Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2014, 6(6):369-373

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Pesticides pollution characteristics in the soil-groundwater system of vegetable greenhouse cultivation in eastern China

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ABSTRACT

Knowledge on the fate of multi-pesticides in the environment is of great importance to their security use and the environmental health. In order to study the seasonal variation of pesticides pollution characteristics in the soil-groundwater system, four times of field investigation from the biggest vegetable cultivation base in China was conducted with soil and groundwater sampling from 2011 to 2012. Results showed that the composition and levels of pesticides in the greenhouse soil varied from different seasons with high levels in spring and summer. In the soil, the levels of traditional organochlorine insecticide (OCI) decreased, while that of acaricide and fungicide increased. In the groundwater, the residue of pesticide, mainly comprised of imidacloprid, was relatively steady from spring to winter. The potential environmental risks of soil were most significant in summer, while that of groundwater were mainly in summer and autumn. This suggested that much attention should be paid to pesticides monitoring and management in the greenhouse environment, especially in summer. It was also essential to monitoring groundwater pesticide in the long run.

Keywords: greenhouse cultivation; soil-groundwater system; pesticides pollution; environmental risk; seasonal variation

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INTRODUCTION

Much higher levels of pesticides residue and pollution risks were reported in the greenhouse soil than the open field vegetables in China [1]. Therefore, the environmental pollution and health risk of pesticides in the greenhouses becomes a very prominent issue in China. Pesticides residues in agricultural soil have been reported frequently in the last decades [2-4], while little valuable information of pesticides resides in the soil-groundwater system were provided [5]. In addition, previous studies mainly focused on the occurrence and distributions of pesticides residues in the environmental compartments, but few study concentrated on the seasonal variation characteristics, even less on the residue distribution in the soil-groundwater compartment. Most of present risk assessment was based on the hypothesis of invariable pesticides residue in the environment [6-7], which would lead to improper evaluation of the pesticides health risk. Consequently, the pesticide environmental risk evaluation in the consideration of the seasonal characteristics may be appropriate.

The aims of this study were: (1) Compare the occurrences and risks of traditional POPs class pesticides (organochlorine insecticides) with the new pesticides (organphosphorus insecticide, pyrethroid insecticide, neonicotinoid insecticide, phenyl pyrazole insecticide, acaricide, and fungicide) in the environmental matrix to enlarge the knowledge of the priority pollutants; (2) Analyze the differences of pesticides pollution between soil and groundwater on greenhouse cultivation area; (3) Probe the seasonal variation characteristics of pesticides residues to evaluate whether the pesticides residue in the soil-groundwater system is steady or not and to master the trend of pesticides risk in the greenhouse environment.

EXPERIMENTAL SECTION

The study area (Longitude: 118°44′23″-118°45′13″E; Latitude: 36°54′59″-36°55′27″N) locates in Shouguang City of Shandong Province, Eastern China (Figure 1). This area lies in a semi-arid and warm temperature zone and belongs to a typical continental climate. The mean annual precipitation is 588 mm and mainly concentrated in June to August. The predominant cropping system is vegetable in the greenhouse. The buried depth of groundwater is 0-70 meters. The recharge for the shallow aquifer mainly comprise of irrigation. The status in the study area are similar to most of other greenhouse area in Northern China, so this study will give more knowledge to the public for the health risks of these huge groups people.

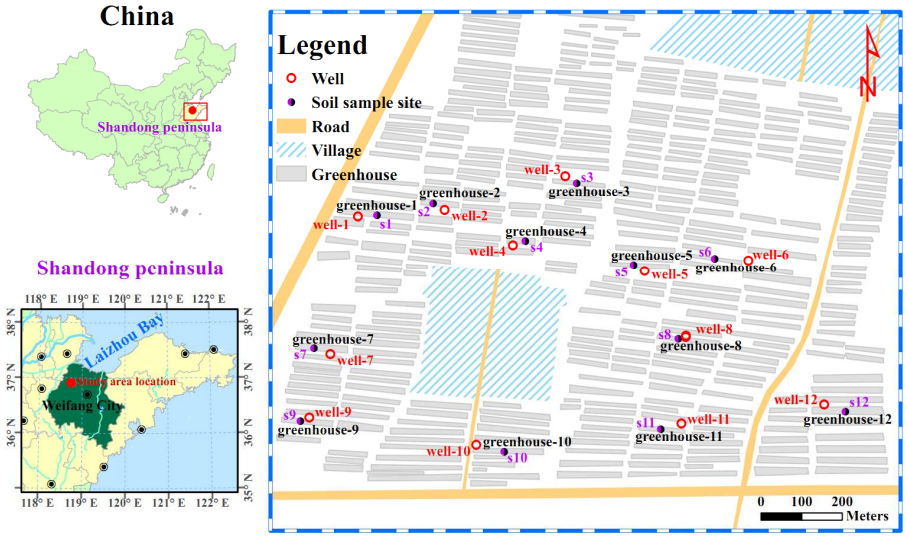

Figure 1. The greenhouses distribution and the sampling sites of study area. well-1-well-12 are groundwater sample sites located outside the greenhouse; s1-s12 are soil sample sites located in the greenhouse. Each of the gray rectangles stands for a greenhouse

The sampling stages were distributed in December in 2011, March, May, September and December in 2012, respectively. Groundwater samples were collected from 12 wells. Soil samples were also collected in the greenhouse when the groundwater sampling finished. Each of the soil sampling point was located in the vicinity of a well. The soil samples were collected with a 10 cm diameter soil core sampler. At each site, the soil was collected from four points randomly and mixed into one sample. Field works were completed in 2 days, and taken back to the laboratory immediately. All the samples were extracted in a week.

The standard solution including 21 kinds of organochlorine insecticides (OCIs), 20 kinds of organphosphorus insecticide (OPI), 9 kinds of pyrethroid insecticide (PI), a nitromethylene insecticide (NI), a phenyl pyrazole insecticide (PPI), an acaricide (pyridaben), and 4 kinds of fungicide including triadimefon, chlorothalonil, vinclozolin and procymidone. Soil samples were extracted by ultrasonic solvent extraction method [8]; Water samples were extracted by solid phase extraction (SPE) method [9].

OCIs were analyzed by gas chromatography tandem mass spectrometry (GC-MS) [10]. OPIs were analyzed by gas chromatography tandem mass spectrometry (GC-MS) [11]. PI, NI, PPI, acaricide, TF, BPIF, DIF and TCIF were analyzed by gas chromatography tandem mass spectrometry (GC-MS) [12]. Quantification was performed using the internal calibration method based on the six-point calibration curve for individual pesticides. The pesticides concentrations reported in this paper were instrument and recovery corrected. The mean recoveries for surrogates were 70% to 110%. The relative standard deviations (RSD) for triplicate samples were less than 12%.

RESULTS

3.1 Seasonal variation of pesticides in the soil

As shown in Figure 2, the levels of pesticides in the soil also varied significantly from seasons. In the winter of 2011, the concentration of endosulfan, DDT (p,p'-DDD+ p,p'-DDE) and quintozene were not detected (nd)-6.62, nd-0.76 and nd-1.28 mg/kg dry weight (dw), respectively. In the spring of 2012, the concentration of chlorothalonil was nd-10.22 mg/kg dw. In the summer of 2012, the concentration of monocrotophos was 5.1-21 mg/kg dw. In the autumn of 2012, the concentration of flucythrinate was nd-3.9 mg/kg dw. And in the winter of 2012, the concentration of pyridaben was nd-2.6 mg/kg dw. This showed that the amount of pesticides applied in spring and

summer were much higher than that in other seasons.

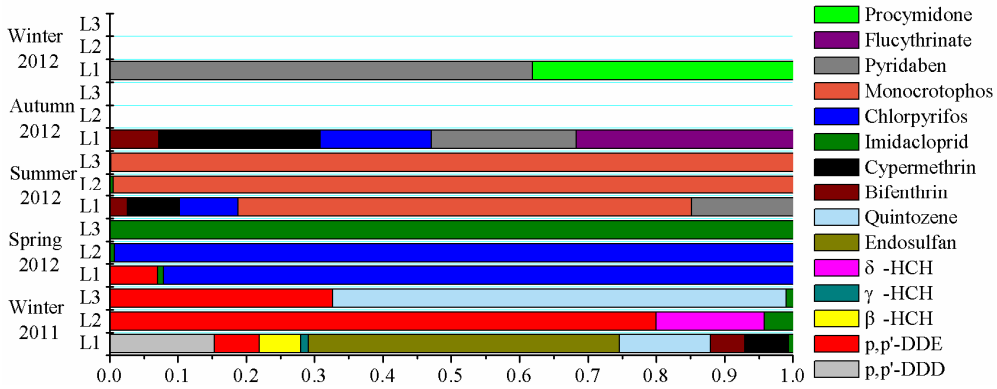

Figure 2. composition of pesticides in the soil from the winter of 2011 to the winter of 2012

The types of pesticides residue in the winter of 2011 was more than that in the winter of 2012, and the level of OCI in the winter of 2011 was higher while the levels of acaricide and fungicide were higher in the winter of 2012, suggesting that the use of traditional OCI decreased in the greenhouse while acaricide and fungicide increased. This may be related to more strict pesticide production standard, use management and the market demands of green organic vegetables.

However, the mean concentration of DDT in the topsoil in the winter of 2011 were much higher than the value of Chinese soil environmental quality standard class 3 (1.0 mg/kg dw) (China EPA, http://www.nthb.cn/standard/standard02/20030414085238.html), which is considered as the limit of human body health risk. Comparing with other countries, the level of pesticides residue in the topsoil in this study was higher than that in the paddy field of India (mean concentration of DDT, 1.005 mg/kg dw, mean concentration of HCH, 1.056 mg/kg dw) [13], and far higher than that on the farmland of Central German (mean concentration of DDT, 0.072 mg/kg dw, mean concentration of HCH, 0.008 mg/kg dw) [14] and Southern United States (DDT, 0.211 mg/kg dw, mean concentration of HCH, < 0.0003 mg/kg dw) [15], while lower than that on the orchard of Waikato of New Zealand (DDT, 8.390 mg/kg dw) [16]. For the lack of data, the comparison of other pesticides in this study with those in other areas can't be made. Fortunately, we can infer that other pesticides pollution may be also more serious than those in most of other areas (see in Table 1).

Table 1 Part of physicochemical properties of the pesticides detected in the groundwater*.

Compound	Soil Half-Life (d)	Vapor pressure (mm Hg, 25°C)	Water Solubility (mg/L, 25°C)	Log K_{oc}
Chlorothalonil	360	4.72E-07	2.60E+01	3.54
Chlorpyrifos	360	2.05E-05	3.57E-01	3.90
Endosulfan	360	1.25E-06	1.49E+00	3.21
Flucythrinate	120	8.55E-08	4.02E-03	4.79
Imidacloprid	120	1.68E-06	7.17E+03	1.53
Monocrotophos	30	2.79E-05	4.91E+04	0.89
p,p'-DDT	360	7.47E-06	7.31E-03	6.00
Procymidone	360	2.73E-08	3.55E+01	2.60
Pyridaben	120	2.93E-08	1.83E-02	4.42
Quintozene	360	2.72E-05	5.80E-01	3.86

** These indexes value were calculated by EPI Suit software (US EPA).*

3.2 Seasonal Variation of Pesticides in the Groundwater

As shown in Figure 3, fourteen kinds of pesticides were detected in the groundwater and the composition of pesticides varied from seasons. The pesticide residue in the groundwater was mainly comprised of imidacloprid, whose proportion ranged from 77.8% to 97.4% from the winter of 2011 to the winter of 2012, suggesting the composition of pesticides in the groundwater were more stable than that in the soil.

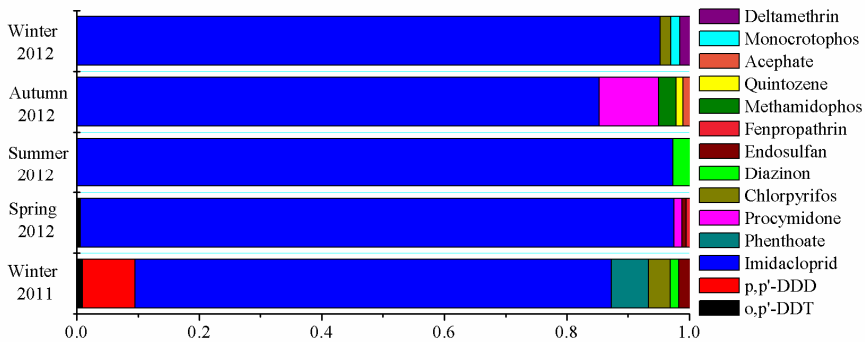

Figure 3. Compositions and levels of pesticide residues in the groundwater from 2011 to 2012

The mean concentration of DDT in the winter of 2011 (0.007 μg/L) and in the spring of 2012 (0.001 μg/L) was the same order of magnitude with the Chinese groundwater water quality standards class 2 (0.005 μg/L, considered as the background value) (China EPA, http://www.nthb.cn/standard/standard05/20030411101228.html). Comparing with other countries, the level of DDT residue in the groundwater in the study area was much lower than that in the urban area of Hyderabad City in India (mean: 0.175 μg/L) [17], and the farmland of Bangladesh (0.051-1.653 μg/L) [18]. However, the concentration of other pesticides in the ground water was much higher than that of DDT. Therefore, the groundwater pesticides pollution was not serious.

DISCUSSION

In the study area, imidacloprid was the dominating pesticide in the groundwater for the investigating seasons. There existed a significant variation of the level of imidacloprid in spatial in the winter of 2011 (ANOVA, $p<0.05$), but there was no significant variation in other seasons. The level of other pesticides had significant variation in spatial in different seasons (ANOVA, $p<0.05$). This showed that NI (imidacloprid) was steady in the groundwater both in different seasons and spaces, which indicated the frequent use of imidacloprid in the study area. Other pesticides showed a large spatial variation, and showed significant differences of pesticides application in different greenhouse. In the winter of 2011, DDT, endosulfan and quintozene had high level in the soil, which had low level in the groundwater, but imidacloprid was quite the opposite. In the spring of 2012, imidacloprid and chlorothalonil had high level in the soil and groundwater; while chlorothalonil had high level in the soil but had low level in the groundwater. In the summer of 2012, monocrotophos had high level in the soil and low level in the groundwater, while imidacloprid was quite different. In the autumn of 2012, chlorpyrifos, pyridaben and flucythrinate had high level in the soil and low level in the groundwater; while imidacloprid was on the contrary. In the winter of 2012, pyridaben and procymidone had high level in the soil and low level in the groundwater; while imidacloprid was in different situations. This was mainly due to the differences of the physicochemical properties of different pesticides [19]. As shown in Table 1, imidacloprid had a lower octanol-water partition coefficient (log K_{oc}: 1.53, 25^{o}C) and a higher water solubility (7.17E+03 mg/L, 25^{o}C) than most of other pesticides detected in the groundwater, indicating imidacloprid had a stronger migration ability from soil to groundwater. But the water solubility of monocrotophos is higher than that of imidacloprid and its octanol-water partition coefficient was lower than that of imidacloprid. Shorter half-life of monocrotophos led to its fast degradation in the soil and few residues leached to the groundwater. These results indicated that imidacloprid had higher allocation proportion in the groundwater than that in the soil, and also indicated that imidacloprid was easy to cause the pollution of groundwater.

CONCLUSION

The pesticides residue level varied significantly from seasons in the soil environment, but that was relatively steady in the groundwater. The levels of pesticides in the soil environment in spring and summer were much higher than that in other seasons, while there was no significant difference in the pesticides residue levels in the groundwater environment all the year round. The main pollutants in the soil in different seasons were quite different from that in the groundwater. Pesticides pollution in the soil should be paid more attention, especially in summer.

Acknowledgements
This research work was financially supported by the National Public Benefit Research Foundation of China (Grant No. 201109009, 201301039), the National Natural Science Foundation of China (Grant No. 41271236 and No. 51279063), and Program for New Century Excellent Talents in University (Grant No. NCET-13-0794) in China.

REFERENCES

[1] Cai, Q.Y., Mo, C.H. Wu, Q.T., Katsoyiannis, A., Zeng Q.Y., **2008**, *Sci. Total. Environ*., 389(2-3), 209-224.
[2] Fu, J., Mai, B., Sheng, G., Zhang, G., Wang, X., Peng, P., Xiao, X., Ran, R., Cheng, F., Peng, X., Wang, Z., Tang, U.W., **2003**, *Chemosphere*, 52(9), 1411-1422.
[3] Shegunova, P., Klánová, J., Holoubek, I., **2007**, *Environ. Pollut*., 146(1), 257-261.
[4] Hao, H.; Sun, B.; Zhao, Z., **2008**, *Environ. Pollut*., 156(3), 1046-1052.
[5] Zhang, C., Liao, X., Li, J., Xu, L., Liu, M., Du, B., Wang, Y., **2013**, *Chemosphere*, 92(4), 337-343.
[6] Peterson, R.K.D., Macedo, P.A., Davis, R.S., **2006**, *Environ. Health Persp*., 114(3), 366-372.
[7] Datta, R., Sarkar, D., Sharma, S., Sand, K., **2006**, *Sci. Total Environ*., 372(1), 39-48.
[8] Vagi, M.C., Petsas, A.S., Kostopoulou, M.N., Karamanoli, M.K., Lekkas, T.D., **2007**, *Desalination*, 210(1), 146-156.
[9] Lambropoulou, D.A., Albanis, T.A., **2004**, *Anal. Chim. Acta*, 514(1), 125-130.
[10] Rocha, C., Pappas, E.A., Huang, C.H., **2008**, *Environ. Pollut*., 152(1), 239-244.
[11] Bravo, R., Driskell, W.J., Whitehead, R.D., Needham, L.L., Barr, D.B., **2002**, *J. Anal. Toxicol*., 26(5), 245-252.
[12] Škerl, M.I.S., Kmecl, V., Gregorc, A., **2010**, B. *Environ. Contam. Tox*., 85(2), 125-128.
[13] Mishra, K., Sharma, R.C., Kumar, S., **2012**, *Ecotox. Environ., Safe*. 76, 215-225.
[14] Manz, M., Wenzel, K.D., Dietze, U., Schüürmann, G., **2001**, *Sci. Total. Environ*., 277(1), 187-198.
[15] Bidleman, T.F., Leone, A.D., **2004**, *Environ. Pollut*. 128(1), 49-57.
[16] Gaw, S.K., Wilkins, A.L., Kim, N.D., Palmer, G.T., Robinson, P., **2006**, *Sci. Total. Environ*. 355(1), 31-47.
[17] Shukla, G., Kumar, A., Bhanti, M., Joseph, P.E., Taneja, A., **2006**, *Environ. Entomol*., 32(2), 244-247.
[18] Matin, M.A., Malek, M.A., Amin, M.R., Rahman, S., Khatoon, J., Rahman, M., Aminuddin, M., Mian, A.J., **1998**, *Agr. Ecosyst. Environ*., 69(1), 11-15.
[19] González-Pradas, E., Ureña-Amate, M.D., Flores-Céspedes, F., Fernández-Pérez, M., Garratt, J., Wilkins, R., **2002**, *Soil Sci. Soc. Am. J.*, 66(6), 1821-1828