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Research Note

Determination of Persistent Pesticide Residues in Ground Water of Agra Region Using Solid Phase Extraction and Gas Chromatography

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Abstract: Water samples collected from ground water of Agra region were analyzed for the presence of pesticide residues using solid phase extraction and gas chromatographic techniques. Both organochlorine and organophosphorous pesticides viz., malathion, chloropyriphos, γ-HCH, α-HCH, endosulfan (α and β isomers) and isomers of DDT (p´-DDE and p´-DDT) were detected in concentrations much above the prescribed limits. Seasonal variations were observed in the level of pesticide residues.

Key words: Pesticides, groundwater, solid-phase extraction.

Introduction

The widespread use of pesticides has led to their being detected in various environmental matrices such as soil, air and water (Shailaja and Nair, 2001). If the credits of pesticides include enhanced economic potential in terms of increased production of food and fiber, and amelioration of vector-borne diseases then their debits have resulted in serious health implications to man and environment (Bruce and McMohan, 1996; Cerejeria et al., 2003). The city of Agra, located on the banks of river Yamuna is known internationally for its historic Taj Mahal and visited by several tourists from around the globe. The city is a major centre for various industrial and agricultural activities in northern India and in recent years has witnessed unpredictable increase in population, industrialization and urbanization. This has resulted in limited and deteriorated surfacewater supply; thus majority of the city's population has reverted to ground water for drinking and other domestic purposes, considering it relatively free from toxic substances. This paper discusses the seasonal variations in the level of various pesticide residues detected in ground water of Agra city. Ground water being the major source of drinking water, it is important to monitor its fitness for human consumption.

Materials and Methods

Study Area and Sample Collection

The study area is located between 27.17 ºN latitude and 77.58 ºE longitude on the banks of river Yamuna, Uttar Pradesh, India. The city was divided into thirteen sampling locations so as to cover the entire area. 500 ml of groundwater samples were collected from each site in sterilized glass bottles previously rinsed with hexane, from India Mark II hand-pumps installed by Government of India. Sampling was carried out during January to December, 2005. Duplicate samples were collected from each sampling location.

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Analytical Methodology

500 ml water sample was percolated through C18 cartridges (Millipore, Bedford) and the sorbed solutes were eluted with 5 ml each of methanol, dichloromethane and hexane (HPLC grade for spectroscopy). The eluates were dried under a gentle stream of nitrogen and pooled together in 1 ml hexane. one µl of sample thus prepared was injected and analyzed using HP 5890 gas chromatograph equipped with a 30 m × 0.25 mm i.d DB-17, 0.25 µm film thickness capillary column and supported by an Electron Capture Detector (ECD). Accuracy of determination was checked routinely by using standard samples (Promochem, Augsburg, Germany) and running ultra pure water blanks. The injector, oven and detector temperatures were maintained at 200 ºC, 220 ºC and 275 ºC respectively.

Results and Discussion

The results of analysis of groundwater samples collected from various sites of Agra city showed the presence of both organochlorine and organophosphorous pesticides. The distribution patterns of these pesticide residues have been illustrated in Table 1 and Figure 1. Out of the total 39 samples analyzed 84.6% of the samples exceeded the EC and BIS drinking water standards (5 mg/l of total pesticide level and 0.1 mg/l of individual pesticides is permissible). Seasonal variations were observed in the concentrations of pesticide residues, with the highest levels registered during monsoons (July-Sept). All the samples analyzed, showed the presence of at least one of the pesticide residues detected. During monsoons γ-HCH, an isomer of HCH, was prevalent in 92.3% (12/13) samples, while α-HCH was detected in 46.15% (6/13) (Table 1, Figure 1).

Table 1: Range of detection of pesticide residues in drinking water of Agra region

Sl. No.	*Pesticides*	*Summers (mg/l)*	*Monsoons (mg/l)*	*Winters (mg/l)*
1	γ-HCH	0.259-1.60	0.080-11.600	0.040-2.00
2	α-HCH	0.200-0.433	0.030-0.890	0.336-0.338
3	α-endosulfan	0.20-0.472	0.021-0.900	-
4	β-Endosulfan	0.050-0.1.375	0.460-0.780	0.050-0.890
5	Malathion	0.500-2.400	2.240-6.500	0.150-1.050
6	Chloropyriphos	0.430-0.600	0.30-0.600	0.892-0.892
7	p-DDE	0.20-0.330	0.020-0.553	-
8	p-DDT	-	-	0.500-0.890

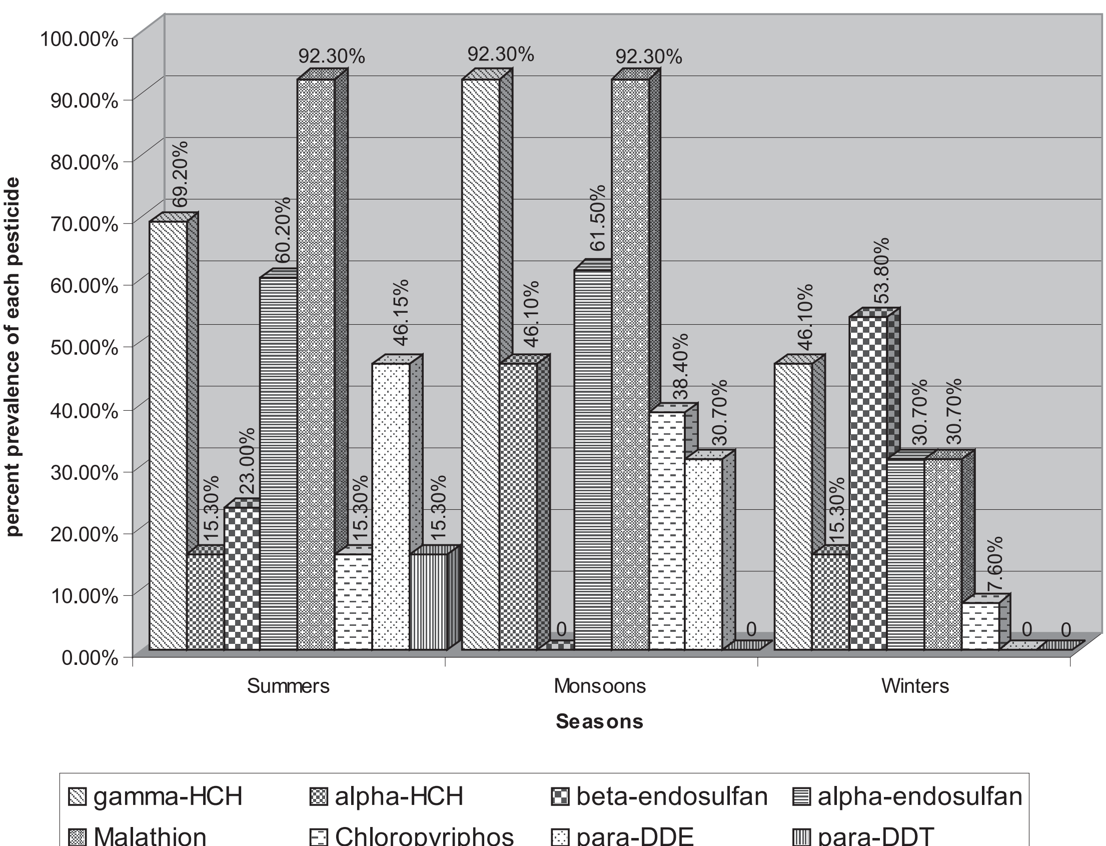

Figure 1: Percent seasonal prevalence of pesticide residues in groundwater of Agra region.

Malathion was also detected in 92.3% samples during monsoons. β-endosulfan was prevalent in 53.8% samples with concentrations ranging from 0.021-0.900 mg/l. However the concentrations of endosulfan exceeded the prescribed limits only in three samples. The alpha isomer of endosulfan was prevalent in 61.5% samples. The alpha isomer was more prevalent as compared to the beta isomer and was detected in 61.5% of the samples. 38.4% samples showed the presence of chloropyriphos and isomer of DDT, p-DDE was detected in 30.7% samples. p-DDT was not detected during monsoons (Figure 1, Table 1). The summer months also showed pesticide concentrations much higher than the set limits, but were comparatively less as compared to the monsoons. 69.2% (9/13) samples showed the presence of γ-HCH while the alpha isomer was detected in 15.3% samples. Malathion was the most prevalent during summers, being detected in 92.3% samples. Alpha and Beta isomers of endosulfan were detected in 23.0% and 69.2% samples respectively. Like the monsoons p-DDT was not detected in any of the samples, while p-DDE was prevalent in 46.15% samples but only two samples exceeded the prescribed limits.

Chloropyriphos was present in 15.5% samples and its concentrations were 0.43-0.600 g/l (Figure 1, Table 1). The concentrations of pesticides drastically reduced during winters. Unlike monsoons and summers only 46% samples showed the presence of γ-HCH and 15.3% of α-HCH. Malathion was present in 30.7% of the samples analyzed. The beta isomer of endosulfan was not detected during winters; however the alpha isomer was present in 30.7% samples at 0.050-0.80 mg/l. Chloropyriphos was detected only in one of the samples. During winters unlike other seasons p-DDE was not detected, while p-DDT was detected in one sample (Figure 1, Table 1).

A statistically significant difference using ANOVA was observed between the concentrations of different pesticides during different seasons $p > 0.005$ in all cases. The predominance of HCH and malathion residues in water samples analyzed indicates their liberal applications by local farmers, mainly because of their lower cost. Owing to their insecticidal properties and long lasting effects, they are extensively used for human vector control programmes (Soutter and Pannatier, 1996). Moreover the large number of cold storages in Agra city and its adjoining areas depend mostly on lindane, malathion and DDT for protection against pests, despite a ban on the use of lindane and DDT for preservation of food grains, pulses, oil seeds etc. and in storage by the Ministry of Agriculture, Govt. of India (Mathur, 1998).

Run off and leaching of pesticides from various industrial establishments, several agricultural farmlands in the city and its adjoining areas and domestic waste is a major cause of ingress of these pesticide residues into groundwater reservoirs. Pesticides are generally applied in the fields before the crop covers the soil, which provides easy access of these pesticides to the soil surface and there is a high risk of leaching. Moreover, the soil in this region being of coarse sandy loam, it aids in their leaching into the water saturated zones. This also explains the occurrence of pesticides in higher concentration during the monsoon (Papadopoulou et al., 2003). Most of the pesticides detected are highly persistent and due to their slow rates of degradation contamination at one location showed up years later at a different site, since ground water moves both vertically and horizontally (Iwata et al., 1994).

The hand pumps which were used for sample collection are a major source of drinking water for the nearby population; if this stays unchecked, could pose serious health effects including immuno-suppression, hormone disruption, reproductive abnormalities, diminished intelligence and cancer (Funari et al., 1998). Agra being a major tourist spot, needs immediate alternatives as tourists have to depend on the bottled water which could also be refilled with these polluted groundwater as a recent study reveals the presence of pesticides in bottled water and soft drinks (*Times of India*, February 4, 2003). Since groundwater contamination is largely irreversible and its purification is a difficult task, the best policy thus is to prevent hazardous substances from getting into it. This can be achieved to a great extent by reducing the application rates per season, reclassification of the pesticides into the restricted use category, educating farmers about safe application technology and various soil conservation practices that decreases pesticide run off. More detailed monitoring studies need to be conducted to study the leaching behaviour of these pesticides into the ground water.

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