RESIDUAL CHARACTERISTICS OF DDTS AND HCHS IN WATER BODIES OF CHINA: A REVIEW

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Abstract

In the past decades, a large volume of persistent organochlorinated pesticides, especially, DDTs and HCHs were produced and used in China, moreover, the over-dose and illegal use aggravated the serious environment pollution. In this study, the residual levels and distribution characteristics of DDTs and HCHs in environmental water bodies all over the China were investigated, and the regional variation, vertical distribution, and temporal changes were analyzed as well. It was found that, after prohibiting the agricultural use of DDTs and HCHs in China in 1980s, their residual levels decreased gradually in water although new pollution occurred occasionally. As for vertical distribution in water, the residues in surfacial layer were higher than that in bottom layer, and the residues in middle layer were the lowest. Among the different regions in China, high residues appeared in Minjiang River, Daya bay, Tonghui River, where both of DDTs and HCHs were more than 100ng/L, however, the low residual level appeared in Yangtze River, Yongding River, where both of DDTs and HCHs were less than 10ng/L, and the middle residual appeared in Pearl River, Jiulongjiang River etc. The higher residues in lakes than in rivers, and the new pollution input should be paid more attentions.

Introduction

Organochlorinated pesticides have been spread in agriculture production since 1940s due to their low cost and high efficiency in agriculture protection, both of production and consumption rose to the peak in the world by the end of 1960s. China began to produce and use organochlorinated pesticides since 1950s, the consumption of organochlorinated pesticides continuously increased during the followed three decades, and organochlorinated pesticides shared 78 percentage of total pesticides market in China in early 1980s. Totally, about 4.46 and 0.43 millions tones of technical HCHs and DDTs were produced and extensively used in China before 1985 (Figure 1). The agricultural application of DDTs and HCHs has been forbidden for more than 20 years, moreover, the production, sale, use, import and export of DDTs has been banned in China from May 17, 2009 as required by the Stockholm Convention. However, organochlorinated pesticides have been of great concern because of their large production and illegal use, contribution from other pesticides, deleterious effect on non-target organism, ubiquity, bio-accumulatibility and persistence in environment, organochlorinated pesticides such as DDTs and HCHs were still detected out frequently from the environmental media in China[1,2]. Water body plays as an important environmental medium would be polluted by various pathways, such as atmospheric deposition, runoff, agricultural and industrial drainages. Therefore, in this study, the residual levels of DDTs and HCHs and their trends in environmental water bodies were summarized and analyzed.

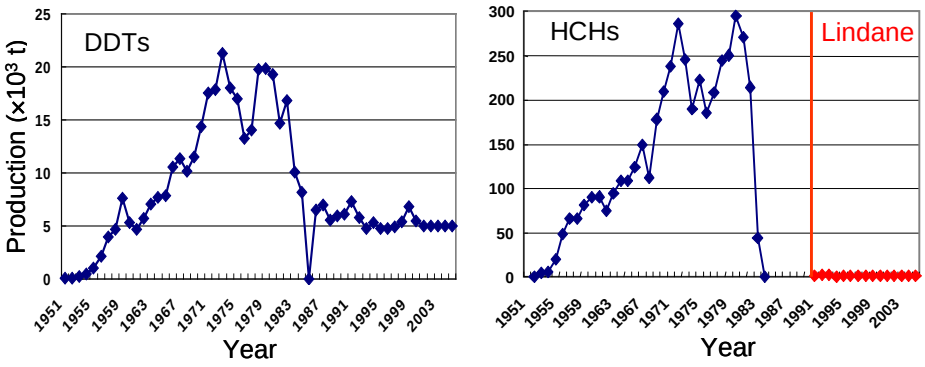

Figure 1. Historical production of DDTs and technical HCHs in China

Results and Discussions

Regional distribution

As we know, the spatial and temporal distribution of water resource in China is quite imbalance, rich in the southern areas and poor in the northern areas, which is inconsistent with the distribution of population, farmland and economy. Therefore, most surveys of organochlorinated pesticides in surface waters focused on some large water systems in southeastern coastal area of China where economic developed quickly, such as Pearl River, Jiulong River, Minjiang River and so on. There are only a few researches on the rest water systems in China, especially in west China, while this is accordance with the less river distribution in China. From the collected data, it could be found that the pollution level of pesticidal POPs in Minjiang River, Jiulongjiang River and Daya Bay in Fujian Province and Guangdong Province, were relatively serious, residual level of DDTs ranged from 12.8 to 175.0ng/L, and HCHs levels were 62.5-264.7ng/L, belonged to high pollution level (DDTs>100ng/L, HCH>100ng/L). However, both of DDTs and HCHs in these rivers still reached the environmental quality standards for surface water GB 3838-2002 (DDTs <1000ng/L, HCHs <5000ng/L) of China. Pearl River, Xiamen Harbor, Shiziyang, Macao Inner Harbor fell into middle pollution level (DDTs:10-100ng/L, HCH:10-100ng/L) and low pollution level (DDTs <10ng/L, HCHs <10ng/L), DDTs and HCHs concentrations usually covered within 0.10 to 10ng/L, and maximum concentration did not exceed 100ng/L[3-5]. What should be emphasized is that, the residues of pesticides were much higher in lakes than those in rivers, for example, γ-HCH concentrations in Fuxian Lake, Yunnan Province, ranged from 106.0ng/L to 7354.0ng/L, which was much worse than the standard requirement of GB3838-2002[6]. Another study on DDTs and HCHs concentrations in industrial wastewater and groundwater in Liantangzhen area of Jiangxi Province indicated that, concentrations of DDTs and HCHs were 106.7ng/L and 317.5ng/L, respectively[7].

Comparing with the pollution in water system of South China, rivers in East China seemed to be a little cleaner. Sun et al monitored organochlorinated pesticides in the Yangtze River (Nanjing section) for one year, the results indicated that average DDTs ranged from 1.46 to 2.26ng/L, and HCHs covered from 4.26 to 5.57ng/L[8]. Pollution situation of Taihu Lake was at same level to Yangtze River[9]. However, within the basin of Huaihe River, DDT was used to prevent from disease vector, the DDTs concentrations (4.45-78.87ng/L) was higher than other rivers, while the HCHs concentration (1.11-7.55ng/L) was similar with other rivers in this area[10].

In north China, some of rivers and lakes, e.g. Haihe River, Baiyangdian Lake and Tonghui River, were polluted

seriously as well, which were attributed to the chemical industrial and agricultural production. HCHs concentrations in Haihe River, the largest water system in North China, ranged from 225.0 to 1269.0ng/L[11], the average concentrations of DDTs and HCHs in Tonghui River in 2002 were 91.8 and 356.4ng/L, respectively[12]. An investigation indicated that during 1994 to 1995, residual levels of DDTs and HCHs in Baiyangdian Lake were ND-900ng/L and 300-2000ng/L, respectively[2]. Fortunately, Guanting Reservoir and Yongding River became clearer after the protection action was conducted, several investigations carried out in 2000 which indicated that both of DDTs and HCHs concentrations were less than 10ng/L[13,14]. In northeast of China, the DDTs and HCHs residues still belong to middle pollution level. Songhua River, Liaohe River, two large rivers play important roles in supplying drinking water and irrigation water for the wide area along the rivers, which were polluted seriously in the past decades, however, with the active protection actions in recent years, water quality become better and better although it still takes a long period to recover completely. The investigation in late 1990s indicated that HCHs concentrations were tens to hundreds ng/L level in Liaohe River and Songhua River, and DDTs concentration was about 29.9ng/L[15]. Another study on Wujintang Reservoir, Liaoning Province, indicated that the DDTs level was undetectable, but average HCHs concentration was 35.6ng/L[16].

Unfortunately, there are few reports about pollution level of water bodies in west of China. DDTs and HCHs in water from two Tibetan lakes, Lake Yamzho Yumco and Lake Co Ngoin, were analyzed, it was found that DDTs concentrations in two lakes were 0.27ng/L and 0.30ng/L respectively, HCHs concentrations were 3.83ng/L and 1.81ng/L, respectively. The occurrence of DDTs and HCHs, the absence of an up-profile decreasing trend around the surface layer, as well as the higher concentrations of DDTs and HCHs in Lake Yomzho Yumco compared to the northern Lake Co Ngoin may probably suggest a significant long-range atmospheric transport of pesticidal POPs by air flows from the Bay of Bengal to Tibet. Although the DDTs and HCHs concentrations in water from the two Tibetan lakes still belonged to low pollution level, it strongly warned us that an accumulation of POPs in Tibetan lacustrine environment[17].

Seasonal variation

As we know, China stretches from the south to the north the equator belt, torrid zone, sub-torrid zone, warm temperate zone, temperate zone and cold temperate zone, and there exists in these regions great discrepancies of natural conditions and evident diversities. As for different seasons, the concentrations of organochlorinated pesticides in water bodies are quite different. Yang et al monitored the pollution levels of DDTs, HCHs and some other of pesticidal POPs in Pearl River and Shiziyang River in 2001 spring (March) and autumn (August), respectively. The results indicated that the pollution level of two rivers were similar, DDTs concentrations in Pearl River and Shiziyang River were 5.33-8.03 and 5.85-9.53ng/L in 2001 spring, HCHs levels were 81.4-99.7 and 13.8-39.8ng/L, respectively. In autumn season, DDTs concentrations in Pearl River and Shiziyang River were 0.76-1.13 and 0.52-1.02ng/L, HCHs levels were 7.0-16.2ng/L and 5.8-20.6ng/L, respectively. Furthermore, concentrations of DDTs, HCHs measured in spring season in both rivers were almost 10 times higher than those in autumn season at each sampling site, which was due to the difference of the total flow in spring and autumn[3].

Sun et al. continuously monitored organochlorinated pesticides including DDTs and HCHs of samples collected from Yangtze River (Nanjing section, Jiangsu Province) for one year from December 1998 to October 1999 (Figure 2). It was found that the concentration of DDTs and HCHs covered from 0.30 to 1.73ng/L and 4.24 to 5.54ng/L, respectively, the highest concentration appeared in January and lowest one appeared in August,

concentrations of spring and autumn stood between those of winter and summer, while samples collected in September and October was a little lower than those collected in May and June[8].

Zhou et al collected surface water samples at 45 sampling sites from the Qiantang River and analyzed concentrations of 13 organochlorine pesticides during six surveys in 2 years of 2005-2006. The results are shown in Figure 3, it can be seen that the maximum levels of OCPs in water appeared in July, while significantly lower OCP concentrations were measured in January. Considering the sampling sites, most of them located on downstream of farmland or traditional agriculture area in Zhejiang Province, which meant that organochlorinated pesticides DDTs and HCHs could be released from wet deposition or soil eroding to waters with much rainfall during summer season in 2006 in Zhejiang province. In addition, significant linear correlation was found between the concentration of HCH and that of total 13 organochlorinated pesticides in water, which may be due to the high percentage of HCHs concentrations among 13 tested organochlorinated pesticides[18].

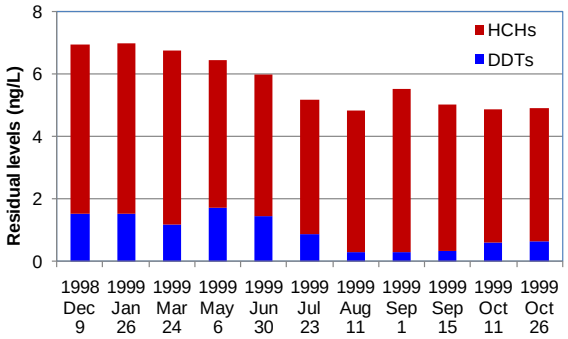

Figure 2. Variation of DDTs and HCHs residues during 1-year sampling in Yangtze River

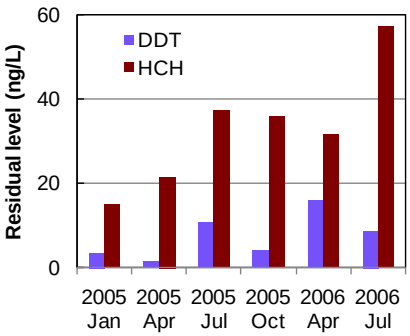

Figure 3. Variation of DDTs and HCHs residues in water from Qiantang River

Chronological trends

The environment monitoring and assessment research in China just started from recent several years, and the historical monitoring data for environment pollution was quite scarce, and there are only little reports on the chronological trends of pesticidal POPs pollution in river water of China, and almost no long-term continuous monitoring. Summarized the reports by Cai et al and Bodo et al., it was found that, the national average concentration of HCHs reduced from 1673.0ng/L in 1979 to 467.0ng/L in 1983, and further decreased to 24.0ng/L in 1992. A survey on water qualities of Yangtze River shown that HCHs concentrations changes before and after prohibition of HCHs use in agriculture are shown in Figure 4, it can be seen that after prohibition, the concentration of HCHs decreased significantly[1].

As mentioned above, there are relatively more monitoring data for those water bodies in south of China. As shown in Figure 5, the residual concentrations of DDTs and HCHs in Pearl River had great reduction between 1994 to 2001, since then, the residues keep a stable level, which was attributed to the DDTs application as anti-corrosive paint on watercrafts.

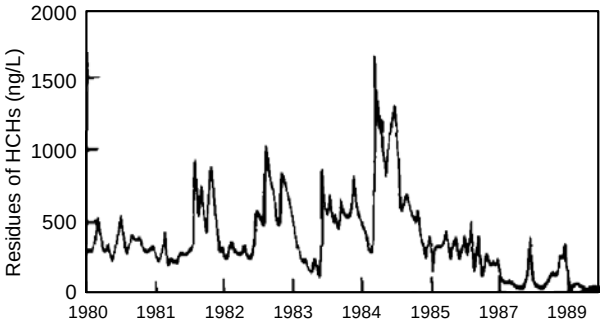

Figure 4. Residual trends of HCHs in Yangtze River (Wuhan section)

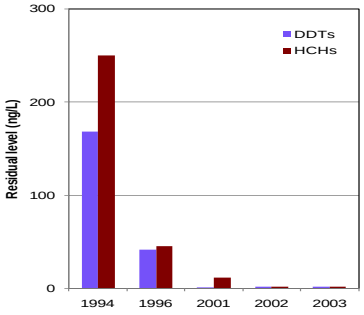

Figure 5. Temporal changes of DDTs and HCHs residues of Pearl River

Vertical distribution

The vertical distribution of pesticidal POPs in water body is quite difficult to study due to the complex watercourse conditions and hydraulic disturbance of sampling, so there are only few measurement results. Yang QS et al investigated the concentration distribution of DDTs, HCHs and some other pesticidal POPs in Macao Inner Harbor along the depth of water. As for DDTs and HCHs, the changes of their residual concentrations depended on the depth of water (Figure 6), that is, the deeper the water was, the residual concentrations of them would be lower. However, within the interface zone between bottom water and sediment, the concentration of pesticides increased near to the level of surface water again[4]. However, there is a difference between the concentrations changes of DDTs and HCHs in surfacial layer and sub-layer, that is, the residue of HCHs in surfacial layer is lower than that in the sub-layer, which may be attributed to the evaporation of HCHs from the surfacial layer into air, while as for DDTs, the residue in surfacial layer was higher than that in sub-layer, which indicated the new input from air deposition. In addition, the residues of both DDTs and HCHs at bottom interface increased significantly which was due to the releasing of target substances from sediment. Recently, Yang et al investigated their vertical distribution in Hu'men estuary of Pearl River, the trends of residues distribution of DDTs and HCHs in this area was similar with that in Macao Inner Harbor, and DDTs levels covered from 0.16 to 3.28ng/L, while HCHs ranged from 19.29 to 59.29ng/L[19].

Another survey on DDTs and γ-HCH residual concentrations at 0.5m and 15m depth in Fuxian Lake, Yunnan Province, the results indicated that, γ-HCH concentrations were 106.0-7354.0ng/L at 0.5m depth, while 104.0-4048.0ng/L at 15m, which indicated that some new pollution of HCH occurred in the study area[6].

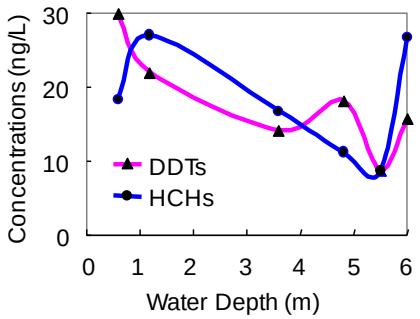

Figure 6. Vertical distribution of DDTs and HCHs in Macao Inner harbor

Conclusions

The agricultural use of DDTs and HCHs has been forbidden in China for almost 30 years, they can still be detected out from water bodies frequently although their concentrations are decreasing gradually. Especially, those rivers in south China such as Minjiang River, Daya Bay, both of DDTs and HCHs levels were more than 100ng/L, and the residues in Pearl River, Jiulongjiang River ranged from 10 to 100ng/L. As for East China and North China, the residues of organochlorinated pesticides were complex, which was mainly caused by the chemical industrial and agricultural production, for example, Tonghui River and Huaihe River. Within the basin of Huaihe River, pesticides use and schistosomiasis preventing contributed to the high residues of Organochlorinated pesticides. Totally, the residual levels of DDTs and HCHs in water bodies decreased from southeast to northwest of China. In addition, the higher residual level in lakes than in rivers should be paid more attentions in pollution management. As for the vertical distribution of DDTs and HCHs, surfacial layer > bottom layer (bottom interface) > middle layer, which was due to the new pollution input and releasing from sediment. The most important is that the new pollution input should be controlled and cut off, which will be of benefit to protecting safety of ecosystem and human health.

Acknowledgements

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