Residual Dioxins of Sediments and Soils in the Lake YAO Area of China*

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Abstract

Large amounts of the powerful pesticide sodium pentachlorophenol (Na-PCP) have been sprayed over Lake YAO area of China to control schistosomiasis, an epidemic parasitic disease. Dioxins, a class of toxic, persistent compounds have been detected as impurities in commercial Na-PCP products. These contaminants are released into the environment and significantly contribute to human exposure to dioxins in China. This study focuses on investigation of residual dioxins in sediments and soils in this Na-PCP sprayed area, and compares these results with those of human tissue samples from the same area so as to evaluate the health risks associated with exposure to Na-PCP. Sediment and soil samples from the region where Na-PCP was applied were collected from different sites and different vertical levels. A control sediment sample was collected and analyzed for comparison. All of the samples were analyzed by high resolution gas chromatography/ high resolution mass spectrometry (HRGC/HRMS). The international dioxin toxic equivalent (I-TEQ) values of these samples were calculated. The dioxins detected in Chinese commercial Na-PCP products ranged from 33 to 254 ng TEQ/g. The residual dioxins of sediment and soil samples from schistosomiasis areas were found significantly higher than those from non-schistosomiasis areas, where no Na-PCP was sprayed. In addition, the PCDD/F congener distribution patterns in the sediment and soil samples from schistosomiasis areas were similar to that of Na-PCP, which provided a type of "fingerprint" useful in the studying the transport and fate of residual dioxins in the schistosomiasis areas. These results are very well correlated to our previous findings of elevated I-TEQ levels in human blood and milk samples from schistosomiasis areas. Therefore, we conclude that the chemical pesticide Na-PCP is a source of environmental and human dioxin exposure in the Chinese schistosomiasis area studied.

Introduction

Japanese schistosomiasis had been an epidemic parasitic disease in the Lake YAO area of Jiang Xi province in China for a very long time. In 1972, molluscs were found in more than 80% of the area. Although Na-PCP had been sprayed multiple times over several years, it was

not very effective to kill the molluscs. In April 1973, large amounts of Na-PCP were applied in large-scale over the whole lake area. Nine hundred tons of commercial Na-PCP products were sprayed evenly over the lake area of 50 km^2. With the total volume of 10^8 m^3 water in the lake, the concentration of Na-PCP reached 10 μg/ml. After this action, the majority of the molluscs in the lake area were killed. This action can be considered as an effective preventive measure to reduce the numbers of people exposed to schistosomiasis. However, the adverse health effects of using Na-PCP to control schistosomiasis may outweigh its benefit by causing dioxin contamination in the environment. With awareness of the fact that dioxins are a class of hazardous environmental contaminants, PCDD/Fs have been detected in the Chinese commercial pentachlorophenol (PCP) and Na-PCP.[1-3] Dioxins in Chinese commercial Na-PCP ranged from 33 to 254 ng TEQ/g. In our previous investigations, the PCDD/Fs levels in human blood from schistosomiasis area were 2.6 and 1.9 times higher than general population for old and young group, respectively. The levels of PCDD/Fs in human breast milk samples from schistosomiasis region were elevated by 2.1 fold compared to the control group.[4-5] By comparison of PCDD/Fs congener distribution patterns, it can be concluded that the accumulation of dioxins in human tissues is directly related to the use of Na-PCP. The purpose of this study is to detect the PCDD/F residual levels in the sediment and soil samples from schistosomiasis areas, investigate the migration and transport of dioxins in the environment and establish the relationship between elevated dioxin levels in the environment and human health risk associated with exposure to Na-PCP.

Similar with other lakes in the middle valleys of the Yangtze River, Lake YAO contains many lands, and the level of the water was regulated through flooding gate in the lower streams. The most part of the lake area was used for planting paddy rice. The majority of the planting was done manually, farmers traditionally wear open sandals or walk barefoot while working in the fields. Thus, farmers were potentially exposed to Na-PCP and were at a risk of elevated dioxin body burdens. Additionally, the sediment and soils were ploughed frequently due to the people's work, so it would be interesting to investigate the residual PCDD/Fs in the sediments from schistosomiasis area.

Experimental Methods

Sampling

Sediment samples from the region where Na-PCP was applied were collected from different sites and different vertical levels. A control sediment sample was collected from the same area where no Na-PCP was applied for comparison.

Extraction and Clean-up

Soxhlet extraction followed by clean-up through a multi-layer silica column and a basic alumina column.

HRGC/HRMS analysis

^{13}C-labeled internal method was used. Qualitative/quantitative analysis was performed by HRGC/HRMS. Nine ^{13}C-labeled internal standards with known concentration were added

to the samples before extraction. Two other ^{13}C standards were added right before GC/MS analysis to determine the recovery. Seventeen 2,3,7,8-chlorine substituted toxic dioxin congeners were quantified by isotope dilution HRGC/HRMS.

Computation of TEQ

The TEQs relative to 2,3,7,8-TCDD are utilized internationally to describe the toxicity of all individual PCDD/Fs congeners. The total TEQ for the sample is the sum of seventeen toxic PCDD/Fs congener TEF values multiplied by the concentration of corresponding congeners in the sample.

Results and Discussion

1. Some of the samples were taken from the bank of the lake where Na-PCP had been piled in 1973. With some artificial and natural transition, such as the effect of sunlight, rain and microbiological degradation, most of the PCDD/Fs in the soils were disappeared. The current PCDD/Fs level were 1.7-8.9 pgTEQ/g. The PCDD/Fs level in the control sediment samples collected from the area where no Na-PCP was sprayed was 2.7 pg TEQ/g. The trail in the rice field where had been submerged by Na-PCP in 1973, it had never been flooded again, the residual PCDD/Fs detected in the top soil were only 1.7-6.5 pg TEQ/g.

2. Due to the least amount of sunlight in the lower part of the lake with water all the year round, the detected dioxin levels might reflect the highest residual concentration 20 years after the major spraying. 27.7 pg TEQ/g PCDD/Fs were found in the sediment samples from this region, which is 10 times of the control value. 16 pg TEQ/g PCDD/Fs was detected in the samples collected from the top and at a depth of 40 cm, this might be due to the frequent removal of the soil when farmers planted rice. In addition, 14.4 pg TEQ/g was detected in the sediment sample collected at the exit of the lower stream of the lake. Based on the above results, we can deduce that the usage of large amount of Na-PCP in 1973 cause that PCDD/Fs residual levels in the sediment over vast areas of the lake elevated by about six times compared to the sediment samples collected from the region where no Na-PCP has been applied in the same area. Since the overall dioxin residual levels were significantly higher than the nearby regions, also the farmers traditionally walk barefoot while working in the fields, and they consume water from the contaminated area and eat food grown in contaminated soil, all these factors caused the elevated dioxin levels in the human blood and milk from the schistosomiasis area.

3. For a small part of the land where some molluscs were found after the spray of Na-PCP in 1973, multi-spray of Na-PCP has been applied locally before 1991. Because of the recent usage of Na-PCP, higher level of PCDD/Fs have been detected in the sediment samples collected from that region, ranging from 99.3 to 439 pg TEQ/g. In one set of sediment samples collected from a part from this region, residual PCDD/Fs were detected as 419 pg TEQ/g in the surface, 360 pg TEQ/g in the sample from 20 cm deep, and 402 pg TEQ/g in the sample from 40 cm deep, respectively. Thus, it can be deduced that the residual dioxin levels in the lake area

within five years of the major spraying with Na-PCP in 1973 must be much higher than those of detected today, probably over 150 times higher than that of control value. Therefore, it would be a reasonable explanation for our previous findings that the dioxins levels in the old people are higher than those of young people who were born after 1973, and this leads to our conclusion that the use of Na-PCP can cause elevated PCDD/F levels and dioxin I-TEQs in both the environment and in humans. Concern about dioxin contamination and health risk has resulted in a plan to replace Na-PCP with a new molluscicide.

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