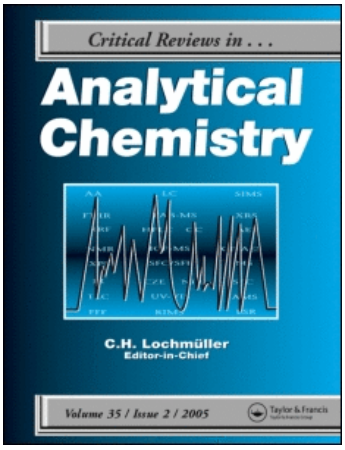

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Analysis of Carbamate Pesticides and Their Metabolites in Water by Solid Phase Extraction and Liquid Chromatography: A Review

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ABSTRACT: Carbamates are an important, broad class of pesticides that are used extensively as insecticides, fungicides, and herbicides. Sensitive, economical, fast, and environmental friendly procedures are constantly developed to investigate their residues in water samples. The state of the art in methods based on solid phase extraction (SPE) and liquid chromatographic determination are examined here. SPE is presently the most extended method for preconcentration of carbamate pesticide residues and their transformation products from water samples. Advantages and limitations of alkyl bonded-silica, and polymeric sorbents, carbon, and mixed-phases in off-line and on-line procedures are discussed. Because some carbamates and transformation products are thermolabile, multiresidue determination is usually carried out by liquid chromatographic techniques. The most interesting reported analytical conditions are presented in a tabular form. Finally, an overview to the levels found in different environmental waters is done; concentrations were usually detected in the sub $\mu g\ l^{-1}$ order.

KEY WORDS: solid phase extraction (SPE), liquid chromatography, carbamate pesticides, environmental water, silica-bonded phases, activated carbon, polymeric phases, mixed-phases, on-line SPE, off-line SPE.

I. INTRODUCTION

Carbamate pesticides were introduced as pesticides in the early 1950s and are used extensively in pest control due to their effectiveness and broad spectrum of biological activity (insecticides, fungicides, and herbicides). Their structures are N-substituted carbamic acid esters ($R_1OCONR_2R_3$). Thiocarbamates ($R_1SONR_2R_3$) are also included into this group. For most carbamates R_1 includes a phenyl or a heterocyclic aromatic ring, although enol and oxime carbamates are also commercialized. The R_2 group is usually a methyl, and the R_3 is either a hydrogen, methyl, or a more complex group. High polarity and solubility in water and thermal unstability are typical characteristics of carbamate pesticides.[1] However, these attributes cannot be generalized to the whole group of carbamate pesticides because their properties vary from one to another (i.e., *N*-methyl oxime carbamate sulfoxides are highly polar, while *N*-methyl aryl carbamates are much less so).[2]

These pesticides have high acute toxicity.[3,4] They act by a mechanism of reversible inhibition of acetylcholine, which is less toxic to mammals than organophosphorus pesticides. The cholinesterase activity has been used as biomarker for assessing the exposure of organisms such as the common carp to carbamates.[5] Even when carbamate pesticides are correctly applied, their residues can be found in the soil itself and in run-offs from the soil[6] as well as in food,[7,8] crops,[8] and waters.[9] Their presence in a wide variety of waters is mainly due to their leachability and high water solubility. This leachability is confirmed by their groundwater ubiquity score defined as (log $t_{1/2}$)(4-log K_{oc}), where $t_{1/2}$ is the half life in soil, and log K_{oc} is the soil organic carbon partition coefficient[10] that identifies carbamates as potential leachers.

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The importance of the presence of the target carbamates and their transformation products (TPs) in water also must be considered. These TPs are formed as a consequence of several processes such as hydrolysis, biodegradation, oxidation, photolysis, biotransformation, metabolic reactions in living organisms, etc.[11-14] These processes lead to compounds more toxic than the parent pesticides[11] and are more persistent in the environment. Therefore, it is of vital importance to be able to measure these pesticides in aquatic media. The general concern about detecting trace levels of pesticides is reflected in the monitoring programs like the one carried out by the Dutch National Institute of Public Health and Environment,[15] the National Pesticide Survey Program of U.S.A.,[16] the Rhine Basin,[17] and the National Water Quality Assessment[18] of the U.S.A.

The presence of carbamates in these waters is one of the best indicators of pesticides sprayed by aircraft, accidental spills, or direct application to crops. Consequently, a number of reports have dealt with how to develop sensitive, efficient, rapid, and reliable methods of determination and to confirm the presence of carbamate pesticides in groundwaters[19] and river or lake[20-22] and well[23] waters.

In real samples is important to have an adequate preconcentration technique[24,25] and a good chromatographic method[8,26,27] to monitor carbamates in water. The most common technique for carbamate pesticide extraction is solid phase extraction (SPE).[24,25] Solid phase microextraction (SPME), liquid-liquid extraction (LLE), and supercritical fluid (SFE) extraction have well-known disadvantages compared with SPE.[9,24,28] Chromatographic methods such as liquid,[27,28] gas,[29,30] micelar electrokinetic capillary,[31,32] supercritical fluid,[33] and thin layer[34] chromatography have been used to analyze carbamates residues in waters. Liquid chromatography (LC) has been applied routinely in the analysis of carbamates due to their suitability for thermally labile and polar pesticides and those on-line pre- and post-column systems are compatible with LC.[27,35] Non chromatographic techniques such as immunoassays,[36-38] biosensors,[39] spectrophotometry,[40,41] and electrochemistry[42] are also used for the determination of these pesticides.

This review summarizes the used SPE and LC techniques to analyze carbamate pesticides and their derivative products in waters, focusing on off-line and on-line SPE with different kinds of sorbents. Concerning the determination, LC is the method reviewed with UV, diode array, fluorescence, and mass spectrometry detectors. Finally, the applications of the described techniques for the analysis of real samples are also summarized.

II. SOLID PHASE EXTRACTION (SPE)

A. General

The final goals of a pesticide analysis are to obtain the cleanest samples, to determine the minimum concentration with the lowest limits of detection (LODs), and to avoid pesticide degradation during transport to the laboratory. All this means that the accuracy and precision of a method of analysis is directly dependent on the sample treatment. In this field, an adequate sampling plan is necessary for every monitoring program. For this purpose, sampling methods for river, lakes, well water, and seawater have been reviewed,[43] taking into account the importance of the influence of the organic matter present in the waters and the interactions of the pesticides with humic substances.

Solid-phase extraction (SPE) has rapidly established itself as an important sample preparation technique for either matrix simplification or trace enrichment. The sorption and desorption processes in the liquid-phase sorbent system have been described,[44] and these preconcentration procedures are considered low-performance liquid chromatography. With SPE, pesticides present in aqueous matrix can be isolated, concentrated, and purified. A typical SPE sequence includes the activation of the sorbent bed (wetting), removal of the excess of activation solvent (conditioning), application of the sample, removal of interferences (clean up) and water, elution of the sorbed analytes, and reconstitution of the extract.[45]

When nonreproducible recoveries are achieved, they can be due to interaction between the analyte and the matrix, leading to the undisponibility of the

analyte because of its adsorption onto solid suspended matter or because the matrix produces a higher polarity of the analyte by its charge. The importance of removing these interfering compounds, the storage of analytes and other factors affecting the SPE process such as the type of sorbents, sample volume, pH, sorbent treatment, and cartridge design have been reviewed.[24,25,46]

Sorbents available in SPE include the common inorganic adsorbents used in column liquid chromatography (silica gel, magnesium silicate, and alumina) as well as activated charcoal, bonded silica phases, and polymers. The most popular phases used for carbamate pesticides are octadecyl- and octyl-silica, styrene-divinylbenzene copolymers, and activated carbon black. The common SPE procedures involve three supports: cartridges, precolumns, and disks. The extraction disk technique was first applied in 1990. Disks have diameters of 25, 47, or 90 mm, but the most common size is that of 47 mm, and 0.5 mm thick, made of PTFE and sorbent particles. The sorbent mass for a 47-mm-diameter disk is about 500 mg. A number of procedures using extraction disks have been developed for the determination of carbamates in both off-line[47-49] and on-line procedures.[50-52] The disks with the C18 phase are used most often, but disks with styrene-divinylbenzene copolymer[47,52] or activated carbon[53] are also used, although much less frequently. The three main advantages of disks over columns are the following: (1) the particle diameter of the sorbent is smaller and mass transfer is therefore faster, (2) the better packing reduces the mean free path of the analyte molecules to the sorbent particle and, (3) the increase in the flow cross-section reduces the linear velocity of the analyzed sample with simultaneous reduction in its flow rate. All this leads to increased efficiency of the sorption/desorption mechanisms. In general, the time required to isolate pesticides using disks is half that needed with cartridges, and a further increase in sample processing productivity can be achieved by using a device for multiple extractions.

The packing materials have particle sizes ranging from 30 to 60 μm, and the flow rate of solution through the support is usually controlled by vacuum suction, depending on the type of sorbent used. The flow rate of the sample through the extraction sorbent in on-line procedures is often lower than off-line, because of that on-line cartridges have smaller particle size being clogging more likely to occur.

The most common elution solvents used for carbamate pesticides are acetonitrile, methanol, or less commonly ethyl acetate when the extractive phase is a silica-bonded phase, methanol, or methanol/dichloromethane mixtures when graphitized carbon black is used, and methanol/acetonitrile mixtures or acetonitrile with buffer addition for polymeric sorbents.

The sample volumes processed range between 25 ml and 2 l depending on the analytes determined and their breakthrough volumes, the pesticide levels present in the sample, the sample flow rate, the type of procedure (on- or off-line), and the type of sorbent used. The sample volume is determined according to the enrichment factors needed, and, as a rule, it can be demonstrated that there is a progressive decrease in recovery efficiencies, while the sample volume increases by standing saturation and/or by deactivation of the cartridge material.[54]

Breakthrough volumes (Vb) depend on the analyte and the extractive sorbent used. Oxamyl and methomyl have very low Vb (about 25 ml) with silica-bonded phases. Nevertheless, when extraction is done with GCB,[53] breakthrough for oxamyl begins to occur between 1 and 2 l, while methomyl did not show breakthrough even for the larger volume of sample (2 l).

Applications of off-line and on-line procedures in water are summarized in Tables 1 and 2, respectively.

The operational flexibility and the simplicity of the equipment required are the major advantages of the off-line approach. However, the possibility of automation, the elimination losses during handling of the eluate, and the high sample throughput of on-line procedure are good reasons for its using in analysis and analytical methods for continuous monitoring of water quality.[85] The two most common commercially available on-line systems are the OSP-2 (Merck) and PROSPEKT (Spark Holland). At present, on-line approach is used relatively small, packed precolumns whose typical dimensions are 2 to 10 mm × 2 to 4.6 mm I.D., although manual slurry or dry packing of a precolumn is also common.

TABLE 1

Off-Line Solid Phase Extraction (SPE) of Carbamate Pesticides and Their Metabolites from Water

Pesticides	Sample (type, volume and spiking level)	Solid phase	Elution	Recoveries (%)	LODs ($ng\ l^{-1}$)	Ref.
Carbaryl Methiocarb Propham Propoxur Thiram	Tap, natural and underground waters (500 ml) (0.16-16.1 $\mu g\ l^{-1}$)	500 mg Supelclean LC-18 cartridges (40 μm)	1 ml of AcN	93-99 79-87 89-95 99-104 -	≥ 50	54
Carbofuran Prosulfocarb Triallate	Milli Q-water (1000 ml) (0.128-0.895 $\mu g\ l^{-1}$)	1000 mg Mega BondElut C18 cartridges	5 x 1 ml of THF/methanol (4:1)	92 91 96	144-309	47
Carbofuran Prosulfocarb Triallate	Milli Q-water (1000 ml) (0.128-0.895 $\mu g\ l^{-1}$)	500 mg Empore C18 disks (47 mm)	3 x 10 ml of acetone/ methanol (4:1)	107 94 35	211-434	47
Aldicarb Carbofuran Methiocarb Methomyl	Milli Q, drinking, ground and sea waters (400 ml) (0.1-1 $\mu g\ l^{-1}$)	360 mg C18 cartridges	1 ml AcN	92-107 91-108 99-112 <25	110-300	19
Aldicarb Carbofuran Methiocarb Methomyl	Milli Q, drinking, ground and sea waters (400 ml) (1 $\mu g\ l^{-1}$)	360 mg C18 Sep-Pak cartridges	2 ml AcN	nd-90 89-110 68-109 <20	110-300	55
Carbofuran Promecarb	Milli-Q water (250 ml) (0.04 and 0.08 $\mu g\ l^{-1}$)	500 mg Supelclean ENVI-18 cartridges	2 ml ethyl acetate	87-101 92	0.011-0.022	56

Pesticides	Sample (type, volume and spiking level)	Solid phase	Elution	Recoveries (%)	LODs ($ng\ l^{-1}$)	Ref.
Aldicarb	River water	500 mg low-carbon	2 ml AcN	95-103	20-30	57
Aldicarb sulfone	(50 ml) (0.1 and 1.0 $\mu g\ l^{-1}$)	C18/OH-bonded silica		83-91		
Aldicarb sulphoxide		(40 μm)		83-93		
Bufencarb				92-96		
Butocarboxim				93-99		
Butocarboxim sulphone				80-88		
Butocarboxim sulphoxide				76-82		
Carbaryl				102-104		
Carbofuran				98-101		
Carbonolate				89-100		
Ethiofencarb				100-108		
Ethiofencarb sulphone				98-106		
Ethiofencarb sulphoxide				55-59		
Methiocarb				98		
Methiocarb sulphone				100-106		
Methiocarb sulphoxide				77-80		
Methomyl				81-90		
Oxamyl				89-111		
Promecarb				96-100		
Propoxur				98-104		
Thiofanox sulphone				102-106		
Thiofanox sulphoxide				38-44		
Tranid				99-106		
Triallate	Drinking water (pH 6) (250 and 1000 ml) (0.5 and 0.1 $\mu g\ l^{-1}$)	750 mg of Bakerbond Speedisk C18 silica disks (50 mm)	10 ml of methylene chloride-methanol (4:1, v/v)	85-95	10	58

TABLE 1 (continued)

Pesticides	Sample (type, volume and spiking level)	Solid phase	Elution	Recoveries (%)	LODs (ng l^{-1})	Ref.
Aldicarb	Distilled water	1 g C18	1 ml methanol and 6 ml	94	-	59
Carbaryl	(100 ml) (5-15 μg l^{-1})	cartridges	methylene chloride/	95		
Carbofuran			methanol	102		
Ethiofencarb			(80:20, v/v)	94		
Methomyl				86		
Molinate				92		
Pirimicarb				95		
Propham				92		
Propoxur				99		
Aldicarb	Surface water	500 mg C-18	1 ml de ethyl acetate	92	30-60	60
Carbaryl	(500 ml) (0.1 μg l^{-1})	Bond-Elute		94		
Carbofuran		cartridges		89		
Methomyl				63		
Carbendazim	Groundwater	500 mg C18	3 x 0.4 ml of methanol	99-108	40-50	61
Methiocarb	(500 ml)	cartridges		116-119		
	(0.1 and 2 μg l^{-1})					
Fenobucarb	Tap and sea water	Envi-18	5 ml methanol	93-125	-	62
Isoprocarb	(500 ml) (10 μg l^{-1})	cartridges		64-108		
Carbaryl	Distilled water (acidified with 0.2 ml concentrated HCl) (250 ml) (20 μg l^{-1})	J.T. Baker C-18 SPE	methanol	108	100	63

Pesticides	Sample (type, volume and spiking level)	Solid phase	Elution	Recoveries (%)	LODs (ng l^{-1})	Ref.
Carbaryl	Lake water	500 mg Bondapack C8	10 ml AcN-	90-99	20-220	22
Carbendazim	(50, 100, 250 500 ml)	column	methylene chloride	44-77		
Carbofuran	(0.02-0.22 μg l^{-1})	(37-55 μm)	(50:50, v/v)	52-61		
Dietofencarb				63-78		
Dioxacarb				15-54		
Fenothiocarb				78-83		
Methylthiophanate				67-76		
Methomyl				-		
Molinate				72-75		
Oxamyl				-		
Thiobencarb				73-92		
Aldicarb	Ultrapure and drinking waters	500 mg Hypercarb PGC	5 ml methanol	54-75	50-300	64
Aminocarb	(1000 ml) (0.1 μg l^{-1})	cartridges		nd-106		
Carbendazim	River water	(40-60μm)		nd-53		
Methomyl	(200 ml) (1 μg l^{-1})			84-100		
Oxamyl				nd-95		
Aldicarb	Drinking water	300 and 1000 mg	1 ml methanol and 6	92-95	2.6-17	65
Aldicarb sulfone	(2000 ml) (0.3-1.2 μg l^{-1})	Carbograph	ml methylene	8-72		
Aldicarb sulfoxide		(74-130 μm)	chloride-methanol	30-91		
Butocarboxim			(80:20, v/v)	89-93		
Butocarboxim sulfoxide				60-102		
Butoxycarboxim				42-98		
Isocarbamid				92-99		
Methomyl				88-100		
Oxamyl				84-101		

TABLE 1 (continued)

Pesticides	Sample (type, volume and spiking level)	Solid phase	Elution	Recoveries (%)	LODs (ng l^{-1})	Ref.
Aldicarb sulphoxide Methomyl Oxamyl	Drinking water (1000 ml) (1 µg l^{-1})	500 mg EnviCarb SPE cartridge (40-100 µm) Empore-activated Carbon disks (47 mm)	1 ml methanol and 2 x 5 ml methylene chloride-methanol (80:20, v/v)	43-75 68-99 68-71	40-500	53
Aldicarb sulfone Aldicarb sulfoxide Butocarboxim sulfoxide Butoxycarboxim Methomyl Oxamyl	Drinking water (4000 ml) (0.2 µg l^{-1})	500 mg Carbograph 1, 4 and 5 cartridges (37-150 µm)	1 ml methanol and 6 ml methylene chloride-methanol (80:20, v/v)	28-95 32-97 55-97 50-98 92-101 87-99	-	66
Aldicarb Aldicarb sulfone Aldicarb sulfoxide	Water (150 ml) (13.3 µg l^{-1} each analyte)	250 mg GCB Supelclean Envi-Carb cartridges	2 ml methanol	99 93 102	1000	67
Carbaryl Carbofuran Chloropropham Methomyl Oxamyl Propham	Drinking water (2000 ml) (0.125-0.750 µg l^{-1})	250 mg Carbopack B cartridges	1 ml methanol and 6 ml methylene chloride/ methanol (80:20, v/v)	98 97 97 92 89 96	3-60	68
Aldicarb	Drinking water (1000 ml) (16 µg l^{-1})	Supelclean ENVI-Carb cartridges	0.8 ml methanol and 2 x3.5 ml methylene chloride/ methanol (80:20, v/v)	101	40	69

Pesticides	Sample (type, volume and spiking level)	Solid phase	Elution	Recoveries (%)	LODs (ng l^{-1})	Ref.
Aldicarb	Tap water	250 mg Carbopack B	1 ml methanol and 2 x 3 ml	83	0.8-21	70
Butylate	(2000 ml)	cartridges	methylene chloride/	82		
Carbaryl	(0.1-1.5 µg l^{-1})		methanol (90:10, v/v)	97		
Carbofuran				99		
Chlorpropham				97		
Cycloate				89		
Eptam				82		
Ethiofencarb				93		
Methomyl				98		
Molinate				91		
Oxamyl				93		
Pirimicarb				95		
Pirimiphos-methyl				100		
Pirimiphos-ethyl				98		
Propham				93		
Propoxur				98		
Sulfallate				99		
Aldicarb	Distilled water	1 g Carbograph 1	1 ml methanol and 6 ml	96	-	59
Carbaryl	(250 ml) (5-15 µg l^{-1})	cartridges	methylene chloride/ methanol	97		
Carbofuran			(80:20, v/v)	100		
Ethiofencarb				95		
Methomyl				94		
Molinate				96		
Pirimicarb				95		
Propham				95		
Propoxur				95		

TABLE 1 (continued)

Pesticides	Sample (type, volume and spiking level)	Solid phase	Elution	Recoveries (%)	LODs (ng l^{-1})	Ref.
Benomyl	River water (250 ml) (20 μg l^{-1})	Empore disks (47 mm)	2 x 5 ml ethyl acetate	80	80	48
Aldicarb Aminocarb Carbendazim Methomyl Oxamyl	LC-grade water (1000 ml) (0.1 μg l^{-1}) Drinking water (1000 ml) (0.1 μg l^{-1}) River water (200 ml) (1 μg l^{-1})	200 mg SDB-1 PS-DVB cartridge (43-123 μm)	2 ml methanol-AcN (50:50, v/v)	73-79 90-103 nd-80 nd-94 nd-85	< 100	71
Carbendazim	Tap water (pH 4.0) (1000 ml) (290 ng l^{-1})	A mixture of 100 mg of a mixture of LiChrolut EN and100 mg LiChrolut RP-18 cartridges	2 x 3 ml methanol and 1 x 1 ml methanol	97	7	72

AcN: Acetonitrile
THF: Tetrahydrofuran
PGC: Porous graphitized carbon
PS-DVB: Polymeric styrene divinylbenzene
SDB: Styrene divinylbenzene

TABLE 2
On-Line Solid Phase Extraction of Carbamate Pesticides and Their Metabolites from Water

Pesticides	Sample (type, volume and spiking level)	Solid phase extraction	Eluents and flow rate	Analytical column	Detectors	Recoveries (%)	LODs (ng l^{-1})	Ref.
Aldicarb	Milli-Q and river water (20 ml) (5 μg l^{-1})	C18 disks (47 mm)	AcN-water (90:10, v/v) and AcN-100 mM dipotassium hydrogen phosphate buffer (pH 7) (5:95, v/v) gradient (1 ml min^{-1})	150 x 4.6 mm I.D. Rosil C18 (5 μm)	DAD-UV (215 nm)	-	1500-5000	50
Aldicarb Aldicarb sulfone Aldicarb sulfoxide Carbaryl Carbofuran 3-Hydroxycarbofuran 3-Ketocarbofuran 1-Naphthol	Drinking water (10 ml) (0.2 μg l^{-1})	10 C18 Empore disks (4.6 mm O.D.)	AcN-methanol-water (40:40:20) and AcN-water (10:90) gradient (2 ml min^{-1})	250 x 4.6 mm I.D. Supersphere 60 RP-8 (4μm)	Fluorescence λ_{ex} 330 nm λ_{em} 465 nm	94 71 73 78 95 73 74 73	5-40	51
Carbaryl	Milli Q water (100, 200 and 300 ml) (0.1 μg l^{-1})	10 x 2.1 mm I.D. RP-18 (5μm)	AcN-water gradient (3 ml min^{-1})	150 x 4.6 mm I.D. Nucleosil C18 (5 μm)	UV (254 nm)	80-98	200	73
Carbaryl	Sea water (pH 6-7) (200 ml) (0.5 μg l^{-1})	10 x 4.6 mm I.D. Spherisorb ODS (5 μm)	Methanol-AcN-water gradient (1 ml min^{-1})	250 x 4.6 mm I.D. Zorbax ODS (5 μm)	UV (220 nm)	80	< 100	74
Methiocarb	LC-grade (150 ml) (1 μg l^{-1})	10 x 2 mm I.D. C18 (40 μm)	AcN-HPLC water gradient (1 ml min^{-1})	250 x 4.6 mm I.D. Shandon C8 (5 μm)	UV (220 nm)	95	70	75

TABLE 2 (continued)

Pesticides	Sample (type, volume and spiking level)	Solid phase extraction	Eluents and flow rate	Analytical column	Detectors	Recoveries (%)	LODs (ng l^{-1})	Ref.
Carbaryl	Milli-Q water	10 x 2.0 mm I.D. RP-	Methanol-water	125 x 3 mm I.D.	UV-DAD	72	1-6	76
Carbofuran	(50-100 ml	18	gradient	LiChrospher 60 RP-		81		
Chlorpropham	(2.4 μg l^{-1})	(20 μm)	(0.6 ml min^{-1})	Select B		70		
Methiocarb				(40μm)		75		
Phenmedipham						59		
Pirimicarb						78		
Propham						77		
Propoxur						80		
Prosulfocarb						61		
Aldicarb	Drinking water	10 x 3.0 mm I.D.	AcN-water (20:80),	250 x 4.0 mm I.D.	Fluorescence	96-102	30-50	77
Aldicarb sulphone	(3 and 5 ml)	C_{18}/OH Bondesil (40	methanol-water	packed with	λ_{ex} 340 nm	84-93		
Aldicarb sulphoxide	(0.1 μg l^{-1})	μm),	(20:80) and AcN-	Supersphere RP-8	λ_{em} 445 nm	76-99		
Butocarboxim		10 x 2.0 mm I.D. and	water (60:40) gradient	(4 μm)		80-110		
Butocarboxim sulphone		10 x 3.0 mm I.D.	(0.75 ml min^{-1})			80-93		
Butocarboxim sulphoxide		PLRP-S (15-25 μm),				73-98		
Carbaryl		10 x 4.0 mm C18/OH				97-102		
Carbofuran		Bondesil (40 μm) .				99-104		
Ethiofencarb						54-103		
Ethiofencarb sulphoxide						95-102		
Methiocarb						83-92		
Methiocarb sulphone						97-107		
Methiocarb sulphoxide						92-110		
Methomyl						85-100		
Oxamyl						91-111		
Propoxur						96-103		
Thiofanox sulphone						nd-104		
Thiofanox sulphoxide						nd-98		

Pesticides	Sample (type, volume and spiking level)	Solid phase extraction	Eluents and flow rate	Analytical column	Detectors	Recoveries (%)	LODs (ng l^{-1})	Ref.
Aldicarb	Estuarine water	10 C18 disks	AcN-methanol-water	250 x 4.6 mm I.D.	Fluorescence	94	< 10	52
Aldicarb sulfone	(pH 3)	(4.6 mm)	(40:40:20) and AcN-	Supersphere 60 RP-8	λ_{ex} 330 nm	90		
Aldicarb sulfoxide	(10 ml)		water (10:90)	(4 μm)	λ_{em} 465 nm	87		
Butocarboxim	(0.2 μg l^{-1})		gradient			93		
Carbaryl			(0.8 ml min^{-1})			80		
Carbofuran						95		
3-Hydroxy-carbofuran						75		
3-Hydroxy-7-phenol-carbofuran						nr		
3-Ketocarbofuran						72		
Methiocarb						96		
Methiocarb sulfone						73		
Methiocarb sulfoxide						78		
Methomyl						88		
Molinate						nr		
Oxamyl						85		
Carbaryl	Deionized water	10 x 4.6 mm	AcN-water gradient	150 x 4.6 mm I.D.	UV (210 nm)	83	10-70	78
Carbendazim	(50 ml)	I.D.	(0.7 ml min^{-1})	Spherisorb C8 (3 μm)		101		
Carbofuran	(1.2 μg l^{-1})	LiChrospher				73		
Dietofencarb		RP-18				96		
Dioxacarb		(10 μm)				79		
Fenothiocarb						69		
Methomyl						71		
Methylthiophanate						103		
Molinate						94		
Oxamyl						99		
Thiobencarb						62		

TABLE 2 (continued)

Pesticides	Sample (type, volume and spiking level)	Solid phase extraction	Eluents and flow rate	Analytical column	Detectors	Recoveries (%)	LODs (ng l^{-1})	Ref.
Carbetamide Chlorbufam Chlorpropham Phenmedipham Propham	Surface water (50 ml) (0.5 and 4 μg l^{-1})	10 x 2 mm I.D. packed with C18 (10 μm)	Methanol-water-AcN gradient (1 ml min^{-1})	150 x 4.6 mm I.D. C18 (5 μm)	DAD (236 nm)		<100	14
Carbaryl Methiocarb Methomyl Oxamyl Propoxur	HPLC-grade water (100 ml) (5 μg l^{-1} each analyte and carbaryl 0.5 μg l^{-1})	10 x 2 mm I.D. CPP-50 (carbon material) (10-20 μm)	AcN-water gradient (1 ml min^{-1})	250 x 4 mm I.D. LiChrocart C18 (5 μm)	UV (220 nm)	78 88 56 40 72	50-1000	53
Aldicarb Barban Carbaryl Carbofuran Methomyl Oxamyl Propoxur	Milli-Q water (25,50 and 100 ml) (1 μg l^{-1})	10 x 2 mm I.D. PLRP-S PSDVB (15-25 μm)	Methanol-0.1 M ammonium acetate (pH 5.0) gradient (0.4 ml min^{-1})	200 x 4.0 mm I.D. Spherisorb ODS2 (5 μm)	DAD (240 nm)	85-94 70-85 90-94 97-102 8-30 20-38 80-95	50-500	79
Aldicarb Aldicarb sulfone Carbofuran 3-Hydroxycarbofuran Methomyl Molinate Oxamyl	River water (100 ml) (5 μg l^{-1})	20 x 3 mm I.D. PRP-1 (10 μm)	Distilled tap water (pH 5.8)-AcN gradient (1 ml min^{-1})	250 x 4.6 mm I.D. LiChrospher C18 (5 μm)	DAD	89 14 102 85 19 87 21	50-1000	21

Pesticides	Sample (type, volume and spiking level)	Solid phase extraction	Eluents and flow rate	Analytical column	Detectors	Recoveries (%)	LODs (ng l^{-1})	Ref.
Oxamyl	LC grade (100 ml) (0.1 μg l^{-1}), drinking (100 ml) (0.2 μg l^{-1}) and river (100 ml) (1.0 μg l^{-1}) waters (all to pH 2)	8 x 2 mm I.D. with SDB-1 PS-DVB (43-123 μm)	AcN-5 10^{-3} M phosphate buffer (pH 7) (1 ml min^{-1})	100 x 4.6 mm I.D. Hypercarb Porous graphitic carbon (5 μm)	UV (220nm)	73-102	100-500	71
Methomyl Oxamyl	Milli Q water (50-100 ml) (2 μg l^{-1})	10 x 3 mm I.D. Hysphere-1 (5 μm)	Milli-Q water (pH 3)-AcN gradient (1 ml min^{-1})	250 x 4.6 mm I.D. Spherisorb ODS 2 (5 μm)	UV (240 nm)	78-90 82	60	80
Methomyl Oxamyl	River water (25 ml) (8 μg l^{-1})	10 x 3 mm I.D. packed with non commercial polymeric resin (50-100 μm)	Milli Q water (pH 3)/ methanol gradient (1 ml min^{-1})	250 x 4 mm I.D. Spherisorb ODS 2 (5 μm)	UV (240 nm)	72 74	200-400	81
Aldicarb Carbaryl Carbofuran Molinate	Milli-Q water (pH 2) + 5 g l^{-1} of NaCl (50 ml) (5 μg l^{-1})	10 x 2 mm I.D. packed with styrene-divinylbenzene copolymer	Methanol-water (acidified to pH 4.5 by adding acetic acid) gradient (1 ml min^{-1})	200 x 4.6 mm I.D. Spherisorb ODS-2 (5 μm)	DAD (240 nm)	86 96 78 89	40	82
Carbendazim Carbofuran Molinate	Water containing humic acid (pH 7) (10 mg l^{-1}) (2 μg l^{-1})	10 x 2 mm I.D. packed PLRP-S (20 μm)	Acetonitrile-water (both containing 0.1% (v/v) of acetic acid (pH 3) gradient (1 ml min^{-1})	150 x 4.6 mm I.D. Octadecylsilica Ultracarb 5 ODS-30 (5 μm)	DAD	94 119 123	70-300	83

TABLE 2 (continued)

Pesticides	Sample (type, volume and spiking level)	Solid phase extraction	Eluents and flow rate	Analytical column	Detectors	Recoveries (%)	LODs (ng l^{-1})	Ref.
Methomyl Oxamyl	Milli Q, tap and Ebro river water (50 ml) (2 μg l^{-1})	10 x 3 mm I.D. non commercial polymeric resin	Milli Q water (pH 3) and AcN gradient (1 ml min^{-1})	250 x 4.6 mm I.D. Kromasil 100 C18 (5 μm)	UV (240 nm)	77-89 85-88	5000	84

nr: not responding to the detector
nd: not detected
UV: Ultraviolet
DAD: Diode array detector
ODS: Octadecylsilica
PSDVB: Polymeric styrene divinylbenzene
AcN: Acetonitrile

B. Off-Line Solid-Phase Extraction

1. Alkyl-Bonded Silica Sorbents

Silica gel began to be used for separate analytes from environmental water samples, but its peak tailing and poor selectivity and efficiency gave rise to the development of phases based in silica with an alkyl- or aryl- group substituted silanol. In this way the surface hydroxyl groups are replaced by different hydrocarbon chains[86] leading to different applications depending on the moiety bonded. The functionality properties of the sorbent also depend on the percentage of carbon loading, bonded-silica porosity, particle-size, and whether the phase is endcapped. Endcapping is used to reduce the residual silanols, but the maximum percentage of endcapping is 70%.[86] The rest of the free silanols groups can directly or indirectly affect to the extraction. To reduce silanol activity, other options can be taken, such as selecting a sorbent with a higher carbon loading or increasing the ionic strength of the conditioning solvent, sample, or wash solvent to compete with the silanols and prevent analyte bonding.

The most popular sorbents from this group in SPE are octadecylsilica (C18) and octylsilica (C8) in either cartridges or disks supports (Table 1).

When extraction was done with cartridges, recoveries greater than 79% for carbaryl, propham, propoxur, and methiocarb were obtained with a C18 sorbent. The exception was thiram, which was not retained because dithiocarbamates easily produce complexes with metal ions.[54] Carbendazim and methiocarb also showed good recoveries (>99%) when they were extracted with a C18 Bond Elut cartridge containing 0.5 g of sorbent.[61] Supelclean ENVI-18 disposable cartridges also containing 0.5 of octadecyl bonded silica solid-phase were successfully applied to the extraction of carbofuran and promecarb, and reached recoveries of 101.1% and 91.7%, respectively, with very low detection limits (11 and 22 pg).[56] Aldicarb carbofuran and methiocarb were effectively extracted from Milli Q, drinking, and ground water with C18 Sep Pak cartridges, but this sorbent proved unable to extract the most polar compound methomyl.[55] On the other hand, this pesticide was recovered, together with aldicarb, carbofuran, and carbaryl at levels higher than 62.6% when they were extracted with C18 Bond Elut cartridges.[60]

Benomyl[48] and carbendazim[87] have been extracted with C18 Empore disks from many different environmental waters, as well as EPTC, molinate, and carbofuran.[88] In this study the pesticides showed lower recoveries from natural surface waters (river, lake, and sea) than from distilled and underground water. Ten carbamate pesticides that exhibit large differences in polarity were determined in environmental waters[49] using three solid phases for cleaning up (neutral aluminium oxide, Florisil, and aminopropyl-bonded modified silica). The final proposed method used C18 disks for extraction. The detection limits were normally in the 10 to 60 ng range, and recoveries were 76 to 100%.

2. Carbon Sorbents

The most widely used sorbent is graphitized carbon black (GCB). An important gain of this sorbent is that recoveries do not decrease when environmental waters with dissolved organic carbon (DOC) are extracted. This is due to the fact that fulvic acids, which represent up to 80% of the DOC content in surface waters, are adsorbed on the anion-exchange sites of the GCB surface, and therefore they cannot compete with nonacidic pesticides for adsorption on the nonspecific sites of the sorbent. Although this fact is possible to occurr, it was found that the only effect caused by the presence of 10 mg l^{-1} DOC of humic substances in water was that the partial saturation of the GCB cartridge.[65]

Two new GCBs (Carbograph 4 and 5) have been assayed, and both exhibited more ability to extract very polar compounds from drinking water containing 20 mg l^{-1} of dissolved organic matter when than the old Carbograph 1.[66]

Despite its wide application, GCB has three main disadvantages: the collapsing of the sorbent,[53,89] the desorption problems in forward elution mode,[64] and the possibility of reactions between the analytes and the sorbent surface with

incomplete sorption and desorption.[90] These reactions are due to the fact that the GCB surface framework is contaminated by few oxygen complexes, that is, hydroquinone groups in equilibrium with their oxidized forms, namely, semiquinones and quinones,[91] that interact strongly with sufficiently acidic compounds. If this effect is unwelcome, it can be eliminated by reducing quinones to less reactive hydroquinones with an aqueous solution of ascorbic acids.[59,65] Some of the mechanisms involving GCB extraction have been examined recently.[92]

3. Polymeric Resins

With these sorbents, the retention behavior of the analytes is governed by hydrophobic interactions similar to C18 silica, but, owing to the aromatic rings in the network of the polymer matrix, one can expect strong electrodonor interactions with aromatic rings of solutes. Recovery values of 95% for carbofuran and 72% for prosulfocarb were obtained with Empore SDB disks; however, this extraction material was not useful for triallate.[47]

A multiresidue extraction procedure including molinate was achieved with highly cross-linked ethylvinylbenzene-divinylbenzene copolymer (LiChrolut EN) cartridges, and the recoveries obtained for a wide range of volumes of Milli Q water (100 to 1000 ml) were in all cases up to 106%.[93] Junker-Buchheit and Witzenbacher[72] concluded that LiChrolut EN has 10 times the loading capacity of any bonded silica phase.

4. Mixed Phases

The advantages that each sorbent present when it is used individually can be increased when a mixture of sorbents is used.[46] Schülein et al.[47] suggested the combination of solid phases for extraction of polar and very polar nonpolar compounds. Despite that, this mixed-sorbent technique has not been used frequently. Very few examples can be found in the literature. However, in one such study in which extraction of carbendazim was done with a mixture of LiChrolut EN and LiChrolut RP-18,[72] the highest recoveries and the lowest interferences from co-eluted components were obtained with the mixed phases, while extraction using each separated phase gave the worst results.

C. On-Line Solid-Phase Extraction

1. Alkyl-Bonded Silica Sorbents

In most published procedures for on-line trace enrichment, C18 or C8 chemically bonded silicas are used as the precolumn packing material, with particle sizes varying from 5 μm,[74] 10 μm,[94] or 40 μm.[95]

A problem presented by conventional apolar SPE phases is that the most polar carbamates (i.e., aldicarb, oxamyl, and methomyl) are not sufficiently retained, and thus they do not provide satisfactory recovery results. This characteristic is due to the structure of the bonded silica material. It is generally accepted that the surface-active sites on silica are Si-OH groups (silanols). Siloxane groups (Si-O-Si) are also present, but the activity of these essentially hydrophobic sites is so low that they are rarely considered to be of any consequence. Silanols serve as attachment points for the covalent silyl ether bonds that anchor bonded phases to the silica support. Therefore, after the silica surface has been modified, numerous unreacted (residual) silanol groups are left within the bonded phase. These residual silanols are weakly acidic, with pK_a values typically between 5 and 7; thus, they can interact with polar compounds through strong hydrogen bond and dipole-dipole interactions. The resulting heterogeneous surface leads to mixed retention mechanisms and peak tailing, particularly when basic solutes are involved. One feature of silanols not generally appreciated is that they are not all alike (free silanols, geminols, vicinols ...). It is suggested that it is not the absolute number of surface silanol groups that is important but rather the relative distribution of free, geminal, and vicinal groups.[47]

Sorbent efficiency greatly varies from one study to another, and the recoveries for a given pesticide when extracted with the same sorbent

differ. Comparative studies are necessary to ascertain, for a determined procedure, which sorbent is the best for each individual compound, such as that extracting carbaryl through a 1.5-cm precolumn packed with a C18-bonded silica or PRP-1 copolymer, and the analytes were separated on a 15-cm C18 analytical column.[73] The packed C18 precolumn was selected because the peak broadening in the chromatograms resulting from enrichment on PRP-1 was significant, and it was difficult to obtain quantitative results with this sorbent. With the selected sorbent the LOD for carbaryl was 0.2 $\mu g\ l^{-1}$.

For the on-line extraction, 12 carbamate pesticides were compared with different sorbents.[78] When extracting 50 ml of spiked deionized water samples, the best recoveries were obtained with the RP18 phase, followed in decreasing order by CN, PS-DVB, C2, and GCB, although the breakthrough volumes were reached earlier with silica gel-based phases than with PS-DVB.

A comparative study of the precolumns of the same geometry slurry packed with Bondesil C18/OH, PLRP-S, EnviCarb GCB, CPP-50, and Empore Activated carbon disks (EACD) for the polar carbamates oxamyl, methomyl, and aldicarb was run.[53] The authors concluded that using 10 membrane extraction disks of C18 bonded-silica material increases the breakthrough volume of many polar carbamates when compared with the other packing material, PLRP-S. This can be ascribed to the higher trapping capacity of C18 membrane disks of 8-μm particle size in an on-line combination.[51] Using the same extraction procedure, another study was carried out,[96] but this time detection was by mass spectrometry instead of UV-VIS or fluorescence.

Commercially available Bondesil-C18/OH was used,[97] and apolar and polar interactions occur (via the alkyl chains and hydroxyl groups, respectively), and breakthrough volumes were increased compared with polymeric phases.

2. Carbon Sorbents

New low carbon sorbents have been developed, with a high level of free silanol groups, applied especially to polar compounds. The efficiency of this sorbent has been controversial, and the results have been compared with those obtained with polymeric or carbon sorbents. However, even with resins, neither oxamyl nor methomyl can be satisfactorily extracted.[79]

The use of Envicarb as extractant is not recommended by several authors[53,89] because of a phenomenon called "collapsing" of the material under the operational pressure of the LC system. However, the commercially available EnviCarb[47] and the noncommercialized CPP-50[53] were used in an on-line procedure coupled to a C18-bonded silica column, but in this case there was a peak broadening caused by the strong sorption of the carbamates on carbon. This effect was suppressed by eluting the precolumn with a separate stream of 0.1 ml min^{-1} of organic solvent that was mixed with the LC gradient in front of the analytical column.[53]

3. Polymeric Resins

As some old polymeric sorbents have proven not to be efficient for the extraction of these polar compounds, new sorbents must be assayed. A comparative study of three commercial polymeric sorbents (PLRP-S, LiChrolut EN, and Envi Chrom P) and a newly synthesized sorbent was carried out[81] involving the application of the three to the extraction of oxamyl and methomyl. The new polymer gave better results for these two pesticides than PLRP-S or Envi Crom P but similar results for other less polar compounds.

On the other hand, modified polymeric resin with an *o*-carboxybenzoyl moiety prepared from a polystyrene-divinylbenzene resin was used to analyze of oxamyl and methomyl, and gave recoveries of up to 77% when 50-ml samples were preconcentrated.[84] A PLRP-S styrene-divinylbenzene copolymer was used for the preconcentration of carbendazim, carbofuran, and molinate, and breakthrough values higher than 300 ml were obtained.[83] The same type of resin was chosen for the preconcentration of molinate,[98] for carbofuran and 3-hydroxicarbofuran,[99] for aldicarb, carbofuran, carbaryl, and molinate,[82] and for the most polar compounds, carbendazim, and aldicarb[20,100,101] in waters, with satisfactory results. This highly hydrophobic polymer (PLRP-S) was also selected com-

pared with C18-bonded silica material for the extraction of aldicarb, propoxur, carbofuran, carbaryl, and barban because of the higher breakthrough volumes for most of the studied compounds.[79]

However, in another study[76] carried out with spherical styrenedivinylbenzene copolymers (PLRP-S and PRP-1), the band broadening led to strong overlapping peaks in the chromatograms, making analysis of complex mixtures impossible and the authors considered the combination of PLRP-S with C18 analytical columns incompatible.

A backflush-mode elution is necessary when polymeric resins are used, and the major drawback to this elution procedure is that matrix interferences are also eluted onto the guard column, causing a build up of strongly retained compounds on the guard column during analysis.[77]

The effectiveness of three different sorbents, Carbopack B, Bond Elut PPL (a functionalized polymeric resin), and HYSphere-1 (a higher crosslinking polymeric resin) were also compared.[80] The study demonstrated that the three sorbents gave similar recoveries for oxamyl and methomyl in surface and tap water.

"Collapsing" of the material has been also observed under operational pressure when LiChrolut EN is not mechanically stable for use on-line enrichment cartridges. This fact can be eliminated by addition of perfluorinated polyethene particles (PolyF®), which mechanically stabilises the enrichment cartridges for repeated use.[102,103]

PRP-1 material is recommended for medium polar compounds, but the fact that different recoveries were found for a single compound when extracted with SDB and with PRP-1 led the authors to conclude that the two polymeric sorbents are of a different nature or that SDB polymer is present at a much lower concentration.[52]

4. Mixed Phases

An on-line study compared three SPE disk systems: (1) 10 C18-bonded silica disks, (2) 10 SDB disks and, (3) four SDB and six C18-bonded silica Empore disks for the preconcentration of some carbamates and TPs.[52] Of the three systems used, (1) and (3) reached higher recovery values for most of the studied compounds. The main trouble was found with the more polar compounds that eluted at the beginning of the LC traces were interfered with humic substances present in the water and/or had low breakthrough volumes.

III. LIQUID CHROMATOGRAPHY (LC)

A. General

The determination of carbamate residues in waters can be achieved by several methods, but nowadays the increasing availability of LC is very patent when comparing liquid vs. gas chromatography.[27] This is mainly due to their suitability for thermally labile and polar compounds, and, to their major advantage, over gas chromatography that on-line precolumn and post-column systems are compatible with LC. In addition, the powerful mass spectrometer detectors have been coupled successfully to LC systems.

The main difference between one and another LC method is the length of the column, the mobile phase, elution mode, the stationary phase, and the detectors used. From Tables 2 and 3, it can be seen that the length of the chromatographic columns normally ranges between 100 and 250 mm, being preferred to those shorter ones of 100 mm when few compounds are analyzed. The most used solvents as mobile phase are acetonitrile, methanol, and/or water in a gradient mode, although isocratic elution is also performed. pH modification of the mobile phase is sometimes achieved with buffer addition, commonly phosphate or ammonium acetate buffer.

Bonded-silica is the most used support material; however, it presents two drawbacks in that it cannot be used at extreme pH values, and the presence of some residual silanol groups, which, in principle, could contribute to undesirable interactions sorbent-pesticide.[104] Hydrolysis occurs rapidly when the column packing is used at low pH and at high temperatures. New technologies tend to improve C18 stationary phases in order to reach more stable and pH- and temperature-resistant phases.[104]

The most common sorbents are octyl-silica and octadecyl-silica, although other less common

TABLE 3
Determination Methods of Carbamates and Their Metabolites After Off-Line Solid Phase Extraction from Waters

Pesticides	Mobile phase (flow rate)	Analytical column	Detectors	Ref.
Carbaryl Methiocarb Propham Propoxur Thiram	AcN:water (42:58, v/v) isocratic (1.5 ml min^{-1})	200 x 4 mm I.D. Spherisorb ODS column (5μm)	UV (220 nm)	54
Carbofuran Prosulfocarb	AcN-buffer solution (1 mmol ammonium acetate diluted to 1 l water) gradient (0.8 ml min^{-1})	250 x 4 mm I.D. Hypersil ODS column (3 μm)	UV-DAD (220 nm)	47
Aldicarb Carbofuran Methiocarb Methomyl	Water-methanol-AcN gradient (1 ml min^{-1})	150 x 3 mm I.D. Hypersil Shandon Green Env. C18 column (5 μm)	DAD (212 nm)	19 and 55
Carbofuran Promecarb	Methanol-water acidified with 0.3% formic acid	100 x 1.0 mm I.D. column C18 (5μm)	ISP-MS	56
Aldicarb Aldicarb sulfone Aldicarb sulphoxide Bufencarb Butocarboxim Butocarboxim sulphone Butocarboxim sulphoxide Carbaryl Carbofuran Carbonolate Ethiofencarb Ethiofencarb sulphone Ethiofencarb sulphoxide Methiocarb Methiocarb sulphone Methiocarb sulphoxide Methomyl Oxamyl Promecarb Propoxur Thiofanox sulphone Thiofanox sulphoxide Tranid	AcN-water (20:80), methanol-water (20:80) and AcN-water (60:40) gradient (0.75 ml min^{-1})	250 x 4.0 mm I.D. Supersphere RP-8 column (4 μm)	Fluorescence λ_{ex} 340 nm λ_{em} 445 nm	57
Triallate	AcN- 5 10^{-3} M phosphate buffer (pH 7) gradient (1 ml min^{-1})	250 x 4.6 mm I.D. Bakerbond Narrow Pore C18 (5 μm)	UV-DAD (220 nm)	58

Table 3 (continued)

Pesticides	Mobile phase (flow rate)	Analytical columns	Detectors	Ref.
Aldicarb Carbaryl Carbofuran Ethiofencarb Methomyl Molinate Pirimicarb Propham Propoxur	Water-1 mmol l^{-1} phosphate buffer (pH 6.7) and AcN gradient (2 ml min^{-1})	250 x 4.5 mm I.D. LC-18 DB (5 μm)	UV (210 nm)	59
Aldicarb Carbaryl Carbofuran Methomyl	AcN-phosphate buffer (pH 7) gradient (1 ml min^{-1})	250 x 4.6 mm I.D. Novapak C18 (5 μm)	Fluorescence λ_{ex} 330 nm λ_{em} 465 nm	60
Carbendazim Methiocab	63% methanol and 37% 0.1 M aqueous ammonium acetate	250 x 4.6 mm I.D. Spherisorb S5 ODS-1	TS/Plasmaspray-MS	61
Fenobucarb Isoprocarb	AcN-phosphate buffer solution (pH 2.6) (45:55)	250 x 4.6 mm I.D. LC-ABZ	UV-Vis (215 nm)	62
Carbaryl	Methanol/DI-DI water gradient (0.2 ml min^{-1})	150 x 2.1 mm I.D.Supelcosil LC-8	ESP-MS	63
Carbaryl Carbendazim Carbofuran Dietofencarb Dioxacarb Fenothiocarb Methylthiophanate Methomyl Molinate Oxamyl Thiobencarb	AcN-HPLC grade water gradient (0.7 ml min^{-1})	250 x 4.0 mm I.D. Spherisorb C18 (5 μm)	UV (210 nm)	22
Aldicarb Aminocarb Carbendazim Methomyl Oxamyl	AcN-$5 \cdot 10^{-3}$ M phosphate buffer (pH 7) gradient (1 ml min^{-1})	250 x 4.6 mm I.D. Supelcosil LC18-DB (5 μm)	UV (200 nm)	64
Aldicarb Aldicarb sulfone Aldicarb sulfoxide Butocarboxim Butocarboxim sulfoxide Butoxycarboxim Isocarbamid Methomyl Oxamyl	Water-methanol (98:2) and AcN gradient (1.5 ml min^{-1})	250 x 4.6 mm I.D. Supelco LC-18 DB (5 μm)	UV (210 nm)	65

Table 3 (continued)

Pesticides	Mobile phase (flow rate)	Analytical columns	Detectors	Ref.
Aldicarb sulphoxide Methomyl Oxamyl	Methanol-water (5:95, v/v) and methanol-water (90:10, v/v) gradient ($1 ml min^{-1}$)	250 x 4.6 mm I.D. Supelcosil C18 (5 μm)	UV (254 nm)	53
Aldicarb Aldicarb sulfone Aldicarb sulfoxide Butocarboxim sulfoxide Butoxycarboxim Methomyl Oxamyl Propoxur	Water-methanol (98:2) and AcN gradient ($1.5 ml min^{-1}$)	250 x 4.6 mm I.D. LC-18 DB (5 μm)	UV (210 nm)	66
Aldicarb Aldicarb sulfone Aldicarb sulfoxide	Water-methanol gradient ($1 ml min^{-1}$)	100 mm C_{18} carbamate column	Fluorescence λ_{ex} 340 nm λ_{em} 455 nm	67
Carbaryl Carbofuran Chloropropham Methomyl Oxamyl Propham	AcN-water gradient ($1.5 ml min^{-1}$)	250 x 4.6 mm I.D LC-18 (5 μm)	UV (225 nm)	68
Aldicarb	Water-AcN (90:10) and AcN gradient ($2 ml min^{-1}$)	LC-18	UV (220 nm)	69
Aldicarb Butylate Carbaryl Carbofuran Chlorpropham Cycloate Eptam Ethiofencarb Methomyl Molinate Oxamyl Pirimicarb Pirimiphos-methyl Propham Propoxur Sulfallate	Water-1 mmol l^{-1} phosphate buffer (pH 6.7) and AcN gradient ($2 ml min^{-1}$)	250 x 4.5 mm I.D. LC-18 DB (5 μm)	UV (220 nm)	70
Benomyl	Methanol-deionized water pH 7 buffer mixture (0.067 M Na_2HPO_4+ 0.067 M KH_2PO_4) gradient ($2 ml min^{-1}$)	Whatman C18 Partisphere	UV (254 nm)	48

Table 3 (continued)

Pesticides	Mobile phase (flow rate)	Analytical columns	Detectors	Ref.
Aldicarb Aminocarb Carbendazim Methomyl Oxamyl	AcN-5 10^{-3} M phosphate buffer (pH 7) gradient (1 ml min^{-1})	250 x 4.6 mm I.D. Supelco C18 (5 μm)	DAD (220 nm)	71
Carbendazim	AcN water (20:80, v/v) isocratic (0.7 ml min^{-1})	125 x 4 mm I.D. Purospher RP-18 (5μm)	UV-DAD (220 nm)	72

AcN: Acetonitrile
DAD: Diode array detector
ESP: Electrospray
ISP: Ionspray
TSP: Thermospray
MS: Mass spectrometry
UV: Ultraviolet

sorbents such as phenyl[87] or PLRP-S[20] are also used.

B. Detectors

1. UV and DAD Detectors

A review of the literature (see Tables 2 and 3) shows that UV absorbance is the most common detector method for the determination of carbamates in water. UV and DAD detectors are the most commonly available in laboratories and also traditionally the most frequently used in LC. The wavelengths used vary according to the pesticides analyzed, finding an important drawback such as the interferences found when working at wavelengths under 205 nm are employed and a certain baseline drift that disturbs correct quantification of the analytes. This last fact was corrected by contaminating water with a small amount of methanol.[65]

The most common wavelengths are of 210 or 220 nm, although many carbamates can be detected at different wavelengths, such as aldicarb, oxamyl, and methomyl, which absorb at 210, 220, or 254 nm.[64]

UV detector has the disadvantage of a lack of selectivity and, sometimes, poor sensitivity. To overcome these two limitations, other detectors have been applied such as diode array detection,[14,19,21,79] or a selective post-column derivatization with fluorescence detection,[57,60,67] which offers a degree of selectivity and sensitivity often an order or more over that offered by UV. The use of DAD allows selection of the wavelengths employed for the determination of each pesticide in order to obtain an improvement in sensitivity and selectivity. LC-DAD system is significantly cheaper, and normally provides sufficient data for early-warning purposes.

2. Fluorescence Detectors

The general structure of the carbamate pesticides is an *N*-methyl substituted urethane with the variation in the ester moiety. The common methylamine functionality provides the possibility for the detection of compounds via a two-stage, post-column reaction. The carbamates in the column effluent are first hydrolyzed at elevated temperature by sodium hydroxide to form methylamine. Methylamine is converted into a fluorophore compound (1-dimethylaminoethylthio-2-methylisoindole) by the addition of *o*-phthalaldehyde (OPA) and 2-mercaptoethanol (MCE) in a borate buffer[57,77,105,106] or OPA and Thiofluor™ (*N*, *N*-dimethyl-2-mercaptoethylamine).[51,60,107] The use of Thiofluor™ has the advantage of its major stability, and that it does not presents the odor of MCE. Excitation and emission wavelengths can vary, as can be seen from Tables 2 and 3.

Derivatization methods have been developed because the carbamate pesticides do not have

natural fluorescence, thus this technique requires reagent solutions to be added, and extra column peak broadening can result from the reactor. However, post-column detection allows the analytes to be separated in their original form, formation of artefacts is at a minimum, reaction does not need to be complete, their products do not have to be stable because the only requirement is reproducibility, and it is easily automated.

The derivatization process has been rather improved and simplified since the reagents (NaOH, OPA and MCE), introduced separately in a beginning, have been put together as a single reagent with just the one pump that was needed.[108] Another simplification of the technique applied was that of making the post-column hydrolysis in an anion exchange resin (Aminex-27) (catalyst) heated to 140ºC.[109] Only the mobile phase, water, acetonitrile, and sodium acetate solution was flowed through the resin. This method does not use strong base reagents and only a single pump to introduce the reagent of derivatization (OPA-MCE) after the chromatographic column and the anion resin is required. The inexpensive general purpose magnesium oxide can be also used because it has very favorable catalytic characteristics for the hydrolysis of *N*-methylcarbamates, but in the practice the relatively rapid blockage of the hydrolysis column due to the wide range of particle sizes. The major advantage of solid-phase hydrolysis compared with NaOH solution hydrol ysis is the omission of an extra reagent pump, which means that no dilution of the HPLC column effluent takes place, thereby avoiding extra band broadening and retaining optimum resolution and peak sensitivity. Eliminating the NaOH hydrolysis also prevents the occasional leaking of the reagent pump seals or blockage of the hydrolysis reaction capillary due to the build up of crystallized NaOH reagent.[57] This was possible because the hydrolysis (borate solution) and derivatization (OPA-MCE) in the mobile phase without anion-exchange resin and strong base reagents.[105]

3. Mass-Spectrometric (MS) Detection

a. General

The application of MS detector is the most powerful tool available for analyzing and to avoid problems observed in other techniques such as LC-DAD caused by matrix interferences that leads to poor recoveries.[110] Such recoveries can be improved by LC-TSP-MS, because in this case analytical measurements were more correctly performed.[87] Good reviews and articles on the different types of interfaces used, including transport systems, direct liquid introduction, thermospray, atmospheric pressure ionization, electrospray and particle beam have been published.[111-115] The drawbacks of coupling LC-MS are that sensitivity is lower than that of GC-MS in all instances, the main problem is the transfer of analytes from the liquid phase into a high vacuum gas phase. Other limitations occur when coupling these two techniques, such as nonvolatile buffers cannot be used, the eluent flow rate is often limited to a to a narrow optimal range, the percentage of organic modifier can affect the sensitivity of detection, and the choice of ionization methods is limited. Unless a greater amount of sample is extracted, difficult quantification, due to variations in sensitivity in day-to-day use, unless calibration and cleaning of the different parts are done, hence it can mostly be recommended for confirmation purposes, and poor structural information, which is particularly true for LC-TSP-MS. The development of LC-PB-MS with the possibility of producing EI spectra has partially overcome these problems, but in this case polar compounds are more difficult to analyze than with the LC-TSP-MS interface.

The main goals in LC-MS techniques are to implement the methods, especially those using API interfacing, on a routine basis or to develop tandem mass spectrometric scanning strategies.[99]

b. LC-TSP-MS

Thermospray (TSP) system is probably the more used for carbamate analysis in waters for off-line[61] and on-line[116] determinations and involves reversed-phase columns and volatile buffers, with or without a filament or discharge; filament-off and filament-on with positive- and negative-ion modes are common choices. The filament-off mode is associated with thermospray ionization; meanwhile, the filament-on mode is similar to chemical ionization and discharge ion-

ization. These two procedures are commonly applied, the filament-on mode being preferred due to the higher sensitivity reached. The TSP interface can be operated under discharge-assisted buffer ionization preparations, sensitivities much higher than those obtained in the filament on mode, or with volatile salt ionization without external ionization media.[117]

The positive-ion mode is used more, and normally yields $(M + H)^+$ and/ or $(M + NH_4)^+$ base peaks. The negative-ion mode yields $(M + acetate)^-$ or $(M + formate)^-$ base peaks, but optimization and repeatability are difficult. The lack of structural information is due to the absence of abundant fragment ions.[115] A method to solve the problem of assigning structures in a coeluted mixture was proposed for the determination of carbofuran, propoxur, and pirimicarb.[118] The method consisted in a multivariate curve resolution technique (MCR), a technique also applied in a degradation study of benomyl and carbendazim;[119] the method permitted distinguishes between the presence of two coeluted compounds with the same mass.

In LC-TSP-MS the nature of the reagent gas is determined by the composition of the LC eluent. Because volatile ionic modifiers are needed, the demands of a suitable eluent can seriously interfere with the optimization of both PI and NI modes. The different clusters between the components of the LC eluent will determine the scan range. A study explored the influence of four different eluent compositions on reversed phase LC. Methanol-water (50: 50) + 0.05 *M* ammonium acetate, methanol-water (50:50) + 0.05 *M* ammonium formate, acetonitrile-water (50: 50) + 0.05 *M* ammonium acetate, and acetonitrile-water (50:50) + 0.05 *M* ammonium formate were assayed in positive- and negative-ion modes during the generation of TSP spectra of carbamates.[120] They used these combinations for the characterization of oxamyl, carbofuran, propoxur, carbaryl, pirimicarb, and chlorpropham, identifying the different adducts formed with each eluent and modifier. An interlaboratory study of a LC-TSP-MS method for selected *N*-methylcarbamates based on AOAC International's blind replicate design with balanced replicates was evaluated.[121] The results indicated that the LC-TSP-MS method might be a viable analytical method for thermally labile compounds. However, the control of certain operational parameters is critical, that is, the tip temperature needs to be monitored and carefully controlled because it plays a major role in adduct formation and ion fragmentation. Although it is not important whether the ammonium adducts ion or the protonated ion is the dominant ion, it is important that the thermospray spectra be consistent between the standard and the sample and from day to day.

Four carbamates were determined with a TSP-MS interface,[116] and the limits of detection for the whole of the pesticides were in the range 2-90 ng l^{-1}.

Several carbamate pesticides were analyzed[96,122] in the TSP-MS mode. Each compound gave two main ions corresponding to $(M + H)^+$ and $(M + NH_4)^+$ in the PI mode. Ammonium formate was chosen as an eluent additive instead of ammonium acetate because it enhanced the chromatographic resolution at pH 3 and also adduct formation as a result of its slightly higher gas-phase acidity. However, the sensitivity was similar in both instances and $(M + NH_4)^+$ appeared to be the base peak for the whole group of carbamates except carbofuran, which had $(M + H)^+$ as its base peak. This behavior meets the expectations for carbamates, except for carbofuran, the ions of which did not match previous findings published[120] showing $(M + H)^+$ as the base peak.

c. LC-PB-MS

Particle beam is a recommended detection technique in US Environmental Protection Agency methods for trace organics in waters that it provides electron impact mass spectra, giving access to comparing with large databases. Unfortunately, the method is not sensitive, induces thermal degradation, and fragmentation.

Even though the PB can be coupled to a conventional LC with flow rates up to 1 ml min^{-1}, it has many disadvantages such as the low sensitivity due to inefficient sample transfer through the interface. On-line coupling to SPE can compensate this drawback.

A new microliter flow rate LC/MS PB interface was applied to a multiresidue analysis, in-

cluding some carbamates. With this interface mobile phase (water/acetonitrile), flow rates ranging between 1 and 5 μl min^{-1} passed into the electron impact ion source of the MS. The aerosol generated by the reduced solvent input allows improved signal response for high water content mobile phases with better chromatographic performance during gradient analysis.[123] In the described procedure the mobile phase was added with a 0.1 *M* solution of ammonium acetate to the water for the separation of basic/neutral pesticides, and with 0.05% TFA in water and 0.25% TFA in acetonitrile for the acidic ones. This was done because, as demonstrated previously,[124,125] the addition of certain substances to the mobile phase can enhance both the chromatographic performance and overall particle beam carrier process, with evident advantages in sensitivity and response linearity. Ammonium acetate was also added to the mobile phase (methanol), because it acts as a carrier and extends the PB-MS linear range.[79]

LC-PB-MS, using full-scan electron impact mode detection,[115] has been also applied for the determination of 32 carbamates and 11 transformation products. LODs reached for 17 compounds were 0.1 to 8 μg l^{-1}. Thirty-three carbamates and 14 of their transformation products were analyzed with flow injection PB-MS with electron impact ionization and ammonia and methane positive and negative chemical ionization (CI),[126] the mass spectra of 14 compounds were compared. The mass spectra from the FIA-PB-PCI-MS experiments exhibit higher relative abundance for fragment ions. The influence of the ion source pressure and temperature on the ion abundance under ammonia PCI conditions was studied. Results indicate that thermal degradation of the carbamate pesticides takes place in the FIA-PB-MS system. In addition, the $(M + NH_3 + H)^+$ and $(M + NH_3+H\text{-}CH_3NCO)^+$ ion intensities are strongly dependent on the ion source pressure, especially for carbofuran.

Also using a LC-PB-MS method, the operation of a quadrupole ion trap mass spectrometer (QITMS) as a mass spectrometric detector was described,[128] and studies investigating two methods of QITMS operation implemented with standard ITMS software to eject unwanted solvent ions from the ion trap were realized. This was applied to aldicarb sulfone, carbaryl, methiocarb, and carbaryl. Isocratic LC-PB-QITMS analyses showed lower limits of detection than those reported for LC-PB-MS analyzed on PB systems using quadrupole mass analyzers.

d. LC-APCI-MS

Heated nebulizers under atmospheric pressure chemical ionization mode (APCI) have been applied to the determination of carbamates.[129,130] The main limitation of this interface is that ionization occurs in the gas phase. The volatilization of a sample prior to APCI can only be achieved with the input of a sufficient amount of heat, with inevitable decomposition of thermolabile compounds. Despite this disadvantage, APCI has the great advantage of inducing fragmentation of the primary ions with the application of an appropriate voltage value, so APCI offers the possibility of obtaining additional structural information. This mode of operation is termed cone voltage fragmentation (CVF) or preanalyzer collision-induced dissociation (CID).[94]

The development of atmospheric pressure ionization (API) systems offers new opportunities for the determination of thermolabile and polar compounds such as carbofuran[131] and carbendazim.[132] This study demonstrated that with TSP and PB interfaces the quantification of carbofuran was affected by both the ion source pressure and temperature, whereas quantification using API interfaces, APCI, ESP, and IP is less dependent on these parameters.

Some interlaboratory studies on the performance of some interfaces in the determination of carbamates have shown APCI-MS to be the most sensitive technique with approximately 10-fold better detection limits than ISP and TSP. The PB-MS was in some instances almost four orders of magnitude less sensitive than APCI-MS,[133] which is in agreement with the study[94] where it was concluded that with the APCI interface a greater number of compounds may be determined than with the PB interface and that it was more sensitive.

e. LC-ESP-MS and ISP-MS

The use of ESP ionization is used for the instances in which pesticides cannot be detected by TSP such as the analysis of thermally degradable pesticides. This ionization technique depends on the dispersion of a sample solution into an electrically charged aerosol. Once electrically charged droplets are formed, evaporation of the solvents takes place at atmospheric pressure, which provides a rather soft ionization technique, that is, with little or no fragmentation of the protonated molecule. Together with the fact that no heat is applied during the introduction of the target compounds into the MS, thermal degradation is prevented and thus this permits the protonated molecules of the carbamates to be mainly formed. This advantage also holds for Ionspray (ISP) and high-flow ISP interfaces. In the high-flow version of the interface a so-called liquid shield is incorporated, which in principle allows the use of low rates of up to 1 ml min^{-1}. Mexacarbamate[134] was determined using a 4.6 mm I.D. analytical column and a 1 ml min^{-1}. Again a high-flow interface was used for the analysis of 10 carbamates[49] coupled to a 3-mm I.D. column, the eluent flow was 0.3 ml min^{-1}, applied without splitting of the eluent before its entrance in the mass spectrometer. Quantification showed the concentration level to be ca. 5 μg l^{-1} or about 1 ng l^{-1} in the initial water sample. The ISP interface parameters were optimized for the study of carbofuran and promecarb using a narrow bore analytical column.[56] The optimization was focused in the liquid flow-rate entering the interface. Flow rates from 10 μl min^{-1} to 60 μl min^{-1} were delivered to the ionspray probe. Although the signal response remained unchanged, the use of the lower flow rates improved the baseline stability in the full scan mode, thereby increasing the signal to noise ratio. This confirms the general observation that sample detection under ISP conditions is sensitive to the concentration, and not to the sample mass flow rate delivered to the source. The major drawback of this developed method, compared with conventional MS-MS in a triple analyzer instrument, is that chemical noise is not removed from the parent and fragment ion signals.

Another advantage is that LODs could be 100 times lower than those that can be obtained by using TSP.[135] In addition, much better structural information is obtained when compared with TSP-MS. Electrospray nebulization works well when a sample is dissolved in methanol, ethanol, acetonitrile, chloroform, or some other suitable organic solvent that has a low surface tension. It is more difficult to spray solutions in water, which has a much higher surface tension and opposes the separation of droplets from the liquid front. The spray is less stable and the droplets are bigger. A solution given to overcome this problem is to achieve a coaxial arrangement of two tubes.[111]

Electrospray is a low flow rate technique. When the flow rate is increased for a given sample concentration, the sample ion signal does not increase. So, in terms of sample concentration, the sensitivity remains constant, but in terms of mass flow the sensitivity drops when the flow rate of the sample solution is increased. The apparent concentration sensitivity of electrospray can be attributed to a decrease in droplet-charging efficiency and a shift toward larger diameters in the droplet-size distribution if the liquid flow rate is increased. The practical upper limit to flow rate in pure electrospray is 10 to 20 μl min^{-1} depending on the composition of the solvent. Pneumatically assisted electrospray has been used up to 200 μl min^{-1}, and high-flow pneumatically assisted electrospray with up to 1 ml min^{-1}. The possibility of using conventional-size analytical columns is not available with the ESP interface, where flow-rates are so small. However, the application of post-column splitting of the LC eluent combined with a 1-mm I.D. column provided a full scan positive-ion MS/MS mass spectrum of propoxur at a level of 60 pg.[136]

IV. ENVIRONMENTAL ANALYSIS OF CARBAMATES AND THEIR TRANSFORMATION PRODUCTS

Because of the intensive agricultural use of pesticides and possible health effects, a monitorization of the surface waters draining agricultural areas is necessary. Some of these areas are taken into account in environmental programs, such as the re-

gions of the Central Columbia Plateau included in the Columbia Basin Irrigation Project. Data obtained from monitoring studies are useful for determining the occurrence and temporal distribution of pesticides and their metabolites in the evaluated areas, as it was done in a very rigorous paper for the determination of pesticides in Arkansas Surface waters.[48] There are seasonal variations that show the different environmental behavior, and this is directly dependent on their solubilities, that is, methomyl is much water soluble than carbofuran. The type of pesticide detected depends directly on the type of culture in the zone; carbamates such as molinate or carbofuran are frequent in rice cultures; meanwhile, aldicarb and its metabolites are normal when citrics are cultivated. Moreover, some carbamates such as carbofuran have Maximum Contaminant Level Goals (MCLG) proposed by the EPA for primary drinking waters. That is the reason for what this pesticide was analyzed in private wells from an agriculture area such as Central Maine.[23] The normal period for application of these compounds is plotted from late spring to early summer months. Sometimes pesticides are detected out that reported period as it occurred with carbaryl in Crab Creek Lateral (Columbia). Because this pesticide has a relative short life, its detection suggests its use outside its period of application rather than its persistence in the environment.[5]

Table 4 summarizes the place of withdrawal of the sample, pesticides detected, concentration range found, analytical parameters, detection system, and LOD.

Different matrices are analyzed such as aquifer, drinking, sea, river, lake, wells, and surface and ground waters, being that the levels of pesticides found vary depending on the sampled zone. Meanwhile, levels reached in waters from the Plateau of Lassithi are lower than the EU maximum acceptable concentration of 0.1 $\mu g\ l^{-1}$ for an individual pesticide,[60] other zones such as the Albufera Lake and surrounding irrigation channels are hardly contaminated with high pesticide levels, as was demonstrated from two long-term periods of monitorization.[22,141] Other studies also demonstrate that pollution by carbamate insecticides exceeds the limit of 0.5 $\mu g\ l^{-1}$ for total pesticides allowed by the European Directive. These high pesticide levels occurred in various regions; a major supplier of green vegetables region such as Almeria (Spain), where carbofuran, methomyl, and methiocarb were detected in waters from the Campo de Nijar aquifer,[110] or in the Ebro Delta,[49] where carbofuran was found at a concentration level of approx. 5$\mu g\ l^{-1}$.

V. CONCLUSIONS

SPE is one of the most important techniques for trace enrichment of carbamate pesticide and metabolites from waters. That is because a sample preparation by SPE is easy to handle, fast, environmentally friendly, and gives high recoveries with reproducible extractions. The use of alkyl-bonded silica, styrene-divinylbenzene copolymers, and activated carbons commercialized as cartridges, precolumns, and disks is frequently referenced as solid phases. Retention mechanisms of the silica sorbents are well known, and a lot of cheap, available phases are on the market. Carbon-based phases are less influenced than the silica-based phases by the organic matter contained in water. Polymeric sorbents present high loading capacity and unique retention properties to some carbamate and transformation products. The use of mixed phases is scarcely cited. Such mixed phases can be useful for extracting carbamates of different polarities in a single extraction.

On-line SPE procedures minimize the operator handling and can be completely automated, thus they are helpful for the routine evaluation of water quality. The off-line approach is simple, versatile, allows *in situ* sampling, can be performed in any common laboratory, can reach good limits of detection by extracting high volumes of sample, and many solid phases with a broad spectrum of properties are commercially available for performing it. In the future, the SPE will probably be progressively replaced by other emerging techniques such as solid-phase microextraction (SPME). At the moment, the use of SPME coupled to LC is limited to a few compounds.

After SPE, liquid chromatography is usually performed with octyl- and octadecylsilica analytical columns; other stationary phases are used rarely. In on-line procedures, the use of the same type of phase for extraction and determination

Table 4
Residues of Carbamates and Their Derived Products in Environmental Waters

Sample	Pesticide	Concentration range ($\mu g\ l^{-1}$)	Ref.
Groundwater from Almería (Spain)	Carbofuran	3.5-4.8	19 and 55
	Methiocarb	0.4-5.5	
	Methomyl	2.2-2.8	
La Albufera Lake water (Valencia, Spain)	Carbaryl	11.5	22
	Carbofuran	1.3-8.9	
	Dietofencarb	4.0-36.0	
	Fenothiocarb	4.0-16.0	
	Molinate	1.3-20.1	
Field water from the phreatic horizon of the Axios River basin of a rice field from Macedonia (Greece)	Carbofuran	0.09	21
Ground water from the Axios River basin from Macedonia (Greece)	Carbofuran	nd	21
	Molinate	0.42	
Groundwater from the raw water intake line of the Murphree Water Treatment Plant in Gainesville,FL (USA) and linestone from an outcrop of the Floridan Aquifer in Ocala, FL (USA)	Aldicarb	36-249	137
	Aldicarb nitrile	nd	
	Aldicarb oxime	3.2-32	
	Aldicarb sulfone	25-250	
	Aldicarb sulfone nitrile	nd	
	Aldicarb sulfone oxime	7.8-78	
	Aldicarb sulfoxide	20-200	
	Aldicarb sulfoxide nitrile	22-220	
	Aldicarb sulfoxide oxime	3.8-38	
Streams and ponds	Benomyl	40.8	138
	Carbendazim	9.9	
Raw water from the Ebro Delta (Spain)	Carbofuran	5	49
Nitra river (Slovakia) (pH 7.5-8.5)	Aldicarb	0.05-3	139
Well water in Central Maine (USA)	Carbofuran	0.08-0.38	23
River Rhine (Germany)	Barban	0.05	100 and 101
Aquifer from Almería (Spain)	Carbofuran	0.32	110
	Methiocarb	0.3	
	Methomyl	0.8	

Table 4 (continued)

Sample	Pesticide	Concentration range	Ref.
Pond water from Uttar Pradesh (India)	Carbofuran	0.07-0.96	140
Surface and ground water of Lassithi Plateau, Crete (Greece)	Aldicarb Carbaryl Carbofuran Methomyl	nd nd nd nd	60
River and streams surface water in Mississippi, Lawrence, Phillips, and Jefferson Counties in Arkansas (USA)	Benomyl	0.5-1.2	48
La Albufera Lake water and irrigation channels from Valencia (Spain)	Molinate Thiobencarb	nd-1383 nd-505	141
River of delta Ebro (Spain)	Molinate	nd-2.39	82
Groundwater from the Water Research Centre private borehole water (UK)	Carbendazim	0.2	61

nd: not detected

(analytical column) is recommended to avoid a band broadening effect. DAD and UV detection are the most often cited. Nevertheless, interferences at the low wavelengths used for carbamate detection and a limited sensitivity are inherent to such detectors. Carbamates do not exhibit native fluorescence; therefore, a derivatization is required if the sensitive fluorescence detector is to be used. Mass spectrometric are ideal detectors. LC-MS has become a robust and routinely applicable tool in environmental laboratories with a reasonable price. LC-MS interfaces are continuously perfected and thermospray and electrospray interfaces are the most utilized for analysis of carbamate residues. On the other hand, the nitrogen contained in the carbamic structure facilitates the positive-ion formation for atmospheric pressure chemical ionization.

Considering the SPE-LC reviewed applications, it can be assumed that typical concentration levels of carbamate pesticides and metabolites in environmental waters are of the low to sub $\mu g\ l^{-1}$.

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