

The Role of Agricultural and Residential Land-uses on Organophosphorus and Organochlorine Pesticides Residues in Water and Sediments of Siahrud River, Qaemshahr

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Extended Abstract

Introduction

Non-point source water pollution comes from a wide range of human activities in which input source pollutants are not visible and certain. It is clear that much more difficult to measure and control non-point source pollution from point sources of contamination. In many countries, all types of agricultural activities are considered as non-point sources. In the present days, there are more concerns about using pesticides and its effects on environment and human health and this concern is to some extent that needs the programs for decreasing to use pesticides as a part of the agricultural major strategy and the other uses. The lack of basic information about pesticides in environment is a limitation for determining standard values, so according it setting up the programs for decreasing to use pesticides is possible.

Materials and Methods

Pesticide standards were purchased from Sigma-Aldrich and all reagents purchased from Merck.

The area of Siahrud with its Watershed is over 10070 hectares that placed in Mazandaran province in Qaemshahr city in Iran. The length of this river is 5 km. In this research, sampling was done in three season, summer (August), autumn (November) and spring (May) 2012. For selecting sites, it was used land-use map. Each site was placed between two Land-uses and it was identified 7 site based on it (Table 1). In each site, it was taken 3 water samples, (3 replications) using horizontal water sampler and 3 sediment samples by using sediment core sampler. The sediment samples were taken from the upper 5cm of the sediment surface and all samples were placed in glass containers and were transported to the laboratory.

Table 1. Number, name, Land-use type and location of the sampling stations

sampling site num	Site name	Land-use	Location	
			Longitude	Latitude
1	Seyed Abu-Saleh	Forest	36°26'44.20"N	52°59'49.77"E
2	Kutena	Agriculture & Garden	36°26'29.07"N	52°55'1.23"E
3	Sarukola	Agriculture-1	36°26'27.96"N	52°54'5.34"E
4	Qaemshahr	Residential-1	36°29'19.19"N	52°53'28.94"E
5	The jomeh Bazar Bridge	Agriculture-2	52°55'2.29"E	36°37'26.59"N
6	Sikapol	Residential-2	52°56'6.24"E	36°38'52.38"N
7	Larim	Agriculture-3	52°57'48.07"E	36°46'2.60"N

First, samples were filtered by glass fiber filter with the spores in 0.5 µm. 500 ml was separated from each samples and 50 µlit internal standard PCNB with 5 µgr/lit concentrations added to each of them. For Extracting and pre-concentration of Organophosphorus and Organochlorine pesticides was used solid phase cartridge (TELOS SPE Column ENV 200 mg/3ml model). 500 ml water sample with flow velocity 10 ml/min was passed. Following it the solid phase was dried by sucking air inside the cartridge. Then, the cartridges were eluted with 10 ml of ethyl acetate. The extracts were reduced in volume by N₂ blow-down. The last volume was reached 500

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µlit. For identifying and measuring pesticides, it was injected 1 µlit from the last extracted soluble to gas chromatography (GC).

After transferring sediments samples to laboratory, they were put to dry in the Freeze Dryer for 18 hours. Then samples were screened with 63 micro-meter sieve. 5 gr dried and sieved sample with 2 gr activated copper were mixed by using diluted Nitric acid (4%) and 1 gr Sodium sulfate (activated in 120°C for 12 hours). Then, 50 micro liters from internal standard 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 added to residue sediment, and maintained 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 (or rotavap) then to 0.5 ml by Gentle stream of Nitrogen. For cleaning up was used florisil that was semi activated with distilled water (wt/vol 6%). 1 µlit of this soluble was injected to GC/ECD.

Identifying organophosphorus and organochlorine in water and sediment samples was done by comprising observed pick inhibitory time in chromatograph obtained from sample and injecting standard soluble. The concentration was accounted by the level below pick of samples than the internal standard and putting it in standard calibration curve equation of pesticides. The obtained LOD values in this method were 2 to 8 ng/lit for organochlorine pesticides and 1 to 5 ng/lit for organophosphorus pesticides in the water samples. The recovery percent of this method for organochlorine pesticides was among 95% to 104% and recovery percent for organophosphorus pesticides was among 90% to 110%.

Results and Discussion

For determining the relation among the forest, agriculture, gardens and residential uses with the concentration of pesticides both in the water and the sediment it was accounted the average 9 concentrations of each pesticide in each station (3 seasons and 3 replicate for each season) it was identified the effect degree of each stations and in turn each uses by statistically comparing these numbers. These relations were significant for all pesticides (excepted β-HCH and Delderin in the water) and in general, there has been an increasing trend for all pesticides (excepted β-HCH and γ-HCH) the sediment along the river. As it was mentioned, every station is an agent for one uses that according to it, the results of statistical analysis has been surveyed and provided with any pesticides.

The relation of land-use with the pesticides concentration in the water by surveying relation of use with DDTs concentration (Figs. 2 to 9), it was concluded that the station N.6 related to residential use (Juibar city) has had the highest effect on the concentration of 2,4'-DDD, 2,4'-DDT, 4,4'-DDD, 4,4'-DDT, but the highest concentration increasing observed for 2,4'-DDE, 4,4'-DDE is in the agriculture area (station 5). This use has the most effectiveness area among the other stations and for this reason, the most decomposition and decay of DDTs to DDEs is occurred in this distance whether in the soil of region or in the water and in the sediment and therefore it has been seen more amount of DDE, too. Generally, the concentration of DDE than DDT and DDD is more and for describing this case, it can say when DDT degrades under aerobic conditions by microorganisms, DDE and when it degrades under anaerobic conditions, DDD are the most important compounds which obtained and so the proportion of DDE /DDD can be a good index for deformation of DDT under oxidation conditions that in this research is an indication for being dominant of aerobic conditions in order to degrading DDT along the river.

The relation of use with γ-HCH pesticide concentration is Significant in the water and is not Significant for β-HCH. The most concentration of chlorpyrifos has been 0.174 µg/lit for station 7 in the summer. In station 3 that is related to agriculture 1, it is seen increasing in chlorpyrifos, these changes in stations 4 and 5 is remained Significant, in the station 6, it is seen much more increasing for this toxic that is possibly due to intensive agriculture in the residential area of Juibar and also using this pesticide in the green spaces of city, and it must be noted that established runoff in the residential area than the other uses is much more and the lowest influence and evaporation is occurred in this use and thus in the consumption unit, naturally it has more effect on the pesticide residue in the water and sediment.

Diazinon has high consumption in the region and has the highest concentration among the other toxins both in water and sediment, of course in the summer. The amount of this toxin is changed from average 0.008 µg/l in the first station to 0.900 µg/l in stations 6 and 7. This toxin has the highest consumption in June and July months and the early August. The highest concentration is for summer and station 7 that equals to 1.867 µg/l. The lowest concentration amount observed in the forest Land-use and has had the highest effect on this pesticide concentration in station 6 and then 5. Despite of more consumption in Stations 2 and 3, this increase is not significant that it can be inferred due to the small distance of this stations from each other and less effective area of the region on the river span studied and increasing this pesticide in station 6 is due to urbanism along with agriculture of Juibar city and also it is possible to use diazinon in nonagricultural consumptions in this city.

Edifenphos has the lowest concentration amount with the average 0.212 $\mu\text{g/l}$ in station 1 and the highest amount with average 0.965 $\mu\text{g/l}$. the highest concentration is observed in station 7 and summer in 1.581 $\mu\text{g/l}$. EPA of allowable limit of edifenphos was announced 0.17 $\mu\text{g/l}$ in fresh water that is affected on non- pointed contaminations, so considering to it, the amount of edifenphos is more than this allowable limit in all stations. The relation of land use with pesticides concentration in sediment Considering to the results obtained from aldrin has no significant correlation. The concentration of organochlorine pesticides HCH has different trend than the other pesticides in sediment along the river and it can be mostly said had a descending trend. For the reason of decreasing concentration of these two pesticides in the sediment and along the river, it must be considered to the physicochemical characteristics β -HCH and γ -HCH in sediment. The average of β -HCH concentration was between 0.024 and 0.54 $\mu\text{g/gdw}$ and the most high observed concentration for this pesticide was in the summer and in station 1 and 5 were 0.089 and 0.088 $\mu\text{g/gdw}$, respectively. The average of γ -HCH concentration was between LOD to 0.109 $\mu\text{g/gdw}$ and the highest concentration is observed for this pesticide in the summer and was 0.173 $\mu\text{g/g}$ dry weight in the station 1. The highest amount and descending trend toward the end of river is observed in station 1, so the last three stations were lower than the LOD limit. The highest effect of decrease was in the station 4, so its reason can be attributed to suddenly more increasing in organic materials in sediment, as it was pointed that the concentration of this pesticide and also β -HCH has a inverse correlation with organic carbon amount. The average alteration in Chlorpyrifos concentration is between 0.031 $\mu\text{g/gdw}$ and 0.131 $\mu\text{g/gdw}$ in the station 1. The lowest amount in the station 1 is related to forest use. It is observed a significant increase in concentration that its reason can be more consuming pesticides in Citrus groves. It is observed a significant increase in the station 5 and there is increasing trend in the stations 6 and 7 in residential 2 and agricultural 3 uses, respectively. The average concentration of diazinon is about 0.101 $\mu\text{g/gdw}$ in the station 1 1.795 $\mu\text{g/gdw}$ in the station 6. The highest concentration measured for this toxic was in the station 7 and summer that has been measured 3.299 $\mu\text{g/gdw}$ Diazinon in the sediment. There is significant difference among the stations. It was observed a significant increase in Diazinon concentration in the station 2, so it was pointed it is due to excessive usage against garden pests in the area. Then, it was observed the gentle increasing trend in the stations 3 and 4 and again the significant increasing trend in the station 5 as it was claimed its granule was used against rice stem borer. It was observed relatively high increase in the concentration of this pesticide in its sediment in the station 6, so its reason can be attributed to agricultural usage in this land use and also against home insects, town, ornamental gardens, and healthy and animal's pests in this use. The average of edifenphos concentration among this station is 0.061 to 0.217 $\mu\text{g/gdw}$. The lowest concentration measured was in the station 1 and the highest concentration in the station 7 was 0.442 $\mu\text{g/g}$ dry weight. There is to increase in concentration in sediment, but it has been Significant in the first three stations that its previous use was forest, the station 5 by agricultural Land-use 2 that its previous use was residential and the station 6.

Conclusion

In surveying the land use role on the pesticides concentration in the water and sediment, in general the highest effect was for residential 2 and agriculture 2 land uses its reason is probably more effective areas, urbanism along with agriculture and more using pesticides in agricultural and nonagricultural consumption, the highest concentration of pesticides except β -HCH and γ -HCH (in sediment) was in the station 7 and β -HCH and γ -HCH had decreasing trend in contamination of organic materials in sediment along the river. In all stations and all seasons, the concentration of organophosphorus pesticides is much due to current consumption.

Keywords: GC, organotoxin, pollution, sediment, water.