

SOLID PHASE EXTRACTION OF HALOGENATED, ORGANOPHOSPHORUS AND NITROGEN-CONTAINING PESTICIDES FROM RIVER WATER SAMPLES. ANALYTICAL QUALITY PARAMETERS.

MARIA E. BAEZ, SOLEDAD NAVARRO AND ALEJANDRA SOLAR

Departamento de Química Inorgánica y Analítica, Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Casilla 233, Santiago, Chile.

SUMMARY

A study of matrix effects arising from river water samples using C18 SPE columns in the determination of 38 pesticides having different chemical properties is presented. Recoveries from river water samples of different origin and the influence of prefiltration step, pH and ionic strength were tested. A calibration equation for the extraction method was calculated by using the statistical method of linear regression, the independent variable being the amount of analyte added and the dependent variable, the amount of recovered analyte. Extractions were carried out in waters spiked with 65 to 1600 ng L⁻¹ of organophosphorus and nitrogen-containing pesticides, and with 12.5 to 320 ng L⁻¹ of halogenated pesticides. Only trifluralin, captan, aldrin, tri-allate, α -BHC, γ -BHC, and azinphos-methyl behavior could not be described through a linear relationship due to low precision and, possibly, to interferences caused by the matrix sample. Linearity, analytical sensitivity, precision and limit of detection were established for 31 compounds. Slope values in the regression equation ranged from 0.68 to 0.98, the exception being amitraz (0.43), dieldrin (0.51), and 4,4' DDT (0.58), which accounted for losses produced in the extraction process. Systematic errors were detected for most of the compounds and they could be corrected by using the calibration data obtained for the whole analytical process. The detection limits established through the model in most of the cases were lower than the maximum allowed limit for waters by the European Union (100 ng L⁻¹), ranging from 7 to 21 ng L⁻¹ for pesticides determined by GC-ECD, and from 20 to 102 ng L⁻¹ (except triadimefon, 220), for those determined by GC-NPD.

KEY WORDS: Solid phase extraction, pesticide residue analysis, river water, matrix effects, performance characteristics.

RESUMEN

Se estudia el efecto de matriz en la determinación de 38 plaguicidas pertenecientes a diferentes clases químicas en muestras de agua de río. Se establecieron los porcentajes de recuperación de éstos desde muestras de distinto origen y se evaluó la influencia del pH, fuerza iónica y de la etapa de pre-filtración. Se calculó una ecuación de calibración para el método de extracción utilizando el modelo estadístico de regresión lineal, anteriormente aplicado en muestras de agua ultrapura. La variable independiente fue la cantidad de analito agregada y la dependiente fue la cantidad recuperada. Las aguas fueron contaminadas en concentraciones que variaron entre 65 y 1600 ng L⁻¹

*To whom correspondence should be addressed.

para los plaguicidas organofosforados y nitrogenados y entre 12,5 y 320 ng L⁻¹ para los halogenados. Entre los compuestos estudiados, el comportamiento de trifluralin, captan, aldrin, tri-allate, α -BHC, γ -BHC y asinphos-methyl no puede ser descrito a través de una relación lineal, debido a una baja precisión y, posiblemente, a interferencias causadas por la matriz. Se estableció la linealidad, sensibilidad, precisión y límite de detección para 31 compuestos. Los valores de la pendiente de la ecuación de regresión varían entre 0,68 y 0,98, excepto en el caso de amitraz (0,43), dieldrin (0,51) y 4,4' DDT (0,58), los que dan cuenta de pérdidas producidas en el proceso de extracción. Se detectaron errores sistemáticos para la mayoría de los compuestos, los que pueden ser corregidos usando los datos de calibración del proceso analítico total. Los límites de detección son menores al límite máximo permitido para aguas por la Unión Europea (100 ng L⁻¹), fluctuando entre 7 y 21 ng L⁻¹ para los plaguicidas determinados por GC-ECD y entre 20 y 102 ng L⁻¹ (excepto triadimefon, 220), para aquéllos determinados por GC-NPD.

PALABRAS CLAVES: Extracción en fase sólida, análisis multiresiduos de pesticidas, efectos de matriz, agua de río, parámetros analíticos.

INTRODUCTION

Solid phase extraction (SPE) mainly on octadecylsilane (ODS), with membrane extraction disks or cartridges with the alkyl-bonded silica packing has been widely used as an isolation and concentration tool for multiresidue analysis of organic compounds in environmental water samples¹⁻¹⁹. In spite of this wide application, losses of analyte or matrix effects are frequently mentioned.

Previously, a critical study was carried out of a SPE method for the determination of 23 halogenated pesticides and 21 organophosphorus and nitrogen-containing pesticides determined by gas chromatography with electron capture (GC-ECD) and nitrogen-phosphorus detection (GC-NPD), mainly in ultrapure water samples^{15,16}. Several interferences were established, and the effect of minor changes in conditions such as sample volume or flow rate was observed on recoveries in this class of matrix. However, the general procedure under study was considered appropriate for most of the pesticides, except for several triazines and triazole-derived compounds, amitraz, dimethoate and captan, affected by changes in extraction conditions.

The aim of this study was to evaluate matrix effects arising from surface waters for the developed method and to estimate its performance characteristics for the determination of the pesticides above mentioned. River water samples of different origin were spiked with the compounds under study. On the other hand, performance characteristics were estimated using the statistical method of linear regression²⁰⁻²¹. This method was tested with a Mapocho river sample. To this end, recoveries from the real water sample spiked with pesticides mixtures at four concentration levels were determined, the independent and dependent variables being the added and recovered amounts, respectively. These levels included the maximum pesticide residue to be found in drinking water according to European Community (EC) regulations limits (0.1 μ g/L). The statistical model of linear regression has been employed for the evaluation of total analytical systems including SPE associated with chromatographic methods to detect pesticides residues in ultrapure water^{22,23} and environmental waters^{6,12}. In this work, linearity, analytical sensitivity, precision, and limit of detection (LOD) for 31 compound were obtained, and a calibration with spiked water samples treated as the real samples is proposed, the aim being to reduce quantitation errors caused by the matrix effect.

EXPERIMENTAL

Chemical and reagents

The pesticides used had a purity \geq 99% unless otherwise stated, and they were: alachlor, aldrin, atrazine, azinphos-methyl, dieldrin, diazinon (98%), endrin, ethoprophos, 4,4' DDE, 4,4' DDD, 4,4' DDT, malathion (95%), methoxychlor, methidathion, napropamide, parathion-methyl, prometryn, propazine, trifluralin (95%), tri-allate, endosulfan I and II (mix of isomers, 96%), BHC (mix of isomers 30% α , 30% β and 40% γ) (all from Polyscience), amitraz, chlorpyrifos, dichlorvos, mevinphos, phosmet, tetradifon, triadimefon, penconazole, simazine and vinclozolin (Pestanal®, Riedel de Häen), captan and propiconazole

(96%, mix of two isomers, Chem Service).

All solvents used were residue analysis grade (Merck, J.T. Baker). Pentachloronitrobenzene (PCNB) and triphenyl phosphate (TPP) from Aldrich were used as internal standards for chromatographic determinations.

Stock solutions were prepared in acetone at 1 g L^{-1} except aldrin, endrin, dieldrin, endosulfan, 4,4' DDE, 4,4' DDD, methoxychlor, dieldrin and PCNB, which were prepared in hexane; and azinphos-methyl, which was prepared in toluene. Working standard solutions for GC analysis were diluted with hexane and with methanol for sample spikes.

Water used

Water samples were collected from the Teno, Lontue, Claro and Maule rivers in the VII Region of Chile, and from the Mapocho river in the Metropolitan Region. The first four ones were used to study matrix effects only on SPE of organophosphorus, triazines and triazole-derived pesticides. The Mapocho river sample was used to establish the analytical quality parameters of the method for all the pesticides under study. Total suspended matter, pH and conductivity of these samples were determined.

Chromatographic conditions

GC-ECD

A Hewlett Packard 5890 Series II gas chromatograph equipped with split/splitless injector, electron-capture detector, HP 3395 integrator and HP-5 capillary column (30 m x 0.32 mm i.d., 0.25 μm film thickness) was used. Helium and nitrogen were selected as carrier gas and auxiliary gas, respectively. Determinations were carried out under the following conditions: injector temperature, 250°C; detector temperature 300°C; column temperature program, 160°C for 1 min, increase from 160 to 210°C at 2°/min, hold at 210°C for 2 min; and increase to 250°C at 15°/min, hold for 6 min. A 1 μL volume of the sample was injected in the split mode (split ratio, 1:15).

GC-NPD

A Shimadzu GC-14B gas chromatograph equipped with a split/splitless injector, a nitrogen-phosphorus detector (NPD) FTD-14 and PTE 5TM capillary column (30 m x 0.32 mm i.d., 0.25 μm film thickness) was used. Chromatography data acquisition and processing were accomplished with a Shimadzu data processing unit C-R7A Chromatopac. The GC operating conditions were the following: splitless injector temperature, 250°C; injector purge activation time, 2 min; NPD temperature, 280°C. The oven temperature program used was as follows; 60°C for 2 min; increase from 60 to 140°C at 30°C/min, hold at 140°C for 2 min; increase to 190°C at 3°C/min, hold at 190°C for 2 min; and increase to 280°C at 20°C/min, hold at 280°C for 5 min. Helium was used as the carrier gas and 1 μL volume of the sample was injected.

Solid phase extraction

The method used to condition cartridges (Octadecyl (C₁₈) of 500 mg, J.T. Baker) and to process samples was the same as that used to evaluate SPE in ultrapure water and it has been described in detail elsewhere^{15,16}. Briefly, 1 L of water spiked at different levels was passed through the column under vacuum in order to obtain a flow rate of 16 mL/min; pesticides were eluted by successive passing of ethyl acetate and iso-octane. The eluate was dried on 1 g anhydrous sodium sulfate supported in an empty cartridge, and washed with an additional 0.5 mL of each solvent. Extracts were evaporated to dryness under a stream of nitrogen and residues were redissolved in 1 mL hexane. 50 μL of TPP at 6 mg L^{-1} or PCNB at 1 mg L^{-1} were added for GC-NPD and GC-ECD determination, respectively.

Recovery tests

Matrix effects were studied by spiking in duplicate 1 L of the river water samples with a mixture of organophosphorus, triazine and triazole-derived pesticides, napropamide and amitraz, at the following concentration levels: ethoprophos and dichlorvos, 150 ng L^{-1} ; chlorpyrifos and methidathion, 200 ng L^{-1} ;

azinphos-methyl, diazinon, mevinphos, parathion-methyl and malathion, 300 ng L⁻¹; simazine and propiconazole I, 400 ng L⁻¹; atrazine, propazine, and prometryn, 500 ng L⁻¹; penconazole and propiconazole II, 600 ng L⁻¹; triadimefon and napropamide 800 ng L⁻¹. The concentration levels of halogenated pesticides were α -BHC and δ -BHC 30 ng L⁻¹; γ -BHC 40 ng L⁻¹; aldrin, dieldrin, endosulfan I and II, 25 ng L⁻¹; trifluralin, vinclozolin, chlorpyrifos, tetradifon, methoxychlor, endrin, 4,4' DDE, 4,4' DDD and 4,4' DDT 50 ng L⁻¹, and tri-allate 70 ng L⁻¹. Unspiked samples from the same sources were also extracted to check for background interferences. A recovery test with ultrapure water spiked at the same level was used to evaluate the prefiltration effect, and blank tests for columns used in the present study were constantly performed to evaluate the elution of some impurities generated by extraction materials.

To calibrate the extraction method, water samples were spiked at four concentration levels, depending on the pesticide under study, between 65 and 2000 ng L⁻¹ for those pesticides determined by GC-NPD (Table II), and between 12.5 and 300 ng L⁻¹ for those determined by GC-ECD (Table III). The concentrations used to spike waters were in the ratios 1, 2, 3, and 4. Each level was repeated four times for those pesticides determined by GC-NPD and three times for those determined by GC-ECD, and recoveries were calculated by comparing with area ratios obtained for the reference standard at the same concentration level and prepared at the same time as the sample extraction. Surface water samples were always filtered through a 0.45 μ m regenerated cellulose filter (Sartorius AG) after the addition of the spiking solution to eliminate particulate matter.

Calculation of performance characteristics of the SPE method

Linearity ($1-S_b/b$), sensitivity ($S_{y/x}/b$), and limit of detection ($3(S_{y/x}/b)[n-2/n-1]^{1/2}$) of each compound were calculated from data sets obtained for the four concentration levels above mentioned. The equation established was $Y = a + bX$, where Y was the amount of recovered analyte; X, the amount added; $S_{y/x}$ and S_b are the regression standard deviation and the slope standard deviation, respectively.

Equations used to define precision [$S_c(\%)$] were as follows:

$$S_c = [1/N + 1/n + (Y_u - Y)^2/b^2 \sum(X_i - X)^2]^{1/2} S_{y/x}/b$$

$$S_r(C) = [S_c/C] 100$$

where n = number of pairs of points

N = number of Y_u determinations

Y_u = recovered amount at the corresponding concentration level

S_c = concentration standard deviation^{24,25)}

RESULTS AND DISCUSSION

Table I shows the results of recoveries obtained on different river water samples for organophosphorus and nitrogen-containing pesticides. First, a blank of each sample was analyzed in order to see whether different peaks appeared in the chromatogram at the same retention times as the pesticides under study. Several compounds were detected: at the same time as dichlorvos in sample 1, ethoprophos and diazinon in sample 3, and atrazine in samples 3 and 4, but signals were < 4% of the corresponding standard. The prefiltration step, studied with ultrapure water, led only to lower recoveries of chlorpyrifos (81%). Losses of dichlorvos, mevinphos, prometryn, penconazole, propiconazole and amitraz for this matrix, under the general extraction conditions without the prefiltration step, had been described in a previous study¹⁶⁾.

Before the study of matrix effects, pH and ionic strength effects were tested on ultrapure and river water samples. The percentage of recovery of simazine, atrazine, propazine, dichlorvos, mevinphos, malathion, chlorpyrifos, triadimefon and napropamide at pH 9 was lower than that obtained at pH 4, while prometryn, penconazole and the first eluting isomer of propiconazole were better recovered (70-80%), both situations with ultrapure water samples. The organophosphorus pesticides mentioned above are hydrolyzed in basic media whereas napropamide, triazines and triazoles under study are reported as stable compounds, so for these compounds a real effect of this factor was attributed. An increase in the ionic strength only led to increased recovery of prometryn. These effects were not observed on river water samples. Napropamide and prometryn were recovered at pH 4 and 9, and the other triazines were well recovered at pH 9. Data from different river water samples show positive or negative matrix influence,

TABLE I. Mean recoveries (%) obtained on different water samples. Organophosphorus, triazine and triazole-derived pesticides.

Sample	1	2	3	4	Filtered Ultrapure Water
pH	7.0	8.5	8.0	9.0	
Conductivity ($\mu\text{s}/\text{cm}$)	486	204	225	4720	
Suspended solids (mg/L)	99	25	3	10	
Dichlorvos	74	102	94	62	81
Mevinphos	80	109	93	89	62
Ethoprophos	81	96	96	81	91
Diazinon	86	102	87	89	87
Parathion-methyl	82	96	87	81	86
Malathion	88	89	91	86	92
Chlorpyrifos	81	75	60	81	81
Methidathion	92	101	95	93	92
Azinphos-methyl	99	104	105	110	94
Simazine	88	102	100	97	89
Atrazine	87	98	99	97	97
Propazine	88	98	96	94	93
Prometryn	84	93	92	92	71
Triadimefon	92	94	90	94	89
Penconazole	105	121	115	131	52
Propiconazole I	101	115	112	123	60
Propiconazole II	95	104	104	107	72
Napropamide	88	92	89	92	91
Amitraz	7	10	14	30	0

regardless of pH, mainly for dichlorvos, mevinphos, ethoprophos, chlorpyrifos, penconazole and propiconazole. For example, matrix 1 and 4 with pH 7 and 9, respectively, show lower recoveries than those obtained with the other matrices for dichlorvos and parathion-methyl while chlorpyrifos is better recovered. On the other hand, high recoveries (between 95 and 130%) were obtained for penconazole and the two isomers of propiconazole. In previous studies with ultrapure waters [15, 16] for these compounds we obtained response enhancement ratios relative to standards prepared in a matrix-free solvent in excess of 100%, mainly at the lowest concentration levels under study. This phenomenon was attributed to the co-elution of some compounds from the cartridges which would have an influence increasing the transference of the analytes from the injection port to the chromatographic column by either reducing thermal degradation or by blocking active sites within the injector. This effect or a similar one produced by natural compounds from the water matrix would be present. Severe matrix effects explained by this phenomenon have been reported for more complex matrices^{26,27} mainly for polar or less stable compounds, which has involved an additional clean-up step²⁷. Losses of amitraz were always obtained either with ultrapure water (the pH adjusted to 9) or river water; it is unstable at pH < 7 and it can be considered as a fat soluble compound ($\log K_{ow} = 5.5$), and poor recoveries could be explained by irreversible adsorption of the analyte on the sorbent.

Matrix effects for the halogenated compounds were evaluated only on the Mapocho River sample and the influence of the prefiltration step, pH, and ionic strength was also tested. The prefiltration step led to lower recoveries of aldrin (30%), dieldrin (66%), 4,4' DDT (76%), tri-allate and captan (71%). Captan and vinclozolin are unstable at basic pH; they were poorly recovered at pH 9.0 with ultrapure and river water samples while a positive effect of the matrix (pH 7.9) was observed only for vinclozolin (71%). Signals from the matrix were observed at the same retention time as trifluralin, α -BHC, γ -BHC and tri-allate. In spite of this effect, remarkable losses were produced for these compounds. No significant effects were obtained for the halogenated compounds under study with an increase in the ionic strength of the water sample.

Variable data for solid-phase extraction recoveries of pesticides belonging to different chemical classes have been reported in the literature for environmental water samples, using octadecylsilane as

the stationary phase either on cartridges or extraction disks. So, triazine compounds (atrazine, simazine, prometryn and cianazine) have been recovered from distilled and underground water samples at relatively high levels compared with river, lake and marine waters (40-80%), the main problem being the decreased recoveries of prometryn from marine and lake waters; organophosphorus compounds have shown a similar behavior¹¹⁾. Propazine and prometryn have the 2' position of the heterocycle ring occupied by a chlorine atom and a methylthio group, respectively; this structural change could explain a different retention behavior on the reversed-phase C18. On the other hand, atrazine, simazine, malathion, azinphos methyl, chlorpyrifos, diazinon or malathion have been well recovered (80-115%) from ground water, stream, runoff, river and lough water^{10,14,17,18)}. Low recoveries have been reported for river water containing naturally dissolved humic acids and this has been attributed to their capability to enhance the solubility of organic pollutants by adsorbing part of them or blocking the active sites of the adsorbents^{5,19)}. Hydrophobic pesticides (log $K_{ow} \approx 6$) show a strong tendency to be adsorbed onto the particulate matter and onto the filter^{18,20)}, prefiltering would therefore yield lower recoveries for this class of compounds in real environmental waters.

Values that define the equation of the calibration curve for the whole extraction method (intercept a , and slope b) and the corresponding error estimators (S_a , S_b and $S_{Y/X}$) for 31 compounds are presented in Tables 2 and 3. Data from ultrapure water²³⁾ have also been included. Only pesticides which presented a similar behavior at the four levels of concentrations under study were considered, so analysis of trifluralin, captan, aldrin, tri-allate, α -BHC and γ -BHC was not performed. Azinphos-methyl presented a behavior better described through a logarithmic equation. Figure 1 shows the calibration lines of diazinon and azinphos-methyl at the same concentration range, and the corresponding equations. For those compounds determined by GC-NPD, the slopes obtained with river water are higher than 0.68 (except amitraz, 0.43); intercepts range from -6.1 to 35, except for triazole-derived compounds, mevinphos, napropamide and amitraz. The same compounds show the highest imprecisions in the estimation of the regression parameters. These high standard deviations can be attributed to the severe losses of amitraz, to recoveries at the lowest concentration level in excess of 100% of mevinphos, propiconazole and penconazole, and to the high relative standard deviation for recoveries at the lowest concentration level of napropamide. In addition, triazolic compounds, napropamide and amitraz are not detected very sensitively by GC-NPD, so the extent of working ranges was broader than that employed with organophosphorus pesticides. When data are compared with those obtained with ultrapure water, error estimators are always lower, except for napropamide and dichlorvos. For those compounds determined by GC-ECD, slopes with river water are higher than 0.80 except for dieldrin, 4,4' DDT; 4,4' DDD and chlorpyrifos (0.51, 0.57, 0.79 and 0.77); the intercepts ranging from -5.0 to 5.0. Tetradifon and alachlor show the highest imprecisions.

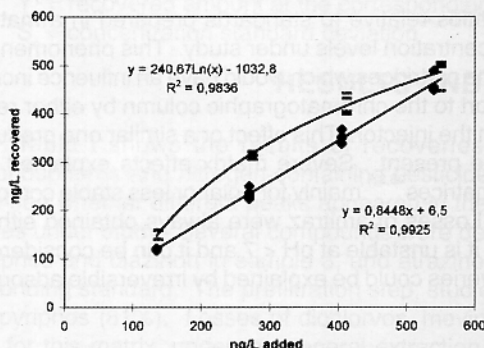


FIG. 1. Diazinon (♦) and azinphos-methyl (-) behavior during the whole extraction method.

When the slope and intercept values are 1 and zero, respectively, systematic errors will not be present^{24,25)}. S_b , S_a and the t-critical factor corresponding to $\alpha = 0.05$ with $n-2$ degrees of freedom were employed to calculate the confidence range of slope and intercept for each compound in order to test whether 1 and zero values were included within the respective ranges ($\pm t S$). Systematic errors were detected for all the compounds under study, except tetradifon. The higher precision in the estimation of regression parameters of halogenated compounds leads to the detection of systematic errors both with ultrapure and river water, whereas for N- and P-containing compounds, with ultrapure water, are detected only for dichlorvos, ethoprophos, simazine, napropamide and amitraz. Calibrations with spiked river waters subjected to the same extraction treatment as real samples could be used to reduce the quantitation errors caused by either the general extraction conditions or matrix effects arising from them.

TABLE II. Calibration data set ($Y = a + bX$) for river and ultrapure water samples extraction method. Organophosphorus, triazine, and triazole-derived pesticides.

	Concentration range in fortified water (ng/L) ¹	a	S _a	b	S _b	S _{Y/X}
Dichlorvos	80-320	-4.7	9.2	0.681	0.042	15
	100-750	0.7	11.7	0.829	0.024	24
Mevinphos	140-560	63.8	11.8	0.708	0.031	19
Ethoprophos	65-260	4.4	3.5	0.837	0.020	5.7
	100-750	-14.5	11.2	0.971	0.023	22.7
Diazinon	140-560	6.5	7.3	0.845	0.020	11.9
	100-750	-16.6	13.2	0.990	0.027	26.8
Parathion-methyl	130-520	6.7	7.1	0.828	0.020	11.6
	100-750	-20.2	13.3	1.054	0.028	27.0
Malathion	150-600	7.5	5.1	0.863	0.013	8.3
	100-750	12.8	13.0	0.981	0.027	26.5
Chlorpyrifos	110-440	-6.1	5.0	0.720	0.017	8.2
	100-750	-36.4	16.4	1.045	0.034	33.3
Methidathion	100-400	16.8	7.1	0.836	0.025	11.6
	100-750	-1.0	11.6	0.967	0.024	23.6
Simazine	200-800	35.3	6.8	0.882	0.012	11.1
	100-750	5.6	13.6	0.862	0.028	11.1
Atrazine	250-1000	25.4	7.7	0.871	0.011	12.5
	100-750	-8.5	10.8	0.980	0.022	21.5
Propazine	250-1000	20.8	7.4	0.881	0.011	12.0
	100-750	-18.1	11.3	0.985	0.023	22.9
Prometryn	260-1040	29.1	8.7	0.846	0.012	14.2
Triadimefon	400-1600	58.2	36.6	0.788	0.033	59.8
	100-750	32.6	26.5	0.828	0.055	53.9
Penconazole	325-1300	224.6	19.1	0.6967	0.021	31.2
Propiconazole I	200-800	100.9	10.6	0.770	0.019	17.3
Propiconazole II	300-1200	115.6	11.1	0.797	0.013	18.1
Napropamide	400-1600	44.0	18.6	0.859	0.017	30.3
	100-750	7.5	7.1	0.850	0.015	14.4
Amitraz	500-2000	-53.5	53.3	0.429	0.038	87.1

¹In Tables II and III river water range fits the first row and ultrapure water range the second one.

TABLE III. Calibration data set ($Y = a + bX$) for river and ultrapure water samples extraction method. Halogenated pesticides.

	Concentration range in fortified water (ng/L)	a	S_a	b	S_b	$S_{Y/X}$
Dieldrin	12.5-50	-0.67	1.12	0.510	0.031	1.58
		-0.15	1.04	0.786	0.033	1.47
δ -BHC	15-60	4.33	1.55	0.898	0.038	2.20
		-0.25	0.76	0.973	0.028	1.08
4,4' DDT	30-120	2.18	1.92	0.576	0.024	2.71
4,4' DDE	25-100	5.50	1.52	0.868	0.020	2.15
		1.27	1.34	0.929	0.020	1.90
4,4' DDD	25-100	-2.00	1.31	0.787	0.018	1.86
		0.92	1.40	0.902	0.020	1.98
Endosulfan I	12.5-50	3.00	1.18	0.806	0.014	1.67
		0.17	0.72	0.945	0.030	1.02
Endosulfan II	12.5-50	-5.00	1.23	0.975	0.014	1.74
		-0.05	0.88	0.980	0.026	1.25
Endrin	33-132	1.00	0.08	0.908	0.009	1.14
	25-100	0.80	1.78	1.010	0.026	2.52
Tetradifon	25-100	0.83	2.99	0.978	0.045	4.23
	37.5-150	-1.57	1.80	1.018	0.026	2.54
Vinclozolin	25-100	1.33	2.22	0.825	0.032	3.14
		2.10	0.81	0.919	0.012	1.14
Chlorpyriphos	30-120	1.67	1.84	0.769	0.023	2.60
	25-100	1.15	2.40	0.883	0.035	3.39
Methoxychlor	30-120	0.17	1.89	0.910	0.024	2.67
	25-100	1.53	1.71	0.934	0.025	2.42
Alachlor	80-320	-1.83	4.84	0.947	0.021	6.84
	50-200	-1.98	3.99	1.017	0.029	5.64

Linearity was measured through the correlation coefficient (r) and from $1-S_b/b$ (Table IV). A value of $S_r(b) = 0.1/t$ could be used as an acceptable limit of calibration of an instrumental method²⁰. According to this criterion only dichlorvos and amitraz among the compounds determined by GC-NPD ($n=16$), and tetradifon and dieldrin among those determined by GC-ECD ($n=12$) showed a linearity below 0.953 and 0.955 (the corresponding linearity limits for $\alpha = 0.05$ with $n-2$ degrees of freedom). The same compounds reached $S_r(C)$ values higher than 5%.

LODs were calculated both from the equation of calibration of the total analytical system^{20,22} and by a conventional method (three times the standard deviation value of the analytical signal at the lowest concentration level detected for each compound). The statistical method reflects the errors associated with the fitting of the calibration, so LODs are higher than those obtained by the conventional method

(Table IV). Better or similar LODs are obtained with river water when comparing with statistical data from ultrapure water, except for napropamide, triadimefon, vinclozolin, tetradifon. Values are < 100ng/L, except triadimefon, penconazole, napropamide and amitraz, for which instrumental LODs are also higher.

TABLE IV. Linearity, sensitivity, repeatability and limit of detection of the method.

	r	Linearity 1-S _y /b	S _r (C) ¹ (%)	Sensitivity (ng/L)	LOD (ng/L) Statistical	LOD (ng/L) Instrumental
GC-NPD						
Dichlorvos	0.974	0.938	7.9(160)	22	64 (98) ²	8
Mevinphos	0.987	0.956	5.6 (275)	27	79	16
Ethoprophos	0.996	0.977	3.0 (130)	7	20 (68)	3
Diazinon	0.996	0.977	3.0 (270)	14	41 (78)	11
Parathion-methyl	0.996	0.975	3.2 (250)	14	41 (74)	14
Malathion	0.999	0.985	1.8 (300)	10	28 (78)	11
Chlorpyriphos	0.996	0.976	3.0 (220)	11	33 (92)	8
Methidathion	0.994	0.970	3.8 (200)	14	40 (70)	8
Simazine	0.999	0.987	1.7 (400)	13	36 (37)	17
Atrazine	0.999	0.987	1.6 (500)	14	42 (63)	25
Propazine	0.999	0.988	1.5 (500)	14	40 (65)	23
Prometryn	0.999	0.985	1.8 (520)	17	49	63
Triadimefon	0.988	0.958	5.4 (800)	76	220 (188)	32
Penconazole	0.993	0.969	4.0 (650)	45	130	51
Propiconazole I	0.996	0.975	3.1 (400)	23	65	20
Propiconazole II	0.998	0.983	2.2 (600)	23	66	20
Napropamide	0.997	0.980	2.6 (800)	35	102 (49)	35
Amitraz	0.950	0.912	11.2 (1000)	203	588	65
GC-ECD						
Dieldrin	0.982	0.939	7.8 (25)	3	9 (5)	1
δ-BHC	0.991	0.958	5.3 (30)	2	7 (3)	1
4,4' DDT	0.991	0.957	5.3 (60)	5	14	2
4,4' DDE	0.997	0.976	3.0 (50)	2	7 (6)	2
4,4' DDD	0.997	0.977	3.0 (50)	2	7 (6)	3
Endosulfan I	0.999	0.983	2.2 (25)	2	6 (3)	2
Endosulfan II	0.999	0.985	1.9 (25)	2	5 (4)	2
Endrin	0.999	0.985	1.2 (66)	2	5 (4)	2
Tetradifon	0.989	0.953	5.9 (50)	4	13 (7)	5
Vinclozolin	0.992	0.961	5.0 (50)	4	11 (4)	2
Chlorpyriphos	0.996	0.970	3.8 (60)	3	10 (11)	2
Methoxychlor	0.997	0.974	3.3 (60)	3	9 (7)	7
Alachlor	0.998	0.978	2.8 (160)	7	21 (16)	9

¹ () = concentration in ng/L used to calculate precision

² () = LOD obtained with ultrapure water

CONCLUSIONS

Solid phase extraction from river water samples is appropriate for most of the compounds under study, but previous evaluation of matrix interferences is advisable. The behavior of trifluralin, captan, aldrin, tri-allate, α-BHC, γ-BHC and azinphos-methyl cannot be described through a linear relationship. According to performance characteristics estimated from the statistical linear regression model, only dichlorvos, amitraz, dieldrin and triadimefon did not reach suitable levels of linearity, precision, sensitivity or limit of detection. Systematic errors detected could be corrected by using the calibration data obtained for the whole analytical process allowing better accuracy levels. Enhanced chromatographic responses for triazolic compounds interferes in obtaining conclusions at the lowest concentration levels. The estimation of the analytical quality parameters through the statistical linear regression model permitted to compare the recovery behavior of different pesticides from two classes of aqueous matrices.

ACKNOWLEDGEMENTS

The authors thank the Fondo Nacional de Investigación Científica y Tecnológica for its financial support (Project FONDECYT N° 1940301).

REFERENCES

1. J. Mañes and Y. Picó, J. Moltó and G. Font. *J. High Resol. Chromatogr.*, **13**, 843 (1990).
2. J. Beltrán, F.J. López, F. Hernández. *Anal. Chim. Acta*, **283**, 297 (1993).
3. J. Moltó, Y. Picó, J. Mañes and G. Font. *J. Assoc. Off. Anal. Chem. Int.*, **75**, 714 (1992).
4. G.H. Tan. *Analyst*, **117**, 1129 (1992).
5. G. Font, J. Mañes, J. Moltó and Y. Picó. *J. Chromatogr.*, **642**, 135 (1993).
6. M. Meyer, M. Mills and E. Thurman. *J. Chromatogr.*, **629**, 55 (1993).
7. M. Psathaki, E. Manoussaridou and E. Stephanou. *J. Chromatogr.*, **667**, 241 (1994).
8. P. Vitali, E. Venturini, C. Bonora, R. Calori and R. Raffaelli. *J. Chromatogr.*, **660**, 219 (1994).
9. S. Bengtsson, T. Berglöv, S. Granat, G. Jonsall. *Pestic. Sci.*, **41**, 55 (1994).
10. C. Crespo, R.M. Marcé, F. Borrull. *J. Chromatogr.*, **670**, 135 (1994).
11. T.A. Albanis, D.G. Hela. *J. Chromatogr.*, **707**, 283 (1995).
12. J. Salau, R. Alonso, G. Battló, D. Barceló. *Anal. Chim. Acta*, **293**, 109 (1994).
13. V. Pacáková, K. Stulik, J. Jiskra. *J. Chromatogr.*, **754**, 17 (1996).
14. R.A. McLaughlin, B.S. Johnson. *J. Chromatogr.*, **790**, 161 (1997).
15. M. Báez, O. Lastra, M. Rodríguez. *J. High Resol. Chromatogr.*, **19**, 559 (1996).
16. M. Baéz, M. Rodríguez, O. Lastra, P. Contreras. *J. High Resol. Chromatogr.*, **20**, 591 (1997).
17. J.J. Jiménez, J.L. Bernal, M.J. del Nozal, J.M. Rivera. *J. Chromatogr.*, **778**, 289 (1997).
18. D. Barceló, S. Chiron, S. Lacorte, E. Martínez, J. Salau and M. Hennion. *Trends in Anal. Chem.*, **13**, 352 (1994).
19. P. Bonifazi, E. Pierini, F. Bruner. *Chromatographia*, **44**, 595 (1997).
20. L. Cuadros, A.M. García, C. Jiménez, M. Román. *Anal. Lett.*, **26**, 1243 (1993).
21. C. de la Colina, F. Sánchez-Rasero, G. Cancela, E. Romero and A. Peña. *Analyst.*, **120**, 1723 (1995).
22. C. de la Colina, A. Peña, M. Mingorance and F. Sánchez-Rasero. *J. Chromatogr. A.*, **733**, 275 (1996).
23. M. Báez, M. Rodríguez, O. Lastra. *Bol. Soc. Chil. Quím.*, **42**, 457 (1997).
24. J.C. Miller, J.N. Miller. *Estadística para Química Analítica*. Addison-Wexley Iberoamericana. Wilmington, Delaware, USA, 2nd edn. (1993).
25. R. Cela. *Avances en Quimiometría Práctica*. Ed. Universidad de Santiago de Compostela (1994).
26. J.L. Bernal, M.J. del Nozal, J.J. Jiménez, J.M. Rivera. *J. Chromatogr.*, **778**, 111 (1997).
27. P.T. Holland, D. McNaughton, C.P. Malcolm. *J. AOAC Int.*, **77**, 79 (1994).
28. S. Lartiges, P. Garrigues. *Environ. Sci. Technol.*, **29**, 1246 (1995).