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Composition and potential risks of agricultural chemical pesticides presented in the potential drinking water sources of groundwater from rural area, eastern China

Hongjun Lei[1]*, Hongwei Pan[1,2], Beidou Xi[2]*, Ting Xu[3]
[1]School of Water Conservancy, North China University of Water Resources and Electric Power, Zhengzhou, (CHINA)
[2]State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Sciences, Beijing, (CHINA)
[3]College of Resources and Environmental Sciences, China Agricultural University, Beijing 100193, (CHINA)
E-mail: hj_lei2002@163.com

ABSTRACT

Groundwater is an important water resource in the lower Yellow River rural area. In recent years, with the arid events occurred more and more frequent, the drinking water problem in the rural areas has been deteriorating. For the releasing the pressure of drinking water scarce, more and more groundwater has been explored and used as drinking water. However, the information on the studies of groundwater quality and human health risks brought by drinking polluted groundwater greatly lacks. In this study, the rural area locates in the Shandong Province of lower Yellow River with heavy agricultural chemical pesticides application amount was chosen to study the composition, levels and potential human health risks of pesticides residue in the groundwater. Results showed that forty-two types of pesticides were analyzed, among which seven types of pesticides were detected in the groundwater samples. Among the detected pesticides, imidacloprid had the highest level with a concentration of 58.915±16.114 μg/L, and p,p'-DDD, phenthoate, diazinon, chlorpyrifos, endosulfan and o,p'-DDT had a concentration of 2.596, 2.170, 1.198, 0.946, 0.665 and 0.280 μg/L, respectively. This indicated that imidacloprid was easier to transport into the groundwater than other pesticides in the study area. However, the human health risk evaluation results showed that low level of diazinon exhibited a high human health risk with the HI value of higher than 0.1, while the highest level compound of imidacloprid showed a low human health risk with the HI value of 0.01~0.1. This revealed that low level of pesticides in the groundwater would also pose high human health risk. Therefore, the evaluation of pesticides pollution in the groundwater should not only judged by the investigation of the residue level but also should be evaluated its human health risk. Because diazinon in the groundwater of the study area exhibited high human health risk, therefore this type of pesticides should be paid more attention to be observed and managed in order to insure safety water drinking.

KEYWORDS

Groundwater; Agricultural chemical pesticides; Rural area; Human health risks.

INTRODUCTION

Agricultural chemical pesticides exists worldwide, soil, air, rivers, lakes, seas, sediments, and other environmental matrix[1-5]. This big class of pollutants has been paid much attention by the governments and scientists more than half a century due to its high toxicity to human and the ecological system[6,7]. Groundwater is a typical environmental matrix which is buried under the soil and rock layer. Thereby, it's difficult to collect the water samples to study the pesticides pollution status. In recent years, with the increasing of environmental protection awareness, groundwater pollution has been concerned. Chinese government has been carrying out the National Groundwater Investigation Project (NGIP) from 2011. Agricultural chemical pesticides are also contained in this project. According to the investigation, levels and distribution of pesticides in the groundwater would be well understood by the public, which would be convenient for the future groundwater pollution controlling and the pesticides management.

Shandong province is one of the most important food production areas in the lower Yellow River area, and a large quantity of pesticides were applied on farmland. High levels of pesticides residue in the soil of Shandong Province have been reported[8]. In the recent years, the arid events occurred frequently in the lower Yellow River area, water resource scarce has been a key problem[9]. In some rural areas, groundwater has been explored more and more for life. The residents would drink the polluted groundwater in this trend. However, the status of groundwater quality is not very clear today. Scientist has been more and more anxious about this status. Thereby, the carrying of the work on the investigation of groundwater pesticides pollution characteristics and the human health risk evaluation is meaningful. This would provide some useful knowledge on the levels of pesticides in the groundwater of rural areas from lower Yellow River and give some suggestion on the management for safe drinking groundwater and controlling the risk of pesticide.

The aims of this study were: (1) to determine the composition and levels of agricultural chemical pesticides in the groundwater in the lower Yellow River rural area; (2) to identify the potential human health risks by drinking groundwater containing agricultural chemical pesticides for better groundwater protection and risk decreasing.

EXPERIMENTS SECTION

The studying area locates in the rural area of Shandong province, Eastern China. The water samples were mainly collected from the wells which are mainly used for irrigation. There were totally twelve wells evenly distributed in the study area, which covers about forty thousand square meters of area. The soil type here is mainly comprised of loam, which occupies more than ninety percent of the land. The average groundwater buried depth in the study area is four meters. The crop planting here contains winter wheat, summer corns, beans, peanuts and vegetables, among which vegetable is the prominent crops. The average yearly rainfall is about 600 mm and decreased significantly in the recent arid years. The pesticides application in the study area is very common; the total amount of pesticides used on the farmland in the whole Shandong Province is arranged as one of the largest pesticides application Province in China. In the past thirty years, the composition of pesticides used on the farmland has been changed greatly. Specifically, organochlorine pesticide was the first biggest class of pesticides applied in Shandong Province before it was strictly forbidden to use on agriculture. After that period, the use of other types of pesticides started to increase, and today organphosphorus insecticide, pyrethroid insecticide, fungicide, and other types of pesticides has been the main part of the applied agricultural chemical pesticides. With the climate change recent years, the total volume of water source has been decreased significantly. The scarce of water source has resulted in increasing the exploration amount of groundwater. The drinking of groundwater would arise potential human health risks. However, the composition, level and human health risks of pesticides in the groundwater of the study area are still unclear; thereby, the investigation and evaluation work is necessary.

The sampling was carried in 2011, and the sampling sites (irrigation wells) are mainly distributed in the vegetable planting area. The sampling procedure was described as follows. Firstly, Wash the well before sampling and measure the instable groundwater index, such as EC (electrical conductor), pH, DO (dissolved oxygen) and water tempura using a WTW multiparametric equipment (Multiline F/Set 3; APHA, 2005). When these indexes changed not remarkable, start to collect the water samples from the well using a hand pump. The samples were put in a 1 L clean brown glass bottle which has been washed by methylene chloride and dried over in the oven at 120^{o}C for 2 hours. Totally 2 L of water were collected from a well. The bottle was labeled with the sampling site name. At the same time, recorded the groundwater buried depth and the geographic coordination of the sampling site by a GPS locator. Tighten the glass cap when each water sampling finished, and put the samples in a incubator temporarily with a piece a ice prepared before sampling, brought to the library on the day and conserved under a low temperature (-8^{o}C). The extraction and analysis of the water samples were finished in one week.

A standard solution including twenty-one types of organochlorine pesticides was obtained from Chem Service (USA). The standard solution of twenty types of organphosphorus pesticides and a nitromethylene pesticide was obtained from SigmaeAldrich (Germany). The water samples were first passed though a mesh of 0.45 μm glass fibre (i.d., 50 mm) to remove solid matters before extraction and then concentrated by SPE. The extraction precdure by solid phase extraction (SPE) was a modified and improved version of an analysis developed by Bonansea et al.[10]. In brief, The SPE sorbents were first conditioned by washing with 10 mL of dichoromethane, followed by 10 mL acetonitrile and finally 10 mL of Ultrapureultrapure water by employing a moderate vacuum at about 10 mL/min. And then water samples (2 L) were applied through the SPE cartridge. After that, SPE cartridges were air dried for 10 min under vacuum and 10 min by fluxing nitrogen to remove as much residual water as possible. Retained analytes were eluted with 5 mL of acetonitrile followed by 5 mL of methanol. The second fraction containing pesrticides was solvent exchanged and concentrated to 0.2 ml under a gentle nitrogen stream. Finally, adjust the volume to 1.0 mL with n-hexane before GC-MS analysis.

Organochlorine pesticides were analyzed by GC-MS[11]. Organphosphorus pesticides were analyzed by GC-MS[12]. Nitromethylene pesticide was analyzed by GC-MS[13]. Quantification was performed using the internal calibration method based on the nine-point calibration curve for individual pesticides. The pesticides concentrations reported in this paper were instrument and recovery corrected. The analyzed pesticides concentrations were quantified using an internal calibration method for the individual pesticide. All the correlation coefficients for the individual calibration curves were over 0.99. A series of standard spiked blanks, a solvent blank, and a duplicated sample were analyzed during the treatment and analysis procedures. The coefficient concentrations of the duplicate samples varied less than 10%. The analyzed pesticides in the blank samples were all below the detection limit. In addition, a surrogate was spiked into each of the water samples before extraction to evaluate the contaminant loss from the entire analysis process and the matrix effects. The mean recoveries for surrogates were 82% to 125%. The relative standard deviations for triplicate samples were less than 10%.

Human health risks evaluation used in this study was based on USEPA method[14]. The risk was calculated y formula (1) and (2).

$$CDI = \frac{C \times V \times EF \times ED}{BW \times AT} \quad \textbf{(1)}$$

Where, *CDI* is the daily oral intake pesticide per weight, mg/kg-day; *C* is the concentration of pesticide in the groundwater, μg/L; *V* is the daily drinking volume of groundwater, L/day; *EF* is the days of drinking groundwater per year, day/year; *ED* is the years that a human drinking groundwater in his/her life, year; *BW* is the lifetime of the evaluated body, years; *AT* is the weight of a man, kg. These parameters were determined according to the real status of peasants in the rural areas of China. Specifically, the drinking water of an adult per day is about 2 L. The exposure frequency parameter of *EF* could be considered as 365 days. The exposure period of *ED* could be considered to be equal with the lifetime of the exposure body of *BW*. And *AT* is the average body weight of a adults in the rural areas of China, which is usually considered to be 75 kg.

Then, the human health risk by drinking groundwater could be calculated by the follow formulate:

$$HI = \frac{CDI}{RfD} \quad \textbf{(2)}$$

The parameter of *RfD* in the above formula using the *ADI* value, because most of the pesticides investigated in this study couldn't find a *RfD* value on the USEPA internet of ISIR database. But there has some reference on the *ADI* value[15].

In this study, the histogram and error bar which descript the and composition and levels of pesticides were plotted on Microsoft Excel (Microsoft Corp., USA) and the mosaic which was brought to express the evaluation result of human health risk of pesticides presented in the groundwater by the drawing soft ware of Origin 8.0 (OriginLab Corp., USA).

RESULTS

Occurrence of agricultural chemical pesticides in the groundwater

Among all the forty-two types of analyzed pesticides, seven types of them were detected with a detection rate of 100%. Other pesticides were under detection limits. This indicated that most of the pesticides were difficult to migrate into the groundwater for the low levels detected in the groundwater. However, Due to the differences of nature, there exhibited remarkable differences of migration for different types of pesticides. The levels of pesticides detected in the groundwater were shown in figure 1. The level of imidacloprid is the highest with a mean concentration of 58.915±16.114 μg/L which is 22.7~210.7 times of other six types of pesticides. The mean concentration of p,p'-DDD, phenthoate, diazinon, chlorpyrifos, endosulfan and o,p'-DDT were 2.569±1.520, 2.170±0.960, 1.198±0.207, 0.946±0.552, 0.665±0.218, and 0.280±0.151 μg/L, respectively. In this study, p,p'-DDD and o,p'-DDT were detected, while p,p'-DDT was not detected. Studies showed that p,p'-DDT has a half life of more than 20 years and its metabolite is p,p'-DDD in the anaerobic environment and p,p'-DDE in the aerobic environment[16,17]. High level of p,p'-DDD suggested technical DDT has not been used in the study area and the groundwater is anaerobic environment. The former study also showed that o,p'-DDT was the major component of technical dicofol[18]. There were no o,p'-DDD and o,p'-DDE were detected which are the metabolites of o,p'-DDT. Therefore, o,p'-DDT detected in the groundwater in the study area was mainly derived from the recent input of technical dicofol. Endosulfan was occurred in the groundwater, while its metabolite of endosulfan sulfate was not detected in the groundwater. This indicated that endosulfan may be from the recent input. organphosphorus pesticides and nitromethylene pesticide are east to degrade in the environment. Therefore, imidacloprid, phenthoate, diazinon and chlorpyrifos detected in the groundwater were mainly derived from the recent input.

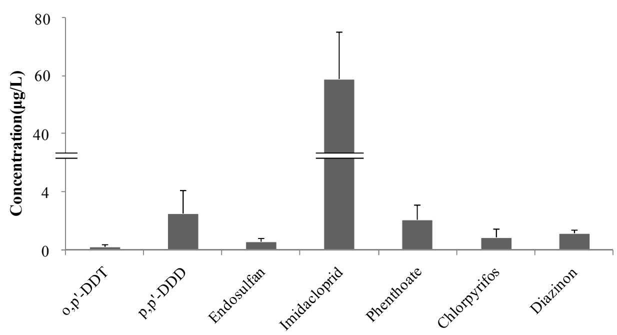

Figure 1: Levels of agricultural chemical pesticides detected in the groundwater of the study area

As shown in figure 2, imidacloprid is accounted for more than 80% of the total mass of pesticides in most of the sampling sites. This could be explained by the higher water solubility and lower absorption by soil particles than other types of pesticides. The mass percentage of other six types of pesticides in figure 1 was much lower than that of imidacloprid, which was mainly due to their low migration. For example, the water solubility of p,p'-DDD was much lower than that of imidacloprid, while the absorption was on the opposite. Therefore, the composition of pesticides in the groundwater could reflect the migaration of pesticides in the study area and also could also show high groundwater pollution vulnerability for the pesticide of imidacloprid. Also shown in figure 2, there was no significant difference for the spatial distribution of imidacloprid. This suggested that the groundwater pollution by pesticides in the study area is steady for spatial distribution. Therefore, the monitoring for the pesticides in the groundwater may only need few sampling data.

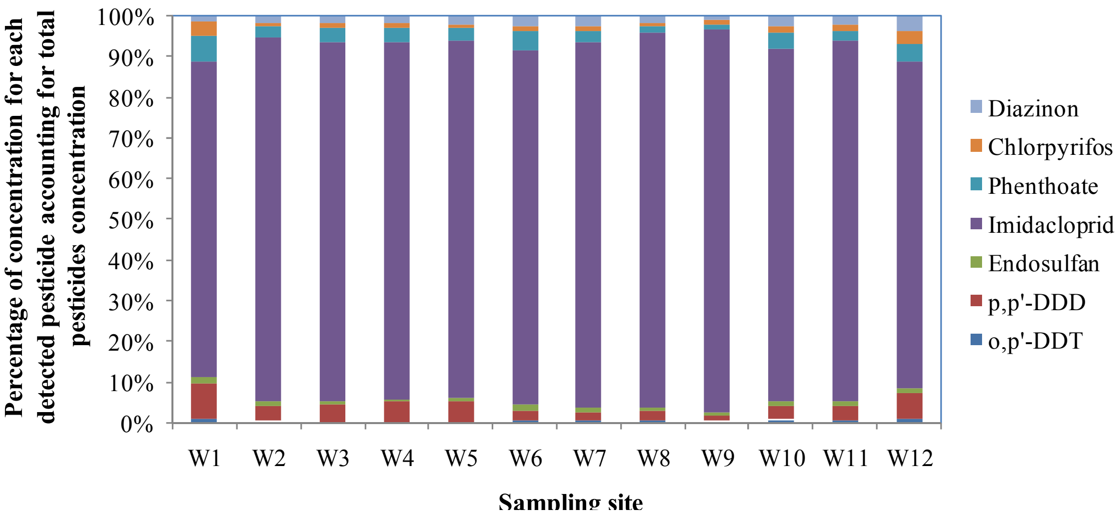

Figure 2 : Composition of agricultural chemical pesticides detected in the groundwater of the study area

Health risk evaluation of major agricultural chemical pesticides detected in the groundwater

There are totally seven types of pesticides were evaluated including diazinon, chlorpyrifos, phenthoate, imidacloprid, endosulfan, p,p'-DDD, and o,p'-DDT. Because only ADI value of DDT could be found, therefore, p,p'-DDD, and o,p'-DDT were not evaluated respectively but DDT was evaluated which equals to sum of p,p'-DDD and o,p'-DDT. ADI value of DDT, endosulfan, imidacloprid, phenthoate, chlorpyrifos, and diazinon are 0.01, 0.006, 0.06, 0.003, 0.01 and 0.0002 mg/kg-day, respectively[18]. As shown in Figure 1, the concentration of diazinon was much lower than that of imidacloprid, however, as shown in Figure 3, diazinon exhibited much higher human health risk than that of imidacloprid. This indicated that the threat of pesticides in the groundwater could not be judged just simple by the concentration of pesticides. Figure 3 also showed that the human health risk level of diazinon in all the sampling sites were higher than 0.1, this indicated that diazinon is the prominent pollutant in the groundwater of the study area and further studies should be carried out to determine whether the groundwater could drink. Besides, the human health risks of organochlorine pesticides in the study area were ranged from 0.001 to 0.01, while that of organphosphorus pesticides were ranged from 0.01 to 0.1. This indicated that the human health risk of organochlorine pesticides in the groundwater is not prominent that that of organphosphorus pesticides and nitromethylene pesticide. Therefore, organphosphorus pesticides and nitromethylene pesticide pollution in the groundwater of the study area should be paid more attention.

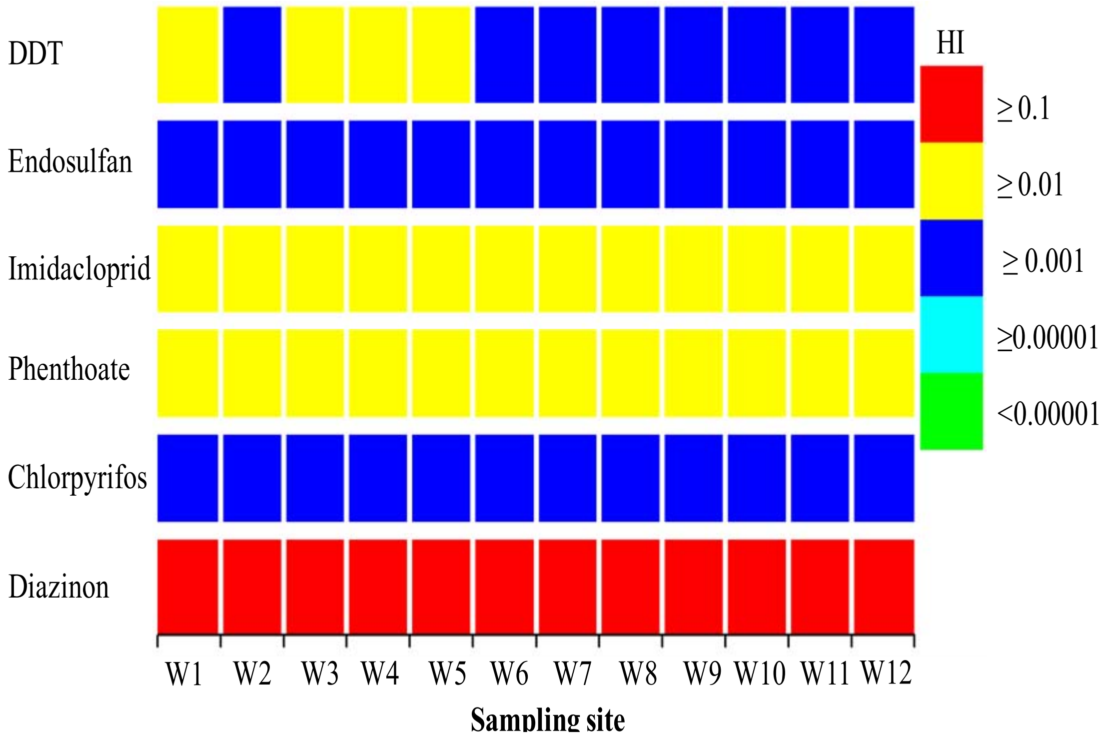

Figure 3 : Mosaic chart of human health risk evaluation results of six major pesticides occurred in the groundwater from rural area of Northern China

DISCUSSION

The investigation of groundwater pesticides pollution in the lower Yellow River rural area was first carried out by this study. An interesting result is that the groundwater pollution may be greatly different from that in the soil. This is because the prominent pollutants in the soil was organochlorine pesticides (especially DDT and HCH) reported by most other studies[19-22], while in this study organochlorine pesticides exhibited low levels and human health risks. Therefore, the prominent pollutants in the soil may be different from that in the soil. However, this is just a hypothesis from this study; more studies were needed to test this hypothesis. In this study, the HI of diazinon in all the groundwater samples was more than 0.1, which exhibited a high human health risk. Even though the groundwater has not been used as drinking water, however, there is no promise that the groundwater would not be used for drinking for ever because the arid events in the lower Yellow River areas happened frequently in the recent years. Therefore, the high human health risk of diazinon in the study area should be emphasized.

CONCLUSION

An investigation was carried out in the lower Yellow River rural area to study the composition, levels and human health risks of pesticides in the groundwater. Few types of pesticides occurred in the groundwater suggested that the groundwater is not easy to be polluted by pesticides. High levels of some pesticides in the groundwater were still observed indicated that groundwater could be polluted by the strong migrating pesticides. Human health evaluation results showed that imidacloprid is the prominent pesticides in the groundwater of the study area. Human health risk of organphosphorus pesticides and nitromethylene pesticide are higher than that of organochlorine pesticides, therefore, these two kinds of pesticides should be paid more attention for the safety drinking water.

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