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Assessment of Pesticide Pollution in Suburban Soil in South Shenyang, China

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Abstract In this study, 35 representative farmland soil samples from suburban areas in south Shenyang, the capital city in Liaoning province, China, were collected to evaluate the pollution of 114 pesticides. Surface soil samples were air-dried and sieved. Ultrasonic extraction was used for pesticides preparation prior to analysis with gas chromatography-mass spectrometry. The total concentrations of tested pesticides in the area ranged in 0–51.32 ng/g and the average of concentrations was 6.86 ng/g. Six pesticides, including butachlor(with detect frequency 71.4%), *p,p′*-DDE (88.6%), *p,p′*-DDT (77.1%), *o,p′*-DDD (82.9%), hexachlorobenzene (88.6%) and δ-HCB (77.1%), were detected most frequently. It indicated that DDTs (N.D.-40.25 ng/g) and HCHs (N.D.-42.79 ng/g) were the predominant pesticide pollutants in soil because of their long term persistence. On the contrary, most of organophosphorus pesticides, pyrethroids and carbamates were not detected. Spatial variation of six pesticides with high detection frequency (>70%) in soil was illustrated. Pollution levels, characteristics and the possible sources were also discussed. The data were helpful to figure out the pollution of the pesticides and could be further used to evaluate the health risk associated with food safety.

Keywords Pesticides · Soil · Suburban · Shenyang

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Pesticides and herbicides have been extensively used for agricultural purposes during the last five decades to protect crops against a wide range of pests and herbs. Organophosphorus pesticides (OPPs), organochlorine pesticides (OCPs), pyrethroids and carbamates are the four main kinds of pesticides once popularly used worldwide. These organic compounds have been frequently detected in soil and constitute an animal and human health hazard (Mwevura et al. 2002). Many pesticides and herbicides, especially organochlorine pesticides have a wide range of acute and chronic health effects, including cancer, neurological damage, birth defects and endocrine disruption. Contamination of organochlorine pesticides in environment, especially in agricultural soils, was reported in many studies (Harris et al. 2000), even if those organochlorine pesticides had been banned for decades of years. Therefore, it is necessary to monitor their residues regularly in the agricultural area and evaluate their potential risks to human heath and ecosystem.

China is a large producer and consumer of pesticides and herbicides. As one of China's greatest metropolises, Shenyang covers about 13,000 km^2 with a population of more than 7.2 million. Pesticides and herbicides were once widely used in the agricultural area in suburban Shenyang districts, especially in Sujiatun District, south of Shenyang. Many species of pesticides were detected in different environmental matrix in Shenyang (Niu and Qin 1991; Zhong and Suo 1996; Kunisue et al. 2004; Liu et al. 2009, 2010).Most previous studies on soil focused on the levels and profiles of pesticides in the whole city(Niu and Qin 1991; Zhong and Suo 1996) or another district Zhangshi known for wastewater irrigation (Sun et al. 2006); sampling sites in the districts like Sujiatun which also supply food to the urban areas were not systematic and detailed enough in those studies; On the other hand, some kinds of pesticides were still produced and released to the environment now, such as DDT as an intermediate of dicofol and butachlor etc., but samples in the latest study on pesticides pollution in the soil in this area were collected before 1996 (Zhong and Suo 1996) to our best of knowledge. The pollution status had not been monitored and evaluated for many years, so it is necessary to conduct a new survey.

Materials and methods

A total of 35 soil samples (0–10 cm soil layer, 1–2 kg each) were collected with a stainless steel scoop and stored in PE bags in June 2010. Sampling sites were illustrated in Fig. 1 according to the GPS values. Each sample was mixed of at least 20 sub samples collected in the $10 \times 10\ m^2$ of sampling sites. All soil samples were stored in dark and transported to the laboratory as soon as possible. Soil samples were air dried and then ground. The samples were stored in −20°C after sieved through a 50 mesh sieve before the sample preparation progress.

The organic solvents including acetone and dichloromethane purchased from Fisher (Fair Lawn, NJ, USA) were pesticide grade. Mixed standards of 114 pesticides (1 mL, 10 mg/L, in acetone) were presented by Institute of Environmental Protection and Monitoring, Minister of Agriculture, China. ^{2}D-labeled chrysene (EPA M-525-IS, 1 mL, 2.0 mg/mL in acetone) was purchased from Accustandard Inc. and used as surrogate (CT, USA). 40 mg/L ^{2}D-chrysene was spiked 2.5 μL before extraction as surrogate in all samples. About 2.0 g of soil sample was ultrasonicated for 30 min with 15 mL of acetone: hexane (v: v/1:1) three times. Then the mixture was centrifuged for 5 min at 4,000 rpm each time. The supernatant was collected, mixed and evaporated to nearly dry in nitrogen flow. The following cleanup procedure was modified from a previous study (Song et al. 2007).The elution was finally concentrated to 0.1 mL with gentle nitrogen flow for GC–MS injection. All the compounds were quantified on Agilent 7890 gas chromatography with Agilent 5975 mass spectrometer with electron impact ion source. The carrier gas (helium) was set in constant flow at 1.0 mL min^{-1}. One μL of the extract was injected with 7673 auto sampler in splitless mode. Twice injections with different SIM parameters (group 1 and group 2 in Table 1) were needed to separate all 114 compounds. A DB-5MS fused silica capillary column (30 m × 0.25 μm × 0.25 mm) was used to separate the pesticides. The ion source and the quadrupole temperature were set at 230, 150°C respectively. The oven temperature program and the SIM mode parameters were also referred to Song's method (Song et al. 2007).The compounds, the retention time, the SIM parameters and the limits of detection were listed in Table 1. Spiked tests indicated that recoveries of all pesticides were from 63.6% to 118.2% with RSD (n = 3) from 3.3% to 17.9%. The detection limits of this method ranged from 0.01 to 8.45 mg/L (Table 1). The recoveries of surrogates in all samples ranged from 77.0% to 112.2%.

Results and discussion

The total concentrations of tested pesticides ranged in 0–51.32 ng/g and the average of total concentrations was 6.86 ng/g. Total pesticides contaminated areas were not found in the studying area. Some organophosphorus pesticides (OPPs), pyrethroids and carbamates were seldom detected mainly because China has banned their application. These kinds of pesticides included methamphetamine, acephate, phorate, methyl-parathion, parathion etc. The fast vaporization rate of these pesticides still in use should account for the low detection frequency of some carbamates including isoprocarb and metolcarb etc. Most of the OPPs, pyrethroids and carbamates investigated can readily degrade in soil with the light, water and microbes from several days to several months which also make it difficult to detect them in time.

Butachlor is one of the three herbicides with the most widely application in China (Yao et al. 2003). Butachlor was detected 25 times in all 35 sites in the present study which indicated the widely use in this area. The concentration of butachlor in soil ranged from 0 to 22.08 ng/g. Considering that the half-life of butachlor in soil is

Fig. 1 Sampling sites

Table 1 SIM programs of the pesticides investigated

Group 1	R.T.	T.ion	Q.ions		LOD*	Group 2	R.T.	T.ion	Q.ions		LOD[a]
Dichlorvos	8.082	185	109	145	0.60	Methamphetamine	7.865	141	94	126	1.85
Acephate	10.064	136	94	183	1.79	Mevinphos	10.048	192	164	127	0.30
Metolcarb	10.414	108	79	77	0.26	Etrofolan	11.425	121	136	91	0.37
Omethoate	12.118	156	110	141	0.24	Baycarb	12.38	121	150	107	0.35
Isoprocarb	12. 431	110	152		0.25	Chlorpropham	12.957	213	171	154	1.14
Ethoprophos	12.745	158	139	200	0.30	Dicrotophos	13.277	127	193	237	1.05
Dibrom	13.1	185	145	109	0.14	Sulfotep	13.494	322	294	266	0.34
Monocrotophos	13.437	164	127	192	2.51	α-HCB	13.734	219	181	183	0.22
Phorate	13.614	260	231	121	0.15	Hexachlorobenzene	13.94	284	286	282	0.78
Dichloran	14.06	206	176	124	0.76	Dimethoate	14.122	87	125	229	0.24
Simazine	14.254	201	186	173	0.43	Carbofuran	14.323	164	149	131	0.23
Atrazine	14.408	200	215	173	0.11	β-HCB	14.494	219	217	254	1.06
γ-HCB	14.665	183	181	221	0.24	Quintozene	14.86	295	265	237	0.35
Terbufos	14.837	231	153	288	0.19	Propetamphos	14.81	236	194	138	0.87
Fonofos	14.922	246	137	109	0.01	Phosphamidon-1	15.254	264	127	193	2.01
Diazinon	15.203	304	179	137	0.48	δ-HCB	15.357	219	183	181	1.25
Disulfoton	15.311	274	186	142	0.22	Propanil	16.254	161	163	217	0.97
Chlorthalonil	15.505	266	268	231	0.19	Phosphamidon-2	16.334	264	127	193	1.97
Pirimicarb	15.963	166	238	72	0.25	Chlorpyriphos-methyl	16.551	286	125	288	0.15
Diclofenthion	16.288	279	251	223	0.02	3-Hydrxy cabofuran	16.6	137	180	151	3.41
Vinclozolin	16.557	285	212	198	0.07	Heptachlor	16.751	272	337	237	0.10
Methyl-parathion	16.557	263	125	109.1	0.10	Fenchlorophos	16.985	285	125	109	0.35
Carbaryl	16.7	144	115	116	0.14	Pirimiphos-methyl	17.465	290	305	276	0.36
Paraoxon	16.957	275	149	247	0.92	Malathion	17.734	173	158	125	0.19
Fenitrothion	17.385	277	260	125	0.11	Fenthion	17.96	278	125	153	0.17
Dichlofluanid	17.614	224	167	226	0.21	Parathion	17.957	291	263	235	0.34
Aldrin	17.757	263	293	329	0.32	Trichloronate	18.123	297	269	109	0.31
Chlorpyrifos	18.031	314	286	258	0.19	Pirimiphos	18.723	333	318	304	0.18
Dicofol	18.065	139	250	141	0.54	Phosfolan	19.134	255	182	210	2.21
Triadimefon	18.391	208	181	293	3.92	Isophenphos	19.277	213	185	255	0.32
Bromophos	18.534	331	329	125	0.15	Methidathion	19.734	145	157	302	0.53
Anilazine	19.008	239	241	178	0.08	o,p'-DDE	19.843	318	316	176	0.32
Mephosfolan	19.225	196	168	140	0.85	Tetrachlorvinphos	20.071	329	331	333	0.41
Quinalphos	19.34	146	157	298	0.70	Plondrel	20.248	299	243	148	0.60
Bromophos-ethyl	19.825	359	331	303	0.30	p,p'-DDE	20.803	318	246	316	0.53
Thiodan-1	20.043	339	341	265	0.17	o,p'-DDD	21.043	235	165	237	0.77
Butachlor	20.191	176	160	188	0.30	Endrin	21.448	345	317	265	0.20
Profenofos	20.7	339	374	297	0.16	Chlorobenzilate	21.763	251	139	253	0.36
Dieldrin	20.808	345	263	277	0.15	o,p'-DDT	22.031	235	165	237	0.44
Thiodan-2	21.732	339	341	265	0.59	Hostathion	22.597	162	172	257	0.29
p,p'-DDD	22.026	235	165	237	0.51	Ediphenphos	22.934	310	173	109	1.13
Ethion	22.22	231	153	384	0.24	Iprodione	24.357	314	245	187	0.40
Famphur	22.79	218	125	217	0.38	Tetramethrin-1	24.551	164	123	135	1.88
p,p'-DDT	23.123	235	165	199	0.25	Tetramethrin-2	24.763	164	123	135	0.33
Phosmet	24.528	160	133	161	0.22	Azinphosmethyl	25.683	160	132	125	0.69
EPN	24.66	157	169	323	0.25	Lambda-cyhalothrin	26.386	181	197	141	0.37
Bifenthrin	24.774	181	166	165	0.09	Pyrazophos	26.717	373	221	232	0.79
Fenpropathrin	24.946	181	265	349	0.46	Coumaphos	27.82	362	226	334	0.96

Table 1 continued

Group 1	R.T.	T.ion	Q.ions		LOD*	Group 2	R.T.	T.ion	Q.ions		LOD[a]
Phosalone	25.688	367	182	154	0.41	Cypermethrin-1	28.957	181	180	152	0.87
Ethyl-azinphos	26.711	160	132	105	0.69	Cypermethrin-2	29.111	181	180	152	1.93
Cis-permethrin	27.488	183	163	184	0.26	Cypermethrin-3	29.231	181	180	152	1.73
Trans-permethrin	27.706	183	163	184	0.18	Cypermethrin-4	29.289	181	180	152	2.94
Cyfluthrin-1	28.46	226	206	199	0.40	Fluvalinate-1	30.826	250	181	252	1.12
Cyfluthrin-2	28.62	226	206	199	1.02	Fluvalinate-2	30.951	250	181	252	1.26
Cyfluthrin-3	28.746	226	199	206	1.02	Deltamethrin-1	31.44	253	181	172	8.45
Cyfluthrin-4	28.797	226	199	206	0.65	Deltamethrin-2	31.883	253	181	172	4.11
Trans-fenvalerate	30.443	225	167	419	0.48						
Cis-fenvalerate	30.814	225	167	419	0.62						

[a] LOD referred to the instrumental LOD in mg/L

generally less than 30 days (Chen and Fan 1988), the application of butachlor must be more frequent than as suggested in this survey. Butachlor was chosen as one of the best herbicides in rice field for its low toxicity and low residues for many years. Few studies on the genetic toxicity of butachlor have been performed by now, but Hill (Hill and Chaudhgi 1997) reported that dialkylquinoneimine, as a herbicide with similar constructer with butachlor was found with genetic toxicity to human beings. Applications of large amount of butachlor should be careful. Butachlor was found with low concentration in the soil. But unlike atrazine (Gruessner 1995), butachlor has not been investigated for its low-dose effect to our best of knowledge. People do not know whether butachlor with low concentrations would poison and kill the amphibians or not which also require us to be careful before we decide to use large amount of butachlor in field.

OCPs, particular in *p,p′*-DDE, *p,p′*-DDT, *o,p′*-DDD, hexachlorobenzene and δ-HCB were detected most frequently for their long-term persistence in the environment. DDTs, HCB and HCHs were still the predominant pesticide pollutants in soil.

Concentrations of total organochlorine pesticides (0.22–56.73 ng/g) were much lower than those of Shanghai (24 kinds of organochlorine pesticides, 3.16–265.24 ng/g) (Jiang et al. 2009). Table 2 showed that *p,p′*-DDE, *p,p′*-DDT, *o,p′*-DDD, hexachlorobenzene and δ-HCB were five pesticides detected most frequently. DDTs and HCHs in soil were further degraded compared to those in 1980s and 1990s. It coincided well with Zhong' study in 1996 (Zhong and Suo 1996). *p,p′*-DDT degrades to *p,p′*-DDE in aerobic environment and to *p,p′*-DDD in anaerobic environment. Surface soil samples in aerobic environment were collected in this study, and these might elucidate the highest detection frequency of *p,p′*-DDE.

The concentrations were in the ranges of N.D.-42.79 ng/g for HCHs (sum of α-, β-, γ- and δ-HCH, median 5.51 ng/g), N.D.-40.25 ng/g for DDTs (sum of *p,p′*-DDT, *p,p′*-DDD, *p,p′*-DDE and *o,p′*-DDT, median 5.53 ng/g). The maximum values in the study were at the same level of those in Shanghai (N.D.-10.38 ng/g; 0.77–247.45 ng/g) (Jiang et al. 2009) and Taiyuan (1.4–45 ng/g; 1.8–100 ng/g) (Fu et al. 2009). For HCHs the maximum and median values were also found at the same level of those in Beijing (1.36–56.61 ng/g;

Table 2 Statistics of the pesticides concentrations

Pesticides	Min.	Max.	Median	Average	Detected
Butachlor	N.D.	22.08	0.78	3.06	25
p,p′-DDD	N.D.	33.48	N.D.	3.55	8
α-HCB	N.D.	27.58	N.D.	1.53	17
Hexachlorobenzene	N.D.	6.47	0.25	0.59	31
β-HCB	N.D.	15.21	0.42	1.46	21
δ-HCB	N.D.	13.21	0.59	3.74	27
o,p′-DDE	N.D.	1.62	0.14	0.19	18
o,p′-DDD	N.D.	13.19	0.63	1.17	29
p,p′-DDE	N.D.	15.57	1.99	3.35	31
p,p′-DDT	N.D.	32.97	0.25	2.15	27

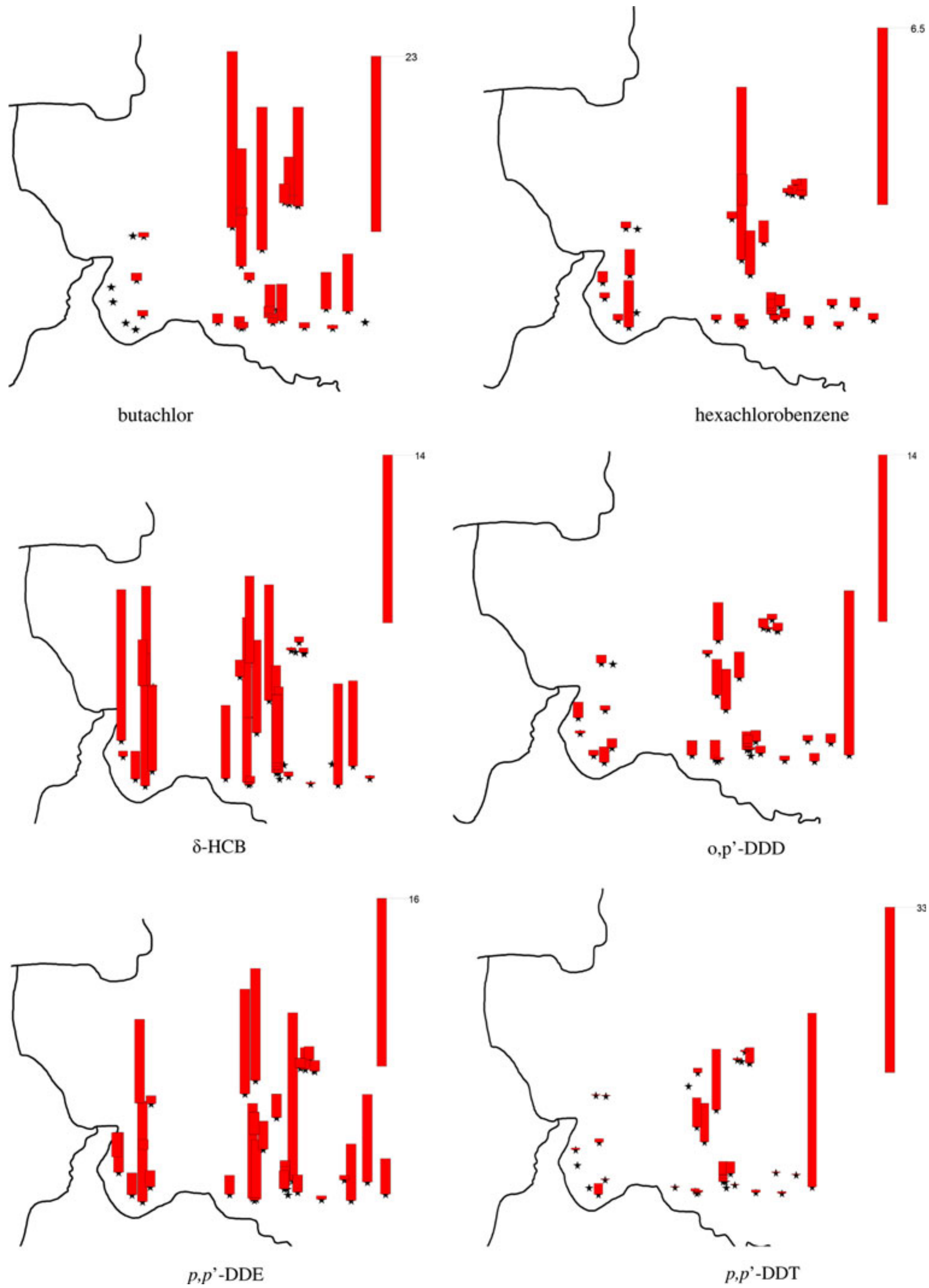

Fig. 2 Spatial distribution of pesticides in the soil of suburban Shenyang (ng/g)

median 5.25 ng/g) (Zhu et al. 2005). The average concentration of p,p'-DDE (3.35 ng/g) was a little higher than that in Hongkong (0.41 ng/g)(Zhang et al. 2006). It indicated that there were still some pesticides residues in soils in Shenyang resulted in reduction of these pesticide residues in soils. But compared to other big cities in China, OCPs pollution was not found in Shenyang. Statistical results of concentrations of individual pesticides in soils were shown in Table 2. Spatial distribution and pollution levels of six typical pesticides at all sites were illustrated clearly with six maps in Fig. 2 which should be very helpful for local government to take corresponding remediation steps.

o,p'-DDT/p,p'-DDT can be used to identify the new input of DDTs (Zheng et al. 2010). In technical DDTs, o,p'-DDT occupy 15% of total components. Considering that the photo- degradation rate of o,p'-DDT in the environment is the same with that of p,p'-DDT, o,p'-DDT/p,p'-DDT in the environment should be 17.5%. China has banned the

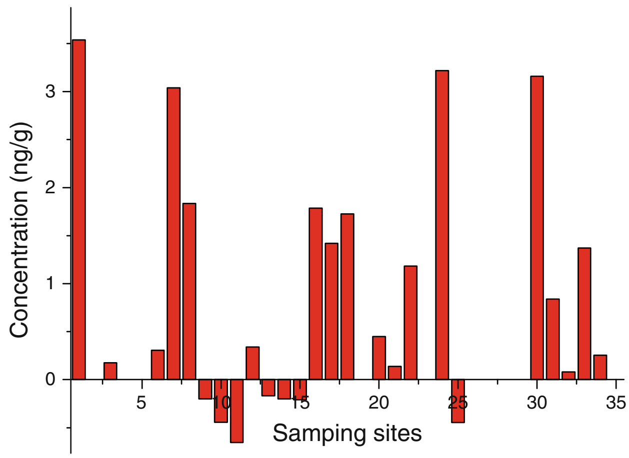

Fig. 3 Concentrations (ng/g) of (β − (α + γ)*0.5) − HCB

production of DDTs for nearly 30 years. But as a by-product of dicofol production in some cities, DDTs were still released to the environment. *o,p′*-DDT/*p,p′*-DDT was about 7 in the dicofol production which should greatly improve the ratios of *o,p′*-DDT/*p,p′*-DDT in the environment (Qiu et al. 2005).In this study, *o,p′*-DDT was detected at only five sites, while *p,p′*-DDT were detected at 27 sites (Table 2). It revealed that of *o,p′*-DDT/*p,p′*-DDT were zero, far less than 0.175 at most sites values. That's to say, No new input of DDTs was found in this area, which was in well agreement to the non-detectable levels of dicofol.

The saturated vapor pressure of β-HCH (3.7×10^{-7} kPa) is significantly lower than α-HCH (3.3×10^{-6} kPa) and γ-HCH (2.1×10^{-5} kPa). α-HCH and γ-HCH are more readily to diffuse to the air in the soil-air interface. β-HCH has symmetrical structure, stable attribute and it is not readily to degrade as other isomers. So in the degradation of HCHs, other isomers can easily transform to β-HCH. The percentage of β-HCH in the soil will keep increasing in the degradation progress. In many studies, the ratios of β-/(α+γ)-HCH were used to identify the historical pollution sources (Zheng et al. 2010). If β-/(α + γ)-HCH is higher than 0.5, it indicates the historical pollution; if it is less than 0.5, it indicates the new introduction of HCH. In the case of α- and γ-HCH in many sites were not detected in this study, the values of β-(α + γ)*0.5 were used as indicator (Fig. 3). 18 values were positive and 7 values were negative which indicated that historical pollution accounted most for HCH pollution at most sites.

In conclusion, butachlor, *p,p′*-DDE, *p,p′*-DDT, *o,p′*-DDD, hexachlorobenzene and δ-HCB were six pesticides detected most frequently in the agricultural soil in south Shenyang, while organophosphorus pesticides (OPPs), pyrethroids and carbamates were seldom detected. DDTs, HCB and HCHs were the predominant pesticide pollutants in soil, but compared to other big cities in China, OCPs pollution in Shenyang was not found. Butachlor was detected 25 times in all 35 sites in the study which indicated the widely use of Butachlor in this area, further surveys and studies on butachor were suggested. Spatial distribution and pollution levels of the six typical pesticides at all sites were illustrated clearly. No new inputs were found through the source analysis of DDTs and HCBs. The soil in the studying area was safe from the pesticides investigated at present.

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