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Review

Environmental Protection Agency and other methods for the determination of priority pesticides and their transformation products in water

D. Barceló

Environmental Chemistry Department, CID–CSIC, c/Jordi Girona 18–26, 08034 Barcelona (Spain)

ABSTRACT

The different priority lists of pesticides in water from the European Economic Community (EEC) and the US Environmental Protection Agency (EPA) in water are listed and discussed. The chromatographic protocols of the EPA employed in the National Pesticide Survey for a total of 101 pesticides and 25 transformation products are reviewed. A comparison with the official methods of the United Kingdom Standing Committee of Analysts (SCA) is shown. Critical comments aimed at improving the present Official methods are made. Special emphasis is devoted to the development of new analytical techniques based on solid-phase extraction combined either off-line or on-line with chromatographic separations. The main aims of the different approaches are the development of screening methods for pesticides and their transformation products in water, the achievement of low limits of detection, especially in the case of the EEC Drinking Water Directive which sets a limit of 0.1 μg/l for individual pesticides, and the use of confirmation methods based on mass spectrometric approaches.

CONTENTS

1. INTRODUCTION: PRIORITY LISTS OF PESTICIDES AND GENERAL ANALYTICAL CONSIDERATIONS

Several hundred pesticides of diverse chemical nature are currently widely used in the USA and Europe for agricultural and non-agricultural purposes. Some are substitutes for the organohlorine pesticides, which were banned after evidence of their toxicity, persistence and bioaccumulation in environmental matrices was found. According to a report published by the US Environmental Protection Agency (EPA), a total of $5 \cdot 10^8$ kg of pesticides was used in 1985 [1]. Pesticide consumption in European countries such as the UK was in the

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region of $14 \cdot 10^6$ kg per year during the period 1980–83 [2]. As far as specific pesticides are concerned, world-wide consumption of malathion and atrazine in 1980 amounted of $24 \cdot 10^6$ kg and $90 \cdot 10^6$ kg, respectively [3,4]. In the Mediterranean countries $2.1 \cdot 10^6$ kg of malathion (active ingredient) were sprayed during the same period *versus* $9.7 \cdot 10^6$ kg in Asia [3].

A recent report published by the Commission of the European Communities (CEC) indicated the total turnover of the major pesticides used in Denmark, France, Germany, the UK, Greece, Netherlands, Italy, Spain and Sweden. The report included non-agricultural uses [5]. Atrazine, one of the herbicides most widely used in the USA and European countries over the last 30 years, is employed for pre- and post-emergence weed control of corn, wheat, barley and sorghum, and on railways and roadside verges. In this respect, in England and Wales the non-agricultural use of this herbicide represented 140 000 kg of active ingredient, whereas for France it was 43 000 kg during 1989 [5]. Not surprisingly it has been detected in ground and surface waters through the world (*e.g.*, in some USA ground waters at concentrations in the range 0.1–3 μg/l [1]), and in ground waters in various European countries [5] and in estuarine areas such as the Rhône river in France [6] and the Ebro delta in Tarragona, Spain [7]. An example of the level of contamination by herbicides in the Ebro delta area is shown in Table 1 with the different contamination levels of the river and the canals. A higher level of pollution (*ca.* ten times higher) was found in the canals owing both to their proximity to the fields where pesticides are being applied and to their low water flow as compared with the Ebro river.

Owing to the environmental impact of pesticides, several priority lists, also called "red" and/or "black lists" have been published to protect the quality of drinking and surface waters. In Table 2, the different pesticides listed in the 76/464/EEC Directive (the so-called black list) are indicated [8]. Following the three general parameters (toxicity, persistence and input) for selecting the priority list of pollutants [9] in the UK, a red list of substances that include several pesticides, most of them common to the EEC list, was established [9].

In order to prevent the contamination of ground and drinking water by pesticides in Europe, a priority list [5], which considers pesticides used over 50 000 kg per annum (and over 500 are indicated) and their capacity for probable or transient leaching, was recently published. This is shown in Table 3. There are a few other pesticides, such as demeton-S-methyl, fentin acetate, mancozeb, propineb, thiobencarb and zineb, for which, although they are used in amounts over 50 000 kg per annum, at present there are insufficient data to evaluate the

TABLE 1

CONCENTRATIONS OF HERBICIDES IN TWO SAMPLING STATIONS (RIVER AND DRAINAGE CANAL) OF THE EBRO DELTA AREA (TARRAGONA, SPAIN) DURING 1991

Compound	Concentration (ng/l)					
	April		May		June	
	River	Canal	River	Canal	River	Canal
Atrazine	36	308	17	58	190	190
Simazine	28	302	35	87	138	440
Molinate	n.d.[a]	1400	38	254	n.d.	3187
Alachlor	206	50	31	862	n.d.	n.d.
Metolachlor	132	68	32	n.d.	69	35
Bentazone	n.d.	n.d.	n.d.	n.d.	n.d.	5520
Trifluralin	14	n.d.	n.d.	n.d.	n.d.	n.d.

[a] n.d. = Not detected (below 0.1 ng/l, except for bentazone, for which it means 10 ng/l).

TABLE 2

PESTICIDES LISTED IN 76/464/EEC COUNCIL DIRECTIVE ON POLLUTION CAUSED BY CERTAIN DANGEROUS SUBSTANCES DISCHARGED INTO THE AQUATIC ENVIRONMENT OF THE COMMUNITY (BLACK LIST)

Aldrin	Disulphoton	Monolinuron
Atrazine	Endosulphan	Omethoate
Azinphos-ethyl	Endrin	Oxydemeton-methyl
Azinphos-methyl	Fenitrothion	Parathion-ethyl
Chlordane	Fenthion	Parathion-methyl
Coumaphos	Heptachlor	Phoxim
2,4-D	Hexachlorobenzene	Propanil
DDT	Linuron	Pyrazon
Demeton	Malathion	Simazine
Dichlorprop	MCPA	2,4,5-T
Dichlorvos	Mecoprop	Triazophos
Dieldrin	Metamidophos	Trichlorfon
Dimethoate	Mevinphos	Trifluralin

probability of leaching. Consequently these are not included in Table 3. In addition, glyphosate and thiram were not included in Table 2 because large differences in the ground water ubiquity score (GUS) index were found. This index is a measure of the leaching capacity of a pesticide through soil [5].

Another important point regarding the different pesticides reported in Table 2 is that although no transformation products (TPs) are included, in the report published by the CEC [5], it was indicated that there is much interest in the determination of such TPs for triazine, organophosphorus, carbamate and chlorinated phenoxy acid herbicides. In this respect, although the EEC Directive on the Quality of Water Intended for Human Consumption sets a maximum admissible concentration (MAC) of 0.1 μg/l for individual pesticides and related products and 0.5 μg/l for total pesticides, it is unclear what can be considered as "related products". It has been indicated that these "related products" refer to TPs that are toxic, which in the context of ground water contamination could be interpreted as exceeding a water quality standard derived from toxicological considerations [5]. In this respect, it is clear that some specific TPs, *e.g.*, fenitrooxon (from fenitrothion) and 1-naphthol (from carbaryl), are more toxic to aquatic organisms than the parent compounds. This also applies to ethylenebisthiourea (ETU), which is a well known TP of maneb and related pesticides and is more toxic than the parent pesticides [5].

Following considerations based on usage information, physico-chemical properties and persistence, a priority list of herbicides was established for the Mediterranean countries France, Italy, Greece and Spain. The list, which is shown in Table 4, considers selected herbicides that can cause contamination of estuarine and coastal environments. The selection of pollutants was based on the availability of usage data and the consideration of half-lives so that pesticides that do not exceed a total of 10 000 kg after 90 days of application have been omitted [10]. Note that some of these pesticides are common to Table 3. We should emphasize that pesticides in drinking water derived from ground water should be considered in a different way to pesticide that reach estuarine waters. The transport of pesticides from river waters to estuarine areas and coastal environments will be dependent on several parameters, *e.g.*, how they are absorbed into the suspended particulates and how they are affected by the higher salinity and pH. An example of such contamination corre-

TABLE 3

PESTICIDES USED IN EUROPE IN AMOUNTS OVER 50 000 kg PER ANNUM WHICH WERE CLASSIFIED AS PROBABLE OR TRANSIENT LEACHERS

Pesticides used in amounts over 500 000 kg are in italics.

Alachlor	Dinoseb	*Methabenzthiazuron*
Aldicarb	*Diuron*	Methiocarb
Amitrole	DNOC	Oxydemeton methyl
Atrazine	EPTC	Phenmedipham
Benazolin	Ethofumesate	*Prochloraz*
Bentazone	Ethoprophos	Propham
Bromofenoxim	Fenamiphos	Prometryn
Carbaryl	Fluoroxypyr	*Propiconazole*
Carbendazim	Iprodione	Propyzamide
Carbetamide	*Isoproturon*	*Pyrethrin*
Chloridazon	Linuron	Simazine
Chlorpyrifos	*Maneb*	Terbutylazine
Chlortoluron	*MCPA*	Terbutryn
Cyanazine	*MCPP*	Triademinol
2,4-D	Metamitron	Trichlorfon
Dalapon	*Metazachlor*	*Trichloroacetic acid*
Diazinon	*Metham-sodium*	Vinclozolin
Dichlobenil	*Metolachlor*	Ziram
Dimethoate		

TABLE 4

HERBICIDES OF POTENTIAL CONCERN IN THE MEDITERRANEAN REGION

Alachlor	EPTC	Metribuzin
Amitrole	Ethalfluralin	Molinate
Atrazine	Ethofumesate	Napropamide
Bentazone	Flamprop-M-isopropyl	Neburon
Bromoxynil	Glyphosate	Paraquat
Butylate	Isoproturon	Pendimethalin
Carbetamide	Linuron	Phenmediphan
Chlortoluron	MCPA	Prometryn
2,4-D	Mecoporp	Simazine
Di-allate	Metamitron	Trichloroacetic acid
Dichlobenil	Metazachlor	Terbumeton
Dichlofop-methyl	Metabenzthiazuron	Terbutylazine
Dinoterb	Metobromuron	Terbutryn
Diquat	Metolachlor	Tri-allate
Diuron	Metoxuron	Trifluralin
DNOC		

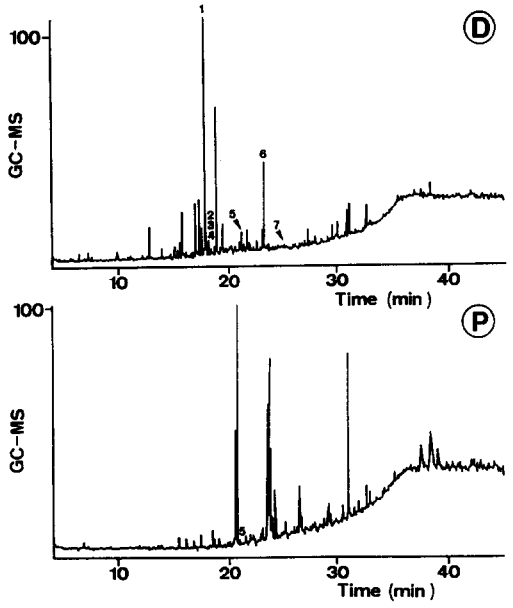

Fig. 1. Total ion current GC–MS of dissolved (D) and particulate (P) matter of river water extract from one of the stations located at the Rhône river estuary. Sampling was carried out during November 1990. Extraction of 5 l of river water sample was carried out using dichloromethane [6]. Compounds identified corresponded to: 1 = tributyl phosphate; 2 = deethylatrazine; 3 = simazine; 4 = deisopropylatrazine; 5 = atrazine; 6 = caffeine; 7 = propanil. Concentration levels for deethylatrazine, simazine, deisopropylatrazine, atrazine and propanil were 4, 10, 3, 17 and 2 ng/l, respectively. A DB-1701 capillary GC column was used.

sponds to the Rhône estuary in the Camargue region, as indicated in Fig. 1, which shows the total ion current chromatogram obtained after extraction of 5 l of river water extract with dichloromethane of the dissolved (D) and particulate (P) organic matter. The levels of the different chlorotriazine herbicides varied from 1 to 17 ng/l in the dissolved phase, whereas in the particulate matter the levels found were below 1 ng/l [6]. This indicates that for this particular group of herbicides transport from river water to the sea occurs mainly in the dissolved phase.

It is estimated that ground water is the source of drinking water for 90% of rural households and three quarters of USA cities. In total, more than half of the USA citizens rely on ground water for their everyday needs. Owing to the amount of information indicating the presence of pesticides in ground water in the different USA States [1], a joint research project between the EPAs Office of Drinking Water (ODW) and the Office of Pesticide Programs (OPP) involved a statistically based survey of pesticide contamination of drinking water wells. During the National Pesticide Survey (NPS), 1349 drinking water wells were sampled and analysed for 101 pesticides, 25 pesticide TPs and nitrate, with a total of 127 analytes. The results of the NPS were released in November 1990 (Phase I) and January 1992 (Phase II) [11,12]. The selection of the different analytes was based on the use of at least 10^6 lbs. (1 lb. = 7000 g) in 1992, a water solubility greater than 30 mg/l and a hydrolysis half-life longer than 25 weeks. Pesticides and pesticide degradation products previously detected in ground water and pesticides regulated under the Safe Drinking Water Act were automatically included in this priority list [13]. The compounds were grouped according to their analysis; seven methods were used that covered all the 126 analytes and are indicated in Table 5 [14]. Of the pesticides listed in Table 5, stability was checked for 147 analytes, 121 being stable for at least 14 days when stored in well water at 4°C. Among the 26 unstable pesticides (with a loss of 100% after storage under the conditions mentioned above) were many organophosphorus pesticides such as azinphos-methyl, disulphoton, fenitrothion, fenthion, malathion and parathion-methyl. It should be noted that these organophosphorus pesticides are included in the priority list of compounds of the EEC (see Table 2). Although they are on this list, their proven degradation when stored at 4°C and for 14 days in well water suggests that they are not so harmful, and their incorporation in a priority list is questionable. Other pesticides, such as ETU and heptachlor, suffered slight degradation (between 15 and 22%) under identical storage conditions, whereas the sample extract generally remained stable [14].

The list shown in Table 5 is so far the most comprehensive list used to conduct a monitoring programme on pesticides. It should be noted that in the last few years (since 1990), an early-warning system for the on-line screening and liquid chromatographic detection of 50 polar pesticides and other pollutants in Rhine river water has been developed in Europe. It involves the Rhine basin, with research groups for Switzerland, Germany and the Netherlands. The first results on the analytical method development have been published recently

TABLE 5

PESTICIDES AND TPs INCLUDED IN THE NATIONAL PESTICIDE SURVEY (USA)

Method 1 (EPA 507)		Endosulphan II	Propachlor
Alachlor	Methyl paraoxon	Endosulphan sulphate	Trifluralin
Ametryn	Metolachlor	Endrin	
Ametraton	Metribuzin		
Atrazine	Mevinphos	*Method 3 (EPA 515.1)*	
Bromacil	MGK 264	Acifluorfen	Dichlorprop
Butachlor	Molinate	2,4-DB	Dinoseb
Butylate	Napropamide	Bentazone	5-Hydroxy dicamba
Carboxin	Norflurazon	Chloramben	4-Nitrophenol
Chlorpropham	Perbulate	2,4-D	PCP
Cycloate	Prometon	Dalapon	Picloram
Diazinon	Prometryn	DCPA acid metabolites	2,4,5-T
Dichlorvos	Pronamide	Dicamba	2,4,5-TP
Diphenamid	Propazine	3,5-Dichlorobenzoic acid	
Disulfoton	Simazine	*Method 4*	
Disulfoton sulphone	Simetryn	Atrazine dealkylated	Linuron
Disulfoton sulphoxide	Stirofos (tetrachlorvinphos)	Barban	Metribuzin DA
EPTC	Tebuthiuron	Carbofuran phenol	Metribuzin DADK
Ethoprop	Terbacil	Cyanazine	Neburon
Fenamiphos	Terbufos	Diuron	Pronamide metabolite
Fenamirol	Terbutryn	Fenamiphos sulphone	Propanil
Fluridone	Triademefon	Fenamiphos sulphoxide	Propham
Hexazinone	Tricyclazole	Fluometuron	Swep
Merphos	Vernolate	3-Ketocarbofuran phenol	
Method 2 (EPA 508)		*Method 5 (EPA 531.1)*	
Aldrin	Endrin aldehyde	Aldicarb	Carbofuran
α-Chlordane	Etridiazole	Aldicarb sulphone	3-Hydroxycarbofuran
γ-Chlordane	α-HCH	Aldicarb sulphoxide	Methiocarb
Chlorneb	β-HCH	Baygon (propoxur)	Methomyl
Chlorobenzilate	δ-HCH	Carbaryl	Oxamyl
Chlorothalonil	γ-HCH	*Method 6*	
DCPA	Heptachlor	ETU	
4,4′-DDD	Heptachlor-epoxide		
4,4′-DDE	Hexachlorobenzene	*Method 7 (EPA 504)*	
4,4′-DDT	Metoxychlor	EDB	*cis*-1,3-Dichloropropene
Dieldrin	*cis*-Permethrin	DBCP	*trans*-1,3-Dichloropropene
Endosulphan I	*trans*-Permethrin	1,2-Dichloropropane	

[15,16]. These results deal only the analytical development stage.

One of the main differences between the USA and European regulations on pesticide programmes is that in Europe each country uses its own analytical method, whereas in the USA the EPA methods are widely implemented. The different approaches used by European governmental laboratories, which prefer to use conventional liquid–liquid extraction (LLE) procedures, and research or other laboratories that prefer to use solid-phase extraction (SPE) techniques, mean that within Europe there are no consensus methods for the determination of pesticides in water. Consequently, it is difficult to employ an NPS monitoring programme approach within the different countries, and intercomparisons and validation of results have not been conducted. This aspect will be discussed in detail in another section of this paper, but is one of the major problems within the EEC, since an agency similar to the EPA does not exist in Europe, although the Council of Ministers agreed in 1990 to create a European Environmental Agency.

Some general comments can be made regarding the different priority lists presented in Tables 2–5. Although in some instances there is agreement on the priority pesticides to be monitored, *e.g.*, atrazine, 2,4-D, linuron and dimethoate, in others there is complete disagreement. This is the case for, *e.g.*, the carbamates, which have been of relatively high importance in the USA monitoring programmes (see Table 5), and the EPA has developed an excellent method of analysis for these pesticides in water with a very low limit of detection (LOD), which will be discussed later. In contrast, in Europe, in the first black list of pesticides they were no carbamates at all (see Table 1). As they were not included in this first list of dangerous substances (Table 2), no tradition of monitoring carbamates has been established, although their use in several countries such as Netherlands, Spain, the UK and Italy has been reported. In addition, the official EPA method for monitoring carbamate pesticides (Method 531.1) has seldom been used in Europe, although it is a highly sensitive and robust method. Another aspect that should be considered is the leachability of these carbamates to ground and well waters, and in this sense they have been studied in different USA well waters through the NPS. However, in Europe, although ground waters are also an important source of drinking water, no such investigation has been undertaken. The percentage of ground water used for drinking water purposes in Europe is close to 100% for Denmark and between 60 and 85% for Italy, Germany, France and the UK, whereas in Spain it is about 30%.

Finally, another remark concerning the different priority lists is that the NPS list (Table 5) is the only one that especifically mentions the TPs of pesticides. This is a very significant aspect, because although in the EEC regulations the importance of TPs of pesticides is indicated [5], no specific TPs are named. This makes it more difficult for laboratories currently involved in monitoring programmes to monitor and select the different TPs. It should also be mentioned that many of the TPs need specific methods of analysis, and are poorly recovered using conventional screening methods. Therefore, in this sense, the efforts made through the NPS with specific methods of analysis and the list of priority pesticides and TPs provided in Table 4 are of great importance and can be implemented, allowing for the different circumstances of each country, worldwide.

As pointed out previously [9], in the selection of priority lists one of the relevant parameters to be taken into consideration is the toxicity of the compound. Such toxicity evaluations depend on the compound and its concentration in water, and should take into account both human toxicity and toxicity to aquatic organisms. For drinking water, the CEC has fixed a level of 0.1 μg/l for individual pesticides and 0.5 μg/l for total pesticides. This is a very strict measure, and analytical methods still need to be developed for a variety of pesticides to comply with this Directive.

The Office of Water of the EPA has established drinking water regulations and health advisory levels for individual pesticides. A selection of the different health advisory levels, also referred to by the EPA as maximum contaminant level goals, are indicated in Table 6. Values given in this table were selected from refs. 12 and 17. Such levels are more correct than the EEC levels, which have been fixed for all the individual pesticides without making any distinction between pesticides of different toxicities. Regarding the levels of the TPs, it can be argued that their levels should follow toxicity values [9].

Establishing the maximum concentration levels for individual pesticides is very important to demonstrate compliance with the different Directives. In the EEC, the strict Directive has the disadvantage that some ubiquitous pesticides, such as atrazine, which is not especially toxic to humans, is found in many instances at levels higher than 0.1 μg/l, and it can be seen from the literature that the levels found in some EEC countries exceed the EEC regulations. However, as the levels set in the EEC Directive were not based on toxicological data, in some instances higher levels are permissible. This restrictive regulation for pesticides in Europe has resulted in the development of analytical methods that can detect pesticides at levels of 0.02 μg/l in order to determine the pesticides at 0.1 μg/l. However, in addition to the lack of information on which pesticides to monitor, it will also be impossible to determine all the pesticides approved for use within the EEC at this level of sensitivity. Because it is difficult to know which pesticides require monitoring, one approach is to focus efforts on those pesticides which are (a) likely to reach water resources, (b) are used in

TABLE 6

HEALTH ADVISORY LEVELS FOR SELECTED PESTICIDES IN DRINKING WATER (EPA OFFICE OF GROUND WATER AND DRINKING WATER)

Compound	Health advisory level (μg/l)	Compound	Health advisory level (μg/l)
Alachlor	2	Diquat	20
Aldicarb	10	Endothall	100
Aldicarb sulphoxide	10	Endrin	2
Aldicarb sulphone	10	Glyphosate	700
Atrazine	3	Methomyl	200
Bromacil	80	Methyl parathion	2
Carbofuran	40	Metolachlor	10
Chlorthalonil	2	Oxamyl	200
Cyanazine	9	Picloram	500
2,4-D	70	Simazine	4
Dalapon	200	Trifluralin	2
Dinoseb	7		

sufficient amounts and (c) have a tendency to be persistent and mobile (see Table 3). The EEC Drinking Water Directive also sets a limit of 0.5 μg/l for total pesticides. It is difficult to carry out proper monitoring of such a parameter, particularly in relation to defining required detection limits and accuracy, unless an arbitrary maximum number of total pesticides is assumed. In the most recent report of the EEC [5] it was stated that analytical methods need a detection limit of 0.02 μg/l or less (ideally 0.01 μg/l) and need to provide data of sufficient accuracy. In the latter respect, around 20% total errors (random and systematic) should be aimed for.

The pesticides of highest priority to the EEC are listed in Table 3. It has also been recommended [5] that significant analytical results need to be confirmed by an additional technique, preferably involving some form of mass spectrometry, because of the likelihood of false positives with the commonly applied methods such as gas chromatography with electron capture (GC–ECD) or nitrogen–phosphorus detection (GC–NPD) and liquid chromatography (LC) with UV detection. For some difficult pesticides such as maneb, ziram and trichloroacetic acid, analytical methods need to be developed in order to reach the LOD indicated in the EEC regulations for water. In the USA, most of the EPA methods in use comply with the Health Guidance levels indicated in Table 6.

In this review, the development of methods of analysis and confirmation for most of the "conventional" organochlorine pesticides will not be considered, as most have been withdrawn and replaced with organophosphorus and carbamate pesticides. However, organochlorine pesticides are covered by method 2 (see Table 5), with a few exceptions such as chlorneb, chlorbenzilate, chlorothalonil, etridiazole, metoxychlor, *cis*- and *trans*-permethrin, propachlor and trifluralin.

In this review, the official methods of analysis for pesticides in drinking water used in the USA (EPA–NPS) and in the UK will be discussed. References will be made to examples of developed methods involving GC using NPD, ECD and flame photometric detection (FPD) and LC using UV, electrochemical and fluorescence detection. As stated previously, it is necessary to use confirmation methods to avoid false positives. In this sense the use of mass spectrometric techniques or two different GC or LC columns of different polarity, which is the common EPA procedure, will be mentioned. Some examples and comments on the different approaches will be given, emphasizing the main advantages and disadvantages.

One of the main decisions to be taken at the beginning of an analysis for pesticides is whether to use GC or LC. In some instances the choice can be very clear and for sufficiently volatile compounds,

such as most of the organochlorine pesticides and some organonitrogen pesticides such as atrazine, or organophosphorus pesticides such as fenitrothion, GC will be preferred. Problems arise when pesticides that are thermally labile and/or polar need to be analysed. The use of derivatization techniques and further GC analysis with a selective detector generally allows good LOD. Other workers prefer to use LC techniques, without prior derivatization, which simplifies the method. There are some specific cases of polar and thermally labile pesticides which, when analysed by GC, need careful attention, because although peaks can be detected in the GC traces, such peaks do not correspond to the compound itself but to a degradation product that is generally formed in the injection port. One such group is the carbamates, compounds with proved thermal instability under conventional GC conditions. It has been pointed out that some of them can be determined by GC with careful selection of the instrumental conditions of analysis [18]. For the determination of carbaryl and other carbamates such as carbofuran, the use of cold on-column injection [19] has been reported to give good recoveries after isolation from water samples. Aldicarb sulphoxide and aldicarb sulphone have also been studied and it has been shown that aldicarb (the parent herbicide of aldicarb sulphoxide and sulphone), degrades at injection port temperatures of 130°C and that longer GC capillary columns do not allow elution in a reasonable time. Consequently, thermal degradation is observed [20]. A previous EPA method oxidized aldicarb to aldicarb sulphone by treatment with peracetic acid and then the aldicarb sulphone was thermally degraded in the injection port, producing the volatile species 2-methyl-2-(methylsulphonyl)propionitrile (EPA, 1981) [21]. It has been also recommended, if GC methods are still to be used, that the problems of decomposition of carbamates giving phenols and isocyanates should be overcome by prior derivatization with appropriate reagents such as acetic anhydride [22]. Similar considerations could be applied to oxamyl and benomyl.

With phenylurea herbicides although linuron can be determined by GC [19,23] with cold on-column injection, monuron and diuron are too thermally unstable and degrade under the GC conditions [23]. To avoid these problems, derivatization with reagents such as heptafluorobutyric anhydride [24] can be applied.

It is difficult, in some instances, to make a choice between GC or LC techniques. In general, a method that offers less manipulation of the sample and which provides good sensitivity is to be preferred. This review will focus on different examples, demonstrating the procedures of the official methods such as those of the EPA, and other methods that are being developed. In many instances the choice of one method over the others depends on the experience of the laboratory, and is dependent on the facilities and know-how available.

2. EPA METHODS OF ANALYSIS

Two reports concerning the revision of methods for the determination of organic compounds in drinking water have recently been published [25,26]. Revision and comments on the different EPA methods for water analyses have been also discussed in two recent papers, which recommended dropping some of the 600 series methods, the encouragement of the use of capillary columns in GC and of microextraction methods and the increasing use of GC–MS methods [27,28]. Of the different methods for determining purgeable organics, it has been recommended that EPA Method 524.2 should be kept, and all others (524.1 and 624) dropped [27].

The philosophy behind EPA methods is clearly stated in their objectives, *viz.*, developing and evaluating analytical methods for organic contaminants in water, determining the response of aquatic organisms to water quality and the development of a quality assurance programme to support the achievement of data quality objectives. The different EPA methods used for pesticide determinations in water can be divided into three groups: (i) those which use GC with selective detection (ECD or NPD), (ii) those which use GC–MS and (iii) those which use LC. The numbering of the different methods is based on the groups of pesticides as given in Table 5. Most of the EPA methods for pesticides in water use LLE procedures, with the exception of Method 525.1, which uses SPE procedures either with C_{18} cartridges or Empore extraction disks. Although in this review it is not the intention to discuss aspects of sample extraction, SPE is gaining in importance as it avoids problems with emulsions and those associated with the consumption and disposal of large volumes of toxic and flammable solvents [29].

The general characteristics of most of the EPA methods are as follows: (i) the acceptance of recoveries in the range from 70 up to 130%, with a maximum relative standard deviation of 30% each; (ii) preservation and storage of the samples is carried out at 4°C, and the recommendations made as to whether a sample should be analysed within a few days of storage or can be kept for a maximum of 14 days [14]; (iii) the description of apparatus and equipment (with safety considerations), reagents, standards and consumable materials; (iv) the use of two columns of different polarity, the so-called primary column, generally a DB-5 or similar, and a second column, called a confirmatory column, such as DB-1701 or equivalent, both in GC determinations; in LC, the primary column is a standard C_{18}-bonded silica and the second column is a cyano type; and (v) the way to proceed with blank samples, internal standards and surrogate solutions, interferences, calibration, standardization and quality control. As the use of surrogates in internal standards can lead to some confusion, definitions of both terms are given. The internal standard is added to measure the relative responses of other analytes and surrogates that are components of the solution. It is a requirement that the internal standard must be an analyte that is not a sample component. In contrast, a surrogate standard is a compound that is extremely unlikely to be found in any sample, is added to a sample aliquot before extraction and is measured with the same procedures as used to measure other sample components. The purpose of a surrogate is to monitor method performance with each sample. The use of a surrogate and internal standard is not common in other official methods as they generally use only an internal standard. A final general comment on the different EPA methods is that although sometimes minimum detection limits (MDLs) are used, estimated detection limit (EDL) and limit of detection (LOD) are used to indicate the same idea, but with a different terminology. It is recommended that in future these criteria be unified, and a single term used to indicate the limit of detection of a method.

A summary of each method used for the determination of pesticides and their corresponding TPs is given in Table 7. In this table, first a microextraction method, using GC–ECD, is mentioned. Although only a small water volume is used (35 ml), the MDLs are acceptable. Conventional analytical methods for organics in drinking water use sample volumes of at least 1 l.

Another EPA method for organonitrogen- and organophosphorus-containing pesticides is shown. In this instance, special attention is given to the storage of the water samples. As mentioned previously [14], it has been shown that 26 organophosphorus pesticides were unstable, with a 100% loss when stored under the usual conditions, at 4°C for 14 days. Among those, disulphuton sulphoxide, diazinon, fenitrothion, pronamide and terbufos deserve special attention as their determination should be carried out immediately after extraction. Other analytes, such as carboxin, EPTC, fluridone, metolachlor, napropamide, tebuthiuron and terbacil, exhibited recoveries of less than 60% after storage for 14 days. For such compounds it was also pointed out that although sample extracts, stored under identical conditions, were stable for 28 days, storage for only 14 days was recommended. Fig. 2 shows two examples of the use of LLE with dichloromethane for the determination of various organonitrogen pesticides in Ebro Delta water. By extracting 5 l of water with a final extract volume of 0.5 ml, an LOD down to 0.1 ng/l can be obtained, as is shown in Fig. 2 [7].

The EPA method for organochlorine pesticides is briefly described in Table 7. Careful attention should be paid to certain pesticides such as chlorthalonil, *cis*-permethrin, *trans*-permethrin and trifluralin, as preservation data are non-definitive, and therefore it is recommended that samples should be analysed immediately. For the other modern pesticides the samples are stable for 7 days at 4°C. For organochlorine pesticides, the method gives very low LODs (in the range 0.01–0.5 μg/l), with the exception of chlorobenzilate. Trifluralin can also be determined by GC–NPD with a low LOD [7].

The method for N-methylcarbamates is also reported in Table 7. No surrogate is used in this instance, as the method involves a direct analysis of water samples, without sample pretreatment. Sample preservation of carbamates is very important, and it has been observed that oxamyl, 3-hydroxycarbofuran, aldicarb sulphoxide and carbaryl can all degrade quickly in neutral and basic waters at room temperature. Therefore, samples should be kept at pH 3 and preserved at −10°C. These compounds

are much more easily degraded than other pesticides reported in EPA methods. An example of the determination of several carbamates using the detection principle of this EPA method is given in Fig. 3, where the LC–postcolumn fluorescence trace for a 10-ml drinking water sample spiked with 0.2 μg/l of a carbamate mixture, and a blank sample, are shown. The water sample was preconcentrated using SPE disks coupled on-line with the LC–postcolumn fluorescence detection system as used by the EPA. LODs in the range 5–40 ng/l are achieved, which are far below those achieved using direct injection of the water sample into the same system.

Analyses for the more volatile pesticides are also indicated in Table 7. A purge-and-trap method with subsequent GC–MS determinations and a microextraction method with *n*-hexane are described. In one instance, the use of MS ensures unequivocal identification of the compounds and the use of a microextraction method avoids volatility problems, giving an acceptable estimated detection limit. The so-called methods for unusual pesticides are also described in Table 7. Such methods have a peculiarity in that each is specific for the pesticide to be determined, *e.g.*, the method for glyphosate can only be used for this compound. These methods are not multi-residue methods and were developed for individual pesticides because of their occurrence in the different waters. The use of specific methods of analysis for one or two pesticides is not advantageous, as this approach increases the analysis time for a laboratory involved in the analysis of a variety of pesticides in water.

One of the most recent methods described in Table 7 is based on SPE techniques. Few EPA methods have been changed during the last few years to incorporate SPE instead LLE. In this method only one GC column is needed as MS confirmation is provided by the fragment ions. Special attention should be paid to possible sources of contamination of the cartridges or disks, which often contain phthalate esters, silicon compounds and other con-

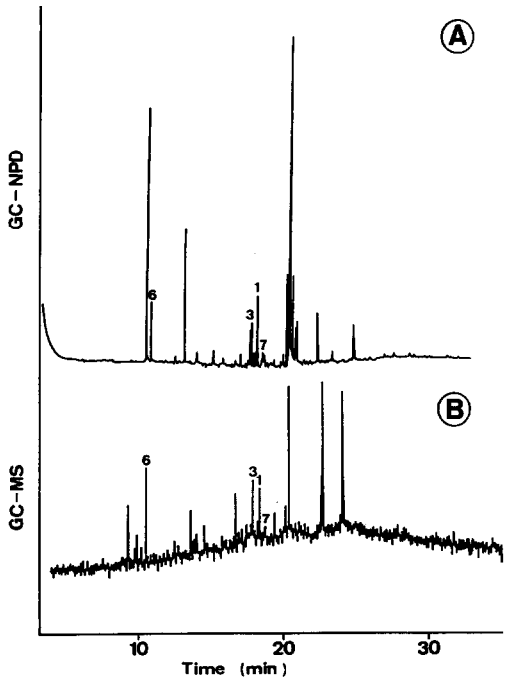

Fig. 2. (A) GC–NPD and (B) GC–MS of an extract of water sample from the Ebro delta containing: (6) molinate (0.050 μg/l), (3) atrazine (0.010 μg/l), (1) simazine (0.012 μg/l) and (7) alachlor (0.005 μg/l). A DB-225 capillary GC column was used.

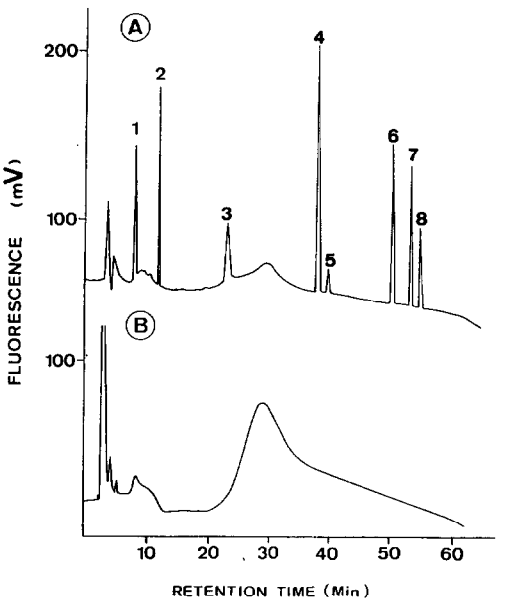

Fig. 3. LC–postcolumn fluorescence detection after preconcentration on C_{18} Empore disks of 10 ml of drinking water spiked with a pesticide mixture at 0.2 μg/l (A) and a drinking water blank sample (B). Compounds analysed: 1 = aldicarb sulphoxide; 2 = aldicarb sulphone; 3 = hydroxycarbofuran; 4 = aldicarb; 5 = 3-ketocarbofuran; 6 = carbofuran; 7 = carbaryl; 8 = 1-naphthol. A 4-μm Superspher 60 RP-8 LC column (Merck) was used.

TABLE 7

SUMMARY OF EPA AND NPS METHODS

EPA Method 505

Determination of organohalide pesticides and commercial polychlorinated biphenyl (PCB) products in water by microextraction and GC–ECD

Dichloromethane extraction

MDLS (only for commonly used pesticides) (μg/l):

Alachlor	0.075	Metoxychlor	0.96	Simazine	6.8
Atrazine	2.4				

EPA Method 507 (NPS Method 1, see Table 5)

Determination of nitrogen- and phosphorus-containing pesticides in water by GC–NPD

Dichloromethane extraction

EDLS (μg/l):

Alachlor	0.4	EPTC	0.2	Perbulate	0.1
Ametryn	2.0	Ethoprop	0.2	Prometon	0.3
Ametraton	0.6	Fenamiphos	1.0	Prometryn	0.2
Atrazine	0.1	Fenamirol	0.4	Pronamide	0.8
Bromacil	2.5	Fluridone	3.8	Propazine	0.1
Butachlor	0.4	Hexazinone	0.8	Simazine	0.1
Butylate	0.1	Merphos	0.2	Simetryn	0.2
Carboxin	0.6	Methyl paraoxon	2.5	Stirofos	0.8
Chlorpropham	0.5	Metolachlor	0.7	Tebuthiuron	1.3
Cycloate	0.2	Metribuzin	0.1	Terbacil	4.5
Diazinon	0.2	Mevinphos	5.0	Terbufos	0.5
Dichlorvos	2.5	MGK 264	0.6	Terbutryn	0.2
Diphenamid	0.6	Molinate	0.1	Triademefon	0.6
Disulfoton	0.3	Napropamide	0.2	Tricyclazole	1.0
Disulfoton sulphone	3.8	Norflurazon	0.5	Vernolate	0.1
Disulfoton sulphoxide	0.4				

EPA Method 508 (NPS Method 2, see Table 5)

Determination of chlorinated pesticides in ground water by GC–ECD

Dichloromethane extraction

EDLS (only for commonly used pesticides) (μg/l):

Chlorneb	0.5	Etridiazole	0.02	*trans*-Permethrin	0.5
Chlorobenzilate	5	Metoxychlor	0.05	Propachlor	0.5
Chlorothalonil	0.02	*cis*-Permethrin	0.5	Trifluralin	0.02
DCPA	0.02				

EPA Method 515.1 (NPS Method 3, see Table 5)

Determination of chlorinated acids in ground water by GC–ECD

Diethyl ether extraction and derivatization (with diazomethane)

EDLS (μg/l):

Acifluorfen	0.1	DCPA acid metabolites	0.02	4-Nitrophenol	0.1
Bentazone	0.2	Dicamba	0.08	PCP	0.08
Chloramben	0.1	3,5-Dichlorobenzoic acid	0.06	Picloram	0.14
2,4-D	0.2	Dichlorprop	0.3	2,4,5-T	0.08
Dalapon	1.3	Dinoseb	0.2	2,4,5-TP	0.07
2,4-DB	0.8	5-Hydroxy dicamba	0.04		

EPA Method 531.1 (NPS Method 5, see Table 5)

Determination of N-methylcarbamoxyloximes and N-methylcarbamates in ground water by direct aqueous injection HPLC with postcolumn derivatization

Direct injection of water samples. After elution, hydrolysis with 0.05 *M* (NaOH at 95°C, reaction with *o*-phthalaldehyde (OPA) and 2-mercaptoethanol to form a highly fluorescent derivative

EDLS (μg/l):

Aldicarb	1.0	Carbaryl	2.0	Methiocarb	4.0
Aldicarb sulphone	2.0	Carbofuran	1.5	Methomyl	0.5
Aldicarab sulphoxide	2.0	3-Hydroxycarbofuran	2.0	Oxamyl	2.0
Baygon	1.0				

(Continued on p. 128)

TABLE 7 *(continued)*

EPA Method 524.2 (NPS Method 7, see Table 5)

Measurement of purgable organic compounds in water by capillary column GC–MS
Trapping of volatile compounds in a tube, heating and desorption
MDL (μg/l):

1,2-Dibromethane (EDB)	0.02	*cis*-1,3-Dichloropropene	Not determined
1,2-Dibromo-3-chloropropane (DBCP)	0.05	*trans*-1,3-Dichloropropene	Not determined
1,2-Dichloropropane	0.02		

EPA Method 504 (NPS Method 7, see Table 5)

1,2-Dibromethane (EDB) and 1,2-dibromo-3-chloropropane (DBCP) in water by microextraction and GC–ECD
n-Hexane extraction
EDLS (μg/l):

EDB	0.01	DBCP	0.01

EPA METHODS FOR UNUSUAL PESTICIDES

EPA Method 547

Determination of glyphosate in drinking water by direct aqueous injection LC, postcolumn derivatization and fluorescence detection
Filtration into a cation-exchange LC column, oxidation with calcium hypochlorite. The product (glycine) is then coupled with OPA–2-mercaptoethanol complex at 38°C to give a fluorophor
MDL (μg/l):

Glyphosate	6 (for drinking water)
	9 (for ground water)

EPA Method 548

Determination of Endothall in drinking water by aqueous derivatization, liquid–solid extraction and GC–ECD
Derivatization with pentafluorophenylhydrazine (PFPH)
MDL (μg/l): 11.5

EPA Method 549

Determination of diquat and paraquat in drinking water by liquid–solid extraction and LC with UV detection
Extraction with C_8 solid sorbent cartridge in the ion-pair mode
MDL (μg/l):

Diquat	0.4	Paraquat	0.8

EPA Method 525

Determination of organic compounds in drinking water by liquid–solid extraction and capillary column GC–MS
Extraction into C_{18} Empore or cartridge. Elution with dichloromethane
EDLS (only for currently used pesticides) (μg/l):

Alachlor	0.09	Methoxychlor	0.08	Simazine	0.12
Atrazine	0.14				

EPA Method 552

Determination of haloacetic acids in drinking water by liquid–liquid extraction, derivatization and GC–ECD
Extraction with MTBE and diazomethane derivatization
MDL (μg/l):

Trichloroacetic acid	0.08

NPS Method 4 (see Table 5)

Determination of pesticides in ground water by LC with UV detection
Dichloromethane extraction
MQL (μg/l):

Atrazine dealkylated	4.4	Fenamiphos sulphoxide	9.4	Neburon	0.6
Barban	3.8	Fluometuron	0.9	Pronamide metablite	6.3
Carbofuran phenol	42	3-Ketocarbofuran phenol	1.9	Propanil	0.6
Cyanazine	4.7	Linuron	0.9	Propham	11
Diuron	0.6	Metribuzin DA	1.2	Swep	0.3
Fenamiphos sulphone	57				

NPS Method 6 (see Table 5)

Determination of ethylene tiourea (ETU) in ground water by GC with NPD
Use of Extralut column, ETU and elution with dichloromethane
MQL (μg/l): 9.0

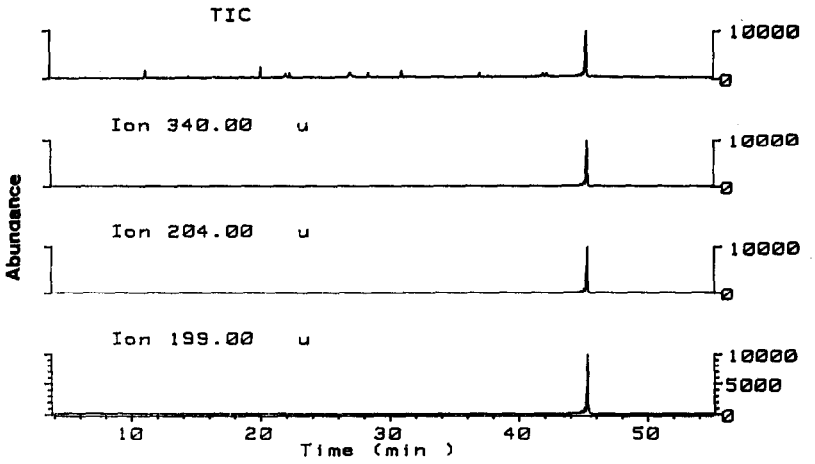

Fig. 4. Total ion current (TIC) and selected ion chromatograms obtained using GC–EI-MS of an estuarine water sample from the Ebro delta which contained 4 μg/l of pyridafenthion. Ions were monitored at *m/z* 340, 204 and 199. An FSQT RSL-300 capillary GC column was used.

taminants [30,31]. Requirements for MS include: (i) scanning should be performed between 45 and 450 u and (ii) the calibrant, bis(perfluorophenyl)phenylphosphine (decafluorotriphenylphosphine, DFTPP) meets all the criteria specified in the method with *m/z* ions varying from 51 up to 443, the most important peaks being at *m/z* 198 and 442. Other relevant ions are at *m/z* 51, 127 and 275. This MS method allows for three different types of MS analysers: magnetic sector, quadrupole and ion trap. The LODs reported in Table 7 correspond to the use of ion trap MS. As an example of the use of Empore extraction discs of C_{18}-bonded silica in combination with GC–MS, Fig. 4 shows the total ion current chromatogram and selected ions of the organophosphorus pesticide pyridafenthion identified in real environmental waters from the Ebro delta area.

The different haloacetic acids determined by EPA methods are also listed. Trichloracetic acid (TCA), which is also very important in the EEC list of pesticides (Table 3), is included. The method reported in Table 7 is also valid for other haloacetic acids and several chlorophenols.

Owing to the need to monitor a variety of pesticides, some of which are not included in the EPA methods for organics in waters, two other methods were developed within the NPS. Method 4 includes most of the TPs of organonitrogen and organophosphorus pesticides, which have shown, in general, good recoveries, varying from 79 up to 97% [13]. For both methods the minimum quantification limit is indicated instead the estimated detection limit (EDL). The value of EDL depends on the degree of interferences to which the method is subjected. So, for methods 4 and 6, the EDL is five and three times lower, respectively [13]. An example of the use of the method indicated in Table 7, although using a water volume of 4 l, is shown on the LC–diode-array detection (DAD) trace in Fig. 5. This corresponds to an extract from a Ebro delta water sample containing low levels of herbicides at 0.1 μg/l, very close to the LOD of LC–DAD. Atrazine (peak 3) could be unequivocally identified from its UV spectrum [7].

3. SCA METHODS OF ANALYSIS

These methods are the Official Methods of the Department of the Environment Drinking Water Inspectorate Standing Committee of Analysts (SCA). Many of these methods, also known as SCA methods, were discussed in two recent reviews [29,32]. Although there are also official methods of analysis for pesticides in water in several EEC countries, these methods will not be discussed here. Differences exist between such official methods of analysis, based on LLE procedures, and other multi-residue methods based on SPE techniques. The number of laboratories that use SPE techniques for the isola-

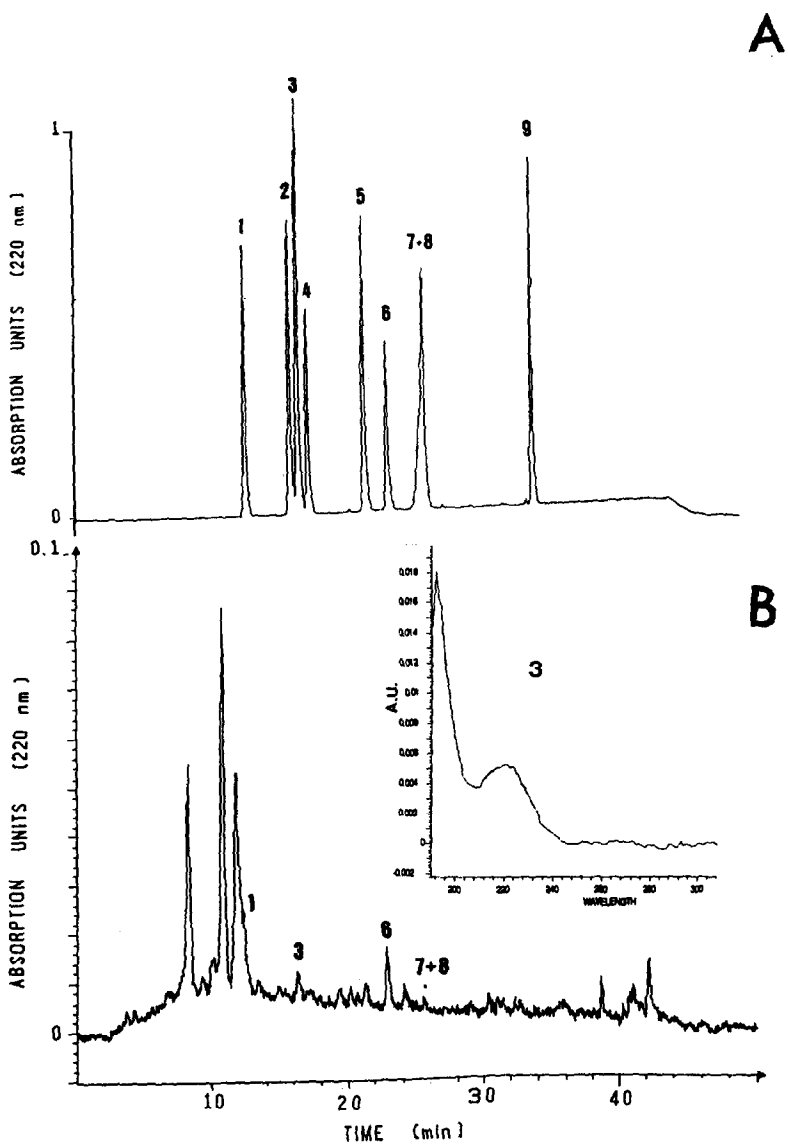

Fig. 5. (A) LC–DAD of a standard sample containing the dichloromethane extract after liquid–liquid extraction of: 1 = simazine; 2 = chlortoluron; 3 = atrazine; 4 = isoproturon; 5 = linuron; 6 = molinate; 7 = alachlor; 8 = metolachlor; 9 = trifluralin. Amount of each pesticide injected, 2 μg. (B) LC–DAD of an extract of an Ebro delta water containing simazine (0.040 μg/l), atrazine (0.010 μg/l), molinate (0.080 μg/l) and alachlor (0.025 μg/l). A Serva LC column packed with 4-μm octadecyl-Daltosil 100 was used.

tion and analysis of pesticides in water in Netherlands [15], Italy [33,34] and Germany [16,35] is increasing. Only selected SCA methods for pesticides in water will be compared with those used by the EPA. One of the current shortcomings in EEC countries is that there is no body similar to the EPA in Europe, so official methods for the whole of Europe have not yet been developed. Similarities and differences between the UK and the USA methods will be shown, with the hope that in the future common EEC methods of pesticides in drinking waters can be discussed.

When comparing the UK and the USA, two aspects need to be mentioned. From the point of

view of pesticides of interest (see Tables 2–5) there are many pesticides which are common. The second important aspect to be mentioned is that in Europe, the levels for any pesticide, as mentioned earlier, have a limit of 0.1 μg/l for drinking water requirements, which is a value much lower than most of the maximum concentration values fixed by the EPA, which are based on health advisory levels (see Table 6). Therefore, in this sense, method development in Europe has been required to produce methods with LODs approximately one order of magnitude lower than the EPA methods, thus causing more difficulties in monitoring a large number of pesticides. The efforts of different research groups working in this area are directed towards achieving the detection limits required by the EEC (which should be at least 0.02 μg/l) in order to determine analytes at 0.1 μg/l. However, many of the UK methods of analysis still do not have LODs as low as the EEC requirements, and only during the last few years has method development been carried out in different European laboratories to achieve such a goal [15,16,33,34].

For the organophosphorus pesticides dichlorvos, dimethoate, malathion, parathion, fenitrothion, chlorfenvinphos, carbophenothion, pirimiphos-methyl and chlorpyrifos, an extraction method involving 25 ml of *n*-hexane and 50 ml of dichloromethane with 1 l of river or drinking water has been employed. The extracts are concentrated to 1 ml in acetone, after evaporation of the dichloromethane extract. Subsequently, 1 μl is injected on to a GC column with flame thermionic detection or FPD [36]. Although the first version of this method used packed GC columns (as in the EPA methods), the SCA method now recommends the use of 25–50-m OV-1 or SE-54 capillary columns [37]. However, the method is less specific than the EPA method and does not include the use of a confirmatory column. The EPA also recommends determining the organophosphorus pesticides as soon as possible, as they can degrade rapidly. The method is based on LLE but uses two extraction solvents, hexane and dichloromethane, instead of only dichloromethane in the EPA method (see Table 7). The use of a mixture of *n*-hexane and dichloromethane allows a better recovery of the less polar organophosphorus pesticides, such as chlorpyrifos, fenitrothion, carbophenothion and pirimiphos-methyl. It is worth mentioning that the SCA method does not result in significant differences in the recoveries between water with high and with low suspended solids. The LOD varies between 0.04 and 0.8 μg/l. In order to compare these results with those of the EPA method (Table 7), it should be mentioned that there are very few organophosphorus pesticides in the EPA method, as degradation of the water solutions kept in a refrigerator occurred rapidly, as reported [14]. One of the compounds, dichlorvos, had an LOD of 0.04 μg/l in the SCA method, which can be attributed to the different way of determining the LOD (by baseline fluctuation and using FPD, which is usually more sensitive to P, as reported [38]).

The SCA method for the determination of triazine herbicides in drinking waters is based on an alkaline extraction (2 ml of ammonia) into dichloromethane (100 and 50 ml), followed by concentration and dissolution in 2 ml of methanol, with injection of 5 μl into the GC–NPD system. A 50-m Carbowax 20M wall-coated open-tubular (WCOT) column is recommended. A detection limit of 0.015 μg/l is estimated for atrazine, simazine, prometryne, propazine and terbutryne [39]. The method does not differ substantially from the EPA method reported in Table 7 for the determination of different organonitrogen and organophosphorus pesticides. It is not necessary to use a 50-m column, as with the EPA method the separation can be achieved using a 30-m column.

A modification of this method has been recently published [40]. This was developed for the determination of the chlorotriazine metabolites deethylatrazine, deisopropylatrazine and hydroxyatrazine. With the use of a mixture of ethyl acetate and dichloromethane with 0.2 *M* ammonium formate, it was possible to increase the extraction recovery of the different chlorotriazine TPs. The final determination was carried out by LC–DAD, which permitted the direct determination of polar metabolites from water samples. Fig. 6 shows the LC–DAD traces for a spiked drinking water sample with 10 μg/l of chlorotriazines extracted with (A) dichloromethane and (B) dichloromethane–ethyl acetate containing 0.2 *M* ammonium formate. The better recovery obtained from the LC–DAD traces is evident, especially for the TPs.

The most extensive list of alternative methods provided by the SCA is for the determination of

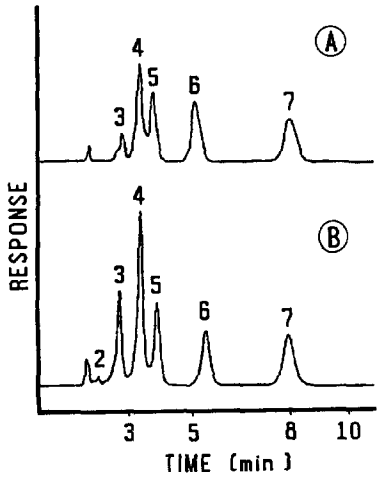

Fig. 6. LC–DAD of a spiked drinking water sample with 10 μg/l of chlorotriazine herbicides extracted with (A) dichloromethane and (B) dichloromethane–ethyl acetate containing 0.2 *M* ammonium formate. Compounds analysed: 2 = chlorodiamino-*s*-triazine; 3 = deisopropylatrazine; 4 = deethylatrazine; 5 = cyanazine; 6 = simazine; 7 = atrazine. DAD detection at 220 nm. A Brownlee cartridge column packed with 5-μm Spherisorb ODS was used.

chlorinated acids [39]. The different methods, as for the EPA (see Table 7), are based on the formation of derivatives followed by GC–ECD. As the SCA method recommends a different derivatization for each of the chlorinated acid herbicides, it is interesting to present a summary of all the alternatives (Table 8). The different methods indicated in this table generally use 1 l of water, with an acidic extraction with diethyl ether, followed by hydrolysis and derivatization and final concentration to 1 ml. Volumes of 5 μl of the sample are injected on to the GC column using a 25-m fused-silica WCOT column containing a methylsilicone stationary phase. The methylation, indicated in Table 8 under Method B, is the most similar to the EPA method. The method for the acidic herbicides it is also valid for other compounds such as polychlorinated phenols.

It should be noted that DCPA (Dacthal or Chlorthal) and DCPA acid metabolites are not included in the SCA methods of analysis, probably because the parent compound is not used in Europe. No evidence of its use was found when ground waters from different European countries were monitored [5]. In contrast, such compounds, as we have seen previously, are the most relevant herbicides detected in the NPS. DCPA acid metabolites can be analysed by Method B in Table 8, which is similar to the EPA method (Table 7). This compound and its TPs are fairly stable in soil, with half-lives of 100 and 365 days, respectively [12]. The incidence of this acidic herbicide is a notable difference between the USA and Europe, as it can affect the water supply of more than 10 million people

TABLE 8

SUMMARY OF SCA METHODS

SCA methods foe the determination of chlorinated phenoxy acids in water

Method A. Extraction, hydrolysis, butylation and GC–ECD
Preferred for: 2,4-D, 2,4,5-T and dalaphon
LOD (μg/l): 2,4-D 0.024; 2,4,5-T 0.004

Method B. Extraction, hydrolysis, methylation and GC–ECD
Preferred for: 2,3,6-trichlorobenzoic acid (TBA), dicamba, polychlorophenols
Also suitable for: 2,4-D, 2,4,5-T and dichlorophenols
LOD (μg/l): 2,4,6-trichlorophenol 0.07; 2,4,5-trichlorophenol 0.2; 2,3,4,6-tetrachlorophenol 0.02; pentachlorophenol 0.02; 2,3,6-TBA 0.0005

Method C. Extraction, perflurorobenzylation and GC–ECD
Preferred for: MCPA, MCPB and MCPP (mecoprop)
Also suitable for: dicamba and TBA
LOD (μg/l): MCPP 0.11; dicamba 0.10; MCPA 0.08; 2,3,6-TBA 0.08; 2,4-D 0.14; 2,3,5-T 0.11; MCPB 0.10

Method D. Extraction, hydrolysis, methylation and GC–MS
Preferred for: MCPA, MCPB, MCPP, 2,4-D and 2,4,5-T
LOD (μg/l): 1 (two suitable ions for each analyte are used in the multiple ion detection)

Method E. Extraction, hydrolysis, nitration, methylation and GC–ECD
Preferrd for: MCPA, MCPB and MCPP
LOD (μg/l): MCPA 0.004

SCA method for the determination of synthetic pyrethroid insecticides in waters by gas–liquid chromatography

Extraction of 1 l of water with *n*-hexane with GC–ECD analysis and confirmation by GC–MS with negative chemical ionization (NCI). A DB-5 column is used
LOD (μg/l): 0.01
Suitable ions for GC–NCI-MS confirmation:

Pyrethroid	Ion (*m/z*)
Cyhalothrin	205, 241
Permethrin	207, 209
Cyfluthrin	207, 209
Cypermethrin	207, 209
Deltamethrin	79, 81

within the USA, whereas in Europe it has not been detected.

The determination of glyphosate does not differ substantially from the EPA method (Table 7) [39]. In the SCA method the sample is concentrated by evaporation and passed through an ion-exchange column. After further concentration the glyphosate (and its major TP aminomethylphosphonic acid) is separated by reversed-phase LC and fluorogenically labelled using OPA and mercaptoethanol, before fluorimetric detection. The LOD is 0.08 μg/l when concentrating 1 l of water sample to 5 ml with injection of 20 μl into the LC system. The difference in the EPA method is that no concentration of the sample is carried out as a large injection loop of 200 μl enhances the detection limit. In the SCA method more manipulation of the sample takes place, thus making possible a better LOD which closely meets the requirements of the EEC Drinking Water Directive.

Carbamates are determined by LC, with either normal- or reversed-phase systems. Here, the method involving reversed-phase systems will be discussed, as it is more frequently used. It allows the determination of most carbamates and urea herbicides in river and drinking waters and in addition allows the determination of soluble dithiocarbamates. A 1-l volume of water sample is concentrated by extraction using 50 + 25 ml of dichloromethane, with prior acidification of the solution to pH 3. After evaporation, the sample is dissolved in 500 μl of acetonitrile or methanol and injected on to the LC column using a 20-μl loop. The method is valid for all the carbamates with the exception of benomyl, which needs adjustment of the pH to 11 with sodium hydroxide prior to extraction. The LODs (μg/l) were 0.08, 0.05, 0.05, 0.02 0.04, 0.04, 0.02 and 0.04 for perbulate, EPTC, triallate, propham, carbaryl, methiocarb, benomyl and dinocap, respectively. The wavelength recommended for the analysis is 220 nm, with the exception of benomyl and dinocap, which are monitored at 364 nm. The method is, evidently, less selective than the EPA method (see Table 7) but is apparently more sensitive with lower LODs. It should be borne in mind that in the EPA method the water samples are directly injected using a 400-μl loop, and considering this fact, the LODs are excellent. When a few millilitres of the sample are concentrated (see Fig. 3), then the EPA method is much more sensitive. A drawback of the SCA method is that it does not specify the column type and, in contrast to EPA, does not indicate the use of a second column for confirmation purposes. This should be recommended as detection at 220 nm is not very selective.

For the determination of dithiocarbamates and related compounds such as maneb, mancozeb, nabam, zineb, ferbam and thiram, the water sample is heated with acid in the presence of tin(II) chloride and 2,2,4-trimethylpentane (isooctane). The carbon disulphide formed dissolves in the isooctane and is determined by GC–FPD [41]. The LOD is 0.48 μg/l (0.84 μg/l as maneb). A great disadvantage of this method is that the result corresponds to the total of the compounds listed, together with any others that undergo the same reaction. During the last few years an elegant LC method based on postcolumn complexation of the dithiocarbamates with finely divided copper to form a coloured complex has been developed [42]. Fig. 7 shows the analysis of a surface water sample spiked with 10 mg/l of thiram.

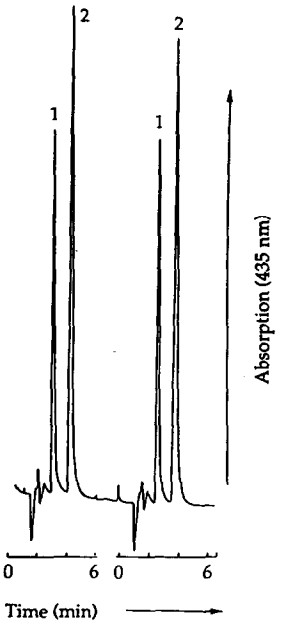

Fig. 7. Chromatograms for the duplicate injection of surface water spiked with 10 mg/l of thiram and 20 mg/l of Cu(dimethyldithiocarbamate)$_2$. LC conditions: column packed with 5-μm Hypersil ODS; copper reactor, 2.0 × 2.1 mm; eluent, acetonitrile–10 m*M* aqueous acetate buffer (pH 5.0) (70:30, v/v); flow-rate, 0.3 ml/min; wavelength, 435 nm.

Synthetic pyrethroids such as permethrin, cypermethrin, α-cypermethrin, fenvalerate and deltamethrin are determined using solvent extraction of 1 l of water with 100 ml of hexane, with clean-up methods involving Florisil (or aminopropylsilica or alumina) and with analysis by GC–ECD with confirmation by GC–MS with negative chemical ionization (NCI) [43]. The method allows an LOD of 0.005 μg/l for each of the studied compounds, which complies with EEC Directives. The columns used are 30 m × 0.33 mm I.D. DB-5 or SE-54. This method is the first that recommends the use of NCI in the selected ion monitoring mode and is in contrast to the EPA methods, which only use GC–MS in the conventional EI mode. In this case, the SCA method also indicates that when MS facilities are not available, another capillary column coated with a different stationary phase should be used for confirmation purposes. This method is clearly more specific and advanced than the EPA method, as (i) more pyrethroids are analysed, (ii) there are three options of clean-up steps and (iii) the use of NCI is recommended. A summary of the method is given in Table 8.

The SCA method for diquat and paraquat involves concentration by ion exchange, reduction with alkaline sodium dithionite and determination of the reduced compound by visible light spectrophotometry by direct or second derivative measurement. The LOD for a 5-l water sample is 0.4 μg/l (direct) or using the second derivative 0.02 μg/l [44]. The problems with this method are the interferences, as any component remaining after the procedure which absorbs light in the relevant region of the visible spectrum will interfere. The maximum wavelengths for measurement are: 396 and 379 nm for paraquat and diquat, respectively. The EPA method has advantages as compounds are separated by LC, with a better elimination of interferences, and further confirmation by DAD.

To summarize the general similarities and differences between the EPA and SCA methods, for SCA methods (i) less emphasis is placed on the use of confirmatory columns (to avoid false positives), surrogates and internal standards, (ii) the number of compounds to be monitored is smaller than the 126 in the NPS–EPA list, so fewer screening methods are available, (iii) DCPA, the most important herbicide within the USA, and its TPs are not monitored although there are generally similarities in compounds and methods between the EPA and SCA, (iv) virtually no information is offered for the analysis of TPs whereas the NPS has already introduced a method that monitors up to 25 TPs, (v) they are based on GC (changing from packed to capillary columns as in EPA methods), whereas few LC methods are used, (vi) two of the methods (for pyrethroids and phenoxy acids) are superior to the EPA methods, as confirmation by GC–MS with NCI with an extended list of pyrethroids is shown and for phenoxy acids they offer three different alternatives of derivatization, depending on the compound to be analysed and also GC–MS confirmation, (vii) less selectivity and sensitivity for the analysis of quats and carbamates compared with the EPA (when concentrating 10 ml of water, the EPA method for carbamates can go as low as 5–10 ng/l) and (viii) for triazines and organophosphorus pesticides there are not many differences compared with the EPA methods.

To conclude this comparison, we can state that, critically, all the official methods of analysis can be improved. In general, it can be commented that within Europe, method development for the determination of pesticides in drinking water is more of a requirement and more needed than in the USA because of the more stringent limits relating to the quality of drinking water. Another general remark concerning all of the methods is that too many official methods are still based on LLE, with the associated problems of solvent disposal. The future within Europe will certainly be the development of screening methods for a wide range of pesticides based on SPE principles, either off-line [33] or on-line [34] with LOD of at least 0.02 μg/l, thus permitting the determination of 0.1 μg/l of each individual pesticide.

An example of a such a way to proceed is shown in Fig. 8 with an on-line LC–DAD analysis obtained after preconcentration on C_{18} Empore extraction disks of 350, 500 and 1000 ml of tap water sample spiked at 0.2 μg/l levels with a pesticide mixture that includes carbamates and TPs. The water volume that needs to be preconcentrated for achieving an LOD that will satisfy the EEC Drinking Water Directive can vary between 150–350 ml.

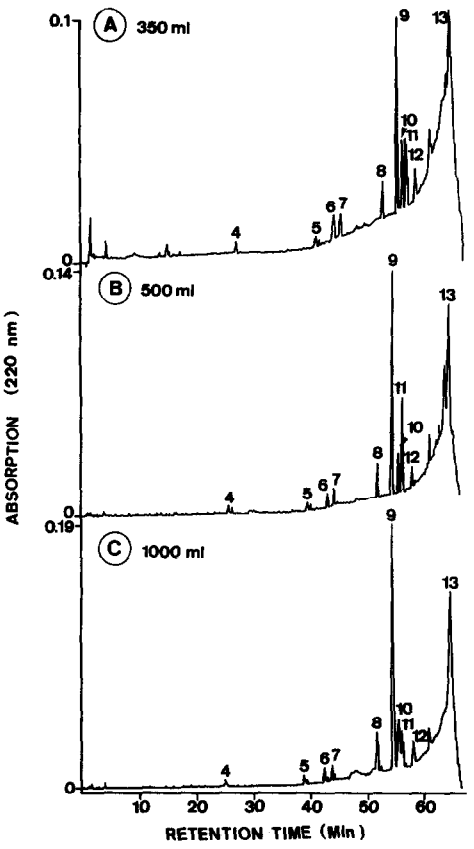

Fig. 8. LC–UV detection after preconcentration on C_{18} Empore extraction disks of (A) 350, (B) 500 and (C) 1000 ml of drinking water spiked at 0.2 μg/l with (1) aldicarb sulphoxide (2) aldicarb sulphone, (3) 3-hydroxy-7-phenol carbofuran, (4) 3-hydroxycarbofuran, (5) 3-ketocarbofuran phenol, (6) aldicarb, (7) 3-ketocarbofuran, (8) carbofuran, (9) carbaryl, (10) chlortoluron, (11) 1-naphthol, (12) isoproturon and (13) metolachlor. A 4-μm Supersphere 60 RP-8 LC column was used.

4. OTHER GC METHODS

Capillary gas chromatography (GC) in combination with selective detection methods, mainly nitrogen–phosphorus (NPD), electron-capture (ECD), flame photometric (FPD) and mass spectrometric (MS), is still the most common technique for the determination of environmental pesticide residues in water, as shown in the above discussion of official methods of analysis. The low LOD, high selectivity and affordability of GC instrumentation is appealing to most laboratories involved in pesticide residue analysis. Several reviews on the use of GC–NPD, GC–ECD and GC–MS have been published [45,46]. Recently, a book presenting various GC and LC approaches, either for multi-residue analysis and for specific groups of compounds, such as carbamates and organophosphorus and organonitrogen compounds, has been published [47].

Examples of the use of GC–NPD for the routine determination of organophosphorus and organonitrogen pesticides in water samples following a multi-screening method similar to the EPA method 507 (Table 7) have been reported [7,48,49]. Examples of organonitrogen and organophosphorus pesticides determined were ametryne, atrazine, atraton, prometryne, metolachlor, fenitrothion, fenthion and parathion-methyl. However, in recent years, as already mentioned, methods based on SPE, instead of the conventional dichloromethane LLE, have been developed. Examples of the use of SPE, using C_{18} silica cartridges followed by either GC–ECD (for atrazine, alachlor, metribuzin and metolachlor [50]), GC–NPD (for carbaryl, carbofuran, fonofos, parathion, alachlor, cyanazine and metribuzin [51, 52]) or GC–alkali flame ionization detection (for organophosphorus pesticides such as pyridafenthion and tetrachlorvinphos or triazines such as atrazine and prometryne [53]) have been reported.

The use of SPE methods has been of increasing interest in the last few years for the isolation of pesticides from water and will probably replace conventional LLE not only in research laboratories (where it is already fairly common), but also in government laboratories, where conventional LLE procedures are still very much in use. The application of SPE has been expanded recently by the use of a novel product, *viz.*, Empore extraction disks containing either C_{18} or polystyrene–divinylbenzene material. These can be used in a similar way to cartridges but with major advantages such as faster extraction owing to the lack of channelling and faster mass transfer owing to smaller pore sizes (8 μm *versus* 40–60 μm). It has been applied to the determination of various pesticides in water matrices, followed by GC–ECD [54]. Recently Empore disks have been coupled on-line with GC–NPD for the direct analysis of 2.5-ml water samples containing various organophosphorus pesticides with LODs of 0.1 μg/l being achieved [55].

Electron-capture detectors (the most commonly

used for classical chlorinated pesticides such as DDT and endrin, which are not discussed here) are resorted to when the molecule contains chlorinated groups (*e.g.*, atrazine, chlorpyrifos, metoxychlor and trifluralin). GC–ECD is the method of choice for the identification of several unstable pesticides which need derivatization prior to GC–ECD determination. Examples are carbamates (trichloroacetyl), chlorinated phenoxy acids (pentafluorobenzyl, methyl esters) and urea pesticides (heptafluorobutyric esters) [22,24,56–58]. Some of these methods include a confirmation procedure, using the derivatives formed, by GC–MS [22,24,58]. Most of the derivatization methods developed are for the acidic herbicides and usually refer to EPA methods (see Table 7). These methods are usually more rapid [56] or introduce refinements related to sampling, clean-up, confirmation of compound identity and quality assurance [58]. For instance, for the detection of acidic herbicides at the 0.02–0.05 μg/l level, the pentafluorbenzyl derivatives are recommended in preference to the methyl esters formed by the classical diazomethane reagent [58], as the latter method lacks sensitivity at the low level of detection required for the monitoring of pesticides in drinking water samples within the EEC.

In order to avoid "false positives" in the determination of pesticides in water samples, confirmatory techniques are needed. As we have seen with the EPA methods, such confirmation is usually achieved by injecting the sample extract on to a second column of different polarity. However, such comparisons do not constitute a foolproof means of confirmation. Another way to carry out confirmation by using a second column is the application of so-called two-dimensional capillary GC, where two columns of different selectivity are combined in such a way that a fraction of the eluate can be directly transferred from one column to another. The different aspects, involving valve switching, pneumatic switching, pneumatic effluent transfer, the different modes of operation (cut, straight and backflush), etc., have been discussed in a review [59]. Examples of the use of linked response data from parallel PFD and ECD instruments with retention data from linear temperature programming [60], and even with the use of three selective detectors (FPD, NPD and ECD types), have recently been published [61]. A third approach is the use of chemical derivatization, which is a technique that has found substantial use in pesticide residue analysis when other means of confirmation were not available. Examples of the use of reagents and chemical reactions for organophosphorus pesticides have been reported recently [38]. The formation of a derivative, *e.g.*, after trifluoroacetylation, means that the original pesticide peak disappears and the derivative, with a different retention time, appears, thus providing confirmation.

GC–MS is the most widely used confirmation technique. The increasing importance of this approach in the determination and confirmation of pesticides in water is linked to the fact that the EPA and SCA methods previously discussed have already implemented GC–MS in some of their protocols, with a tendency to include MS confirmation in the future or in new modified methods. EPA method 525 (see Table 7), based on SPE with either cartridges or disks, has also been evaluated [31], and showed low interferences from the disks in the background mass spectra. A screening method based on the use of SPE with various SPE materials (C_{18}-, amino- and phenyl-bonded) and GC–MS determination for 50 pesticides at sub-μg/l levels, *e.g.*, atrazine, propanil, trifluralin, chlorpyrifos and tetradifon, was developed by the Mario Negri Institute [33]. The isolation of several triazines was evaluated using Sep-Pak C_{18} SPE cartridges [62] and by using a styrene–divinylbenzene copolymer such as PLRP-S [63] in combination with GC–MS with various ionization modes such as EI and positive and negative chemical ionization (PCI and NCI). The use of XAD-2 and XAD-7 in combination with GC–MS with an ion-trap analyser has been reported for several pesticides, *e.g.*, alachlor, diazinon and metribuzin [64]. C_{18} cartridges in combination with isotope dilution GC–MS has been reported for maize herbicides with an LOD of 0.05 μg/l [65].

Applications of the use of LLE based on dichloromethane extraction, similar to the EPA method (Table 7), for oganonitrogen compounds in combination with quadrupole GC–MS [7] and ion-trap GC–MS [66] have been reported for common maize herbicides, such as atrazine, alachlor, metolachlor and simazine.

Although most of the confirmation is carried out by using GC–MS with EI, NCI is increasingly recommended, as has already observed in the SCA

method for pyrethroids. Recent work has also demonstrated the use of this technique for the determination and confirmation of acidic herbicides, *e.g.*, MCPA and dicamba, in natural waters at levels of 0.02 μg/l [67].

In this review, methods for determination of organometallic compounds used as pesticides have not been mentioned. In a recent review references relating to methods for the determination of these compounds are given [45]. It is worth indicating that a common method for the determination of organometallic compounds, *e.g.*, butyltins, involves dichloromethane and tropolone extraction. An LOD of 5 ng/l can be achieved for tributyltin in sea water using GC–MS with an ion-trap detector [68].

5. LC TECHNIQUES

LC systems used for environmental pesticide analyses have been extensively reviewed in two recent papers [45,69]. The increasing use of LC methods for pesticides is chiefly the result of their suitability for thermally labile and polar herbicides, including their TPs, which require derivatization prior to GC analysis. LC methods of analysis also have a major advantage over GC methods in that on-line pre- and postcolumn reaction systems are compatible with LC. LC is therefore becoming an important tool for analysing modern pesticides and their TPs in monitoring programmes, *e.g.*, the different EPA and NPS methods, for the determination of carbamates, unusual pesticides and TPs which are shown in Table 7. This is also due to the development, during the last few years, of UV diode-array detectors with better sensitivity than similar detectors used a few years ago, so making their use in environmental analysis attractive.

The use of a UV detector in LC in conjunction with off-line LLE or SPE is still the most common choice in environmental pesticide analyses of water samples. Information on specific wavelengths, LC eluents and columns for over 200 pesticides is available in the literature. UV detectors are no doubt the most commonly available in laboratories and also traditionally the most frequently used in LC. In Table 9 the UV characteristics of relevant pesticides are shown. These data were summarized from the literature [7,15,16,35,69,70].

Several off-line LLE methods using dichloromethane have been reported covering several groups of pesticides [7,29,71,72]. These methods do not differ substantially from the NPS method reported in Table 7, followed by LC–UV or DAD. In two instances [7,72], further acidification of the water sample to pH <2 allows the extraction of acidic herbicides. Many of the compounds are difficult to determine using GC methods, *e.g.*, isoproturon, linuron and bentazone. Off-line SPE procedures involving packing materials which may contain functional groups of different polarity such as C_8- or C_{18}-bonded silica phases, graphitized carbon black or Amberlite XAD resins have been reported. C_8- and C_{18}-bonded phase cartridges have been used for the development of screening methods for various organonitrogen pesticides such as urons and triazines [35,71] and carbamates and their TPs such as carbofuran, 3-hydroxycarbofuran-7-phenol and 3-ketocarbofuran [73,74]. The use of SPE with acidified water followed by ion-pair LC was developed for the determination of various chlorinated herbicides, *e.g.*, 2,4-D and dicamba in waters [75]. The use of off-line Empore extraction disks in combination with LC–DAD has been developed for the determination of a variety of pesticides, including carbaryl, linuron and fenamiphos in different water matrices, *e.g.*, surface river and simulated sea-water samples. The method, much faster than using C_{18} cartridges, could easily handle 4-l water samples, allowing an LOD of 0.02 μg/l, which is appropriate for the determination of pesticides in drinking waters within the EEC [76]. Graphitized carbon black has been shown to offer effective trapping possibilities for polar pesticides such as aldicarb, diuron and bentazone, and by using flow-rates of 150 ml/min for preconcentrating up to 2 l of river and drinking water [77]. Eighty-nine pesticides of environmental interest were analysed using two different columns, a primary C_{18} and a confirmation cyano column, in a similar way as recommended in the NPS method in Table 7. The good recoveries obtained when using this adsorbent allowed LODs of less than 0.1 μg/l, and consequently it is recommended for demonstrating compliance with the EEC Drinking Water Directives.

SPE methods can be easily converted into fully automated on-line systems coupled to LC. Such systems, also referred to as "precolumn technology", show additional advantages such as lower

TABLE 9

UV CHARACTERIZATON OF PRIORITY PESTICIDES AND TRANSFORMATION PRODUCTS [7,15,16,35,69,70]

Pesticide	UV absorption (nm)	EEC [5]	NPS [14] (nm)	Pesticide	UV absorption	EEC [5]	NPS [14]
Alachlor	200	×	×	Hexazinone	254		×
Aldicarb	207, 220, 247	×	×	3-Hydroxycarbofuran	206		×
Aldicarb sulphone	<200		×	3-Hydroxy-7-phenol carbofuran	<200, 208		×
Aldicarb sulphoxide	<200		×	Isoproturon	201, 243	×	
Ametryn	220		×	3-Ketocarboforan phenol	<200, 215		×
Atrazine	222, 263	×	×	Linuron	211, 249	×	×
Barban	205, 237		×	MCPA	200, 230	×	
Baygon (propoxur)	200, 220		×	Metazachlor	<200, 220	×	
Bentazone	219, 232, 316	×	×	Methabenzthiazuron	223, 269	×	
Bromacil	210, 277		×	Metham-sodium	208, 232	×	×
Carbaryl	220, 270	×	×	Methiocarb	225, 254, 265	×	×
Carbendazim	223, 280	×		Methomyl	220, 232		×
Carbofuran	200, 225, 279		×	Metolachlor	202	×	×
Chloridazon	229, 284		×	Metribuzin	295		×
Chlorpropham	210, 237		×	Mevinphos	218		×
Chlorpyrifos	230, 289	×		Molinate	<200, 208		×
Chlortoluron	211, 243	×		1-Naphthol	210, 232		×
Cyanazine	220	×	×	Napropamide	214		×
2,4-D	208, 224	×	×	Norflurazon	239		×
2,4-DB	208		×	Oxamyl	216		×
Dalapon	No UV	×	×	Permethrin	271	×	×
Desethylatrazine	214		×	Prometon	219		×
Desisopropylatrazine	214		×	Prometryn	223, 254	×	×
Diazinon	248, 288	×	×	Propachlor	<200		×
Dicamba	277		×	Propazine	254		×
Dichlorprop	208, 228, 285		×	Simazine	223, 244, 263	×	×
Dichlorvos	No UV		×	Stirofos (tetrachlorvinphos)	210, 250		×
Dinoseb	211, 269	×	×	2,4,5-T	214		×
Disulfoton	No UV		×	Terbutylazine	225	×	
Diuron	211, 252	×	×	Terbutryn	225	×	×
ETU	231		×	Trichlorfon	<205	×	
Fenamiphos	200, 248	×	×	Trifluralin	211, 233		×
Fenamiphos sulphone	200, 226		×	Vinclozolin	200	×	
Fenamiphos sulphoxide	200, 236		×				

detection limits (analysis of an eluate instead of a sample aliquot), no evaporation losses, no contamination and easy automation. Similarly to off-line techniques, different packing materials have been employed in the precolumn, the most common so far being C_8- or C_{18}-bonded silica [16,78–86]. Coupling of various precolumns of different chemical composition, whether isolated or serially connected, usually packed with C_{18} and PRP-1 (styrene–divinylbenzene copolymer), has been demonstrated to exhibit better clean-up possibilities, as interfering compounds are trapped on the C_{18} precolumn which acts as a filter [78,84]. In other instances the C_{18} precolumn was coupled to a short concentration column containing an "aniline" filter, in order to separate in the same chromatographic run phenylurea herbicides and their corresponding anilines [80]. For the determination of acidic herbicides, *e.g.*, bentazone, the C_{18} precolumn was flushed with phosphate buffer in order to trap these herbicides [82]. The combination of two column-switching devices using longer C_{18} precolumns increases the selectivity by applying a "cutting" technique, and the sensitivity by using large injection volumes. This

technique has allowed the determination of ethylenbisthiourea (ETU) in water samples, providing an elegant way of decreasing the LOD to 0.1 μg/l, which is much lower than that achieved with the EPA method reported in Table 7 [85]. It has also been used for the determination of chloroallyl alcohol, a metabolite of the soil sterilant 1,3-dichloropropene (see Table 7) [83].

In the last few years another styrene–divinylbenzene copolymer, PLRP-S, has become popular. This has been employed in an on-line early-warning system for the monitoring of 50 pesticides in river water [15] and also in combination with the Prospekt apparatus, a fully automated device with a cartridge-exchange system that permits the separation of a variety of compounds with automation of the relevant parameters of the preconcentration step such as pH, volume and ionic strength of the sample. The system combined with UV detection [87] or DAD [88] provided a powerful approach for the automated on-line determination of a broad range of pesticides in water matrices. On-line preconcentration using a two-step approach with PRP-1 in combination with an ion-exchange precolumn has allowed the determination of various chlorotriazines and urons in water at the 10 ng/l level. PRP-1 acts as a powerful filter to remove many neutral interferents present in drinking water samples [89,90]. The on-line coupling of Empore extraction disks with LC–UV [91,92] and LC–postcolumn fluorescence detection and DAD [93] has allowed the determination of various groups of pesticides, *e.g.*, triazines, carbamates and their polar TPs. Empore disks have higher breakthrough volumes and their small particle size (8 μm) eliminates channelling.

Most of the examples of the use of on-line precolumn systems in LC use UV detectors; they are set at different wavelengths according to the pesticides to be determined (*e.g.*, 247 nm for phenylurea pesticides [78–80], 220 nm for carbamates [81,86], 230 nm for phenoxy acids [86] and 233 nm for ETU [85]). Other detectors used include electrochemical and fluorescence [78,84] and DAD instruments, which permit structural information to be obtained; DAD is being increasingly used in monitoring programmes for screening for a variety of non-polar and medium-polarity pesticides in river water samples, *e.g.*, Rhine Basin Programme [15,16,88].

On-line precolumn technology with selective detectors can provide another powerful means of determining pesticides in water, *e.g.*, N-methylcarbamates and O-(methylcarbonyl)oxime pesticides have been determined by employing the same reaction as proposed in the EPA method reported in Table 7. This has allowed low-level determinations of carbamates and their polar TPs in drinking water matrices at 5–40 ng/l [93]. Other examples include the use of oxidation and derivatization reactions with OPA for the determination of glyphosate, a highly polar herbicide, with detection by fluorogenic labelling [94]. One of most complete multi-screening methods developed for the NPS includes the use of postcolumn photolysis followed by fluorescence, electrochemical or conductivity detection, and permitted the detection of over 100 of the pesticides included in this programme (see Table 7) [95].

The combination of LC with MS is the most powerful approach for the detection and confirmation of pesticides in water matrices. It is certainly the preferred approach to avoid false positives. Of the different LC–MS methodologies, thermospray (TSP) and particle beam interfacing (PB) systems are probably the most widely used in water analysis. References to the use of both TSP [96–98] and PB [99–101] have been reported. The most complete screening study based on positive ion LC–MS determination used off-line LLE and SPE [96]. The method permitted the simultaneous determination of 29 pesticides in water samples, with MDLs in the μg/l range, and relative standard deviations of 11–17%. A similar approach to that reported in ref. 96, but with the combined use of positive and negative ionization (PI and NI, respectively) thermospray LC–MS is shown in Fig. 9, which shows chromatograms of a well water extract obtained after LLE with dichloromethane. Another complete multi-screening method which has recently been published uses particle beam LC–MS for the identification and determination of 43 of the 126 NPS pesticides (see Table 5). For these analytes it was feasible to confirm their presence at 0.1 μg/l in water [100].

Buffers and ion-pairing agents present in the LC mobile phases which may interfere with detection can be removed by using a postcolumn extraction system to transfer the organic phase to the detector while the inorganic ions remain in the aqueous layer. This procedure has been used for the ion-suppressed

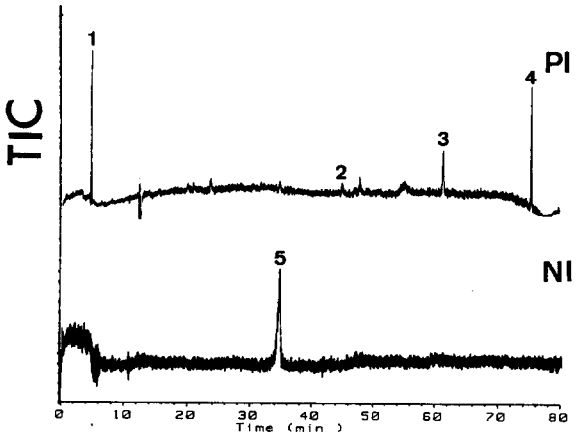

Fig. 9. LC–TSP-MS with PI and NI of a well water extract obtained after LLE using dichloromethane. Compounds determined: 1 = methomyl (13 ng/l); 2 = butocarboxim (18 ng/l); 3 = carbaryl (30 ng/l); 4 = methiocarb (250 ng/l); 5 = methiocarb sulphone (320 ng/l). Ions monitored in PI were $[M + H]^+$ for methomyl and methiocarb at *m/z* 163 and 226, respectively, and $[M + NH_4]^+$ for butocarboxim and carbaryl at *m/z* 208 and 219, respectively. In the NI mode the $[M - H - CH_3COONH]^-$ ion at *m/z* 199 was monitored for methiocarb sulphone.

extraction of chlorinated phenoxy acid pesticides with on-line MS detection [98].

A final remark on the use of LC–MS interfaces for quantitative purposes concerns the problems associated with interlaboratory comparisons of data and validation of results. These aspects have been recently pointed out in a comparison of TSP and PB interfaces [102] and various atmospheric pressure ionization (API) techniques [103] for the determination of a variety of pesticides, including chlorinated phenoxy acids and N-methylcarbamates. From these studies it was shown that the TSP interface gave better sensitivity in the NI mode for the chlorinated phenoxy acid herbicides than did PB. Statistically significant differences in quantification at 50 μg/ml were shown with average relative standard deviations of 36% and 49% for PB and TSP interfaces, respectively [102]. Another interesting study showed more problems with the PB interface, *e.g.*, non-linearity for the determination of carbamates. API with a heated nebulizer interface offered good sensitivity and linearity, providing protonated molecular mass information and abundant fragment ions for structural information [103]. It was concluded that API and TSP performed comparably for the determination of carbamate pesticides, and either was preferable to the PB interface.

6. CONCLUSIONS

From the methods of analysis reported in this review, it is clear that considerable differences exist between the official methods of analysis used in different countries and the newest techniques used in research and other laboratories. The progress in incorporating modern analytical methods, *e.g.*, the use of SPE techniques, capillary GC columns or MS confirmation, into official methods is slow. However, advances are taking place, especially within the EPA.

From the results reported from the National Pesticide Survey in collaboration with the EPA, several general comments can be made concerning the determination of pesticides in drinking water samples. (i) These methods described in detail all the parameters necessary for a good monitoring programme for pesticides, and consist of the most complete study published to date, *e.g.*, storage of samples, with preservation by adding $HgCl_2$ or monochloroacetic buffer; the use of replicate analysis after storage for 0, 14 and 28 days in a refrigerator at 4°C; the use of two different columns (at least), one primary column and a secondary column of different polarity which is used for confirmation purposes. When MS is used, then only one GC column is employed, as confirmation is achieved by MS. (ii) The NPS has for the first time monitored many TPs of pesticides. (iii) The development of microextraction LLE methods, SPE and GC–MS methods is being encouraged and is one of the strongest recommendations of the EPA.

From the final report of the NPS for different drinking water wells, it was shown that DCPA acid (and its metabolites) was the pesticide that occurred in the greatest proportion of community water wells and rural domestic wells, and it has been estimated that over 10 million people are exposed to this pesticide. However, very few are expected to be exposed to levels above the health advisory level. Other pesticides found in 0.1–6.4% of wells were atrazine, simazine, prometon, lindane, ETU, bentazone and alachlor; hexachlorobenzene and dibromochloropropane, ethylene dibromide and dinoseb were also found but their registration has been cancelled by the EPA [12].

Future recommendations for work are as follows. (i) There is a need to develop off-line SPE techniques based on new adsorbent types (*e.g.*, styrene–divinylbenzene copolymers, carbon types or Empore disks) in combination with GC–MS using selective ionization methods, *e.g.*, NCI. In the same way as NCI has been used for pyrethroids in the SCA methods of analysis, it could be a technique recommended for confirmation of organophosphorus pesticides exhibiting electron-withdrawing properties, *e.g.*, the parathion group. (ii) The on-line combination of SPE with LC–(UV)–MS, using either TSP, PB and/or API, will be welcome for screening the more polar pesticides and their polar TPs. Certainly such an approach will allow the determination of pesticides by on-line LC–UV and confirmation by MS, without the need to use derivatization steps. It is worth mentioning that there are still no official methods of analysis involving LC–MS for confirmation. (iii) The development of specific methods of analysis for particular pesticides will be of interest, *e.g.*, the EPA methods for unusual pesticides (*e.g.*, quats or glyphosate). The EEC has defined the need for developing analytical methods with low LODs for difficult pesticides such as maneb, ziram and metham-sodium, among others. (iv) The development of immunochemical methods, radioimmunoassay or enzyme-linked immunoassays will be of interest in the future, especially when linked to chromatographic techniques. Until now most of these techniques have been used for the detection of pesticides in waters and checking the selectivity and sensitivity with conventional chromatographic methods, and in some instances do show a good correlation for quantification purposes. The use of the immunoassay principle for binding specific compounds, *e.g.*, antibodies to the silica surface of the LC precolumn could be an useful method for the isolation of specific pesticides, as it would be a more selective way of using SPE techniques in water analysis. (v) There is a need for validation studies when modern techniques are incorporated into the official and/or routine methods of analysis. This will be the case when using LC–MS for quantitative purposes. From the few studies reported, the intercomparison of results between well established interfaces, such as TSP and PB, is still a problem.

From the above it is clear that much more work still needs to be done on the determination of pesticides in water samples. This particular field of research is also changing each year, as new pesticides are being developed to replace the more toxic ones or those which cause widespread contamination. This is the case for, *e.g.*, atrazine, which is being slowly replaced in some countries by terbutylazine or propazine. In this sense analytical developments need to be continually carried out to determine the new pesticides and the toxic TPs that are being released into the different types of environmental waters.

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