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Gridded inventories of historical usage for selected organochlorine pesticides in Heilongjiang River Basin, China

LIU Li-yan[1], JIANG An-xi[1], REN Nan-qi[1], JIANG Gui-bin[2], LI Yi-fan[3,1,*]

(1. School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harhin 150090, China. E-mail: yi-fan.li@ec.gc.ca; 2. Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China; 3. Atmospheric Environment Service, Environment Canada, Downsview, Ontario, Canada)

Abstract: The use of technical HCH (1, 2, 3, 4, 5, 6-hexachlorocyclohexane), DDT (dichlorodiphenyltrichloroethane) and lindane in Heilongjiang River Basin (HRB) of China was studied. Between 1952 and 1984 the total usage in the HRB was 108900 t for technical HCH, and 4900 t for DDT, respectively, and the use of DDT due to dicofol application in the HRB was 220 t from 1984 to 2003. The usage of lindane in HRB was 109 t from 1991 to 2000. The results show that the highest technical HCH use (41800 t) in HRB was on maize, accounting for 38.3% of the total usage on all crops, followed by the use on wheat (28000 t, 25.7%) and on soybean (26600 t, 24.4%). The highest DDT use (2300 t) was on soybean, accounting for 46.8% of the total usage on all crops, followed by the use on maize (1500 t, 31.3%) and on sorghum (600 t, 13.2%). The major use of lindane was mainly on wheat. Gridded usage inventories of these three OCPs (organochlorine pesticides), in HRB with a 1/6° latitude by 1/4° longitude resolution have been created by using different gridded cropland as surrogates. Some soil samples have also been collected in HRB. Data of usage and soil concentrations of ΣHCH in HRB match quite well to those in Shanghai region, and much higher soil concentration of ΣDDT in Shanghai region could be due to much heavier dicofol use in this region.

Keywords: persistent organic pollutants (POPs); organochlorine pesticides (OCPs); DDT; HCH; lindane; inventories; Heilongjiang River Basin

Introduction

Organochlorine pesticides (OCPs) is a common name of a group of pesticides consisting of benzene and chlorine. Some of OCPs belong to persistent organic pollutants (POPs) that are semi-volatile, bioaccumulative, persistent and toxic (Vallack *et al.*, 1998; Jones and de Voogt, 1999). OCPs are ubiquitous pollutants due to their long-range transport potential. These chemicals have even been found in remote areas like the Arctic (Macdonald *et al.*, 2000; AMAP, 1998, 2004; Li and Macdonald, 2005). Considering their harmful effects on man and wildlife, many international agreements are now coming into effect to reduce future environmental burdens. One such agreement is the Aarhus Protocol in 1998 on POPs under the 1979 Geneva Convention on Long-range Transboundary Air Pollution, which listed 16 POPs substances, 11 of which are pesticides, which are aldrin, dieldrin, endrin, chlordane, DDT, heptachlor, hexachlorobenzene, mirex, chlordecone, lindane, and toxaphene (UNECE, 1998). The other recent international agreement is the Stockholm Convention on POPs, which will eliminate or at least control 12 POPs, 9 of which are OCPs, which are aldrin, dieldrin, endrin, chlordane, DDT, heptachlor, hexachlorobenzene, mirex, and toxaphene (UNEP, 2001; 2003).

In China, technical HCH (1, 2, 3, 4, 5, 6-hexachlorocyclohexane) and DDT (dichlorodiphenyltrichloroethane) were widely used in agriculture, which was the main pesticides accounting for about 78% of total pesticide production and usage before they were banned in 1983 (Hua and San, 1996; Li *et al.*, 1998, 1999, 2001; Yu, 2000). Additionally, a small amount of other OCPs, such as lindane, chlordane, toxaphene, heptachlor, hexachlorobenzene, and mirex have also been produced and applied in China in the past. The Heilongjiang River (also called River Amur), the largest river in East Asia, is 2900 km long, and formed by the confluence of the Shilka and Argun rivers at the Russia-China border. The Heilongjiang River flows generally towards southeast, forming for more than 1610 km along the border of China and Russia, then flows northeast through Russia before entering the Tartar Strait opposite Sakhalin Island (http://www.encyclopedia.com/html/a/amur.asp). The Heilongjiang River Basin (HRB) in China includes almost whole territory of Heilongjiang Province and parts of Jilin Province and Inner Mongolia Autonomous Region (Fig.1). Both agricul-

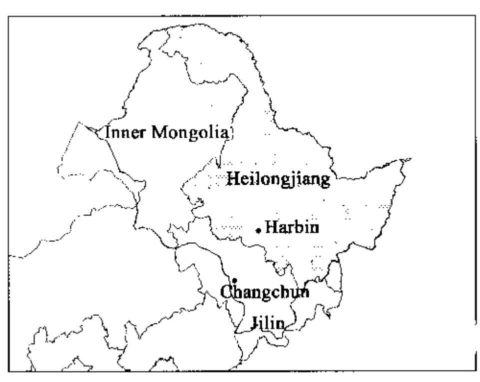

Fig.1 The portion of the Heilongjiang River Basin (HRB) in China.

*Corresponding author

ture and industry are relatively well developed within the basin.

In order to study transport behavior of technical HCH, DDT, and lindane in China and abroad, usage inventories of these three OCPs in China with a 1/6° latitude by 1/4° longitude resolution were compiled (Li *et al.*, 1999, 2001a). Due to limited information on historical usage for these three pesticides, the inventories may not be accurate, especially in the HRB. For example, the data given by Li *et al.* (1999) show that there was no DDT use in the HRB. Although the use of technical HCH and lindane was given in the HRB (Li *et al.*, 2001a), the application distribution of technical HCH in this area needs to be improved.

The present study was to investigate the use of technical HCH, lindane, and DDT in the HRB, and to create gridded historical use inventories for these pesticides in the HRB with a 1/6° latitude by 1/4° longitude resolution.

1 Usage of technical HCH, lindane, and DDT

The production and use of technical HCH and DDT started in the early 1950s in China, and peaked in 1970s (Li *et al.*, 1998, 1999, 2001a). From 1952 to 1984, total 4500000 t of technical HCH and 270000 t of DDT were produced and used in China. Lindane, almost pure γ-HCH, started production and application in China at the beginning of 1990s. Total 11400 t of lindane was produced between 1991 and 2000, among which, only 3200 t were used in China, and the rest was exported or in stock (Li *et al.*, 2001a).

Technical HCH, lindane, and DDT were mainly used in agriculture in China, while only a small portion was used in forestry and public health (Cai *et al.*, 1992; Li *et al.*, 1998, 1999, 2001a). Technical HCH was widely used for pest control in rice, wheat, soybean, maize, cotton, and sorghum production, and DDT was used in wheat, soybean, maize, cotton, and sorghum production. The major use of lindane has been applied on wheat land (Li *et al.*, 2001a). In order to distribute technical HCH usage among different crops in different areas of China, total pesticide usage based on provinces and autonomous regions in 1960 and 1970 (Cai, 1996) was used as surrogates to allocate the usage of technical HCH between 1952 and 1965, and between 1966 and 1975 among these areas, respectively. The usage of technical HCH in these regions from 1976 to 1984 was based on the provincial use of technical HCH in 1980 (Cai, 1996). The total use of technical HCH between 1952 and 1984 in Heilongjiang, Jilin, and Inner Mongolia were 75700, 39600, and 52600 t, respectively.

The similar method as described above was also used to calculate the use of DDT in these regions. Pesticide usage in 1960 and 1970 (Cai, 1996) was used as surrogates to allocate use of DDT between 1952 and 1965, and between 1966 and 1975, respectively; and DDT usage from 1976 to 1984 was based on the provincial use of DDT in 1980 (Cai, 1996), in which the usage of DDT in 1980 was zero in Heilongjiang Province, Jilin Province and Inner Mongolia autonomous region. Thus DDT was assumed not being applied in these three regions between 1951 and 1984 (Li *et al.*, 1999), which is, as we recognize now, not correct.

Based on DDT usage inventories by Li *et al.* (1999), DDT use in Heilongjiang, Jilin, and Inner Mongolia were re-estimated by using crop production data in these three regions as surrogate, which is shown in Fig.2. Fig.2 gives DDT use in Beijing, Shanghai, Tianjin, and different provinces and autonomous regions in China between 1951 and 1984. The results give the total use of DDT between 1951 and 1984 in Heilongjiang, Jilin, and Nei Menggu being 3200, 1900, and 2200 t, respectively.

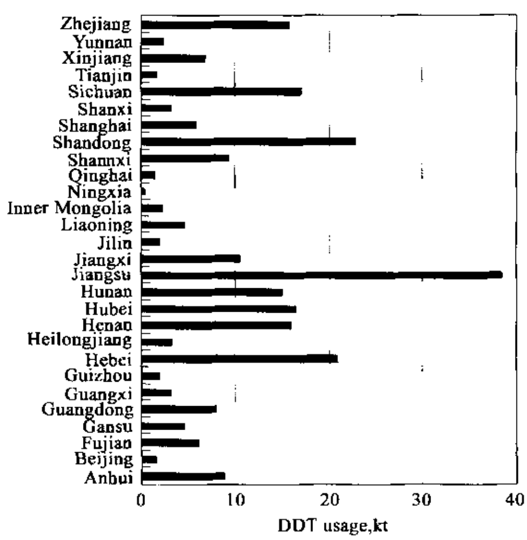

Fig.2 DDT use in part regions in China between 1951 and 1984

2 Usage gridding

2.1 Surrogate data: crop land in HRB

By using the similar method that has been applied to grid the use of pesticides (Li, 2001b; Li *et al.*, 1999, 2001), the gridded maps of different croplands have also been used as surrogate in this study. Digital maps for rice, wheat, soybean, maize, sorghum, and orchard with a 1/6° latitude by 1/4° longitude resolution have been created for Heilongjiang, Jilin, and Inner Mongolia. All these cropland datasets were compiled using an advanced high resolution radiometer (AVHRR) global land database (http://edcwww.cr.usgs.gov/landdaac/1km/) and the Chinese Comprehensive Atlas (Hou, 1990).

2.2 Gridded OCPs use in HRB

Annual usage of pesticides in Heilongjiang, Jilin, and Inner Mongolia was broken for different crops, and then allocated on a grid system with a 1/6° by 1/4° latitude/longitude resolution using different gridded cropland datasets with the same resolution.

Technical HCH usage in HRB was allocated on croplands of maize, wheat, soybean, sorghum, rice, and orchard on a 1/4 ° longitude by 1/6 ° latitude resolution first, and then a gridded inventory for total technical HCH usage was created, which is given in Fig.3.

After the ban on the use of technical HCH in China in 1983, lindane has been used since 1991. Since the use of lindane is mainly on wheat, gridded wheat land is used as surrogate to grid the use of lindane in HRB, as shown in Fig.4.

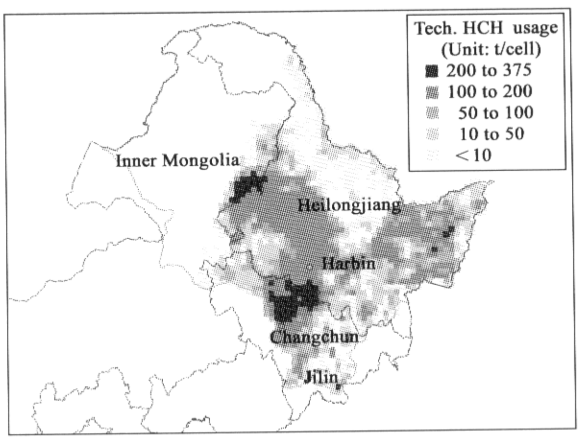

Fig.3 Technical HCH usage on cropland in HRB from 1952 to 1984 on a 1/4°×1/6° longitude and latitude resolution

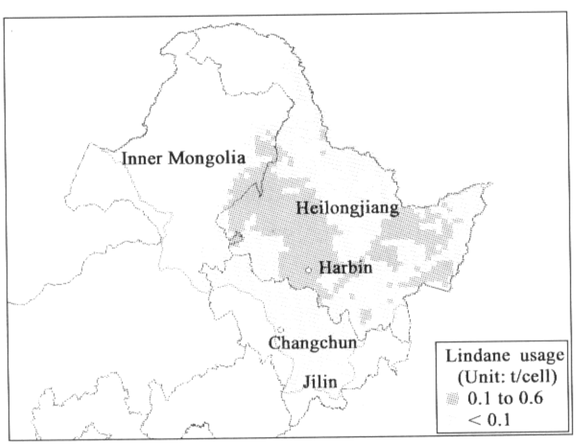

Fig.4 Lindane usage on cropland in HRB on a 1/4°×1/6° longitude and latitude resolution

DDT usage in HRB was allocated on croplands of maize, wheat, soybean, sorghum, and orchard on a 1/4° longitude by 1/6° latitude resolution first, and a gridded inventory for total DDT usage was created, which is given in Fig.5.

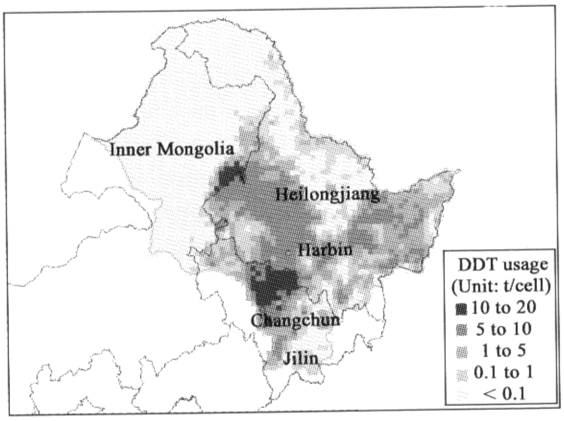

Fig.5 DDT usage on cropland in the HRB from 1952 to 1984 on a 1/4° × 1/6° longitude and latitude resolution

3 Results and discussion

3.1 Total usage of OCPs in HRB

Between 1952 and 1984, total use of technical HCH in HRB was 108900 t among which, 75700 t was used in Heilongjiang, 24600 t in Jilin, and 8600 t in Nei Menggu. Total use of DDT in HRB at the same period was 4900 t among which, 3200 t was used in Heilongjiang, 1300 t in Jilin, and 400 t in Inner Mongolia. The use of lindane between 1991 and 2000 was 94 t in Heilongjiang, 1.3 t in Jilin, and 13.4 t in Inner Mongolia, with total use of 109 t in the HRB. Heilongjiang province made the highest contributions to the use of these OCPs in HRB, 69.6% for technical HCH, 66.3% for DDT, and 86.5% for lindane.

3.2 Usage based on crops

Usage of technical HCH in the HRB between 1952 and 1984 on different crops are given in Fig.6. The largest amount of technical HCH usage (41800 t) was on maize, accounting for 38.3% of the total usage on all crops, followed by use on wheat (28000 t, 25.7%) and on soybean (26600 t, 24.4%). The use on these three crops was 96300 tonnes, accounting for 88.4% of the total technical HCH usage in the HRB.

Fig.7 gives usage of DDT in the HRB on different crops between 1952 and 1984. The highest DDT use (2300 t) was on soybean, accounting for

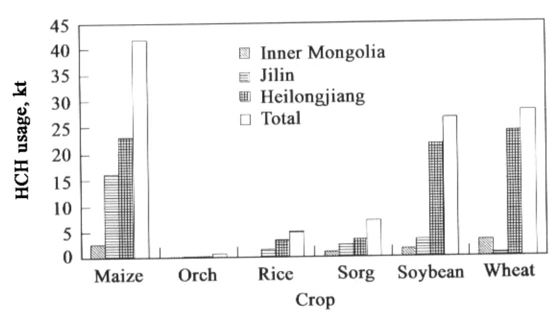

Fig.6 Usage of technical HCH in the HRB from 1952 to 1984 based on crops and provinces

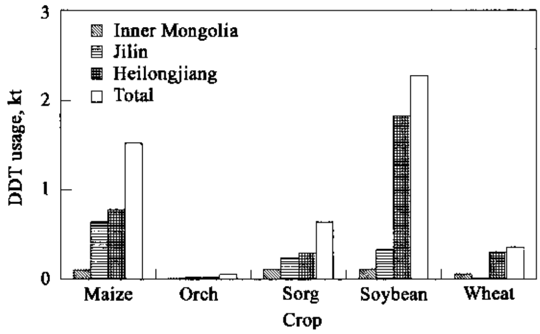

Fig.7 Usage of DDT in the HRB based on crops and provinces

46.8% of the total usage on all crops, followed by use on maize (1500 t, 31.3%) and on sorghum (600 t, 13.2%). The use on these three crops was 4400 t, accounting for 91.3% of the total technical HCH usage in the HRB.

3.3 Soil concentrations of ΣHCH and ΣDDT in HRB

Fourteen soil samples were collected across the HRB for analyzing the soil concentrations of HCHs and DDTs in the region (Liu *et al.*, 2005), not attempting to obtain a comprehensive knowledge of pollution of soil by these pesticides, but hoping to catch a sketchy picture of soil contamination level in HRB caused by application of technical HCH, lindane, and DDT. The results are given in Fig.8 along with soil concentrations of ΣHCH and ΣDDT in other places in China at the beginning of 2000s.

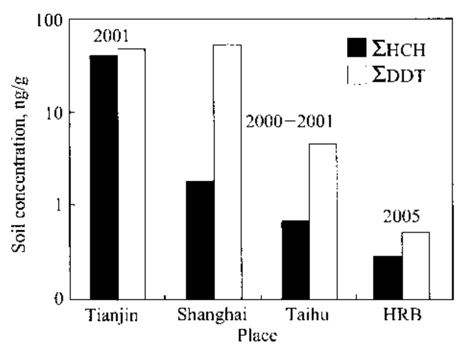

Fig.8 Soil concentrations of ΣHCH and ΣDDT in Tianjin, Shanghai, Taihu, and the HRB (the numbers above the bars are sampling years)
Sources of data: ΣHCH in Tianjin: Gong *et al.*, 2004a; ΣDDT in Tianjin: Gong *et al.*, 2004b; Shanghai and Taihu; Nakata *et al.*, 2005; HRB: this study

The sampling sites in Tianjin have the highest mean soil concentrations of ΣHCH (45.8 ng/g), followed by 1.95 ng/g in soil of Shanghai. The mean soil concentration of ΣHCH in HRB is 0.29 kg/g, the lowest value among the four regions. It is not surprising that soil in Tianjin was heavily contaminated by HCH, since not only technical HCH was applied in this region for may years, but also a chemical plant located in Tianjin (Tianjin Dagu Chemical Plant) had produced technical HCH for more than 40 years (The workshop making technical HCH in the plant was closed in 1999). Usage inventories of technical HCH created by Li *et al.* (2001a) gave that a very large amount of this insecticide had been used in Shanghai cropland, reaching 13000 t in each cell (around size of 25 km by 25 km) for more than 30 years from 1952 to 1983 in the region. By considering that 90% of the land in the cell was cropland, the accumulated application rate was about 370 kg/hm^2, very close to the application rate of 375 kg/hm^2 obtained from a survey in 1983 (Cai *et al.*, 1985; Li *et al.*, 2001a). Our study gave the application rate of technical HCH in HRB 48 kg/hm^2, around 13% of that in Shanghai region. It is interesting to note that the mean soil concentration of HCHs in HRB (0.29 ng/g) is around 15% of mean soil concentration of HCHs in Shanghai region (1.95 ng/g), indicating that HCH residues in soil of these two regions are mainly caused by the historical use of this insecticide.

The highest usage of technical DDT in Shanghai was 1270 t per cell, giving the application rate in the region as 37 kg/hm^2 (Li *et al.*, 1999). Our study shows that the highest usage of technical DDT in HRB was 1270 t per cell, giving the application rate in the region as 2.5 kg/hm^2, around 6.8% of that in Shanghai region. The mean soil concentration of ΣDDT in HRB (0.5 ng/g), however, is less than 1% of that for Shanghai (59 ng/g).

Although the use of DDT was banned in 1983, the production of DDT has continued, mainly for making pesticide dicofol, a nonsystemic acaricide widely used for the control of mites. DDT still remains in the dicofol product as impurities after the synthesis reaction, and the use of dicofol in China could cause a significant DDT contamination in environment. For example, Qiu and co-workers (2004) found out that the use of dicofol applied on cotton fields in the North Yangtze River was the source of high air concentration of DDTs, especially *o, p*'-DDT, over Taihu Lake Basin. This could indicate that, soil residues of DDT in these regions may be caused not only by the historical use of this insecticide, but by the currently used dicofol as well.

According to Zhao (2005), dicofol has applied in Heilongjiang, Jilin, and Inner Mongolia mainly on apple and vegetables, and the use of DDT due to application of dicofol was 124 t in Heilongjiang, 85 t in Jilin, and 61 t in Inner Mongotia from 1984 to 2003. This leads to total use of DDT due to dicofol application in the HRB being around 220 t. On the other hand, the use of DDT due to dicofol application (mainly on cotton, tea, and vegetables) in Shanghai, Jiangshu, and Zhejiang between 1984 and 2003 were 44651, and 361 t respectively, much higher than those in HRB if the geographic sizes are taken into account.

3.4 Uncertainty

Uncertainty estimates for usage data are an important part for an inventory. Many factors could lead to uncertainties for these gridded usage inventories. First, annual production of these three OCPs was considered as annual usage, which could lead the highest uncertainty to the annual usage inventories for these three pesticides. Secondly, in allocation of usage of these two OCPs in each province, the use pattern of these three pesticides in different provinces are assumed to be identical, which is not true, since the use pattern in different places are not always the same. In addition, the temporal difference of use pattern was not considered in our estimation. Finally, the surrogate data (gridded cropland) that we used in gridding the usage of the pesticides in the HRB, could be possible factors for uncertainties.

Based on the usage inventories discussed in this paper, the emission and residue inventories of these OCPs in HRB will be compiled in the near future, and the results will be compared with the monitoring data for these three OCPs in HRB..

4 Conclusions

In comparison with other river basins in China, the study of OCPs in Heilongjiang River Basin is rather limited. Besides the use on crops, OCPs were also used on other sectors such as in forestry and public health. This paper presents the use of technical HCH and DDT on crops between 1952 and 1984 and lindane from 1991 to 2000 in HRB which gives a good picture of temporal and spatial use trends of these pesticides in this region. This effort is especially important since the historical use information for these OCPs in this region is very limited.

The present study shows that, in HRB, total usage between 1952 and 1984 was 108900 t for technical HCH, and 4900 t for DDT, and total usage of lindane from 1991 to 2000 was 109 t. Inventories of gridded usage of technical HCH, DDT and lindane in the HRB with a 1/6° latitude by 1/4 ° longitude resolution have been complied, and will be used in creating the emission and residue inventories in the near future.

Data of usage and soil concentrations of ΣHCH in HRB match quite well to those in Shanghai region, and much higher soil concentration of ΣDDT in Shanghai region could be due to much heavier dicofol use.

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