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RAPID DETERMINATION OF RESIDUAL PESTICIDES AND POLYAROMATIC HYDROCARBONS IN DIFFERENT ENVIRONMENTAL SAMPLES BY HPLC

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Nowadays agriculture represents most important economic activity. Agricultural pesticides that are deliberately used to escalate crop yield unfortunately are endowed with many latent and insidious adverse effects. Pesticides and poly-aromatic hydrocarbons are identified worldwide as toxic environmental pollutants that persist in the environment and bioaccumulates in the food chain. This study was thus designed for the analysis of pesticide residues and Polyaromatic hydrocarbons in fruits and vegetables, water and soil. This work was done with the objective to develop an analytical method for selectively and sensitively detecting pesticides and polyaromatic hydrocarbons in different environmental matrices. For this purpose samples of selected fruits, vegetables, soil and water collected from agricultural land were analyzed to determine the residues of selected organochlorine pesticides (Bifenthrin, Imidacloprid, Difenoconazole) and polycyclic aromatic hydrocarbons (Anthracene , Phenanthrene) by High Pressure Liquid Chromatography. The selected method beautifully allowed the qualitative and quantitative determination of Pesticides and Polyaromatic hydrocarbons in selected samples. Results of study revealed the presence of Anthracene in a concentration ranges from 0.0655-31.632mg/kg, Difenoconazole in concentration ranges from 0.03-18.604mg/kg and Bifenthrin in concentration ranges from 0.024-11.74 mg/kg in different study samples which were exceeding maximum residue limits (MRL) set by Codex Alimentarius Commission.

Keywords: Organochlorinated pesticides, polycyclic aromatic hydrocarbons, high pressure liquid chromatography.

INTRODUCTION

Pakistan economy is largely dependent on agriculture. Directly or indirectly, 68% of its population is dependent on this sector. It contributes more than 21 percent of the total GDP, Gross Domestic Product (Joudejans, 1991). Pakistan's soil is favorable for vegetable and fruit growth and varieties of fruits and vegetables are cultivated here. Vegetables and fruits are juicy so they are more susceptible to pest attacks and pesticides are used for their control. Pesticide is a chemical substance that is used to control, prevent, devastate and diminish any harmful pest that destroys crops. Agricultural pesticides that are deliberately used to escalate crop yield unfortunately are endowed with many latent and insidious adverse effects. Their persistence in the environment is the significant property as the transportation of these compounds can broaden the range of exposure to far beyond the immediate area of their use or release (Rodriguez *et al.*, 2011). Studies revealed that organochlorine pesticides (OCPs) and polycyclic aromatic hydrocarbons (PAHs) are among the most concerning environmental pollutants due to their highly toxic, persistent and bioaccumulative properties (Zhonghua *et al.*, 2016; Hussain *et al.*, 2016; Yang *et al.*, 2016). Therefore, the effects of these ubiquitous compounds are not only limited to human but are extended to environment (Anwar *et al.*, 2011). Due to their chemical properties, they pose significant impact on human health and environment even at low concentrations (Liu *et al.*, 2009). Pesticides when released into the environment have different environmental fate as they may fall into different environmental compartments such as in air, soil or water. When sprayed they may percolate into the soil layer and through soil may reach ground water (Harrison, 1990). Transportation of pesticide from their point of application to other unwanted areas is mainly through rain and wind which may harm that environment. Humans are exposed to pesticides through oral means either by ingesting contaminated food, by inhaling contaminated air or through dermal means. Duration of exposure and toxicity decides the effect of particular pesticide; which may be acute or chronic. Acute include nausea, diarrhea, dizziness, rashes, blindness and death. Exposure of pesticide to living beings may result in chronic effects like neurological deficiencies reproductive disorders and cancers. The trend of pesticide usage in Pakistan is more because climatic conditions are favorable for pest's growth and most of the farmers often grow off season vegetables and fruits that are more vulnerable to pests attack. According to Punjab Private Sector Groundwater Development Project technical report 2002, in Pakistan more than 108 types of insecticide, 30 types of fungicide, 39 types of weedicide, 6 types of rodenticide and 5 types of acaricide are being used (GoP, 2002).

The main objective of this study is to detect and quantify the amount of three organochlorine pesticides (Difenoconazole, Bifenthrin and Imidacloprid) and PAHs (Anthracene and Phenanthrene) by HPLC in environment through its determination in various vegetables, fruits, soil and waste water samples. Several studies have already reported the use of HPLC and GC, GC/MS and other analytical techniques for the determination of different pesticides, PCBs and PAHs in different environmental matrices (Yang *et al*., 2016; Rodriguez *et al*., 2016; Saija *et al*., 2016; Haleyur *et al*., 2016; Zhang *et al*., 2016; Lozowicka *et al*., 2016). Literature demonstrated HPLC as most successful technique to analyze the compounds having similar chemical structure (Obana *et al*., 2002). As compared to other chromatography techniques, it works efficiently avoiding tedious sample preparation (Cserhati and Szogyi, 2012). For this study HPLC with diode UV/Vis detector was used.

MATERIALS AND METHODS

Analytical grade chemicals i.e., Ethyl Acetate, Dichloromethane, Sodium Sulphate, Methanol, Sodium dichloride, Acetonitrile were purchased from RDH/Fluka. HPLC grade methanol was supplied by Merck, Germany and 0.45 µm Magna nylon filters were of Osmonics Inc.

***Introduction to study area*:** Samples for the present study were collected from agricultural field near Abu Zehbi Palace, Rahim Yar Khan which is located at the southern side of Punjab. Climate of Rahim Yar Khan is very dry and hot in summers. Maximum temperature reaches 49.7°C and recorded minimum temperature is 6.8°C.

***Agricultural and environmental profile*:** Based on the production, the main crops of the district are wheat, sugarcane and rice. However the minor production also includes mustard seed, guar seed, oil seed (sun flower), bajra, ground nut, tobacco, moong, masoor and maash. Citrus Fruit, mango, guava and dates are the main fruits of the district. Besides minor (bitterguord, potatoes, bootleguord), main vegetables of the city include carrot, onion, cauliflower, spinach, ladyfinger (Source: Directorate of Agriculture, Crop Reporting Service, Punjab). North-west side of the district faces River Indus. Subsoil quality of water in the area is suitable for industrial purposes. In addition to sugar and textile industries, several other industries i.e. vegetable, fruit juice, beverage, ghee, laundry, fertilizer, etc. are also working in the district.

***Collection of samples*:** As mentioned in Table 1 four types of samples were collected from an industrial and agricultural land in Rahim Yar Khan, City. The sampling was conducted in the month of July, 2014. Fresh vegetables were acquired from fields before their release into the market. Vegetables, fruits and soil samples were collected in polythene bags however the waste water samples were collected in auto claved bottles. Controlled samples for each vegetable, fruit, soil sample and waste water was also collected for the comparative analysis.

***Pretreatment of samples*:** Fruits and vegetable samples were chopped, air dried for 2 days and then grinded into a fine powder form prior to extraction. Soil samples were also air dried and crushed into fine powder.

***Selection of pesticide and PAHs*:** On the basis of field survey and interviews with farmers concerning about the type, amount and frequency of pesticides that are sprayed on the sites. Following pesticides and PAHs mentioned in Table 2 were selected for the research:

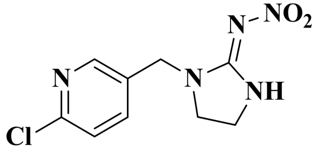
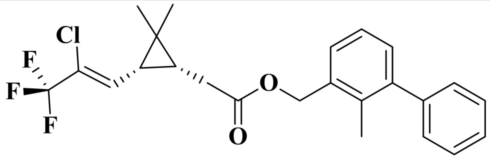
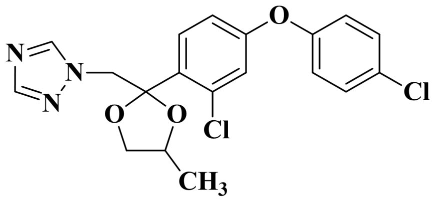
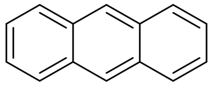
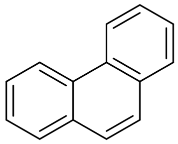
Sample extraction

***Vegetable samples*:** A representative vegetable sample (5g) was taken in a beaker and followed by the addition of 40ml dichloromethane (DCM), 40ml ethyl acetate (EtOAc) (diethyl ether was used for extraction of PAHs), 150 ml distilled water and 5g NaCl. This mixture was kept on a magnetic stirrer for 15 minutes for homogenous mixing and then transferred into a separating funnel, waited for 30 minutes to get well separated organic layer from aqueous layer. The lower organic layer was allowed to separate from aqueous layer. The lower layer which is the organic layer was collected in a beaker. 20ml of DCM and ethyl acetate was added in the aqueous layer to recover any leftover residues. Again the lower layer was collected and mixed with the previous organic layer. The same extraction process was repeated for all vegetable samples 19.

Table 1. Samples used for study.

Sr. No.	Sample Type	Sample Name	Sampling Site
1	Vegetables	Pumpkin	Vegetation site
		Bitter Gourd	Vegetation site
2	Fruits	Mango	Plantation site
		Succari Orange	Plantation site
3	Soil Samples	Soil (Vegetation)	Vegetation site
		Soil (Plantation)	Plantation site
		Soil (Drain)	Drain
4	Wastewater Samples	Canal Water	Canal (Irrigation water)
		Standing Water	Standing water (In fields)

Table 2. Chemical Structures of Selected Pesticides and PAHs.

Pesticide Name	Chemical Name	Chemical Structure
Imidacloprid	1-(6-chloro-3-pyridylmethyl)-N-nitroimidazolidin-2-ylideneamine, 1-[(6-chloro-3-pyridinyl) methyl]-N-nitro-2-imidazolidinimine	
Bifenthrin	(2-methyl-1,1-biphenyl-3-y1)-methyl-3-(2-chloro-3,3,3-trifluoro-1-propenyl)-2,2-dimethyl cyclopropanecarboxylate	
Difenoconazole	1-({2-[2-Chloro-4-(4-chlorophenoxy) phenyl]-4-methyl-1,3-dioxolan-2-yl}methyl)-1H-1,2,4-triazole	
PAHs Name	**Chemical Formula**	**Chemical structure**
Anthracene	$C_{14}H_{10}$	
Phenanthrene	$C_{14}H_{10}$	

Fruit samples: A representative fruit sample (2g) was taken in a beaker and mixed with 40ml of ethyl acetate, 40ml of dichloromethane (DCM), 150ml of distilled water and 5g of NaCl on a magnetic stirrer. This mixture was then transferred to separating funnel and allowed to stand for 30 minutes until two layers were formed. The lower layer (organic layer) was collected in a beaker. 40ml of ethylacetate: DCM (1:1) was added additionally in the upper layer. The lower layer when formed was collected and mixed with the previous organic layer. Same extraction process was repeated for all fruit samples. For cleanup of vegetable samples, 20g of sodium sulphate was added in each sample. Mixture was then filtered through Whattman filter paper. Solvent from the mixture was evaporated in rotary evaporator at 40°C and leftover residues were collected by adding 20ml of methanol.

Soil samples: 5g of soil sample was taken in a beaker and followed by the addition of 40ml of dichloromethane (DCM), 40mL ethyl acetate and 200mL of distilled water. Mixture was placed on a magnetic stirrer for 15 minutes. Then it was shifted into a separating funnel which was kept on a tripod stand for 30 minutes to allow the separation of organic layer from aqueous layer. After 30 minutes the organic layer was collected in a beaker. 20ml of ethyl acetate and dichloromethane each was added again into the aqueous layer. After 10 minutes the organic layer was collected. Both the organic layers were mixed. This extraction procedure was repeated for all soil samples.

Waste water samples: 200ml of water sample along with 40ml of ethyl acetate and 40ml of dichloromethane was taken in a beaker and allowed to mix for 15 minutes on a magnetic stirrer. The mixture of waste water and organic solvents were then transferred into a separating funnel for 30 minutes and was allowed to separate. The organic layer was taken in a beaker after 30 minutes so that organic layer separates from aqueous layer. Lower layer which is the organic layer was collected and the upper layer was followed by the addition of 20ml of ethyl acetate and 20ml of DCM again. After 10 minutes of stay, the organic layer was again collected and mixed with the previous organic layer. Same process was repeated for all waste water samples.

Sample cleanup: For cleanup of all the samples, 20g of sodium sulphate was added in each sample. Mixture was then filtered through Whattman filter paper. Solvent from the mixture was evaporated in rotary evaporator at 40°C and leftover residues were collected by adding 20ml of methanol. For fruit samples 10g of sodium sulphate was used.

Stock standard solution preparation: 3 pesticides i.e., Imidacloprid, Bifenthrin, Difenoconazole and 2 PAHs standard i.e. Anthracene. Phenantherene stock solution was prepared by pursuing the same procedure as for sample preparation with the only difference in amount of sample and solvents. For all the standards, 1g of compound was mixed with 30ml distilled water and 30ml solvents with no addition of NaCl. Then 5ml methanol of HPLC grade was added.

Analysis

Apparatus for Analysis**:** The HPLC system having Agilene 1260 Quaternary Pump Gradient System with ODS 18 Column was used for study.

Mobile Phase was acetonitrile and water (HPLC Grade) in a ratio of 30:70. Both of them were filtered through cellulose filters (0.2 µm). All other parameters were optimized for detection of pesticides and PAHs. The run time was 45 min, flow rate optimized as 1 ml/min, column temperature was kept at 25°C, injection volume maintained at 10µL and UV detection at 245 nm. pH was adjusted to 4.5 with phosphoric acid. Remaining conditions of HPLC are mentioned in Table 2.

Method development and quality control**:** A gradient rapid and sensitive HPLC-UV method was developed and validated to determine pesticides. To achieve method development optimization studies were performed on each HPLC parameter like solvent ratio, pH, temperature of column, sample and injection volume, flow rate, wavelength and post time etc. For optimization one parameter was changed at one time while all others were kept constant.

In order to access the precision in method each sample was analyzed in triplicate to record the variation (if any). Calibration experiments were tested for linearity, accuracy and precision. Limit of detection (3:1) and limit of quantification (10:1) was calculated as signal-noise ratio.

Samples and standards were analyzed in HPLC Agilent 1260, Quaternary Gradient System set at conditions illustrated in Table 2 to obtain chromatogram.

Qualitative and quantitative analysis**:** Qualitative analysis was carried out in order to check the presence of selected pesticides and PAHs in the experimental samples and control groups. This task was accomplished by comparing the retention factor (k) and response of the peak in the chromatogram of the standard chromatogram, with the sample chromatogram.

The comparison revealed the presence pesticides i.e. Difenoconazole, Bifenthrin and PAHs,Anhracene in all the samples of vegetables, fruits, soil and wastewater with different concentrations. However, no pesticide was detected in controlled samples.

After the peaks have been integrated and identified, the next step in the analysis is quantification. Quantification uses peak areas in order to determine the concentration of a compound in the sample.

To achieve the amount of detected byproducts in each sample, quantitative analysis using the formula formulated by chromo academy was used.

$$\text{Response factor} = \frac{\text{Peak area of standard}}{\text{Standard Amount Used in 1ml of Solvent}}$$

$$\text{Amount of standard in sample} = \frac{\text{Peak area (sample peak)}}{\text{Response factor of selected byproduct}}$$

RESULTS AND DISCUSSION

The purpose of the presented study was the determination and quantification of pesticides and polycyclic aromatic hydrocarbons in vegetables, fruits, soil and wastewater samples. To achieve the task of the study high pressure liquid chromatography was employed. The choice of chromatographic technique is very important for the qualitative and quantitative determination of analytes. Several analytical techniques have been adapted for this purpose but HPLC has proved to be the most reliable and time effective technique (Khan *et al*., 2016). Solvent selection of ethyl acetate and dichloromethane gave improved peak resolution. No interfering peaks for the determination of pesticides and PAHs were observed. The existence of pesticides in samples was confirmed by comparing the retention time in the standard chromatogram, with the samples chromatogram. The comparison revealed the presence pesticides i.e., Difenoconazole, Bifenthrin and PAHs, Anthracene in all the samples of vegetables, fruits, soil and wastewater in different concentrations. However, no pesticide was detected in controlled samples. Codex Alimentations Commission of the Food and Agriculture Organization (FAO) UN has established MRLs to avoid the human exposure to pesticide through food consumption. Samples when compared with MRLs all the vegetables and fruit samples were found contaminated with pesticides with the quantities above MRLs. Bifenthrin is an effectively used insecticide for cotton, vegetables and fruits pest control. It is also intended for public health to control mosquitoes. Table 3 shows detected amount of Bifenthrin in all the samples. Vegetable samples were contaminated with bifenthrin at concentration of 6.7488mg/kg in pumpkin and 11.748mg/kg in bitterguord. Fruit samples found to be contaminated at concentrations of 2.55mg/kg in mango and 2.5535 mg/kg in Shakri Orange. In soil samples bifenthrin was quantified as 0.9792mg/kg, 0.9736mg/kg,1.0138mg/kg in vegetation, plantation and drain soil respectively. In wastewater samples bifenthrin was detected in the quantity of 0.02435 mg/L in canal water and 0.02532 mg/L in standing water. Samples when compared with MRLs as shown in Table 3, all the vegetables and fruit samples were found contaminated with pesticides with the quantities above MRLs. Maximum residue limits (MRL) of Codex Alimentarius Commission for Bifenthrin in pumpkin and bitterguord is 0.4 mg/kg alarmingly the concentration of the detected pesticide in the samples of these vegetables were 15 times higher than the standard value for Pumkin while the detected value was 28 times higher than the standard value. The MRL for mango

Table 3. Comparison of determined concentration of pesticides in vegetables (mg/kg), fruits (mg/kg), soil (mg/kg) and wastewater (mg/l) samples with codex standard.

Sr.	Sample	Sample Name	Detected Pesticides			
			Difenoconazole Concentration (mg/kg)	Standard Concentration (mg/kg)	Bifenthrin Concentration (mg/kg)	Standard Concentration (mg/kg)
1	Vegetable	Pumpkin	10.687	0.20	6.7488	0.40
		Bitterguord	18.605	0.20	11.748	0.40
2	Fruit	Mango	4.0380	0.03	2.5500	0.03
		Succari Orange	4.0444	0.80*	2.5535	0.05
3	Soil	Vegetation Soil	1.5507	Not available	0.9792	Not available
		Plantation Soil	1.5418	Not available	0.9736	Not available
		Drain Soil	1.6055	Not available	1.0138	Not available
4	Water	Canal Water	0.0385	Not available	0.02435	Not available
		Standing water	0.0401	Not available	0.02532	Not available

*WTO Standard

is 0.03 mg/kg while the detected value was found to be 82 times higher than the MRL and codex standard for Bifenthrin in citrus is 0.05 mg/kg which is 49 times higher than the Maximum residue limits (MRL). Quantification of bifenthrin residues in soil along with vegetable and fruits is important as about 50% of the total pesticide is absorbed on soil throughout foliar application. Long persistency of Bifenthrin under aerobic and anaerobic conditions has been observed by many researchers. Degradation rate of bifenthrin in soil is much slower as it is revealed that its half-life varies from eight to seventeen months at 20°C (Gan *et al*., 2005). Synthetic pyrethroids (SPs) has a potential of mobility by means of surface runoff into aquatic systems therefore waste water samples were also found to be contaminated with Bifenthrin (Baskaran *et al*., 1999).

Difenoconazole is mainly a fungicide which is used for disease control in fruits, vegetables and other crops. Detected concentration of difenocnazole in all samples is shown in Table 3. Highest concentrations of difenoconazole were found to be present in vegetable samples in the quantity of 10.6874mg/kg and 18.6046 mg/kg in pumpkin and bitterguord samples. In fruit samples the quantified concentrations were 4.038mg/kg and 4.0444mg/kg in mango and Shakri Orange samples. Difenoconazole concentration in soil samples were 1.5507 mg/kg in vegetation soil, 1.5418mg/kg in plantation soil and 1.6055mg/kg in drain soil. However, in wastewater samples, difenoconazole shows the lowest concentration of 0.0401mg/L in standing water and0.0385 mg/L concentration in canal water. Situation seems alarming when these values were compared with Maximum residue limits (MRL) of Codex Alimentarius Commission for Difenoconazole as the found values were found 40-133 times exceeding the standard values for fruits and vegetables. As all the samples were found contaminated with Difenoconazole and Bifenthrin. Vegetable samples particularly bitterguord was the most contaminated. The concentration of difenoconazole was more than bifenthrin in all the samples. Highest concentration of pesticide residues in vegetables than other samples may be the outcome of farmer's negligence and unawareness of good agricultural practices in the study area. Improper irrigation practice results in humidity and ultimately leading to fungal diseases which might be the reason behind the escalated levels of difenoconazole (fungicide) in vegetable samples. Moreover, the samples were not peeled before extraction and as reported in study, the surface of the vegetables and fruits absorb more pesticides than inner pulpy portion and peeling would have resulted in less residual levels (Khan *et al*., 2011). Extensive use and low biodegradability of pesticides may also contaminate soil and other environmental sources. Surface soil collected from the field also shows the residual concentration of pesticide. Though in low concentrations but these pesticides were also observed in canal water which was used for irrigation and drain nearby agricultural fields (Tayade *et al*., 2013). Similar, studies have also shown the presence of different pesticides in other environmental matrixes like oranges, vegetables etc. (Cao *et al*., 2005; Yang *et al*., 2008; Li *et al*., 2017).

Polycyclic aromatic hydrocarbons are ubiquitous pollutants. Their presence in the environment is well documented. Therefore keeping this in mind, samples were also evaluated for the presence of PAHs. Table 4 demonstrates the concentration of Anthracene in all the samples. Among vegetables, anthracene was highest in bittergourd (31.632mg/kg) followed by 18.172mg/kg in pumpkin. In fruits total amount of anthracene was slightly higher in Shakri Orange (6.875 mg/kg) than mango (6.875mg/kg). However in soil samples, drain soil (2.728 mg/kg) was more compared to vegetation soil (2.636 mg/kg) and plantation soil (2.6216 mg/kg). Anthracene concentration was the lowest in canal water (0.0655mg/ L) and standing water (0.681mg/L).

Table 4. Determined concentration of anthracene in vegetables, fruits, soil and wastewater samples (same as in above tables)

Sr.	Sample Type	Sample	Actual Amount of Anthracene in Sample (mg/kg)
1	Vegetables	Pumpkin	18.172
		Bitter Gourd	31.632
2	Fruits	Mango	6.866
		Succari Orange	6.875
3	Soil Samples	Soil (Vegetation site)	2.636
		Soil (Plantation site)	2.621
		Soil (Drain)	2.728
4	Wastewater Samples	Canal Water	0.065
		Standing Water	0.068

Similarly to residual pesticide concentration, the PAH concentration of Anthracene was highest in vegetable samples. PAH presence may be the result of vehicular emissions, industrial activities, nearby domestic combustion, sewage sludge. PAHs have the ability to deposit far away from their source of contamination. These compounds are present in sewage sludge and the application of this sludge on soil may be the cause of contamination (Bishnoi *et al*., 2006). Anthracene is also used in making plastics, dyes and pesticides that may also be the reason of Anthracene detection in pesticide sprayed vegetables, fruits and vegetation and plantation soil. PAH Phenantherene was found to be absent in all the samples as chromatogram of Phenantherene showed no similar to any of the vegetable, fruit, soil or wastewater sample.

The environmental fate of a pesticide is chiefly dependent on chemical properties it possessed (Mukherjee *et al*., 2010). The results of the study shows high concentration of pesticide residues in vegetables than other samples which may be the outcome of farmer's negligence and unawareness of good agricultural practices in the study area. Improper irrigation practice results in humidity and ultimately leading to fungal diseases which might be the reason behind the escalated levels of difenoconazole (fungicide) in vegetable samples. Moreover the samples were not peeled before extraction and as reported in study, the surface of the vegetables and fruits absorb more pesticides than inner pulpy portion and peeling would have resulted in less residual levels (Khan *et al*., 2011). Extensive use and low biodegradability of pesticides may also contaminate soil and other environmental sources. Surface soil collected from the field also shows the residual concentration of pesticide. Though in low concentrations but these pesticides were also observed in canal water which was used for irrigation and drain nearby agricultural fields (Tayade *et al*., 2013). Similarly, to residual pesticide concentration, the PAH concentration of anthracene was highest in vegetable samples. PAH presence may be the result of vehicular emissions, industrial activities, nearby domestic combustion, sewage sludge. PAHs have the ability to deposit far away from their source of contamination. These compounds are present in sewage sludge and the application of this sludge on soil may be the cause of contamination (Bishnoi *et al*., 2006).

Conclusion: A method for stimulus determination of pesticides and polycyclic aromatic hydrocarbons in vegetables, fruits, soil and wastewater samples was developed using HPLC-UV detector. The proposed method beautifully allowed determination of pesticide residues and PAHs at µg/kg levels and offered easy and cheap way for quantification of important pollutants since derivatization is not required and it includes less use of solvents and other chemicals. Quantification analysis illustrates the high levels of anthracene, difenaconazole and bifenthrin in all the samples which is an alarming situation as these persistent compounds badly effects human health and environment.

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