



DETERMINATION OF PESTICIDES IN SURFACE AND GROUND WATER USED FOR HUMAN CONSUMPTION IN GUATEMALA

W. KNEDEL, J.C. CHIQUIN, J. PEREZ, S. ROSALES
Universidad del Valle de Guatemala,
Guatemala City, Guatemala

Abstract

A 15 month sampling and analysis programme was carried out to monitor concentrations of 37 targeted organochlorine, organophosphorus and organopyrethroid pesticides in surface and ground water in Guatemala. The 80 sampling points included 4 points in a lake, one point in each of the four lagoons, 10 municipal water systems of major towns, and 62 points along 52 rivers, most of which are located in the southern coast along borders with Mexico and El Salvador, and are one of the most productive areas in the country. The sampling used provided only preliminary information on the pattern of pesticide contamination of surface and ground water. It showed contamination of surface water in Los Esclavos watershed, Motagua river watershed as well as Villalobos, lake Amatitlan and Michatoya river watershed. Cypermethrin was the ubiquitous pesticides in some areas present in concentrations exceeding toxic levels for fish and other aquatic organisms. Several of the other targeted organophosphorus and ECD detectable pesticides were also detected in surface water. Some municipal water samples also had low levels of pesticides.

1. INTRODUCTION

Guatemala is criss-crossed with many rivers which empty into the Pacific and Atlantic oceans. The watersheds receive water from some rivers passing through areas of high agricultural activity, where farmers frequently use a variety of pesticides. In many agricultural areas cotton was grown in the past and heavy use of organochlorine pesticides was practiced. These pesticides are known to persist in the environment and even though they have been banned since 1984 and 1988 their residues may still be found in the environment. Cotton has been replaced with exportable cash crops in many areas, and the persistent organochlorine pesticides are not used any more. However, some of the newer less persistent pesticides such as the organophosphorus compounds are highly toxic to aquatic organisms such as fish. Therefore, in order to protect the human health and the environment it is very important to monitor environmental matrices, especially water. In this project a 15 month sampling programme was undertaken to collect samples of river, lake, lagoon and municipal water samples to monitor residues of organophosphorus, pyrethroid and organochlorine pesticides.

2. METHODS AND MATERIALS

2.1. Sample handling and preparation

Water samples from the rivers were taken from the center of the rivers. Lake and lagoon water samples were taken along the shoreline. All water samples were taken at least 30 cm below the surface. Samples of municipal water systems were taken from public or domestic drinking water faucets. They were transported in amber glass bottles and kept cold with ice-water mixture. All samples were assigned code numbers for identification and traceability. Pesticides were extracted by adding 50g NaCl to 1 L water sample, stirring until dissolved and stirring with 100 mL dichloromethane for 1 hr. In each round of sample extraction a set of seven spiked laboratory water samples were run as control along with every 82 test samples.

The organic phase was separated, dried on 25g sodium sulfate and concentrated in a rotary evaporator at 40 °C and 30 mm Hg to 0.5 mL. The solvent was changed by adding 50 mL petroleum ether to the solution and concentrating to 0.5 mL. Samples were not allowed to concentrate to complete dryness during this process. The final volume was made to 1.0 mL with iso-octane. All organic solvents were pesticide grade quality and sodium sulfate was pesticide reagent grade, 12-60 mesh, heated at 130 °C and stored in a dessicator.

2.2. Preparation of solutions of analytical standards

Analytical standards of the targeted pesticides were purchased from Chem Service (USA) or Poly Science (USA). Solutions of standards were prepared according to their solubility in acetone or iso-octane. The stock solutions were prepared at a concentration of 1 mg/mL. Working solutions of appropriate concentration were prepared by further dilution of the stock solutions. All solutions were stored at cold temperature and control sheets were maintained for all standards and solutions.

2.3. Analysis

An in-house adapted and validated multi-residue analytical method was used for the analysis of water samples from rivers, lakes and municipal water supply systems. Samples were analysed by gas chromatography (GC) so only volatile compounds were detected and only those compounds were identified for which analytical standards were available. A number of compounds were detected but not identified due to the unavailability of analytical standards required to confirm their identity.

2.3.1. Gas chromatography

Samples were analysed by using a Hewlett-Packard Model 5890 Series II gas chromatograph equipped with an electron capture detector (ECD), a flame photometric detector (FPD) and an HP-5 fused silica capillary column. The column was 60 m long, with 0.32 mm ID, and coated with a 0.25 µm thick film of stationary phase (5% phenyl, 95% methyl siloxane). Nitrogen,

TABLE 1. Gas chromatographic retention times (RT) for 37 targeted pesticides in the calibration solution

	µg/ml	t _{RET}		µg/ml	t _{RET}
DDVP	0.4	12.415	γ-CHLORDANE	0.1	43.399
FOSDRIN	0.4	18.862	o,p'-DDE	0.1	43.858
TRIFLURALINE	0.4	27.709	ENDOSULFAN I	0.1	44.535
PHORATE	0.4	28.352	α-CHLORDANE	0.01	44.795
a-HCH	0.03	28.665	DIELDRIN	0.1	
HEXACHLOROBENZENE	0.02	29.162	p,p'-DDE	0.1	
CYGON	0.4	29.535	o,p'-DDD	0.1	47.742
LINDANE	0.3	30.806	ENDRIN	0.1	49.256
TERBUFOS	0.4	31.102	ENDOSULFAN II	0.1	50.267
DIAZINON	0.4	31.857	p,p'-DDD	0.1	51.276
DISYSTON	4.0	32.149	o,p'-DDT	0.01	51.631
CHLOROTHALONIL	0.4	32.657	ETHION	0.8	51.886
PROPANIL	0.4	34.358	ENDOSULFAN SULFATE	0.3	55.176
METHYLPARATHION	0.2	34.985	p,p'-DDT	0.4	55.692
ALDRIN	0.1	35.518	PROPICONAZOLE	0.2	56.062
CHLORPYRIFOS	0.5	37.708	METHOXICHLOR	1.0	64.818
MALATHION	1.0	38.548	GUTHION	4.0	70.146
HEPTACHLOR EPOXIDE	0.1	41.315	CO-RAL	8.0	78.329
			CYPERMETHRIN	4.0	X=83.9

generated from a Claind ANG generator was used as the carrier and make up gas. The gas was passed through a series of traps set up in tandem and these included a Supelco high temperature trap, a charcoal trap, a moisture trap, an oxygen trap and finally an indicating moisture and oxygen trap. The flow rate for the gas was 1.3 mL/min. (measured at a temperature of 100 °C). The GC was operated in split/splitless mode, and the split vent was opened at 35 seconds after the injection. The split ration was adjusted at 1:5. Injections were made manually and by using Grob technique. The temperature programme was as following:

Oven initial temperature	115 °C
Initial hold time	5 min
Ramp 1	3.5 °C/min
Final temperature	210 °C
Final hold time	0.1 min
Ramp A	1.0 °C/min
Final temperature A	230 °C
Final hold time A	17 min
Ramp B	10 °C/min
Final temperature B	270 °C
Final hold time B	25 min

Due to long retention time for some of the pesticides each chromatographic run was for 90 minutes. Quantitation was based on a single point external standard calibration. Compound identification was based on absolute retention time, supported by the simultaneous detection by two detectors. This was accomplished by splitting the column effluent into two capillaries of equal length, each leading to a different detector. As both detectors responded at about the same time, it was possible to get some qualitative information about the compound detected. For example, a peak detected by ECD for an organophosphorus compound can be verified by the presence of a strong FPD signal at the same retention time.

2.3.2. Method performance tests and quality control procedures:

Quality control procedures included analysis of method performance control samples, recalibration of the GC after every 6 samples, use of control charts, and use of control forms for traceability. The calibration solution of 37 targeted pesticides was injected in the GC twice in the morning, the first for priming the instrument. During each round of analysis (80 samples) nine injections of the calibration solution were made and the results plotted on a control chart. This was done to verify that the analytical system was in control.

During the processing and analysis of field samples a fortified sample was prepared, extracted and analysed along with the field samples. The fortified sample was prepared by spiking laboratory water with acetone solution of the targeted pesticides. The recovery of extraction of the pesticides would give an estimate of the efficiency and reproducibility of the method.

3. RESULTS AND DISCUSSION

3.1. Quality control

The quality control chart for the results of the quantitative analysis of calibration solution of pesticides indicated that the analyses were repeatable as the results were within $\pm 2 \sigma$ (standard deviation of the mean) for the pesticides in the calibration solutions used during the analysis of an entire sampling round which comprised of 80 samples. Quality control chart for GC retention time of pesticides in the calibration solution also verified repeatability of analyses.

The control charts verified that the analytical system was statistically under control quantitatively as well as qualitatively.

Figure 1 shows an example of a chromatogram with mirrored signals from the ECD and the FPD when a sample containing chlorpyrifos, diazinon and dimethoate was injected. Figure 2 shows chromatograms of calibration solutions of the 37 targeted pesticides detected by (a) ECD and (b) FPD. The retention times (RTs) for some pesticides were too close, for example α -endosulfan (44.535 min) and α -chlordane (44.795 min) as well as dieldrin (46.869 min) and p,p-DDE (47.033 min). The resolution of peaks for dieldrin and p,p-DDE was used as an indicator to test the performance of the column. The data on the recovery of the pesticides from the fortified water sample are shown in Table 2. It shows that the recovery of most pesticides was in the acceptable range (70-120%) with low CV (coefficient of variance) values. The exceptions were azinphos methyl and chlorothalonil. Azinphos methyl seemed to have an interfering compound co-eluting with it and it resulted in a false positive recovery value. Recovery of chlorothalonil, on the other hand, was very low, and the reason for this remained unknown. It may be the result of loss of the pesticide due to adsorption on septum in the sample vial cap.

3.2. Trends of pesticide contamination of rivers

The sampling frequency was too low to predict precise trends of pesticide residues in river, lake or municipal waters. Analysis of composite samples taken over a 24 h period with increased frequency would have given a more precise estimate of the levels and scale of pesticide contamination in Guatemalan waters. The sampling programme undertaken, therefore, gives at best only a rough idea about the extent or frequency of pesticide contamination. The results should, therefore, be taken as a general survey of the waters for pesticide contamination.

3.2.1. Pesticide residues in Los Esclavos watershed

Los Esclavos water shed receives water from three other rivers: Panal, Amapa and Utapa. The watershed lies in a region of heavy agricultural activity, with coffee as the main crop. Water samples were taken at sampling point Esclavos 1, located downstream from the merger of the three rivers with Esclavos, and sampling point Esclavos 2, located upstream. Water samples from sampling point Esclavos 1 contained cypermethrin (0.95 $\mu\text{g/L}$), γ -chlordane (0.17 $\mu\text{g/L}$), endosulfan (0.06 $\mu\text{g/L}$) and trace amount of coumaphos. Concentrations of pesticides varied from one sampling round to the next and the pattern of pesticide distribution was not consistent. The highest levels of pesticides were found in water samples taken during the second and third round of sampling. The concentration of cypermethrin in these water samples is quite high. This concentration is higher than that considered toxic to some of the fish and other aquatic organisms.

3.2.2. Pesticide residues in Motagua river

The Motagua river is one of the largest rivers in Guatemala, crossing from west to east and flowing into the Atlantic ocean. The Motagua river watershed receives water from 20 rivers of different sizes, some passing through agricultural areas. Water samples were taken at four sampling points. Residues of organophosphorus pesticides were detected more frequently and at higher concentrations than the other pesticides in these samples. This may be because of tobacco and melon cultivation in this area. Diazinon, with a mean concentration of 0.1 mg/L, was found in all water samples analysed. The other pesticides found included azinphos methyl (1.3 $\mu\text{g/L}$), disulfoton (1.0 $\mu\text{g/L}$ at point 3 and 1.4 $\mu\text{g/L}$ at point 4), malathion (between 0.25-

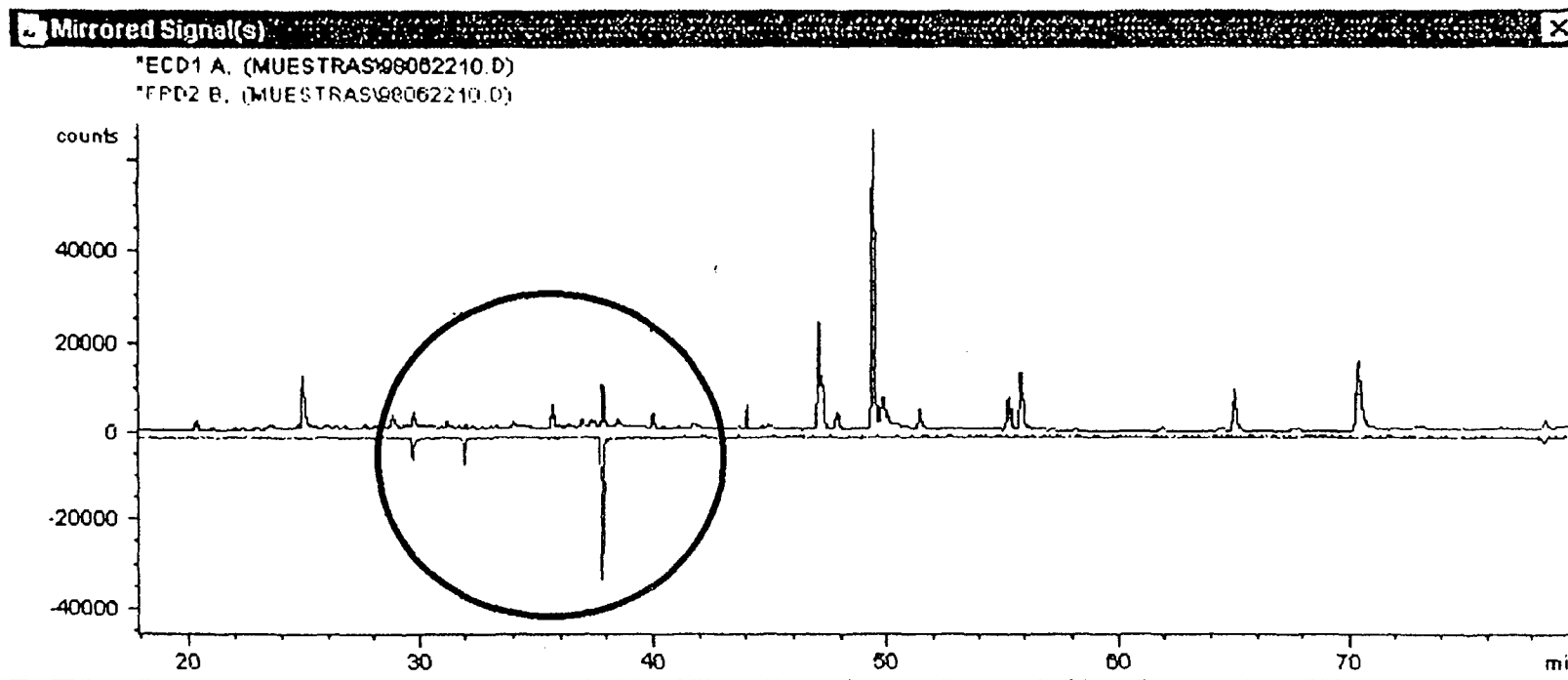


Fig. 1. GC chromatogram showing mirrored signals of three pesticides in a water sample simultaneously detected by ECD and FPD.

TABLE 2. Concentration of 37 targeted pesticides determined in a water sample from the field and their recovery (%) from three fortified laboratory water samples

COMPOUND	98071711	fortn-1	fortn-2	fortn-3	% REC	% REC	% REC	MEAN	STD DEV	Coef. Var.
DDVP	24343	28480	29352	30853	116.99	120.58	126.74	121.44	4.93	4.06
FOSDRIN	21732	22234	23049	21220	102.31	106.06	97.64	102.00	4.22	4.13
TRIFLURALINE	44498	52587	57742	53638	118.18	129.76	120.54	122.83	6.12	4.98
PHORATE	8671	11262	12543	11157	129.88	144.65	128.67	134.40	8.90	6.62
α -HCH	29730	31903	33857	31701	107.31	113.88	106.63	109.27	4.01	3.67
HEXACHLOROBENZENE	25675	27827	27288	28727	108.38	106.28	111.89	108.85	2.83	2.60
CYGON	32965	28782	32303	26240	87.31	97.99	79.60	88.30	9.24	10.46
LINDANE	221939	237332	264262	237630	106.94	119.07	107.07	111.03	6.97	6.28
TERBUFOS	12693	11865	12595	11518	93.48	99.23	90.74	94.48	4.33	4.58
DIAZINON	16421	14522	15825	14994	88.44	96.37	91.31	92.04	4.02	4.36
DISYSTON	9842	9267	9770	8604	94.16	99.27	87.42	93.62	5.94	6.35
CHLOROTHALONIL	44405	2250	1209	2731	5.07	2.72	6.15	4.65	1.75	37.71
PROPANIL	128421	168234	177676	158992	131.00	138.35	123.81	131.05	7.27	5.55
M-PARATHION	76064	67331	73649	68537	88.52	96.83	90.10	91.82	4.41	4.80
HEPTACHLOR	48771	46096	47957	50775	94.52	98.33	104.11	98.99	4.83	4.88
CHLORPYRIFOS	59870	66715	69611	61890	111.43	116.27	103.37	110.36	6.51	5.90
ALDRIN	48664	44721	44329	45638	91.90	91.09	93.78	92.26	1.38	1.50
MALATHION	110259	109684	118597	107564	99.48	107.56	97.56	101.53	5.31	5.23
EPOX. HEPTACI	51831	46396	46189	48868	89.51	89.11	94.28	90.97	2.88	3.16
γ -CHLORDANE	43450	36264	41278	42086	83.46	95.00	96.86	91.77	7.26	7.91
O,P'DDE	52963	40631	45052	53563	76.72	85.06	101.13	87.64	12.41	14.16
ENDOSULFAN I	52044	45984	51171	49379	88.36	98.32	94.88	93.85	5.06	5.39
α -CHLORDANE	147202	116444	128945	136118	79.10	87.60	92.47	86.39	6.76	7.83
DIELDRIN	139420	110682	125907	137022	79.39	90.31	98.28	89.33	9.48	10.62
P,P'DDE	49208	44773	47005	45461	90.99	95.52	92.39	92.97	2.32	2.50
O,P;DDD	58133	50199	53737	56884	86.35	92.44	97.85	92.21	5.75	6.24
ENDRIN	72288	69760	76930	73662	96.50	106.42	101.90	101.61	4.97	4.89
ENDOSULFAN II	42152	39224	44410	39915	93.05	105.36	94.69	97.70	6.68	6.84
P,P'DDD	87223	60734	66121	69133	69.63	75.81	79.26	74.90	4.88	6.51
O,P'DDT	21952	21563	24149	28494	98.23	110.01	129.80	112.68	15.96	14.16
EHTION	96222	83216	90726	90851	86.48	94.29	94.42	91.73	4.54	4.95
SULF. ENDO	80239	80717	87760	76705	100.60	109.37	95.60	101.85	6.97	6.85
P,P;DDT	63676	52668	57685	63484	82.71	90.59	99.70	91.00	8.50	9.34
METHOXICHLOR	131156	164059	177778	173100	125.09	135.55	131.98	130.87	5.32	4.06
GUTHION	147966	739610	713638	500405	499.85	482.30	338.19	440.11	88.70	20.15
CO-RAL	145182	135407	140630	129746	93.27	96.86	89.37	93.17	3.75	4.02
CYPERMETHIRIN	497537	385100	427138	432557	77.40	85.85	86.94	83.40	5.22	6.26

3.2.3. Pesticide residues in the Villalobos river, lake Amatitlan and Michatoya river watershed

In this watershed the concentrations found were very consistent over the entire period of sampling. This fact distinguishes this watershed from those discussed in 3.2.1. and 3.2.2. It is noteworthy that Villalobos river receives effluent from the city of Guatemala and the associated industry as well as the surrounding agricultural areas. The river receives upto 60% of the untreated effluent discharge from the city including domestic and industrial sewage. This may be the reason for the presence of the pesticide residues in the river water throughout the year. Water samples from lake Amatitlan showed consistently low pesticide residues. This may be because the lake receives approximately 60% of its water from the underground

sources. Relatively higher concentration of pesticides were found in samples from Michatoya river, which may be due to intensive farming activity along this river.

In general, higher levels of pesticide residues were detected in the water from the southwestern region, where in some cases total pesticide residues reached a concentration of the ECD and FPD detectable pesticides of 2 to 3.5 µg/L, followed by northeastern region. It should be noted that the total pesticide concentrations referred to here do not include those pesticides which are not detectable by GC-ECD and FPD. Water in the southeastern region had on the average the lowest level of pesticide contamination.

3.2.4. Pesticide residues in water from lake Amatitlan and the lagoons

Analysis of water samples from lake Amatitlan indicated low level of contamination with the ECD and FPD detectable pesticides. The total concentration of ECD and FPD detectable pesticides did not exceed 0.35 µg/L. This is important to know, because lake Amatitlan water will be used in the future as a reservoir to meet the needs of the growing population of Guatemala city. The residues in the lagoons were very low.

3.2.5. Pesticide residues in municipal water systems

The drinking water quality in 8 of the 10 municipalities, in terms of residues of organophosphates, complied even with the European legislation for potable water quality criteria which limits total pesticide residues to a maximum of 0.5 µg/L. However, in the municipal water from Amatitlan municipality the total pesticide concentration, including EC detectable and organophosphates, was 0.83 µg/L. Similarly, the municipal water samples from Villa Canales contained combined residues of EC detectable pesticides at 0.9 µg/L. High levels of cypermethrin were also detected in the municipal water distribution system of the cities of El Jicaró, Usumatlan and Estanzuela. These were above the 0.5 µg/L limit for the sum of pesticides in potable water allowed under European legislation.

3.2.6. Relative frequency of ECD detectable pesticide residues in water

Results of the analysis of water samples taken during round 2 of sampling and analysed by GC-ECD showed a number of pesticides to be detected quite frequently. These included O,P-DDT in 12% of the samples, cypermethrin in 11%, propanil in 10%, endrin and heptachlor epoxide each in 9%, O,P-DDE in 8%, lindane in 7%, chlorothalonil, and α -HCH each in 6%, trifluralin in 5%, HCH in 4%, aldrin, α -chlordane and methoxychlor each in 2% and heptachlor, γ -chlordane, p,p-DDE, endosulfan sulfate and p,p-DDT each in 1% of the samples. Pesticides detected in samples with the frequency of less than 1% included α - and β -endosulfan, dieldrin, o,p-DDD and p,p-DDD.

It is obvious that most of these compounds are old organochlorine pesticides which have been banned under Guatemalan law (DDT since 1984 and the rest since 1988). They have a very low water solubility, yet their presence in the environment is ubiquitous. This can be explained by assuming their presence in the soil and sediment, which is quite likely because, before the persistent organochlorine pesticides were banned, they were heavily used by cotton growers. It is likely that residues are now slowly partitioning from soil/sediment into water. Since many cotton growers are now cultivating exportable cash crops, they are showing increasing interest in having the soil tested for residues of the banned persistent pesticides prior to cultivation of new crops.

3.2.7. Relative frequency of residues of organophosphorus pesticides in water

Results of the analysis of water samples by GC-FPD showed the frequent detection of some of the organophosphorus pesticides. These included coumaphos in 34% of the samples, diazinon in 20%, chlorpyrifos in 12%, dimethoate in 8%, ethion, malathion, methyl parathion and mevinphos each in 5%, dichlorvos in 3%, disulfoton in 2% and azinphos methyl in 1% of the water samples analysed.

4. CONCLUSIONS

Widespread contamination of surface water in rivers and lakes with ECD detectable and organophosphorus pesticides was found in a pesticide monitoring programme carried during 1997 and 1998. Cypermethrin was ubiquitous contaminant of river water and was also found in some of the municipal water supplies. It was detected in 11% of all the samples analysed and in some samples its concentration was as high as 0.90 - 0.95 $\mu\text{g/L}$ which is greater than what is considered toxic to some fish and aquatic organisms. It is also in excess of the maximum limit (0.5 $\mu\text{g/L}$) for sum of pesticides set under European drinking water quality legislation. Several organochlorine pesticides were also detected in water samples, some as frequently as upto 12% of the samples analysed. The compounds most frequently detected included aldrin, α -chlordane, γ -chlordane, o,p-DDE, p,p-DDE, o,p-DDT, p,p-DDT, endosulfan sulfate, endrin, HCH, heptachlor epoxide and methoxychlor. Other pesticides most frequently detected in the water samples included chlorothalonil, trifluralin, propanil, and organophosphorus insecticides azinphos methyl, chlorpyrifos, coumaphos, diazinon, dimethoate, disulfoton, malathion, methyl parathion and mevinphos.

NEXT PAGE(S)
left BLANK