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Organophosphorous Pesticide Residues in Surface and Ground Water in the Southern Coast Watershed of Caspian Sea, Iran

[1]Zahedeh Rahmanikhah, [2]Abbas Esmaeili Sari, [3]Nader Bahramifar and [4]Zahra Shokri Bousjien

[1]Master of Science in Environment, Teacher of Azad University of Arsanjan, Iran
[2]Associate Professor in Environmental Sciences, Tarbiyat Modares University, Noor, Iran
[3]Member of Scientific Mission, Ph.D. in Chemistry, Tarbiyat Modares University, Noor, Iran
[4]Master of Science in Agriculture

Abstract: The southern watershed of Caspian Sea is considered to consume the maximum annual values of pesticides in Iran. Water samples of 31 sites in rivers, 32 reservoirs, 10 wetlands, 21 wells and 21 springs were collected during a period of 1 year, July 2005 to June 2006. The Samples were extracted by solid-phase and analyzed by gas chromatography and nitrogen phosphorus detector (NPD). The average concentrations of them in surface water samples were 0.041µg/l, 0.007µg/l, 0.009µg/l and 0.005µg/l for diazinon, chlorpyrifos, ethion and edifenphos respectively and 0.019µg/ l, 0.016µg/l, 0.012µg/l and 0.012µg/l respectively in ground waters. This research suggests that the residues of pesticides threaten the aquatic life in these ecosystems.

Key words: Organophosphorous pesticide · Surface water · Ground water · GC

INTRODUCTION

Pesticide contamination of fresh water, which has emerged as an important environmental problem in the last few decades, is causing concern with respect to the long-term and low-dose effects of pesticides on public health as well as non-target species [1]. Because some insects and fungi gradually become resistant to chemical compounds many farmers feel they must apply higher concentrations after a period of time to achieve the same results for agricultural use [2].

The use of pesticides in agriculture may lead to contamination of surface and ground water by drift, runoff, drainage and leaching. Surface water contamination may have ecotoxicological effects for aquatic flora and fauna and for human health if used for public consumption [3, 4]. Surface water contamination usually depends on the agricultural season and does not last long, while ground water contamination has a strong inertia, which may cause a continuous human exposure [5].

Before 1970, attention was primarily focused on contamination by organochlorine insecticides. Since that time, a broad array of medium-to- polar pesticides with less persistence is used in agriculture, partly to reduce the potential for residue contamination of surface waters [6]. Organophosphorous pesticides (OPPs) are much less stable than organochlorine compounds and their use is therefore not associated with biomagnification and food chain transfer problems. However, they are general biocides that are toxic to nearly all animals. They are highly toxic to bees, to natural insect parasites and predators [7].

Hence, there is an increasing demand for determination of OPPs in water. To our knowledge, no data on levels of OPPs in eastern waters of northern Iran are present in the literature. One of the most important provinces in this area is Mazandaran, where considerable water resourses are used both for agriculture and human drinking water supply. Located between the Caspian Sea and Alborz mountains, Mazandaran province is considered one of the main rice cultivation regions in Iran (Figure 1). Typically, rice is cultivated under submerged flooded conditions and as a result pesticide concentration in water bodies is considerably higher because irrigation increases the likelihood of transport of pesticides via runoff to surface water. This province consumes approximately 19% of annually applied pesticides in Iran.

Corresponding Author: Zahedeh Rahmanikhah, Master of Science in Environment, Teacher of Azad University of Arsanjan, Iran. Tel: +98-917-791-1292, Fax: +98-711-8214981, E-mail: rahmanikhah@yahoo.com.

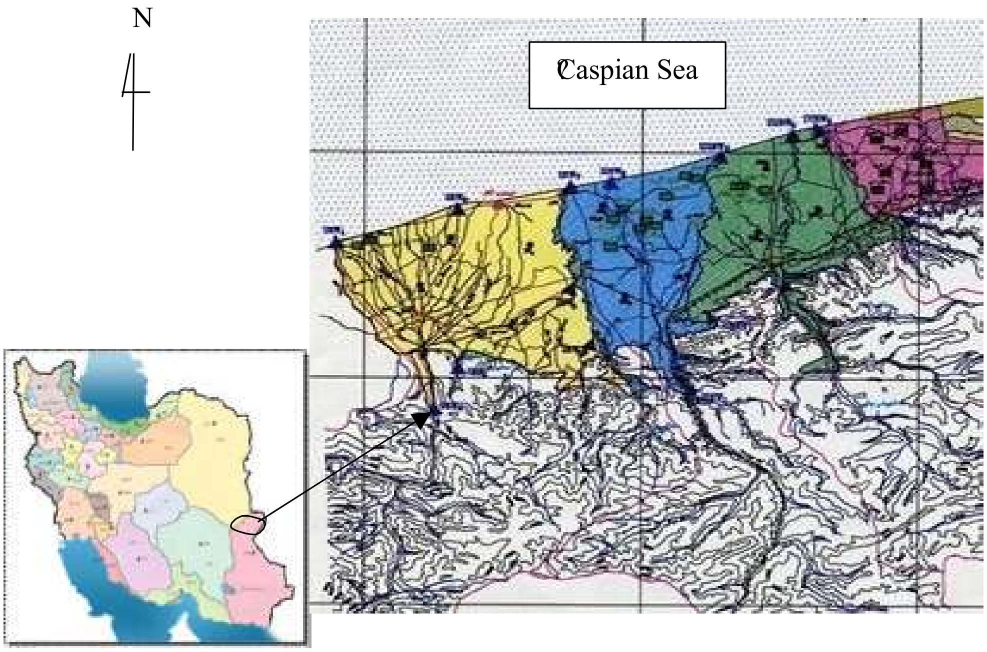

Fig. 1: The map of provinces of Iran and the location of studied area in Mazandaran province and sampling sites

In this investigation, the aqueous matrices studied were surface waters (rivers, reservoir pools, wetlands) and ground waters (wells, springs). The primary insecticides detected (Diazinon, Chloropyrfos, Ethion, Edifenphos) correspond to applications during previous agricultural use.

This study describes the seasonal distribution of organophosphorus pesticides in both surface and ground waters of the eastern side of Mazandaran province in the north of Iran (Figure 1).

MATERIALS AND METHODS

Sampling: Surface water samples were collected monthly from the larger rivers, reservoirs and wetlands included more expanded basins in addition to wells and springs, in the middle of every season from July 2005 to June 2006. Well and spring were taken at twenty-one locations in August, November, February and May. Thirty-one locations, mostly from the upper and estuarine reaches, were chosen for river samples. Thirty-two reservoir and 10 wetland locations were sampled.

At each location, one liter (What does it mean by 1-L) samples were collected in glass bottles with Teflon-lined caps. The samples were stored on ice on location and then transferred to the laboratory and were kept at 2°C prior to analysis.

Chemicals and Instrumentation: Pesticide analytical standards were bought from Riedel-de Han (Seelez, Germany). Stock standard solution consisting of 1 mg/L of a mixture of four organophosphorous pesticide standards was prepared in methanol and used for preparation of spike solutions.

In this investigation, organophosphorous pesticides were measured using a gas chromatograph (GC) and detected using a, nitrogen-phosphorous detector (NPD). The GC (model 1000, DANI Co., Italy) was equipped with a fused silica capillary column (Optima 5 location) of 6-m height, 0.25 mm inner diameter and 0.25 μm film thickness. Carrier gas was helium (99.999% purity) with 3.6 mL/min flowrate In Table flowrate is given 3 mL/min(3.6 mL/min is correct). Operating conditions for the GC are shown in Table 1.

Analytical Methods: Water samples (300 mL) were filtered first through a 125 mm filter (Fchleicher and Schuell 589.3, Germany) and then through a 0.5 μm glass microfiber filter. Filtered samples were extracted by solid-phase extraction using Envir Elut PAH cartridges (Varian, U.S.A) containing 6 ml of volume with 1 g of expletory phase. The cartridges were washed by eluting methanol and distilled water through them [8]. Water samples were pumped into the cartridges at a rate of 10 mL/min and then 10 mL of distilled water was passed through the cartridges to

Table 1: Gas Chromatograph (GC) condition

Condition	value
Injection valume	1µl
Flow rate	3.6ml/min
Injector temperature	250°c
Detector temperature	320°c
Oven temperature	100°C-300°C
Total time	40 min

clean them. The cartridges weren't allowed to dry [6]. The pesticides trapped in the cartridges, were eluted by 10 mL dichloromethane solvent [6] and collected in 15 mL vials fitted with Teflon-lined caps while 1 g Na_2SO_4 was added to the vials for dehydration [1]. The solvent of the extracted water sample was evaporated under nitrogen [9, 1] at 50°C. Finally, the residue of pesticides remaining in the vials was dissolved in 0.3 mL n-hexane [1, 10] and the vials were stored at -15 °C to -20 °C [1]. One microliter of the extracted sample was injected to the GC [10].

RESULTS

Figure 2 shows the chromatogram obtained from distilled water spiked with 0.25 µg/L of four organophosphorous pesticides and the chromatogram obtained from one sample analyzed in this research. The organophosphorus pesticides analyzed in this investigation were Diazinon, Chloropyrfos, Ethion and Edifenphos. Their mean concentrations in the studied area were 0.041, 0.007, 0.009 and 0.005 µg/L, respectively, in surface waters, 0.019, 0.016, 0.012 and 0.012 µg/L, respectively, in groundwater. Comparing these results showed that there was no significant difference between surface and ground water concentrations for Ethion, but the concentrations of the other three compounds differed significantly. Among surface waters, Diazinon was found in highest concentration in rivers, but the concentration of the other organophosphorus pesticides showed no difference on rivers, wetlands and reservoirs. Among all three surface water sources, Diazinon occurred most frequently, reflecting its higher application rate compared with the other pesticides in this region. In the studied area, Diazinon is used mostly for rice fields and deciduous trees, both of which are the main agricultural applications for pesticides. Of Chloropyrphos and Ethion is nearly equal in different parts of the Mazandaran province for controlling pests of deciduous and citrus trees. Diazinon concentration was higher in springs than in wells, but Ethion has been seen in higher concentrations in wells.

In surface waters, Diazinon was detected most frequently, followed by Ethion, Chloropyrphos and Edifenphos. Concentration differences between surface and ground waters and also among three surface and two ground waters are shown in Table 2 and Figure 3.

The Ministry of Environment of British Colombia has determined guidelines for pesticide concentrations in the water column [11]. Quantities for Diazinon and Chloropyrfos have been reported in this guideline but not for the other two orgnophosphorus pesticides. According to this guideline, Diazinon must be lower than 0.1 µg/L and Chloropyrfos must be lower than 0.0035 µg/L to protect fresh water aquatic life short-term and lethal effects. Comparing our results with these standard values showed that surface and ground water concentrations of Chloropyrfos greatly exceeded recommended values, highlighting the need for immediate monitoring and establishment of environmental studies and quality control for these regions. With regard to Diazinon, some of the observed values were more than recommended

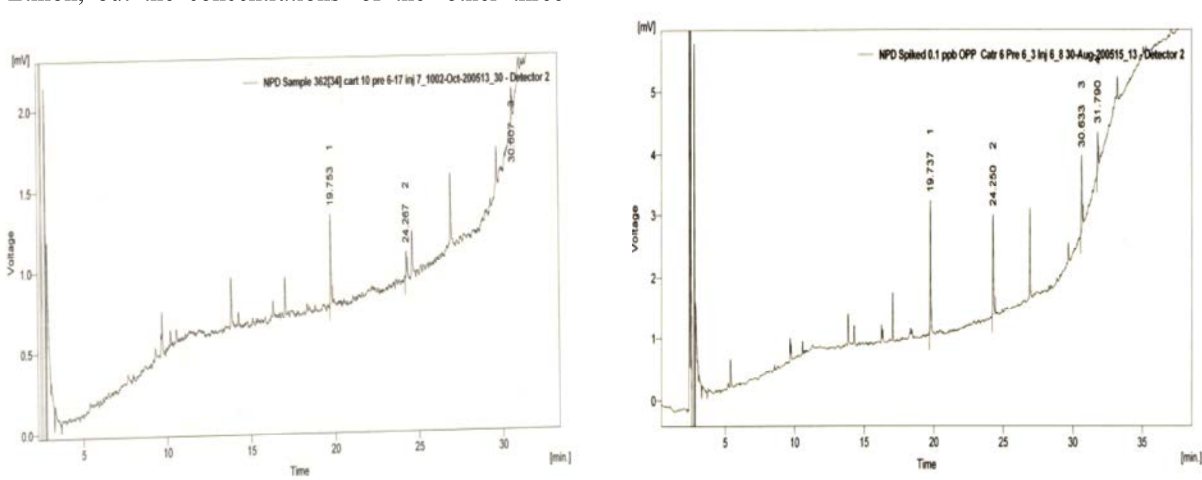

Fig. 2: (a): The chromatogram of water spiked whit 0.25µg/l of four organophosphorous pesticides (peak 1,2, 3, 4) and (b) the chromatogram obtained from one sample analyzed. This sample contains 0.095µg/l diazinon (peak 1), 0.027µg/l chlorpyrifos (peak 2) and 0.039µg/l ethion (peak3).

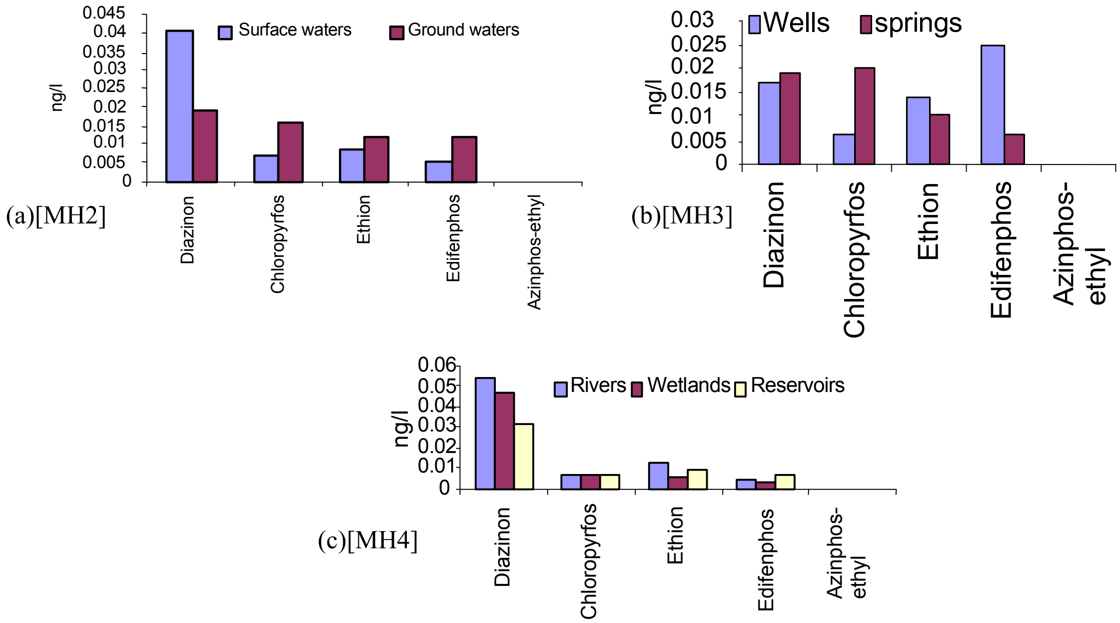

Fig. 3: Comparison of average concentrations of pesticides detected in (a) Surface and ground waters, (b) Rivers, wetlands and reservoirs and (c) Wells and springs

Table 2: The average concentrations of organophosphorus pesticides in surface and ground waters

	Diazinon (µg/l)	Chloropyrfos (µg/l)	Ethion (µg/l)	Edifenphos (µg/l)
Surface waters	0.041	0.007	0.009	0.005
Rivers	0.054	0.007	0.012	0.004
Wetlands	0.047	0.006	0.005	0.003
Reservoirs	0.031	0.007	0.009	0.006
Ground waters	0.019	0.016	0.012	0.012
Wells	0.017	0.006	0.014	0.025
Springs	0.019	0.020	0.010	0.006

What is n.w.s.

limits. To protect fresh water aquatic life from long-term and sub-lethal effects, Diazinon concentrations should be lower than 0.003 µg/L and our results exceeded this value.

Seasonal Patterns: Critical factors for the time elapse from application of pesticides during agricultural cultivation and their occurrence in rivers include the characteristics of the catchments (size, climatologically regime, type of soil or landscape), as well as the chemical and physical properties of the pesticides [12].

The results of seasonal mean values of organophosphorus pesticides are shown in Table 3. In all water samples, significant differences were seen among seasons except for Chloropyrfos in wells. As can be seen from these results, surface water concentrations of Diazinon is highest in summer months for rivers and wetlands and is highest during spring months for

Table 3: Mean values of pesticides during four seasons (July 2005 to June 2006)

	Diazinon (ng/l)	Chloropyrfos (ng/l)	Ethion (ng/l)	Edifenphos (ng/l)
Rivers				
Spring	0.029	0.002	n.d*	n.d
Summer	0.117	0.007	0.011	n.d
Autumn	0.054	0.016	0.023	0.008
Winter	0.017	0.003	0.013	0.009
Wetlands				
Spring	0.008	0.002	n.d	n.d
Summer	0.072	0.008	0.004	n.d
Autumn	0.034	0.015	0.018	0.015
Winter	0.01	0.003	0.014	0.01
Reservoirs				
Spring	0.12	n.d	n.d	n.d
Summer	0.03	0.003	n.d	n.d
Autumn	0.028	0.021	0.014	0.008
Winter	0.005	n.d	0.006	0.004
Wells				
Spring	———	———	———	———
Summer	0.007	n.d	0.001	n.d
Autumn	0.029	0.013	0.026	0.014
Winter	0.016	0.005	0.017	0.06
Springs				
Spring	n.d	n.d	n.d	n.d
Summer	0.017	0.092	0.059	0.021
Autumn	0.022	0.007	0.013	0.012
Winter	0.04	0.041	0.009	0.003

*nd: no detect

Table 4: Properties of pesticides

Pesticide	Water solubility (mg/l)	Soil half life (days)	Water half life (days)	K_{oc}
Diazinon	40[1]	32[1]	7-15[4]	83[1]
òEthion	1[1]	20[1]		4350[1]
Chlorpyrifos	0.4[2]	30.5[3]		6070[3]
Edifenphos				

1- [16] 2- [17]
3- [18] 4- [19]

reservoirs. Highest concentrations of Chloropyrfos, Ethion and Edifenphos, however, are found mostly in autumn except for springs (Exception in case of Springs, Table 3). This is probably due to their application time. The major inputs of these pesticides into rivers, wetlands and reservoirs occurred during the summer period (July-September) after their application in agricultural fields, as a result of surface runoff [13].

In some cases, in this study, the lowest concentrations occurred during spring months (Table 3) because of dilution effects due to high rainfall events and the increased degradation of pesticides after their application. Thus, pesticides were flushed to the surface water systems as pulses in response to high rainfalls during spring [14]. This trend was followed during the current study for the occurrence of pesticides in spring waters.

CONCLUSION

The frequency of pesticide detection exhibits an inverse correlation with Koc values [8]. As shown in Table 4, the Koc value is lowest for Diazinon, another reason for its rate of detection in well water in comparison with the other pesticides.

This research clearly demonstrated deterioration of the quality of surface and ground water in the southern watershed of the Caspian Sea by nonpoint source contaminants. It is important to note that oversight of the use of pesticides in the watershed is very difficult. Because organophosphorous pesticides have a very short half-life, their identification in water supplies shows how frequently they are applied. Further, higher concentrations and frequency rates of Diazinon application indicates its huge consumption in this part of Iran.

It can be seen from Table 2 that Edifenphos was found in lower concentrations as compared to the other pesticides. It is used in low amounts, however.

Obtained results show that Diazinon is likely being applied throughout the year in this region. Therefore, according to its soil half-life of 32 days and its widespread and huge consumption, it is expected to be detected at high concentrations and for a longer time every year, as the results of this investigation confirm. In addition, higher water solubility (40 mg/L) in comparison to Chlorpyriphos and Ethion could be another reason for increased detection of Diazinon.

Because wells are shallow and the application of pesticides is high, it is expected that high concentrations in ground water, but the results are in contrast. In this region, the loam-clay soils adsorb these pesticides before they enter the water wells, so pesticides were leached weakly. In spring waters, higher concentrations of pesticides were detected in comparison to wells. The lower depth of the wells makes the pesticides leach strongly and accumulate to surface waters.

Comparing the results of Chlorpyriphos and Ethion residues confirms that an increase in the pesticides in surface waters follows increased agricultural application, while a pesticide with a higher application rate doesn't always result in a higher residue concentration, because of the physical characteristics of the pesticides. Chlorpyrifos, for example, is applied in higher values, but not found in higher concentrations. Table 4 shows some of the physical characteristics of the pesticides. As observed in this table, the water solubility values of both Chlorpyriphos and Ethion are low. This value is somewhat higher for Ethion, so the average concentration of Ethion in surface waters was higher. The higher frequency rate of Chlorpyriphos residues resulted from a higher soil half-life. The sorption coefficient, K_{oc}, indicates the leaching potential from soil and consequently the potential for transmission to ground waters. This value is high for Chlorpyriphos and Ethion.

It is very important to note that the rates of pesticide application in Mazandaran Province threaten the aquatic life in its ecosystems and this study can be a warning for potential decreases in ecosystem biodiversity.

Although the concentrations of pesticides in well water samples were below the drinking water standards and revised health advisory levels by EPA's Office of water [15] not expected to cause any adverse noncarcinogenic effects (for diazinon is: one-day HA: 20µg/l, ten-day HA: 20µg/l and life-time HA: 0.6µg/l)*, we cannot confirm no adverse impacts by pesticides for drinking water considering their synergy effects when they are together.

Obtained findings in this research reveal that farmers are applying huge amounts of pesticides and it shows the weakness of management and lack of an exact supervision of rate of pesticide consumption. Also it is a sign of illiteracy and unawareness from its tragic consequences.

As the results of this paper confirm, at the present time, farmers presume the necessity of the pesticide application in this region so that the most annual values of pesticides are consumed in Mazandaran province. Therefore considering the abundance of rainfall and water supplies and also rich of biodiversity in this province, the problem of water pollution by pesticides requires deliberation. We hope that this paper would be a perspective for designing an effective policy and performance of functional management in future to prevent from adverse environmental impacts.

Most of performed studies associate to industrial countries but worrying concentrations of pesticide residues were detected from developing ones, so it is necessary to do same studies in a large amount of pesticides in the recent countries.

One-Day HA: The concentration of a chemical in drinking water that is not expected to cause any adverse noncarcinogenic effects for up to one day of exposure. The One-Day HA is normally designed to protect a 10-kg child consuming 1 liter of water per day.

Ten-Day HA: The concentration of a chemical in drinking water that is not expected to cause any adverse noncarcinogenic effects for up to ten days of exposure. The Ten-Day HA is also normally designed to protect a 10-kg child consuming 1 liter of water per day.

Lifetime HA: The concentration of a chemical in drinking water that is not expected to cause any adverse noncarcinogenic effects for a lifetime of exposure. The Lifetime HA is based on exposure of a 70-kg adult consuming 2 liters of water per day. The Lifetime HA for Group C carcinogens includes an adjustment for possible carcinogenicity.

Taken Useful Information for Using Organophosphorous Pesticides in the Other Areas: The results of this monitoring show that the detection and permanence of pesticides in water, depend on causes such as the pesticides halftime and solubility in water, the spread and amount of pesticide applications and the soil kind to leach pesticides into ground waters. The results indicate that the widespread and huge amount of pesticide application is the main reason for detecting of organophosphorous pesticides (especially in rainy regions).

Perhaps, it is impossible to forbid organophosphorous pesticides in present condition, but this research emphasizes the importance of combinative (natural chemical) pest control to decrease the application of these kinds of pesticides.

This controlling style can be a peaceful method between natural resources and agro ecosystems.

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