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Multiresidue Analysis of Pesticides by Gas Chromatography with Electron-capture in Rice Samples from Different Geographical Regions of Pakistan

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Abstract: Since last few years Pakistani rice exporters have become very conscious about the residual level of pesticides in rice and they prefer to have a certificate for residues free rice prior to shipment. 1000 samples of rice were collected from different containers ready to export representing different geographical regions of Pakistan and were tested at the Pakistan Council of Scientific and Industrial Research. The residue levels of 37 chlorinated hydrocarbons including major groups like hexachlorocyclohexane (∑HCH) isomers (α-HCH, β-HCH, γ-HCH and δ-HCH), Dichloro-diphenyl-trichloroethane (∑DDT) congeners (p,p-DDE, o,p-DDT, p,p-DDD and p,p-DDT), heptachlor isomers and Chlordane isomers, aldrin, dieldrin and endrin and chloripyrifos in rice were determined by GC-ECD. Residues of ∑DDT and ∑HCH were detected in 30 and 45% of the samples and during 2005 their average values were found to be 0.001 mg/kg and 0.005 mg/kg repectively. In 2006 level of ∑DDT and ∑HCH was 0.071 mg/kg and 0.191 mg/kg showing increased contamination of these pesticides. Similarly residual level of ∑heptachlor and ∑Chloradane was 0.003 and 0.002 mg/kg in 2005 and these were at the level of 0.191 and -0.005 mg/kg during 2006 repectively. The maximum permissible limit for DDT and HCH metabolites were determined on the basis of an average factor to be 0.2-0.5 mg/kg which is just near to codex limit. Mean recoveries from three replicates ranged from 85.5-106.0%, with coefficients of variation from 0.3-9.9%. The limit of detection was in the range of 0.02-0.01 mg/kg for all organchlorines in average of 37 compounds.

Key words: Export quality rice, pesticide residues, GC/ECD analysis

INTRODUCTION

Pakistan comes among the major rice exporter countries and an average export of rice is 2.5 MMT, consisting of 1.7 MMT of IRRI and 0.8 MMT of Basmati every year. The private sector has been controlled rice trade and the state-owned. (Rice Export Corporation) was abolished several years ago. Today, another state trading agency, the Trading Corporation of Pakistan (TCP), plays a limited role in the rice trade by facilitating government-to-government exports through the private sector. The GOP in consultation with the Rice Exporters Association of Pakistan (REAP) has established a quality review committee to certify the quality of Pakistani rice prior to shipment in an effort to boost the image of Pakistani rice and especially Basmati rice.

The major destinations for Basmati rice exports are included United Arab Emirates (172,339 MT) Oman (68,360 MT), Saudi Arabia (64,680 MT), Qatar (44,678 MT), United Kingdom (27,452 MT), Bahrain (23,398 MT) aND Kuwait (23,163 MT). 12,040 MT of Basmati rice aND 1,679 MT of IRRI rice was shipped to the United States. No doubt more than 90 % rice of the world rice id grown and consumed in Asia and one of the major crop of Pakistan. Pakistan Export promotion Bureau has implemented WTO standards for the import and export of agriculture products and according to that, pesticide residues should not be permitted beyond the permissible limits in food commodities particularly rice as a major component of daily diet all over the world (Caldas and Souza 2004).

Pakistan being agriculture country consumption of pesticides is considerable like other South Asian countries because pesticides residues have been found in soil and water samples from agricultures land. Intensive cultivation and broad adoption of fertilizer responsive varieties have resulted in widespread pest infestation. The extent of pest-related diseases has grown more in the past two decades in Pakistan. Rising pest problems and availability of pesticides due to market development have increased the use of pesticides in crop pest management. Pakistan is soon likely to would come in the list of pesticide consumer countries in the world (Jabbar *et al*., 1993). Pesticide use in grain production has more than doubled within 10 years. Among grains, rice uses pesticides the most intensively however the following pesticides and like many other are totally banned in Pakistan to spray in agriculture field as stated in a Country report issued by Department of plant protection (Rashid, 2006).

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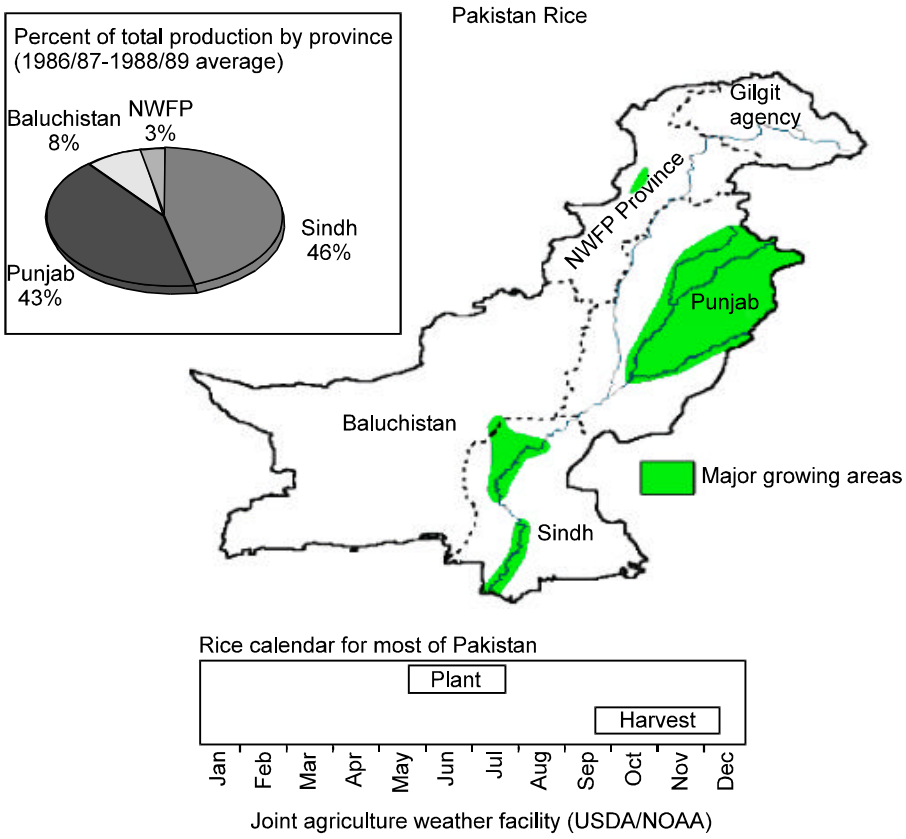

List of pesticides banned in Pakistan

Active Ingredients	Formulations	Pesticides Not Registered
B.H.C	Dichlorvos (above 500 g/l)	Aldrin (POP/PIC)
Binapacryl	Phophamidon (above 500 g/l)	Mirex (POP)
Bromophos ethyl		Chlordane (POP/PIC)
Captafol		Dinoseb (PIC)
Chlordimeform		Ethylene di bromide (PIC)
Chlorobenzilate		Parathion (PIC)
Chlorthiophos		Fluroacetate (PIC)
Cyhexatin		
Dalapon		
DDT		
Dibromochloropropane +		
Dibromochloropropene		
Dicrotophos		
Dieldrin		
Disulfoton		
Endrin		
Ethylene dichloride +		
Carbontenachloride		
Leptophos		
Mercury Compound		
Mevinphos		
Toxaphene		
Zineb		
Heptachlor		
Methyl Parathion		
Monocrotophos (all formulations)		

The contamination of rice by chemical hazards is a worldwide public health concern and is leading cause of trade problem internationally. The determination of pesticides residues in rice has become increasingly essential requirement for consumers, producers and authorities responsible for quality control. Monitoring of

rice for pesticide contamination being an important alimentary source throughout the world and the quality of the grain is not be compromised by the presence of pesticide residues. Pesticide contamination of rice is due to illegal or non-scientific use of pesticide at the time of planting and storage Pesticide residues although in negligible amount or in traces but in fact be a threat to human health.

Studies on dietary intake of pesticide residues have been carried out in the various parts of the world by a number of workers like Shukla *et al.* (2002), Kathpal and Beena (2009), Godfred Darko and Osei Akoto (2008) and Battu *et al.* (2005).

Pakistan Council has conducted a two years study in coordination of exporters to estimate the extent of contamination with 37 compounds of pesticides.

MATERIALS AND METHODS

Analytical method is based on AOAC 2005

Sampling: Rice samples been supplied by a number of clients from consignments ready to shipment at Karachi seaport for the analysis of pesticide residues. These samples have been procured from different parts of Pakistan.

Chemical reagents: All reagents (hexane, acetone, n-hexane, dichloromethane) were double distilled before use. Florisil absorbent was also purified and activated for 02 h at 130°C before use.

Preparation of sample: Quartering and well mixing of whole sample prepare sample, take out approx. 100-200 g is grinded and sieved and a fine particle sample is prepared by passing through 20-mesh size.

Extraction and cleanup of sample: 20-50 g duplicate ground sample of rice was blended with 350 ml H_2O-CH_3CN (7+13) mixture at high Speed in a stainless steel blender for 05 min or unless a well, homogenized blend is prepared. Filtered with suction through Buckner funnel in to 500 mL suction flask and transferred filtrate of residues to Petroleum ether. The measured volume (with a measuring cylinder) of extract/filtrate and was added 100 mL petroleum and transferred to 1 L separator. It was shacked vigorously 1-2 min and added 10 ml saturated sodium chloride (Na_2SO_4) and 600 ml H_2O and volume was Approx. 15 g anhydrous sodium sulfate (Na_2SO_4) was added and shacked vigorously. (Do not let extract remain with Na_2SO_4 > 01 h or losses of solution directly to Florisil column. Solvent was concentrated to 15-10 ml in K-D concentrator by starting evaporation and transferred solution directly to Florisil column for clean up prior to determination (Griffitt, 1983).

Column chromatography: Florisil column (22 mm id) was prepared with (activated at 675°C) containing 10 cm after setting of Florisil topped with 1 cm anhydrous Na_2SO_4. 40-50 mL petroleum ether passed through the column. Petroleum ether extract or concentrate passed through Florisil column and eluted column at about 5 mL/min with 200 mL 6%. 200 ml 15% and 200 ml 50% Petroleum ether solvent at $\leq$5 ml/min in separate receivers. Concentrate each elute to suitable definite volume in K-D concentrator.

Gas Liquid Chromatography (GLC): Determination of chlorinated pesticides was done by Perkin Elmer Gas Chromatograph, Clarus-500 equipped with Electron Capture Detector (ECD) using N_2 as carrier gas. Hydrogen at 2 ml min^{-1} and nitrogen gas at 30 ml min^{-1} was used as the carrier and makeup gases respectively. Analysis is performed on cross bond 5% biphenyl, 95% dimethyl polysilicone capillary column having 30 meter length, 0.35 mm ID and 0.50 µm df.

Initial oven temperature was 100°C, was increased with the rate of 4°C/min up to 240°C. Holding time at 100°C was 5 min and at 240°C was 10 min respectively. Injector temperature was 200°C and detector temperature was 270°C and attention-3.

Pesticides standards and the concentration is mixed standard solution of 37 compound were purchased from Dr. Ehresnstorfer' s laboratory, Germany and certified reference material (IAEA -406) from international Atomic Energy Agency. Working standards were prepared by combining the standard mixture with corresponding is stock solution respectively to prepare calibration solution in the required range.

Analysis of rice samples: recovery studies: A recovery study was carried out by the standard additions technique, by spiking the samples with the surrogate compound prior to applying the extraction procedure at a level of 10 µg kg^{-1}. For spiking studies, a measured 20 g test portion of rice sample with no pesticides detected previously was spiked with appropriate standard solution to a final concentration of 0.05-0.50 mg/kg was vigorously vortexed to distribute the pesticide residues. Data of average recovery and R.S.D. (n = 10) for organochlorines in the samples are shown in Table 1. These results demonstrated that recoveries were almost quantitative.

Quality assurance and quality control measures included the use of reagent blanks, surrogate and matrix spike recovery were done accordingly. Calibration and calibration verification were routinely checked at the beginning and end of each batch of 6 samples. All laboratories batches of samples were contained one procedural blank, one laboratory control sample, a duplicate sample. The procedural blank was spiked with the solvent and a surrogate internal standard pesticides mixture 5 and 11 from Dr. Ehrnestoffer laboratory, Germany. All samples were spiked with the surrogate compound to determine efficiency. Results are calculated on the basis of the mean value of specimens. % recovery, %RSD, LOD and LOR calculated during the analysis and values are given in Table 1.

Table 1: Recovery of pesticides from rice samples

Organochlorine	Recovery (%)	R.S.D (%)	LOD mg/kg	LOR mg/kg
Alpha-HCH	95.4	4.6	0.002	0.005
HCB	97.8	5.1	0.003	0.01
Beta-HCH	92.4	5.0	0.002	0.006
Gamma-HCH	98.5	4.1	0.003	0.01
Delta-HCH	97.9	5.2	0.007	0.02
Epsilon-HCH	95.4	4.5	0.003	0.01
2,4,4-Trichlorobiphenyl	97.8	5.2	0.003	0.008
Heptachlor	92.4	6.0	0.002	0.005
2,2,5,5-Tetrachlorobiphenyl	98.5	4.3	0.003	0.01
Aldrin	97.9	5.4	0.002	0.005
Isodrin	95.4	4.7	0.002	0.005
Heptachlor-exo-epoxide (cis-isomer B) + Oxy-chlordane	97.8	5.2	0.003	0.01
Heptachlor-eNDo-epoxide (trans- isomer A)	92.4	6.0	0.003	0.01
Trans-chlorodane(gamma)	98.5	4.3	0.007	0.02
Cis-Chlordane(alpha)	95.4	4.7	0.003	0.01
Oxy-chlordane	97.8	5.2	0.003	0.008
Trans-Chlordane(gamma)	92.4	6.0	0.002	0.005
2,4-DDE	98.5	4.3	0.003	0.01
2,2,4,5,5-Pentachlorobiphenyl	97.9	5.4	0.002	0.006
Cis-Chlordane(alpha) + alpha-ENDosulfan	95.4	4.7	0.003	0.01
4,4-DDE	97.8	5.2	0.002	0.005
Diedrin	92.4	6.0	0.003	0.01
2,4-DDD	95.4	4.7	0.002	0.006
2,2,4,4,5,5-Hexachlorobiphenyl	97.8	5.2	0.007	0.02
4,4-DDT + 2,2,3,4,4,5-Hexachlorobiphenyl	92.4	6.0	0.003	0.01
Methoxychlor	98.5	4.3	0.007	0.02
2,2,3,4,4,5,5-Heptachlorobiphenyl	97.9	5.4	0.003	0.01
Methoxychlor	95.4	4.7	0.007	0.02
Chlorpyrifos	97.8	5.2	0.003	0.01
Mirex	92.4	6.0	0.003	0.008
Heptachlor-endo-expoxide	98.5	4.3	0.002	0.005
Heptachlor-exo-epoxide (cis-isomer B) + Oxy-chlordane	97.9	5.4	0.003	0.01
Endrin+beta-Endosulfan	95.4	4.7	0.002	0.005
Dichlorvos	97.8	5.2	0.003	0.01
2,2,3,4,4,5-Hexachlorobiphenyl+4,4-DDT	92.4	6.0	0.002	0.006
2,2,4,4,5,5-Hexachlorobiphenyl	98.5	4.3	0.007	0.02
4,4-DDT + 2,2,3,4,4,5-Hexachlorobiphenyl	97.9	5.4	0.003	0.01

The same methodology and instrumental conditions have been employed for measurement of pesticides in sample during 2005-2006.

RESULTS AND DISCUSSION

The chromatograms of standards and blanks have been shown in Fig. 1 and 2. No interferences from sample matrix was observed.

Agriculture is the single largest sector of Pakistani's economy with 21% contribution to GDP employing about 44% of the workforce. More than two-third's of Pakistan's population lives in rural areas and their livelihood continues to revolve around agriculture and allied activities (Economic Survey of Pakistan, 2007-08).

The use of pesticides in Pakistan commenced in 1952. It started with the introduction of an aerial spraying program on the key crops such as, cotton, rice and sugarcane. Agricultural Pesticides Ordinance (APO) was promulgated in 1971 to regulate import, manufacture, formulation, sale, distribution, use and advertisement of pesticides but no importance was given to health hazards due to pesticide residues.

As a part of daily analysis of samples at Pakistan Council of Scientific and Industrial Research (PCSIR), 1000 samples of rice procured by customers for export from rural and urban areas representing different geographical regions of Pakistan. Samples been analyzed for residues of a mixture of 37 organochlorines and organophosphorus compounds. Residues of DDT and HCH, respectively, were detected in about 38 and 43% of the samples analyzed. Medians of both DDT and HCH in rice samples were around 0.01 mg/kg. Concentrations of α-, β-, γ- and δ-HCH exceeded the maximum residue limit of 0.05 mg/kg for each isomer in rice fixed by the Government in rice. Estimated intake of DDT and isomers of HCH through consumption of rice contaminated at their median and 90th percentiles constituted a small proportion of their acceptable daily intakes.

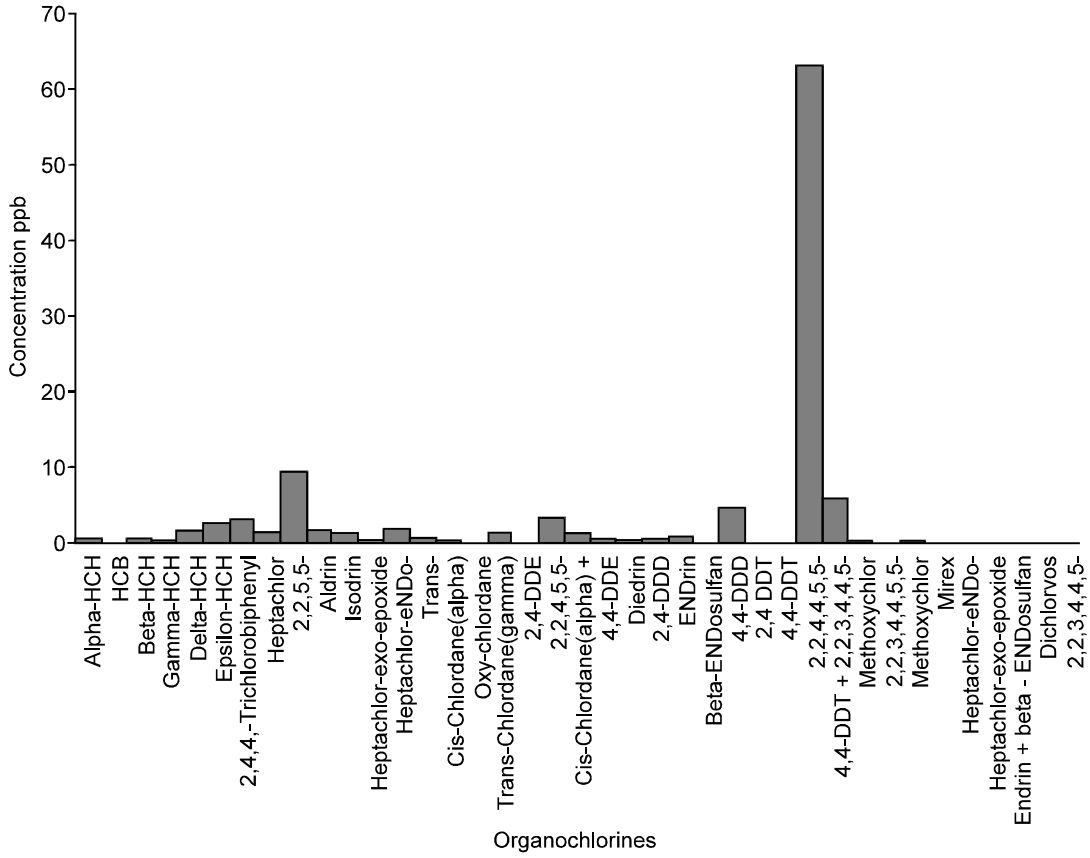

Fig. 1: Organochlorine concentration in export quality rice of Pakistan in 2005

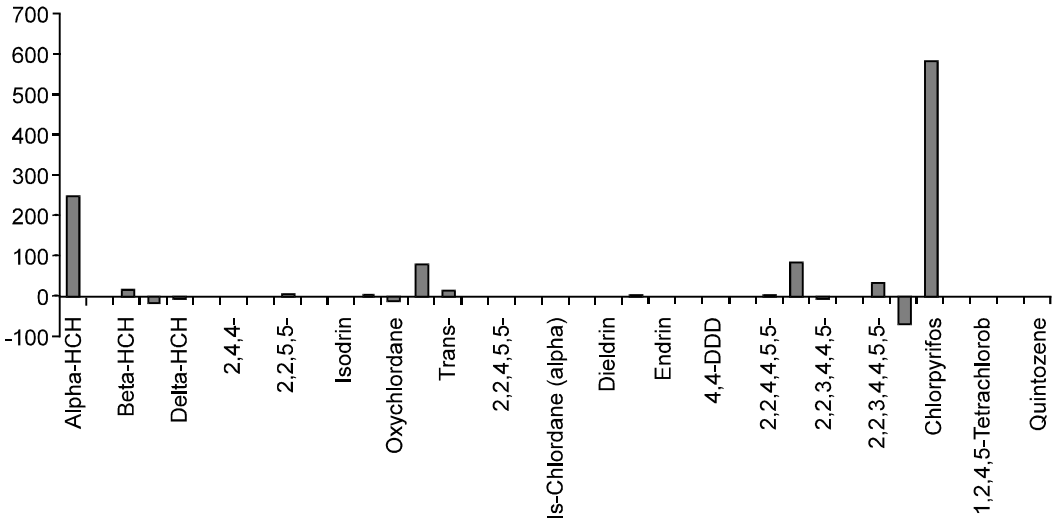

Fig. 2: Organichlorine concentration in export quality rice of Pakistan in 2006

The concentrations of Organochlorine Pesticides (OCPs) in the rice samples during 2005 and 2006 were presented in Table 2 and 3, respectively. Concentrations of Organochlorine Pesticides (OCPs) in the rice were in the range 0-0.005 mg/kg for ∑HCH during 2005 and in 2006 it was 0.191 mg/kg and 0-0.001 mg/kg for PDDT in 2005 and in its 2006 ranged from 0-0.071 mg/kg. The typical HCH generally contains 55-80% of a-HCH, 5-14% of b-HCH, 8-15% of c-HCH, 2-16% of d-HCH. ∑Heptachlor was ranged from 0-0.003 mg/kg in 2005

and in 2006 0.079 mg/kg, respectively. The detection rates of total HCH and DDT in the 2006 were 22.8% and 35.9% compared with 26.0% and 30.0% in 2005. The other five OCPs, except ∑HCH, ∑Heptachlor, ∑Chlordane and ∑DDT, were detected below the LOR. Chlorpyrifos (organophosphorus), has created a serious problem for exporters due to its higher concentration in rice collected from some specific region of Pakistan. Basmati rice is the best quality rice of the world and its major portion being exported to different countries and having great demand. OCPs residues in rice can be bioaccumulated in humans eventually.

The investigations of OCP levels in different food commodities showed their wide occurrence in the environment. In Pakistan, pesticides levels in rice have been decreased sharply after being banned, but could still be intensified by the crop and bio-accumulated to a final high residue level in humans because of their low biodegradability and high persistence. Compositional differences of HCH isomers or DDT congeners in the environment could indicate different contamination sources (PCCRARM, 1997). Typically, technical HCH consisted of 60-70% a-HCH, 5-12% b-HCH, 10-15% g-HCH, 6-10% d-HCH and 3-4% e-HCH and smaller amounts of other isomers and congeners among all isomers, only g-HCH is considered to be the only isomer with insecticidal properties. Although the use of technical HCH is now virtually discontinued in most countries, pure g-HCH (lindane) is still used in some countries around the world.

The physicochemical properties of these HCH isomers are different. β-HCH has the lowest water solubility, vapour pressure and is the most stable and relatively resistant to microbial degradation (Ramesh *et al*., 1991). Also it should be noted that α-HCH can be converted to β-HCH in the environment (Wu *et al*., 1997). Many studies have reported that β-HCH was dominant in environmental samples after long-term migration and transformation (Jiawei *et al*., 2008). The average compositions of HCH isomers measured in the rice were α: 19.7%, β: 80.3%, γ: 0%, d: 0%. Technical DDT generally contains 75% p, p'-DDT, 15% O.P'-DDT, 5% p,p'-DDE and less than 5% others. DDT can be biodegraded to DDE under aerobic condition and to DDD under anaerobic conditions (Kalantzi *et al*., 2001). Comparing the concentrations of p,p0-DDT and its metabolites can distinguish whether the DDT input is recent or not (Phuong *et al*., 2001).

Level of each compounds of pesticide (35-37 compounds) was determined in rice sample during 2005 and 2006 shown in Table 2 and 3.

Status of 2005: During 2005 more than 500 rice samples were analyzed and the contamination of 37 compounds was determined.

∑HCH was the found in 35% rice samples during 2005 was contaminated cumulatively as 5.69 ppb and not detected in a number of samples but the concentration of ∑heptachlor was found to be 3.385 ppb. The other major group of contamination is ∑DDT was found in the range of 0.002-5.878 ppb with a sum value of group as 11.977 ppb and among which pp-DDT was found in maximum concentration as compared to other metabolites of this group but its permissible limit was observed to be found under control limit. The chloropirifose was not dominant s in all samples during 2005 and a total concentration was found as 3.865 ppb.

Status of 2006: During 2006 concentration of ∑HCH was found in 70% samples of rice and its contamination was observed up to 245.87 ppb which is alarming and pp-DDT was found at the level of 92.514 ppb. The most dominant pesticide was found during the 2006 was chlorpyrifos that was 580.83 ppb.

∑Heptachlor and ∑Chlordane were 248.52 and 8.20 ppb in an average value found in 29% samples.

By taking mean of each compound of pesticide concentration, concentration of Chloropirifos was found at higher level during 2006 as compare to 2005 that is reason a number of Pakistani rice consignments were retained by FDA during 2006 and a team has done efforts to determine causes of contamination and it was found that rice from few fields were contaminated with chloripirifos and farmers as well as farm owners were intimated to stop use of spray of that pesticide in which chloripirifos was mixed in composition beyond the recommended amount and analysis of rice samples received during 2007 (Unpublished data) were not found in critical situation. Another main reason is lack of awareness for use of particular pesticide for particular pest. The farmers have inadequate knowledge about pesticides as to their suitability, application techniques and safety measures. This is one of the reasons of poor pest control, environmental pollution and health problems in some areas.

Government of Pakistan have been planned to arrange a number of programs for guidance of the farmers. Intensive studies carried out at PCSIR to control pesticide contamination in fishes, vegetables, water as well as in main crop of Pakistan including rice. The pesticide industry does not put sufficient resources on dissemination of knowledge on pests, pesticides, environment and management techniques. In this area there is great scope of extension work in the public sector is also required.

Use of pesticides is steadily rising in Pakistan' agriculture. Rice is the second highest export of Pakistan earning sizeable foreign exchange. With a view to aver possibility of contamination of this commodity with undesirable quantities of pesticide residues which

Table 2: Mean residual level of pesticides in rice during year 2005

Compounds	Sn1	Sn2	Sn3	Sn4	Sn5	Sn6	Sn7	Sn8	Sn9	Sn10	Sn11
Alpha-HCH	0.195	ND	ND	0.195	ND	ND	ND	ND	ND	ND	0.283HCH
HCB	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Beta-HCH	0.179	0.055	ND	0.179	0.040	ND	0.050	ND	ND	ND	ND
Gamma-HCH	0.181	ND	ND	0.181	ND	ND	ND	ND	ND	ND	ND
Delta-HCH	0.670	ND	ND	0.670	ND	ND	ND	ND	ND	ND	0.171
Epsilon-HCH	1.170	ND	0.001	1.170	ND	ND	ND	ND	ND	ND	0.300
2,4,4-Trichlorobiphenyl	0.973	0.441	0.001	0.973	0.212	0.243	ND	ND	ND	ND	0.336
Heptachlor	ND	ND	ND	ND	ND	ND	1.213	ND	ND	ND	ND
2,2,5,5-Tetrachlorobiphenyl	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	9.428
Aldrin	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.500
Isodrin	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.268
Heptachlor-exo-epoxide (cis-isomer B) + Oxy-chlordane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.205
Heptachlor-eNDo-epoxide (trans- isomer A)	0.900	0.524	ND	ND	0.284	ND	ND	ND	ND	0.001	0.258
Trans-chlorodane(gamma)	ND	ND	ND	0.775	ND	ND	ND	ND	ND	ND	ND
Cis-Chlordane(alpha)	ND	ND	0.001	0.470	ND	ND	ND	ND	ND	ND	ND
Oxy-chlordane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Trans-Chlordane(gamma)	0.775	0.345			ND	ND	ND	ND	ND	ND	ND
2,4-DDE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,2,4,5,5-Pentachlorobiphenyl	0.951	ND	ND	0.951	ND	ND	ND	ND	ND	0.001	1.523
Cis-Chlordane(alpha) + alpha-ENDosulfan	0.470	0.134	ND		0.105	0.082	0.141	ND	ND	0.001	0.232
4,4-DDE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.726
Diedrin	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.258
2,4-DDD	0.226	0.253	ND	0.226	ND	ND	ND	ND	ND	ND	ND
Endrin	0.132	0.102			0.159	ND	0.436	ND	ND	ND	ND
Beta-Endosulfan	ND	ND			ND	ND	ND	ND	ND	ND	ND
4,4-DDD	0.997	1.073	ND	0.997	0.670	0.921	ND	ND	ND	0.002	ND
2,4 DDT	ND	ND	0.006	ND	ND	ND	ND	ND	ND	ND	ND
4,4-DDT			0.002	ND							
2,2,4,4,5,5-Hexachlorobiphenyl	2.465	16.213	ND	ND	20.774	11.356	11.415	0.019	0.007	0.007	1.186
4,4-DDT + 2,2,3,4,4,5-Hexachlorobiphenyl	2.463	0.910	0.042	2.463	ND	ND	ND	ND	ND	ND	ND
Methoxychlor	0.370	ND			ND	ND	ND	ND	ND	ND	ND
2,2,3,4,4,5,5-Heptachlorobiphenyl	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Methoxychlor	ND	ND	ND	0.370	ND	ND	ND	ND	ND	ND	ND
Chlorpyrifos	ND	ND	ND	ND	0.053	0.974	ND	0.251	1.56	1.023	0.004
Mirex	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Heptachlor-endo-expoxide	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Heptachlor-exo-epoxide (cis-isomer B) + Oxy-chlordane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Endrin+beta-Endosulfan	ND	ND	0.001	ND	ND	ND	ND	ND	ND	ND	ND
Dichlorvos	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,2,3,4,4,5-Hexachlorobiphenyl+4,4-DDT	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

*Sn = Average of 10 samples of rice

Table 3: Mean residual level of pesticides in rice during year 2006

Compounds	Sn1	Sn2	Sn3	Sn4	Sn5	Sn6	Sn7	Sn8	Sn9	Sn10	Sn11	Sn12	Sn13
Alpha-HCH	66.043	96.826	ND	ND	0.962	ND	ND	81.903	0.137	ND	ND	ND	ND
HCB	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Beta-HCH	20.234	34.363	ND	ND	ND	ND	ND	-33.579	ND	ND	ND	ND	ND
Gamma-HCH	ND	ND	ND	ND	ND	ND	ND	-13.511	ND	ND	ND	ND	ND
Delta-HCH	ND	ND	ND	ND	ND	ND	ND	-5.532	ND	ND	ND	ND	ND
Epsilon-HCH	ND	ND	ND	ND	ND	ND	ND	0.673	ND	ND	ND	ND	ND
2,4,4-trichlorobiphenyl	0.087	ND	ND	ND	0.021	ND	ND	1.099	ND	ND	ND	1.047	ND
Heptachlor	ND	ND	ND	ND	ND	ND	ND	-2.044	ND	ND	ND	ND	0.001
2,2,5,5-tetrachlorobiphenyl	7.233	ND	ND	0.216	0.175	ND	ND	0.72	ND	ND	ND	ND	ND
Aldrin	ND	ND	ND	2.042	0.095	ND	ND	-4.22	ND	ND	ND	ND	0.003
Isodrin	ND	ND	ND	ND	ND	ND	ND	-0.533	ND	ND	ND	ND	ND
Heptachlor-exo-expoxide	ND	ND	ND	ND	0.123	ND	ND	5.558	ND	ND	ND	ND	ND
Oxychlordane	ND	ND	ND	ND	ND	ND	ND	-7.88	ND	ND	ND	ND	ND
Heptachlor-endo-expoxide	ND	ND	2.198	2.453	0.276	1.409	ND	ND	69.803	ND	2.672	4.382	0.065
Trans-chlorodane(gamma)	ND	ND	ND	ND	0.189	ND	ND	10.56	1.946	ND	0.668	1.854	ND
2,4-DDE	ND	ND	ND	ND	ND	ND	ND	-0.007	ND	ND	ND	ND	ND
2,2,4,5,5-Pentachlorobiphenyl	-0.001	-0.001	-0.001	-0.001	0.027	-0.001	-0.001	0.298	ND	ND	ND	ND	ND
Alpha-Endosulfan	ND	ND	ND	ND	0.097	0.072	ND	ND	ND	ND	ND	ND	0.002
Cis-Chlordane(alpha)	ND	ND	ND	0.441	ND	ND	ND	ND	0.257	ND	ND	0.165	ND
4,4-DDE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Table 3 Continured

Compounds	Sn1	Sn2	Sn3	Sn4	Sn5	Sn6	Sn7	Sn8	Sn9	Sn10	Sn11	Sn12	Sn13
Dieldrin	ND	ND	ND	ND	0.146	-0.002	ND	-0.002	ND	0.575	ND	ND	ND
2,4-DDD	ND	1.045	ND	ND	ND	ND	ND	3.205	ND	ND	ND	ND	ND
Endrin	ND	ND	ND	ND	0.391	ND	ND	0.384	ND	ND	ND	ND	ND
Beta-Endosulfan	ND	ND	ND	ND	ND	ND	ND	0.124	ND	ND	ND	ND	0.003
4,4-DDD	ND	0.674	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,4 DDT	ND	0.093	ND	ND	ND	ND	ND	0.495	ND	ND	ND	ND	ND
2,2,4,4,5,5-Hexachlorobiphenyl	ND	ND	0.634	0.744	ND	ND	ND	2.525	ND	ND	ND	ND	ND
4,4-DDT	ND	ND	ND	ND	ND	ND	ND	87.008	ND	ND	ND	ND	0.001
2,2,3,4,4,5-Hexachlorobiphenyl	ND	1.141	ND	ND	ND	ND	ND	-9.185	4.157	ND	ND	ND	ND
Methoxychlor	ND	ND	ND	ND	ND	ND	ND	-0.346	ND	ND	ND	ND	ND
2,2,3,4,4,5,5-Heptachlorobiphenyl	ND	ND	ND	ND	31	ND	ND	-0.013	ND	ND	ND	ND	ND
Mirex	ND	ND	ND	ND	1.811	ND	ND	-69.224	ND	ND	ND	ND	ND
Chlorpyrifos	ND	ND	ND	ND	0.053	0.974	ND	184.35	316.574	18.809	27.888	32.185	ND
1,2,4-Trichlorobenze	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
1,2,4,5-Tetrachlorob	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Hexachlorobhenzene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Quintozene	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.001

*Sn = Average of 10 samples of rice

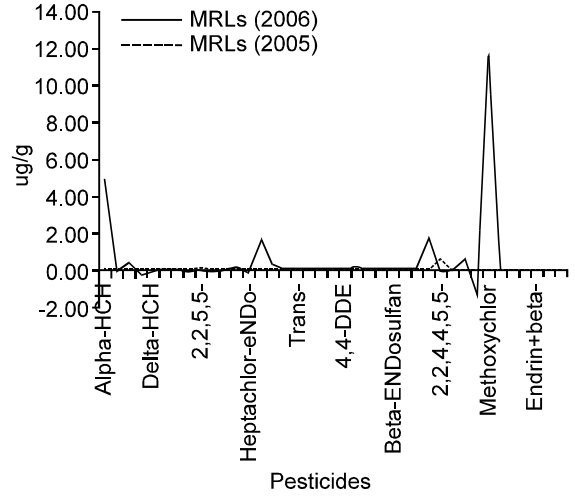

Fig. 3: MRLs calculated during 2005-2006 at mean of 1000 rice samples

may adversely affect country's foreign trade. studies were undertaken with there pesticides popularly used on this crop; viz., diazinon (an organophosphate). Lindane (an organochlorine) and carbaryl (a carbamate). Results obtained indicated that residues of all the pesticides do fall to negligible levels (Nil to 0.6, Nil to 0.46 and Nil to 0.5 ppm respectively) (Hussain, 1992) as well in a variety of fruits and vegetables available at Karachi (Munshi *et al*., 2001).

In conclusion, the OCPs residues in rice have increased sharply during 2006 even being banned for two decades Chlorpyrifos, HCH and DDT were the major detected isomers in rice but still their level is lower than found in rice from other country. It can be concluded that trace OCPs residues in the environment can be bio-accumulated to a final high level in rice. This study indicates that proper presentation is required to stop the propaganda against rice export of Pakistan. A large-scale investigation of OCP residues in different farms in the rice should be launched in order to meet adequately increased demand for Pakistani Banaspati rice in good price and to evaluate the potential health risk to humans.

Conclusion: This study concluded that although all the rice samples were found within the permissible limits suggested in Codex convention in 2003 still one or the two pesticides were found in higher range beyond the permissible limits.

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