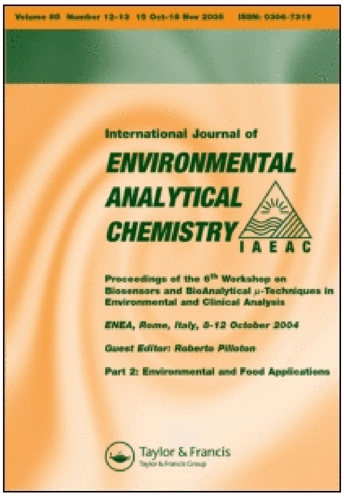

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INFLUENCE OF SALINITY AND DISSOLVED HUMIC ACIDS ON PESTICIDES EXTRACTION FROM WATER USING SOLID-PHASE EXTRACTION DISKS

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The influence of water salinity and dissolved organic matter (DOM) on pesticide extraction recoveries using solid phase extraction disks was investigated. Eleven selected pesticides, belonging to different chemical groups were spiked at 1–5 μg/L in 500 ml distilled water containing sodium chlorine at 0, 5, 10, 15, 20, 25, 30 and 35 ‰ or humic acids at either 0, 1, 5, 10, 25, 50 and 100 mg/L dissolved organic carbon (DOC). Samples were prefiltered and their extraction was done by using C_{18} Empore solid phase extraction disks and filter aid glass beads. The pesticides eluted from the disks were analysed by gas chromatography with flame thermoionic detector (FTD) and mass selected detector (MSD) in the selected ion monitoring (SIM) mode. Higher recoveries of most pesticides were obtained as the water salinity increased from 0 to 35 ‰. Concentrations of DOC in humic acid had less effect on extraction efficiency, which was probably due to greater nonpolar interactions of pesticides to the charge-neutralized humic acid polymer.

Keywords: Pesticides, solid-phase extraction, salinity, dissolved humic acids

INTRODUCTION

Solid-phase extraction has been extensively applied to the extraction of pesticides present in water samples. The adsorbed compounds are then eluted from the solid phase by an organic solvent[1]. C8 and C18 bonded-phase cartridges[2,3], XAD resins[4-6] activated charcoal[7,8], graphitized carbon blank and tenax GC[9,10] have all been employed for the analysis of a variety of pesticides. In the last 4 years, SPE disks containing octadecyl (C18) bonded silica have been employed as an alternative method for the trace enrichment of organic compounds, includ-

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ing pesticides, in water. This technique provides (a) reduced volume of potentially / liquid extraction (LLE)[11], (b) decreased sample preparation time and labor needed than LLE[11], and (c) inreased stability of pesticides after filtration compared to pesticides stored in water[12–15]. At present such disks have been tested for different groups of compounds, including pesticides, organotins and pthalates[16,17]. The system has also been applied on line with LC for the concentration of triazine herbicides and chlorophenols from river and seawater[18].

Extraction results of pesticides from surface water present a variety of recoveries due to their different nature and characteristics as, pH, conductivity, salinity, dissolved organic carbon, suspended matter and containing microrganisms. The recoveries of 22 studied pesticides belonging to different chemical groups (triazines, organophosphorous, substituted ureas, substituted anilides, carbamates and other) were higher in distilled and ground water compared to those from surface waters (river, lake and marine waters)[16]. The main differences among these studied surface waters were the high salinity and conductivity of marine water as well as the higher concentration of the total organic carbon in lake and river water samples. This negative influence of marine waters on the pesticide levels obtained is stronger in the cases of monocrotophos, picloram, terbufos, prometryne, and MCPA the recovery values of which reach below 50% in marine water samples[16]. The influence of marine water was more active for more polar compounds. This behaviour in the case of atrazine and simazine agrees with that reported in Chakeespeare Bay and Ebro river estuaries[18,19]. In contrast, a positive salting-out effect on adsorption on C18 bonded silica has been reported for some herbicides and organophosphorus insecticides[20,21].

Non polar pesticides have been shown to interact with dissolved organic matter[22]. This interaction could reduce extractable pesticides from aqueous solutions, adversly affect method sensitivity, and ultimately make it difficult to draw conclusions from the environmental assessment. A study involving the interaction of increased solution concentrations of DDT with dissolved humic substances indicated that at pH 6, more DDT was bound to humic acid than at pH 9.2[23].

Possible interferences due to varying levels of humic acid extraction efficiency from water were evaluated using solid-phase extraction cartridges containing octadecyl (C18) bonded silica[24]. The significantly lower persistence recovery from water containing humic acids was attributed to lower pesticide affinity to C18 columns when associated with humic acid in suspension[24].

The purpose of this work is to carry out a systematic study on the influence of water salinity and dissolved organic carbon on pesticide extraction efficiency from water using solid-phase extraction disks. The final goal of the article is to improve the quality assurance parameters in relation to pesticide extraction in environmental water analysis, and to apply the present approach to on-going monitoring program in estuarine waters.

EXPERIMENTAL

Chemicals

HPLC-grade water, methanol, dichoromethane, ethyl acetate and isooctane from Pestiscan (Labscan Ltd, Dublin, Ireland) were passed through a 0.45-μm filter before use. Alachlor, atrazine, carbofuran, desethyl-atrazine, malathion, molinate, parathion ethyl, parathion methyl, propanil, simazine and trifluralin were purhased from Promochem (Wesel, Germany). Empore extraction disks were manufactured by 3M and distributed by Varian (Harbor City, CA). The disks used were 47 mm in diameter and 0.5 mm thick. Each disk contained about 500 mg of C18 bonded silica (92±2%) and 10±2% PTFE. The particle characteristics were: 8 μm particle size; 60A pore size; and irregular shape. Empore filter Aid 400 glass beads (St. Paul, USA) for use as a filtration aid when extracting samples with high particulate content using extraction disks. Humic acid was purhased from Aldrich Chemical Company Inc. (Milwaukee, WI-USA).

TABLE I Characteristics of selected pesticides

Pesticides	*Activity*[a]	*Water solubility (mg/L)*	*Vapor pressure (MPa)*[b]	*Soil sorption (LogKoc)*[C]	*Soil Half-life (days)*[b]	*HLC*[d] *(Pa.m^3/mole at 20°C*
Alachlor	H	148	1.9×10^{-9}	2.07	18	3.46×10^{-3}
Atrazine	H	35	3.9×10^{-11}	2.20	64	2.46×10^{-4}
Desethyl-atrazine	H			1.69		
Carbofuran	I	351	2.7×10^{-9}	1.44	40	1.70×10^{-3}
Ethyl Parathion	I	24	$5,1\times10^{-9}$	4.04	15	6.22×10^{-2}
Malathion	I	145	5.3×10^{-9}	3.25	10	1.21×10^{-2}
Methyl Parathion	I	50	$2,0\times101^{9}$	3.70	15	1.05×10^{-2}
Molinate	H	800	7.5×10^{-7}	2.62	60	1.75×10^{-1}
Propanil	H	500	5.3×10^{-9}	2.15	6	2.31×10^{-3}
Simazine	H	5	2.9×10^{-12}	2.10	75	$1,16\times10^{-4}$
Trifluralin	H	0.05	1.5×10^{-8}	3.86	132	$1,00\times10^{+2}$

[a] H = herbicide, I = insecticide, [b] Data extracted from Wauchope et al.[25], [c] Data extracted from Jury et al.[26] and Fielding et al.[27]. These data represent values measured at 20–25°C, [d] HLC = Henry Law Constant in Pa.m^3/mole at 20°C.

Preparation of Water Samples

A sodium chloride solution with a concentration of 10 % (w/v) was prepared in 1 L distilled water. Aliquots of different volumes were removed and placed in the appropriate 1 L bottles and brought to a volume of 500 ml with distilled water to create sodium chloride (salinity) concentrations 0, 5, 10, 15, 20, 25, 30 and 35 ‰ (w/v).

One liter humic acid solutions with dissolved organic carbon (DOC) concentration of 500 mg/L was prepared by dissolving 2.392 g of the Aldrich humic acid. Aliquots of 100, 50, 25, 10, 5, 1 and 0 ml of this solution were removed and placed in 1 L bottles and brought to a volume of 500 ml with distilled water to create DOC concentrations of 100, 50, 25, 10, 5, 1 and 0 mg/L. These concentrations of DOC were used according to relative DOC concentrations used and detected in reported work from the literature[26,28]. The samples were covered and temporarily stored in 4°C overnight until the spiking with pesticide solutions.

The water samples amended with sodium chloride and humic acid were fortified with 0.5 and 0.2 ml respectively, of a 1–5 µg/mL methanol fortification solution containing the mixture of eleven selected pesticides. This brought concentration of all pesticides in water to 1–5 µg/L. Blank quality-control samples received 0.5 ml of methanol and contained no pesticides. The samples were then placed on an orbital shaker for 1 h at 80 rpm to allow equilibrium between pesticides and water samples with sodium chloride and humic acids.

Sample Extraction and Concentration

Empore extraction disks were conditioned with aceton 10 ml for 2 hours. Methanol modifier (5 ml) was added to 1 L water samples to allow better extraction[29,30]. The sample pH was adjusted to <3 with sulfuric acid 1:1 (v/v).

Twelve grams (about 1 cm) of glass beads were poured on the disk already placed in the conventional Millipore apparatus, and both were washed with 10 ml of dichloromethane with the vacuum on and with 10 ml of methanol for 3 min with the vacuum off. The disk was not allowed to become dry, as recommended[31,32]. The sample was mixed well and allowed to percolate through the disks with a flow rate of 50 ml/min under vacuum. After sample extraction, the pesticides trapped in the disk were collected by using 2 × 5 ml of solvent mixture dichloromethane:ethyl acetate (1:1, v/v) as eluting solvent. The fractions were evaporated to 4 ml on a rotary evaporator (35°C). After careful evaporation of solvent to 0.5 ml in a gentle stream of nitrogen, extract residues displayed into 2ml isooctane and were evaporated to a final volume of 1 ml for GC injections. Retention times and recoveries obtained for the different pesticides and waters are indicated in Tables II, III and IV.

TABLE II Retention times (min) of 11 selected pesticides in the GC-FTD system with column DB–1, 30 m, i.d. = 0.32mm as well as in the GC-MS QP 5000 Shimadzu equipped with capillary column, 007 Quatrex-Methyl 5% phenylsilicone 30 x 0.32 mm x 0.5 μm

	GC-FTD + DB-1		*GC-MS + 007Quatrex*	
Pesticides	*t_R (min)*	*RRF (Vinclozolin)*	*t_R (min)*	*Selected ions (m/z)*
1. Molinate	27.77	0.67	25.79	187, 189
2. Desethyl-atrazine	30.84	0.52	26.35	172, 187
3. Trifluralin	31.61	1.07	32,54	335, 337
4. Carbofuran	32.32	0.98	33.59	221, 223
5. Simazine	32.44	0.32	30.73	201, 186
6. Atrazine	32.75	0.37	30.96	215, 200
7. Propanil	35.96	1.58	33.72	217, 161
8. Methyl Parathion	36.80	0.23	34.27	263, 265
9.Alachlor	37.84	0.97	34.71	269, 188
10. Linuron	39.30	1.98	35.83	248, 160
11. Malathion	39.54	0.27	36.33	127, 173
12. Ethyl Parathion	40.74	0.11	37.02	291, 293

Chromatographic Conditions

GC-FTD. Single pesticide standards and 1.5 μl of extracts from the Empore disk preconcentration step were injected in the splitless mode in a Shimadzu 14A capillary gas chromatograph equippped with flame thermionic detector (FTD) at 250°C. The DB–1 column, 30m x 0.32mm i.d., used contained 5% methylsilicone (J & W Scientific, Folsom, CA). The column was programmed from 55°C (2 min) to 210°C (20 min) at 5°C/min and to 270°C (4 min) at 20°C/min. The injection temperature was 220°C.

Helium was used as the carrier and make-up gas. The detector gases were hydrogen and air, and their flow rates were regulated according to results given through the simplex optimization of the analytical variables, in this instance air and hydrogen flow-rates in the detector. The ion source of FTD was an alkali metallic salt (Rb2SO4) bonded to a 0.2 mm spiral of platinum wire.

GC-MS. A GC-MS QP 5000 Shimadzu equipped with capillary column 007 Quatrex-Methyl 5% phenylsilicone 30 × 0.32 mm x 0.5 µm was used. Helium is used as the carrier gas at 14 psi. The chromatographic conditions are: Injector temperature 270°C, Column programme of temperatures 55°C (2min), 55-210 °C (5°C/min), 210°C (15 min), 210–270°C (20°C/min), 270°C (4 min). The ion source and transfer were kept at 200°C and 300°C respectively. The spectra are obtained at 70 eV.

Two ions for each pesticide were chosen for screening analysis in selected ion monitoring (SIM). The ions traces were divided into five groups that were recorded sequentially during the injection, on the basis of the retention times of the single substances; the first group was from 17.1 to 27.2 min, the second from 27.2 to 29.0 min, the third from 29.0 to 31.3 min, the fourth from 31.3 to 34.0 min and the fifth from 34.0 to 50.2 min.

RESULTS AND DISCUSSION

The mean recoveries of three analyses, obtained for the 11 selected pesticides spiked in water solutions of sodium chlorine 0–35‰ and humic acid with a concentration of dissolved organic matter at 0–100 mg/L are shown in Tables III and IV. Differences in the mean percent recovery of pesticides from SPE disks due to salinity and DOC content in water are shown Table V and Figure 1. First it should be noticed that recoveries obtained for the sodium chloride solutions in distilled water were higher than 80 % for 9 compounds and lower for molinate and trifluralin, thus indicating that the use of the disks does not pose any problem to the analysis of such a type of water. Low recoveries found for molinate and trifluarlin can be explained by their high volatility and Henry Law Constant (HLC) as compared to the other compounds (Table I). Molinate has higher value of vapor pressure than trifluralin, but due to the lower solubility of trifluralin its HLC is higher than that of molinate.

From studied pesticides, trifluralin, alachlor and malathion show the smaller increasing on their recovery as the water salinity increases from 0 to 35‰ (level of marine waters). This small influence of salinity is observed mainly in the cases of trifluralin which is the more lipophilic compound. It is possible this negative influence to be stronger than the increase of extraction efficiency by the ionic strength of aqueous samples (Table V and Figure 1). The positive salting-out effect reaches the highest values for desethyl-atrazine (23.5%), carbofuran (19.0%), propanil (19.5%) and methyl parathion (17.0 %) (Figures 2-4).

TABLE III Percent recovery of 11 selected pesticides fortified at 1–5 μg/L and anlysed by GC-FTD

Peak No / Pesticides	*Mean recoveries %*						
	Salinity of solutions (‰)						
	0	*5*	*15*	*20*	*25*	*30*	*35*
1. Molinate	79.5	78.2	80.9	82.3	84.4	92.7	96.2
2. Desethyl-atrazine	97.5	105.2	110.0	110.5	107.6	117.3	121.0
3. Trifluralin	77.6	79.3	80.6	80.8	80.9	81.7	81.9
4. Carbofuran	92.2	95.0	96.2	98.5	104.4	107.6	111.2
5. Simazine	89.2	91.3	95.1	97.4	98.6	102.6	105.3
6. Atrazine	92.4	94.3	96.3	99.0	99.2	100.4	103.6
7. Propanil	90.5	92.1	93.1	96.6	97.3	99.2	110.0
8. Methyl Parathion	86.4	88.9	90.1	96.5	97.4	99.1	103.4
9. Alachlor	99.6	101.7	103.5	103.3	103.9	105.7	106.9
10. Malathion	92.3	92.5	94.6	95.5	96.6	97.6	98.9
11. Ethyl Parathion	101.4	106.2	108.4	108.7	109.4	111.3	113.7

* Spiking levels at 1–5 μg/l, N=3.

TABLE IV Percent recovery of 11 selected pesticides fortified at 1–5 μg/L and analysed by GC-FTD

Peak No / Pesticides	*Mean recoveries %*						
	Dissolved organic carbon in water solutions at mg/L:						
	0	*1*	*5*	*10*	*25*	*50*	*100*
1. Molinate	79.5	74.3	69.2	67.2	65.3	61.5	59.8
2. Desethyl-atrazine	97.5	96.2	95.0	91.5	90.7	89.2	87.2
3. Trifluralin	77.6	73.9	67.6	67.8	63.9	63.6	60.6
4. Carbofuran	92.2	91.0	88.9	88.6	87.4	85.4	82.6
5. Simazine	89.3	89.3	85.1	77.7	75.6	68.6	57.1
6. Atrazine	92.4	85.1	82.3	78.4	75.4	72.6	67.6
7. Propanil	90.5	88.5	90.3	85.4	84.3	83.6	80.9
8. Methyl Parathion	86.4	84.9	82.0	81.0	80.2	77.5	74.8
9. Alachlor	99.6	98.4	97.4	97.3	93.2	92.9	88.5
10. Malathion	92.3	89.2	87.6	85.5	84.6	83.6	81.9
11. Ethyl Parathion	101.4	100.3	96.7	88.6	89.4	87.6	79.5

* Spiking levels at 1–5 μg/l, N=3.

TABLE V Influence of salinity and DOC on pesticide recoveries from water

Peak No / Pesticides	*Difference in the mean % recovery among solutions of:*	
	Salinity: 0 to 35‰	*DOC: 0 to 100 mg/L*
1. Molinate	+ 16.7	– 19.7
2. Desethyl-atrazine	+ 23.5	– 10.3
3. Trifluralin	+ 4.3	– 17.0
4. Carbofuran	+ 19.0	– 9.6
5. Simazine	+ 16.1	– 32.2
6. Atrazine	+ 11.2	– 24.8
7. Propanil	+ 19.5	– 9.6
8. Methyl Parathion	+ 17.0	– 11.6
9. Alachlor	+ 7.3	– 11.1
10. Malathion	+ 6.6	– 10.4
11. Ethyl Parathion	+ 12.3	– 21.9

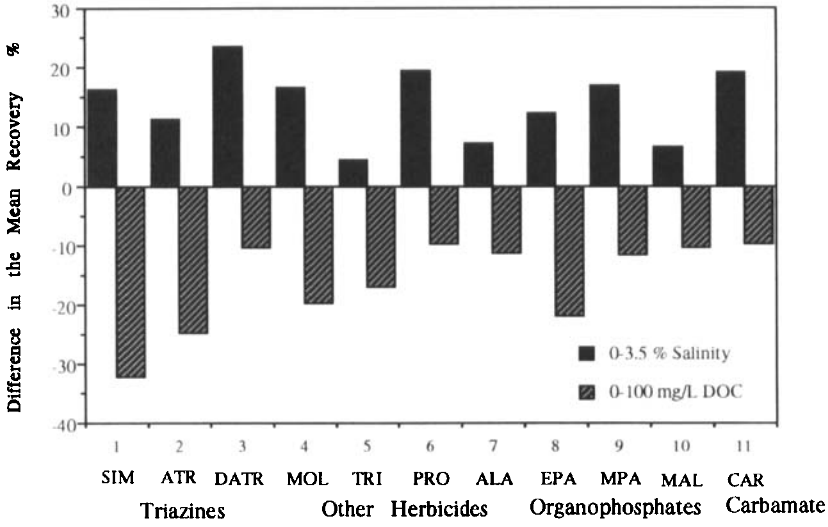

FIGURE 1 Influence of salinity and dissolved organic carbon on pesticide mean recoveries from water

Recoveries obtained from humic acid solutions to a concentration of DOC 25 mg/L (a typical concentration of natural surface water from rivers, estuaries and lakes) were kept higher than 80% only for 7 compounds (desethyl-atrazine, carbofuran, propanil, alachlor, methyl parathion, ethyl parathion and malathion) (Figures 5–7). All pesticides seem to have a reduction in their recoveries as the concentration of DOC in water increases from 0 to 100 mg/L. The influence of humic acids on pesticide recoveries seems to be statisticly significant at concentrations above 5 mg/L. Similar results were found for organophosphates, propanil and carbofuran. The difference in mean percent recovery due to humic acid on the extraction efficiency from SPE disks is higher, over 20% for molinate (19.7%), simazine (32.2 %), atrazine (24.8 %), ethyl parathion (21.9%) and methyl parathion (11.6%). It is well known that compounds as atrazine, simazine with nitrogen groups and a basic stucture exhibit high interactions with humic acids. Ethyl and methyl parathion containing para-nitrophenol stucture in their molecules can also easily interact with humic substances that can act as electron acceptor deficient quinone moieties [24,33,34].

The results in this study correlate with pesticide recovery from earlier work by Senseman et al.[15] where the percent recovery of alachlor, atrazine, methyl parathion, propanil, simazine and trifluralin, extracted using C18 bonded silica disks, was generally lower in the samples containing humic acid than in pure water in pH values 6 and 8.

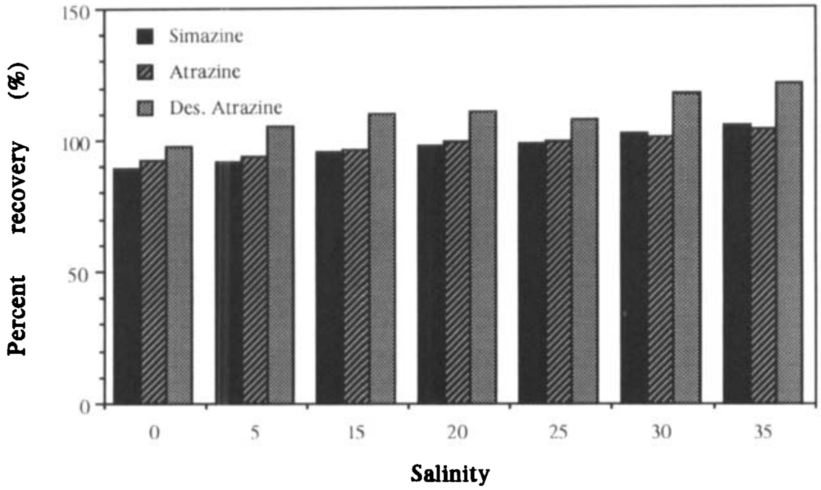

FIGURE 2 Influence of salinity on simazine, atrazine and desethyl atrazine mean recoveries from water

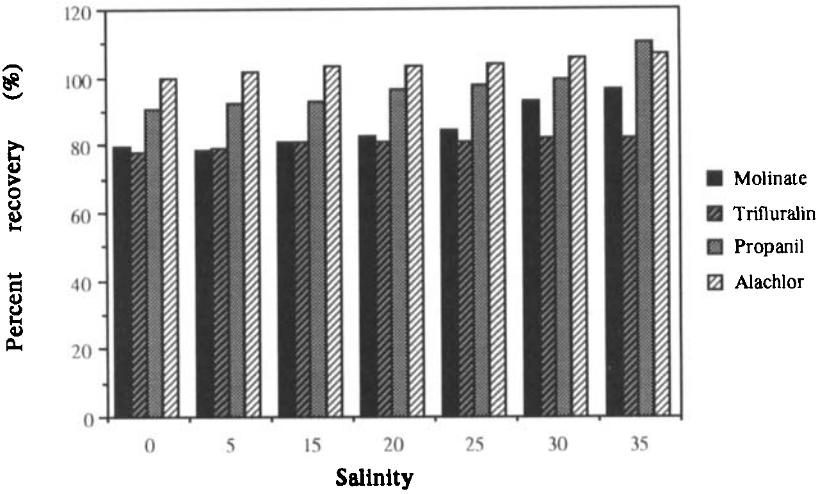

FIGURE 3 Influence of salinity on molinate, trifluralin, propanil and alachlor mean recoveries from water

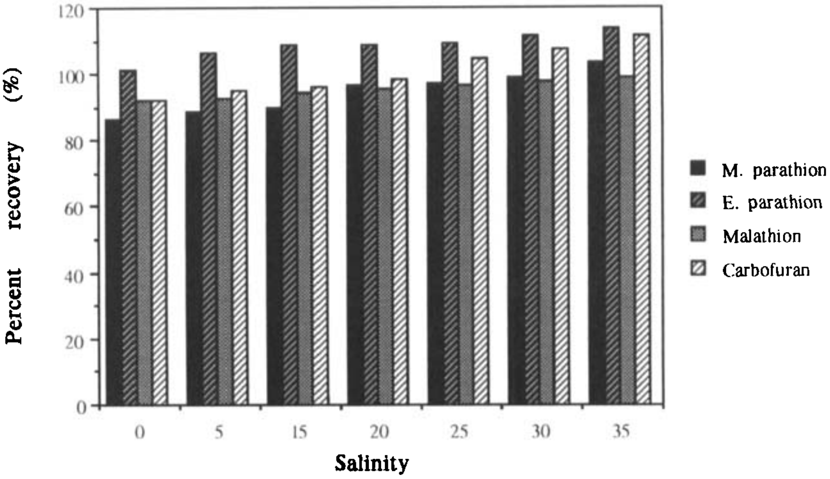

FIGURE 4 Influence of salinity on methyl parathion, ethyl parathion, malathion and carbofuran mean recoveries from water

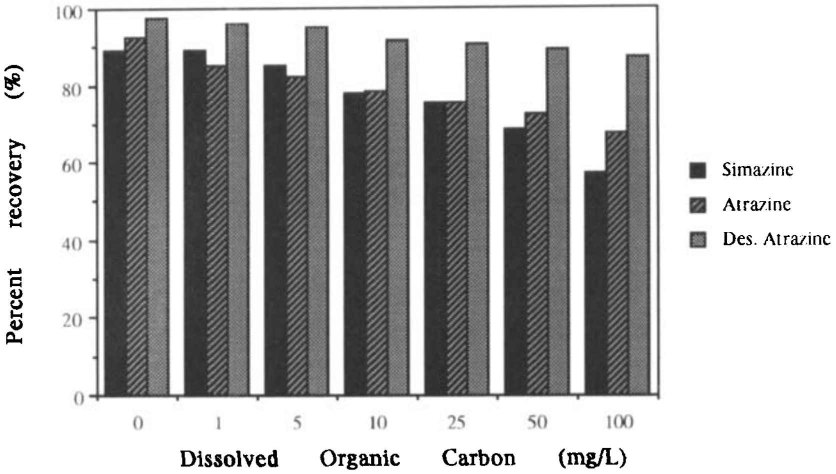

FIGURE 5 Influence of dissoved organic carbon (DOC) on simazine, atarzine and desethyl atrazine mean recoveries from water

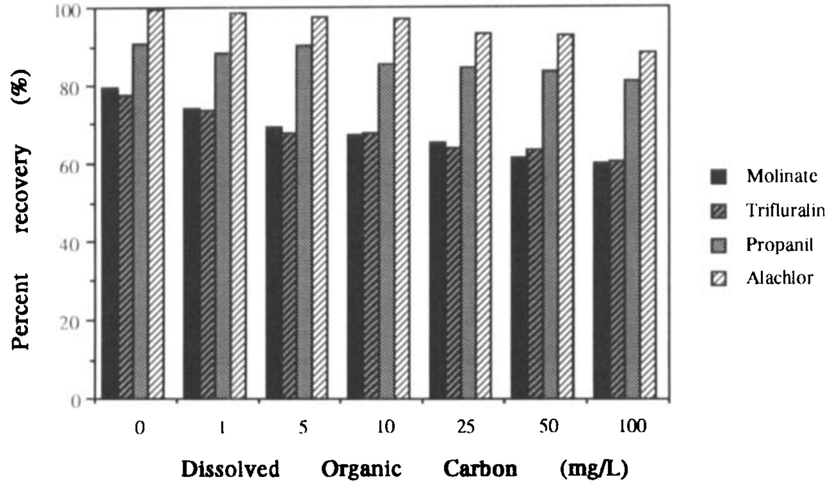

FIGURE 6 Influence of dissoved organic carbon (DOC) on molinate, trifluralin, propanil and alachlor mean recoveries from water

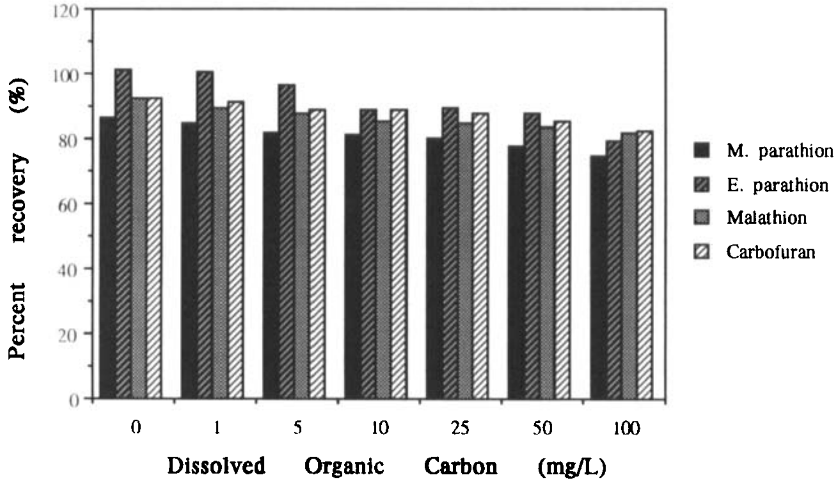

FIGURE 7 Influence of dissoved organic carbon (DOC) on methyl parathion, ethyl parathion, malathion and carbofuran mean recoveries from water

CONCLUSIONS

In conclusion, the dissolved humic acids in water affected similarly the efficiency of solid phase extraction for pesticides within chemical families. The effect of humic acid on pesticides extraction was the reduction of mean percent recoveries as the DOC concentrations reached 100 mg/L. It should be noticed that pesticide recoveries obtained from water solutions with humic acid (DOC concentrations, 25 mg/L) were higher than 80 % for 9 compounds with the exception of molinate, trifluralin, simazine and atrazine, thus indicating that the use of the disks does not pose significant problems to the analysis of such a type of water. A dark brown residue was observed on the SPE disk during and after extraction from humic acid from water occured by partitioning onto C18 material. By partitioning a part of humic acid onto the disk, the portion of the pesticide that was bound to humic acid would have been subjected to the dichloromethane-ethyl acetate mixture disk rinses, thereby minimizing the loss of the pesticide during the extraction procedure.

A positive salting-out effect on adsorption on C18 bonded silica has been observed for all studied pesticides. A small salting out effect was observed for recoveries of three compounds, trifluralin, alachlor and malathion, to be stronger than the increase of extraction efficiency by the ionic strength of aqueous samples. The positive salting-out effect reaches over 25% for molinate, desethyl-atrazine, carbofuran, simazine, propanil and methyl parathion.

The influence of salinity and humic acid on percent pesticide recoveries is substantial enough to adversely affect method sensitivity of these compounds. It also demonstrates the importance of taking into account the effect of salinity and humic acid on pesticide extraction efficiency when surface water samples are analysed.

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