 persons as a group with 4 ml blood or milk per person.

The top 5cm sediment samples from a lake was collected where Na-PCP had been sprayed. Background sampling from non-schistosomiasis areas was conducted.

2.2 Cleanup procedures

A 10g sample of sodium pentachlorophenate was dissolved in 250 ml deionized water, 5 ng ^{14}C -labelled 2,3,7,8-TCDD was spiked into the sample. The solution was extracted two times with benzene. The benzene extract was treated with 1 mol/L NaOH and concentrated sulfuric acid respectively and then washed with water and dried over Na_2SO_4 .

The concentrated extract was extracted with equal volume of DMSO two times, and an equal volume of deionized water was added to the DMSO. The PCDD/Fs in resulting DMSO/ H_2O mixture was back extracted with petroleum ether twice (Orazio, 1989).

The concentrated extract was further fractionated on two basic alumina columns which were containing 25g and 2.5g alumina respectively. Fraction containing the PCDDs and PCDFs which was eluted with (1:1) petroleum ether/ CH_2Cl_2 (Hanspaul, 1987) was collected and analyzed by HRGC/HRMS.

2.3 HRGC/HRMS instrument

Autospect - Ultima; EI (35eV); Resolution: 10000; 60 m DB-5 column; column temperature program: 50°C for 1 min, to 220°C at 20°C/min, to 280°C at 4°C/min, hold for 40 min.

3 Results and discussion

Blank system determination showed free of interferences from dioxins and furans. Quantitative results of the PCDD/PCDFs in Na-PCP are summarized in Table 1. The HRGC/HRMS/SIM chromatograms for tetra- through octachlorinated dioxins and furans in Na-PCP are illustrated in Fig. 1 - 6.

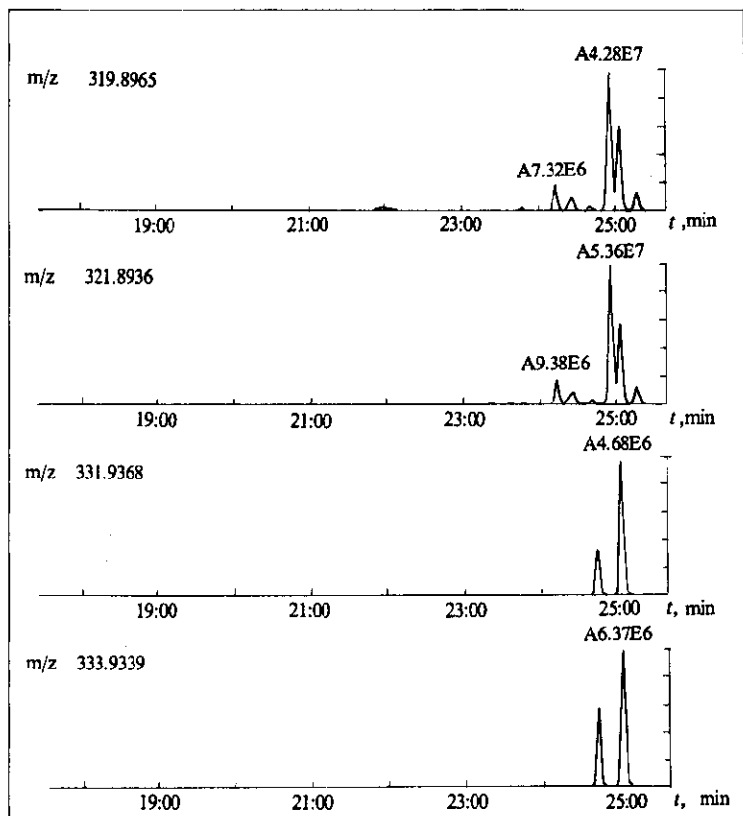


Fig. 1 Mass fragmentograms of TCDD for Na - PCP sample

Table 1 PCDDs/PCDFs in Chinese Na - PCP

Compound	Quantification ions, m/z		Concentration in Na - PCP ppb
	1st	2nd	
2,3,7,8- TCDD	319.8965	321.8936	2.6
Total TCDDs	319.8965	321.8936	9.2
Total PeCDDs	355.8546	357.8516	22.8
Total HxCDDs	389.8157	391.8127	976
Total HpCDDs	423.7766	425.7737	1045
OCDD	457.7378	459.7348	906
2,3,7,8- TCDF	303.9016	305.8987	0.7
Total TCDFs	303.9016	305.8987	10.7
Total PeCDFs	339.8597	341.8567	24
Total HxCDFs	373.8208	375.8178	97.9
Total HpCDFs	407.7818	409.7789	24
OCDF	441.7428	443.7398	440
Total PCDDs			2960
Total PCDFs			597
Total PCDD/Fs			3557

* Quantification of PCDD/Fs was achieved by the comparison of the response factors of ^{13}C -2,3,7,8- TCDF, ^{13}C -1,2,3,7,8- PeCDF, ^{13}C -1,2,3,7,8- PeCDD, ^{13}C -1,2,3,4,7,8- HxCDF, ^{13}C -1,2,3,7,8,9- HxCDD, ^{13}C -1,2,3,4,6,7,8- HpCDF, ^{13}C -1,2,3,4,6,7,8- HpCDD and ^{13}C -OCDD to that of ^{13}C -2,3,7,8- TCDD standard, and the recoveries of these compounds were assumed identical.

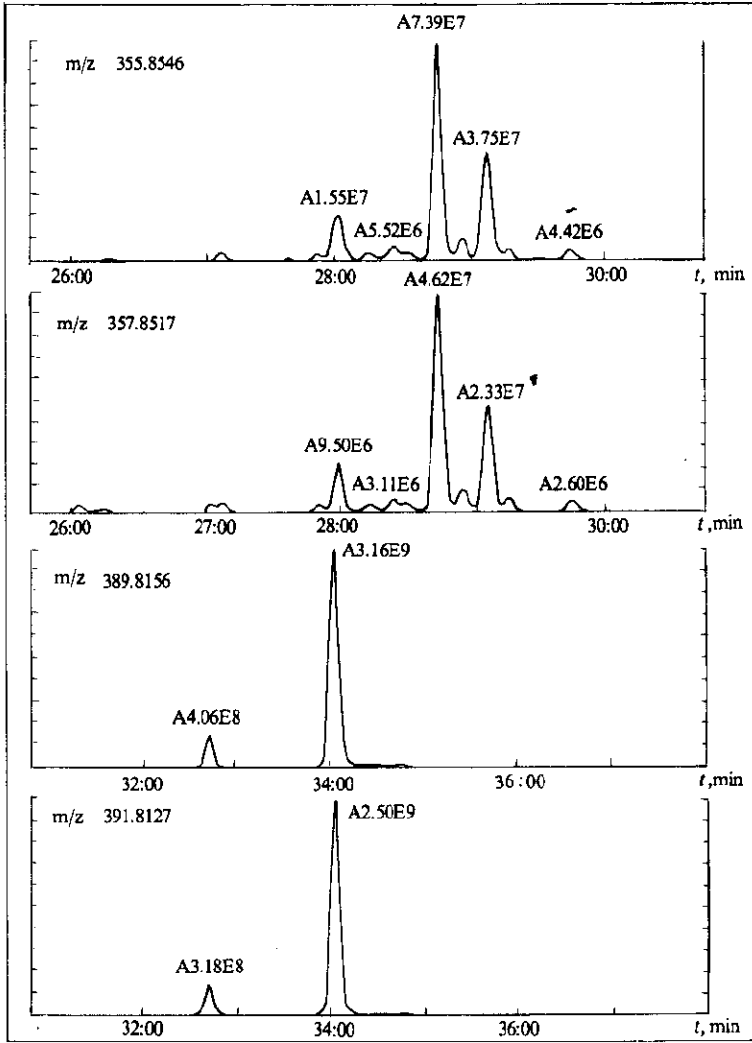


Fig. 2 Mass fragmentograms of penta - and hexa CDD for Na - PCP sample

The results revealed that the content of total PCDDs was significantly higher than that of PCDFs. Although the level of total TCDFs was a little higher than that of TCDDs, the level of toxic isomer 2,3,7,8-TCDF was only 0.7 ppb, much lower than that of 2,3,7,8-TCDD. Thus, relative higher content of TCDF did not contribute much to the toxicity of Na - PCP.

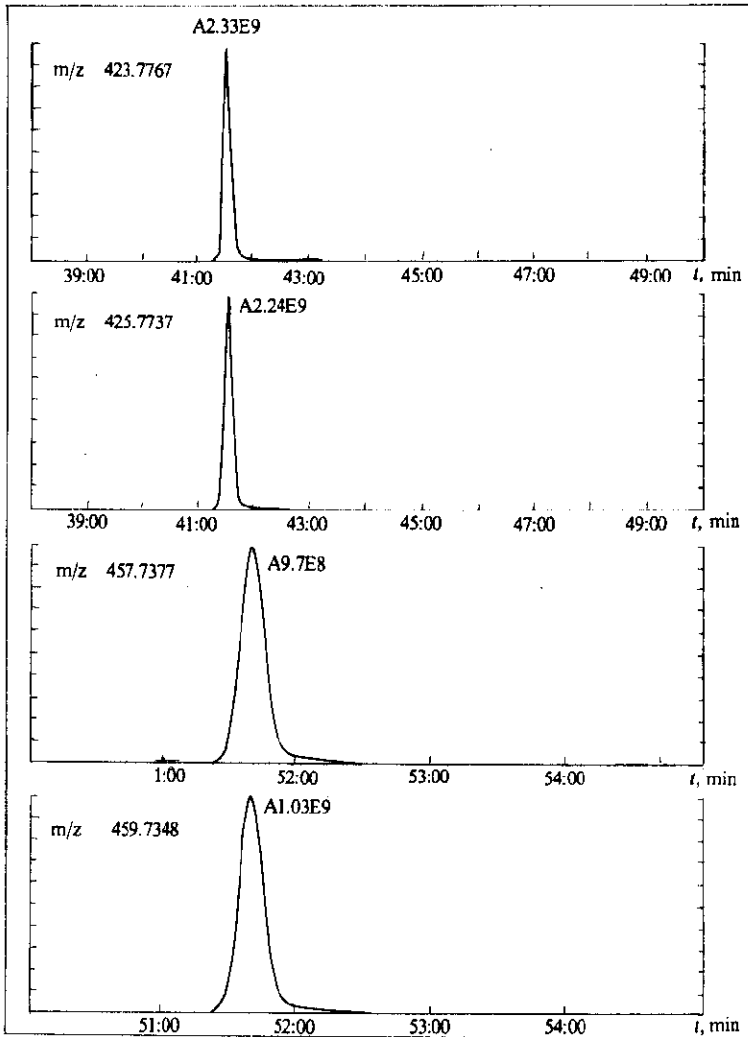


Fig. 3 Mass fragmentograms of hepta - and octa CDD for Na - PCP sample

The results in Table 2 suggest that PCDD/Fs levels in sediment samples, human blood and milk samples (Schechter, 1993; Jiang, 1993) from schistosomiasis areas were higher in various degree than those of control regions (where no Na - PCP was sprayed), and the main contribution to TEQ was due to elevated levels of PCDDs, which seems apparently related to the spray of Na - PCP in schistosomiasis areas, since the values of PCDDs were significantly higher than that of PCDFs which was revealed in the analysis of PCDD/Fs in Na - PCP.

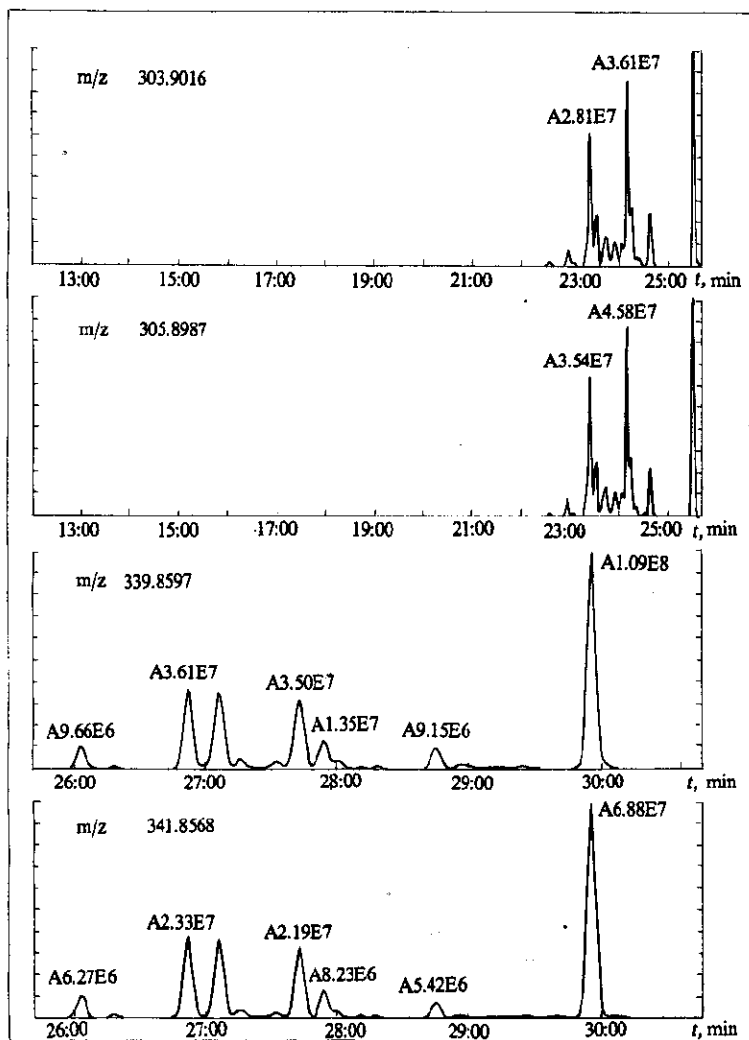


Fig. 4 Mass fragmentograms of tetra- and penta CDF for Na - PCP sample

From the comparison we made in the above table (Table 2), we can learn that TEQ value in blood samples from this area was far below that of central region of Vietnam (Schechter, 1993, Jiang, 1993), it almost equals the background level in the north of Vietnam. Therefore it might be considered that the blood and milk PCDD/Fs levels from schistosomiasis areas have not yet formed a hazard to the health of local residents. However, it has considerable significance to conduct this study. The results demonstrated that the use of Na - PCP can cause elevated PCDD/Fs levels in eco - environment and human blood and milk. It is necessary to conduct the determination of seventeen 2,3,7,8 - substituted PCDD/F congeners and comparison of "fingerprint" compound pattern between Na - PCP and human body and sediment samples from Chinese schistosomiasis areas so as to find out the definite relationship between the use of Na - PCP and eco - environmental effects.

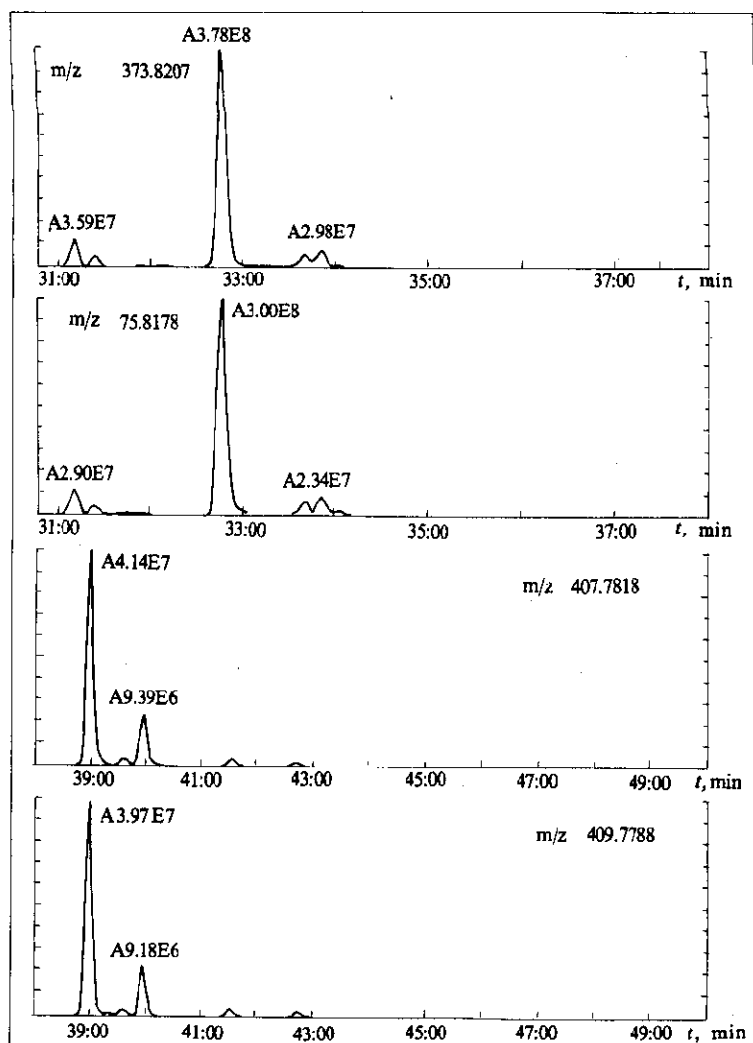


Fig. 5 Mass fragmentograms of hexa- and hepta CDF for Na-PCP sample

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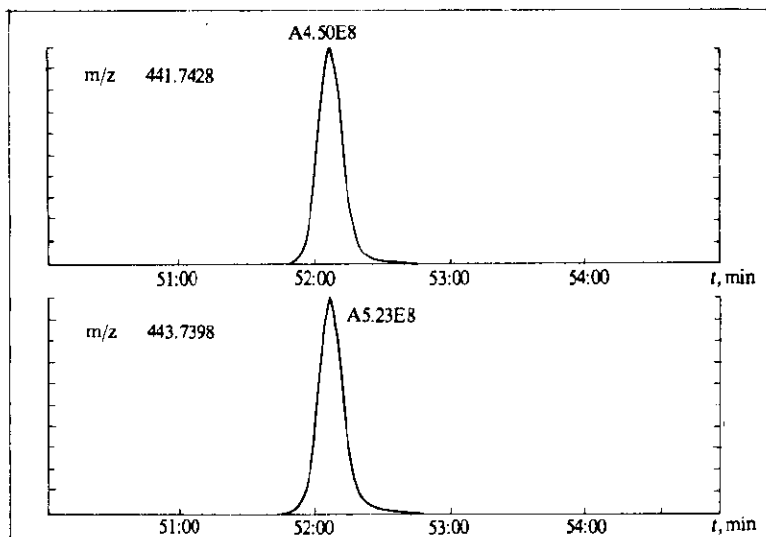


Fig. 6 Mass fragmentograms of octa CDF for Na - PCP sample

Table 2 Comparisons of PCDD/Fs values and dioxin toxic equivalents for human blood, breast milk and sediment samples between Chinese schistosomiasis areas and vietnam geographic regions (Scheeter, 1993; Jiang, 1993)

Compounds	Sediment sample, ppt		Breast milk samples, ppt, lipid		Human blood samples, ppt, lipid		Vietnamese blood, ppt, lipid	
	Control	Schistosomiasis areas	Control	Schistosomiasis areas	Control	Schistosomiasis areas	Central	North(non agent orange sprayed)
			N=50	N=50	N=50	N=50	N=183	N=82
2,3,7,8-TCDD	ND	3.1	0.64	1.4	ND	4.6		
2,3,7,8-TCDF	2.3	ND	2	0.47	2.7	1.4		
Total PCDDs	200	32799	34.34	128.9	148.9	816.8	931	186
Total PCDFs	44.8	861	7.17	4.8	27.2	16.5	214	101
Total PCDD/Fs	244.8	33660	41.51	133.8	176.1	831.4	1145	287
Total TEQ	1.11	62.77	2.6	5.41	5.7	16.5	50	15.3

ND—Not detected; N—The number of persons being collected for a pooled specimen

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