

Determination of Concentration and Sources of HCHs Isomers in Sediments of Siahrud River, Qaemshahr, Iran

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Introduction

Along with increasing population, technology has had more developments for raising the efficiency of agricultural production. Modern agriculture must keep its production against destruction risk by pests. Then, for maintaining the production and crops against pests and diseases, large amounts of pesticides are used each year. Addition to the environment, this also threatens consumers' health. Pollution resulting from pesticides in the water due to long term effects and the high toxicity of pesticides as an environmental problem in the recent decades has been led to concerns about public health and non-target species. It should be considered that some insects and fungi will become resistant against chemical compounds over the time and therefore, farmers use ever more concentration after a while of use, so it causes to worry about toxins residues and its effects on the environment. In the present days, there are more concerns about using irregular use or misusing pesticides and its effects on the environment and human's health. This concern] needs to some extent the programs for decreasing the use of pesticides as a part of the agricultural major strategy. The lack of basic information about concentration and source of pesticides is a limitation for determining standard values that make it possible to set up the programs for decreasing the use of pesticides.

Materials and Methods

Pesticide standards were purchased from Sigma-Aldrich Corporation and all reagents purchased from Merck Company. The Siahrud Basin with an area of over 10,070 hectares is placed in Mazandaran province in Qaemshahr city in the north of Iran, the length of this river is 5 km.

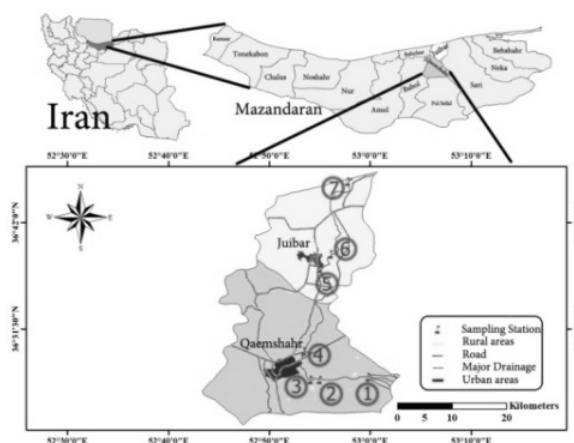


Figure 1. Geographical location of the study area and the sampling stations at Siahrud River-Iran

In this research, sampling was done in three seasons, summer (August), autumn (November) and spring (May) 2012. For selecting sites, we used land use map and identified 7 sites. In each site, 3 sediment samples have been taken by using Sediment core sampler that taken from the upper 5 cm of the sediment surface and all the samples were placed in glass containers and were transported to the laboratory in ice and were immediately put into freeze dryer for 18 hours and were screened with 63 μ m sieve. 5gr sample with 2 gr activated copper

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were mixed by using diluted Nitric acid (4%) and 1 gr Sodium sulfate (activated in 120°C for 12 hours). Then 50 µl of PCNB with 5 mg/lit was added to it and then extraction was done by 100 ml from *n*-hexane and dichloromethane in 1:1 ratio for 40 minutes in the ambient temperature and in the ultrasonic bath. The upper solution of extracted soluble was separated by filter and for the second time, 60 ml of above mentioned solvent with the same ratio was added to residue sediment, and retained in the ultrasonic bath for more 40 minutes. The extracted soluble was added to the previous solutions and its volume was reached about 10 ml by rotary evaporator then to 0.5 ml by gentle stream of Nitrogen. For cleaning up, glass column was used with 30 cm height. The concerned column was filled by the following material from down to up, respectively: One piece of paper filter SS, one piece of Fiberglass, 10gr florisil that was in 90°C in the oven for one night, activated and it was semi activated with distilled water (wt/vol 6%). In the highest part in 1 cm it was put sodium sulfate and before passing, the soluble of column was pre-washed by 20ml normal hexane. Then the soluble was passed from it. Following that, the 50 ml of Solvent of diethyl ether and *n*-hexane soluble in 10:3 ratios was passed from the column and at last total collected soluble was reached volume of 0.5 ml by rotary evaporator and gentle stream of nitrogen. Its solvent was exchanged to *n*-hexane by MTBE Solvent. Finally, the last volume was reached 500 µlit. 1 µlit of this soluble was injected to GC/ECD. Identifying and measuring the residue of HCHs in the samples extracted from sediment was implemented by GC model 1000 DANI Company equipped with capillary column Optima-5 (60m length × 0.25 mm i.d × 0.25 µm film thickness). Helium and nitrogen were employed as the carrier and made up gas, respectively. The column temperature was kept in primarily temperature for 1 minute, then heated to 240°C at 10°C per minute increments, after 1 minute stop, then heated to 260°C at 1°C per minute increments and remained in this temperature for one minute, at last heated to 300°C at 10°C per minute increments, kept in this temperature for ten minutes. Identifying HCHs in sediment samples was done by comprising observed pick inhibitory time in chromatograph obtained from sample and injected standard soluble. The concentration of each pesticide was accounted by the level below pick of samples than the internal standard and putting it in Standard calibration curve equation of pesticides. It was used the ratio of the level below sample pick to the level below internal standard pick as analytical response for calculating concentration. The obtained LOD values in this method were 2 to 8 ng/lit and the recovery percent was 90% to 110%.

Results and Discussion

α HCH concentration at all stations was below the limit of detection (LOD) and β -HCH mean concentration was between 0.024 and 0.054 µgr/gdw. The highest concentration was observed in the summer and Station 1 and was 0.089 µgr/gdw. Average concentration of γ -HCH was between LOD and 0.109 µgr/gdw. The highest concentration was 0.173 µgr/gdw and observed in the summer and Station 1. The concentration of HCHs has different trend than the other pesticides in sediment along the river. For the reason of decreasing concentration of these two pesticides, it is important to consider the physicochemical characteristics of β -HCH and γ -HCH in sediment. HCHs are more polar and soluble in the water than the other organochlorine pesticides and are almost rapidly metabolized to soluble production in the water. Also increasing organic materials in sediment causes to degrade HCHs in this phase and consequently increase the amount of sediment organic material, and the amount of pesticides concentration of HCH will be decreased. The difference among isomeric components of HCH can reveal the resource of contaminant in the environment. Technical HCH contains 60-70% α -HCH, 5-12% β -HCH, 10-15% γ -HCH, 6-10% δ -HCH, but Lindane contains more than 99% γ -HCH. Each of HCH isomers has different physicochemical characteristics. α -HCH and γ -HCH easily degrade in sediment due to high constant coefficient of Henry's law. It is also possible that α -HCH and γ -HCH are altered into β -HCH in the environment, so β -HCH in most sediments, that was not currently entered technical HCH, is predominant isomer. If γ -HCH is predominant isomer, this may indicate new Lindane to enter the environment.

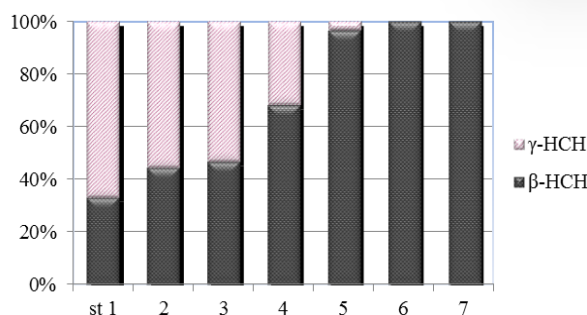


Figure 2. The differences in the percentage composition of HCH isomers in each station (α -HCH in all stations were below the LOD)

Lack of α -HCH in all stations is indicative of new non entry technical HCH and in the first three stations, the high percent of γ -HCH shows consumption of Lindane in these uses, so using Lindane is more in rice nursery. From station 4 to next stations, rapidly decreasing in isomers is indicative of non-consuming Lindane and degrading and altering it into β -HCH.

Keywords: gas chromatography, Lindane, pollution, Technical HCH.