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Review

Extraction methodology and chromatography for the determination of residual pesticides in water

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Abstract

The contemporary state of the determination of pesticide residues and some of their transformation products is reviewed. The review covers the chromatographic determination of herbicides, insecticides and some important fungicide residues and their toxic transformation products (substituted anilines, chlorophenols, ethylenethiourea) in various types of water samples. Advantages and drawbacks of gas and liquid chromatography in this type of analysis are discussed. The emphasis is placed on multi-residue analytical methods with the required limit of quantification (LOQ $< 0.1\ \mu g\ l^{-1}$) and recovery. Various aspects of the isolation, preconcentration and clean-up of pesticide residue extracts from water samples are discussed (liquid–liquid extraction, liquid–solid extraction and supercritical fluid extraction). The characteristics of a modern chromatographic method for the determination of pesticide residues and their transformation products are summarized and trends in the development of GC and LC methods are discussed.

Keywords: Reviews; Water analysis; Environmental analysis; Extraction methods; Pesticides

Contents

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1. Introduction

Water is a very important constituent of the ecosystem on the Earth. The importance of water quality preservation and improvement constantly increases. Intensification of agricultural production, the cultivation of monoculturals for human nutrition and industrial elaboration require the regulation of pesticides usage.

According to Pimentel and Levitan [1], of $455 \cdot 10^6$ kg of pesticides applied yearly in the USA, herbicides represent about 60%, insecticides 24% and fungicides 16%. Approximately 74% of the overall consumption of pesticides is used for the treatment of soybeans and corn. The yearly consumption of atrazine [2] was estimated to be $34.5 \cdot 10^6$ kg per year in the USA and $0.7 \cdot 10^6$ kg per year in the UK. According to Buser [3], the yearly consumption of atrazine in Switzerland (in 1986) was 120 tons; 105 tons was applied in agriculture and 15 tons on railroads. The use of herbicides (simazine, diuron, bromacil) in the citrus industry [4] plays a role in well water contamination by herbicide residue in California. Atrazine was found in ground and surface water in maize production areas [5] of the Transvaal (South Africa) during the maize production season in 1991–92. About 20% of both waters was contaminated (from 0.29 to 4.36 $\mu g\ l^{-1}$). Leaching of atrazine and deethylatrazine into ground water in Germany [6] and Denmark [7] was studied. Residues of triazine herbicides in lakes and rain in Switzerland [3] and contamination of well water in central Maine [8] with atrazine, alachlor and carbofuran were found. Several groups [2,9–11] have monitored the concentration levels of pesticide residues in river or estuarine waters and pond water [12].

Natural waters are contaminated with various pesticides or their transformation products. Herbicides and nematicides are potential contaminants of natural waters because they are directly applied to the soil and are transported into ground water or leached to the surface water. Insecticides are transported into ground water in dust or rain water, which are washed out by precipitation and fall on to the soil.

The EEC Directive 80/778 [13] concerning the quality of water designated for human consumption, establishes the maximum admissible concentration of each individual pesticide at 0.1 $\mu g\ l^{-1}$ and the total amount of pesticides at 0.5 $\mu g\ l^{-1}$.

Table 1
WHO recommended classification of pesticides by hazard [14]

Class		LD_{50} for the rat, oral (mg kg^{-1} body mass)	
		Solids	Liquids
Ia	Extremely hazardous	≤5	≤20
Ib	Highly hazardous	5–50	20–200
II	Moderately hazardous	50–500	200–2000
III	Slightly hazardous	>500	>2000
III+	Unlikely to present hazard in normal use	>2000	>3000

The WHO recommended the classification of pesticides by hazard [14] into five classes on the basis of LD_{50} values (p.o. for rat). Most herbicides belongs to the class III + (Tables 1 and 2). The IARC (International Agency for Research on Cancer) classifies chemical agents into working groups according to the degrees of evidence for carcinogenity towards humans and experimental animals. Some pesticides and their transformation products (chlorophenoxy acid herbicides, DDT, ETU, chlorophenols, some aniline derivatives) are listed into group 2B—agents possibly carcinogenic to humans [15].

The groundwater ubiquity score (GUS) [16] is a simple parameter for assessing the leachability of pesticides. The GUS index can be written as

$$GUS = \log(DT_{50}) \cdot [4 - \log(K_{OC})]$$

Persistence (expressed by DT_{50}) and mobility (expressed by K_{OC}) are key parameters that seem to be particularly representative of the overall leaching potential of non-ionic compounds. Bottoni and Funari [17] evaluated the impact of 48 herbicides on groundwater quality. The tendencies to contaminate groundwater are (a) non-leacher ($GUS < 1.8$), (b) transition ($1.8 < GUS < 2.8$) and (c) leacher ($GUS > 2.8$).

The EPA elaborated lists of pesticides properties which indicate their groundwater contamination potential (see Table 3).

Table 2
Distribution of pesticides according to hazard classes [14]

Pesticide group	Class					Total
	Ia	Ib	II	III	III+	
Rodenticides	11	10	4			25
Insecticides	26	51	62	13	13	165
Fungicides	6	5	21	30	67	129
Herbicides		5	26	57	119	207

Barceló [19] discussed the differences in priority lists of pesticides in water elaborated by the EEC and EPA. WHO requirements on pesticide residue concentrations have been presented [20], providing information about the contemporary requirements on analytical methods for the determination of priority pesticides and their transformation products in water samples.

2. Determination of pesticide residues in water

Separation methods (especially gas and liquid chromatography) play a very important role in the determination of pesticide residues, their metabolites and transformation products in environmental waters. TLC on silica gel can be used as a screening method. Screening of 265 pesticides in water by TLC with automated multiple development was published [21]. A TLC method on silica gel with selective biochemical detection based on inhibition of Hill reaction allows the determination of herbicide residues in water at concentration levels of 0.1–0.5 $\mu g\ l^{-1}$ [22,23]. The Hill reaction is one of the sequence of biochemical reactions constituting the process of photosynthesis in plants [24]. The reaction also takes place in isolated plant chloroplasts and can be carried out and visualized on a thin-layer chromatogram. Metabolites and degradation products do not inhibit the Hill reaction and therefore the herbicide can be confirmed in their presence. Herbicides can be classified according to the power of inhibition of the Hill reaction into three groups (strong inhibitors, weak inhibitors and non-inhibitors; see Table 4).

The list of pesticide compounds reviewed here is given in Table 5.

Table 3
Properties of pesticides which indicate their high groundwater contamination potential [18]

Parameter	Value
Water solubility	>30 mg l^{-1}
K_d	<5, usually <1
K_{oc}	<300
Henry's law constant	$<10^{-2}$ atm m^{-3} mol
Speciation	Negatively charged, fully or partially at ambient pH
Hydrolysis half-time	>25 weeks
Photolysis half-life	>1 week
Field dissipation half-life	>3 weeks

Table 4
Inhibition of Hill reaction by different herbicide groups [25]

Herbicide group[a]		Inhibition power[b]
Ia,b	Triazines and triazinones	++
II	Phenylurea	++
III	Carbamates	++
IV	Phenoxyalkanoic acids	–
V	Arylphenoxypropanoic acids/esters	–
VI	Sulfonylureas	–
VII	Bipyridylium cations	–
VII	Uracils	++
IX	Chloridazon	+
X	Others:	
	Bentazone	+
	Monalide	+
	Thiazafluron	+

[a] Structural groups of herbicidal compounds [26].
[b] ++ = strong inhibitor, LOD <1 ng per spot; + = weak inhibitor, LOD 1–30 ng per spot; – = does not inhibit Hill reaction.

Table 5
List of pesticide compounds reviewed and references relating to their residue analysis in water samples

Pestidide group	Class[a]	Pesticide	Water solubility (mg l^{-1})	Ref.
Anilides	H	Alachlor	212	[8,9,28,46]
	H	Metazachlor	17	[40,96]
	H	Metolachlor	530	[9,28,40,46,90,96]
	H	Propachlor	700	[34,46]
	H	Propanil	2.3	[31,34,65]
Bipyridyl cations	H	Diquat	Well	[69,108]
	H	Paraquat	Well	[69,108]
Carbamates	I,A,N	Aldicarb	600	[35,37,68,92,95,121]
	I	Carbaryl	1000	[31,34,37,39,65,68,92,95]
	I	Carbofuran	425	[8,34,37,68,92,95]
	H	Chlorpropham	89	[34,40]
	H	Desmedipham	7	[22]
	H	EPTC	375	[46]
	I	Oxamyl		[34,68,78]
	I	Methiocarb		[37,68,95]
	I	Methomyl		[34,68,78]
	H	Phenmedipham	10	[22]
	I	Propoxur	2000	[37,68,95,119]
	H	Propham	250	[34,40]
	I	Pirimicarb	270	[68]
Coumarin	R	Warfarin	17	[78]
Diazines	H	Bentazone	500	[9,23,34,56,59,61,62,78,92,120]
	H	Chloridazone	400	[22,34,35,121]
EBDC	F	Maneb	10	[89] (determination of ETU)
	F	Zineb	10	[89]
Nitriles	H	Bromoxynil	130	[34]
	H	Ioxynil	2	[78]
Nitroanilines	H	Benfluralin	1	[46]
	H	Ethalfluralin	1	[77]
	H	Isopropalin	0.1	[46]
	H	Pendimethalin	0.3	[28,46,77]
	H	Trifluralin	1	[9,46,77]
Organophosphorus	I	Azinphos-ethyl		[46,34,50]
compounds	I	Azinphos-methyl	30	[46,48]
	I	Chlorpyriphos-ethyl		[46,50,119]
	I	Chlorpyriphos-methyl	4	[46,50,119]
	I	Diazinon	40	[36,46,48,50,51,119]
	I	Dichlorvos	8000	[35,46,51]
	I	Dimethoate	25000	[35,46,48]
	A	Ethion		[46,49]
	N,I	Ethoprophos	700	[33]
	N	Fenamiphos	700	[31,33,65,92]
	I	Fenitrothion	30	[31,34,36,48,65]
	I	Fenthion	55	[33,48,119]
	I	Fonophos	13	[46,49]
	I	Malathion	145	[36,48–51]
	I	Methamidophos	2000	[46]
	I	Mevinphos	Well	[33]
	I	Parathion-ethyl	24	[31,34,36,46,49,65]
	I	Parathion-methyl	55	[31,36,46,49]

Table 5 (*continued*)

Pestidide group	Class[a]	Pesticide	Water solubility (mg l^{-1})	Ref.
Phenolic	H	Dinoseb		[34]
pesticides	H	Dinoterb		[34]
Phenylureas	H	Buturon	30	[31,45,44
	H	Chlorbromuron	35	[31,42,44,102]
	H	Chloroxuron	3.7	[31,34,40,44,96,102]
	H	Chlortoluron	70	[9,10,31,37,40,42,44,45,96,102,111]
	H	Difenoxuron	20	[31,44,102]
	I	Diflubenzuron	0.2	[31,45]
	H	Diuron	42	[10,31,40–42,44,45,96,102,111,121]
	H	Fenuron	3850	[10,31,40,42,44,45,102]
	H	Fluormeturon		[10,31,42,44,45,102]
	H	Isoproturon	170	[9,10,31,37,40,42,44,45,96,102,111]
	H	Linuron	75	[9,10,31,34,40–42,44,45,65,96,102,111,121]
	H	Methabenzthiazuron	59	[31,40,42,96,111]
	H	Metobromuron	8.8	[10,40,42,44,96,102,111]
	H	Metoxuron	678	[10,31,34,35,40–42,44,45,96,102,111]
	H	Monolinuron	580	[31,34,40,41,42,44,102,111,121]
	H	Monuron	230	[10,31,34,42,44,45,96,102,111]
	H	Neburon	5	[31,41,44,45,96,102]
Sulfonylureas	H	Chlorsulfuron		[71–73,125]
	H	Metsulfuron-methyl		[71,72,125]
Phenoxy acids	H	MCPA	300	[53–56,58,59,61–63]
	H	MCPB	44	[34,56,58,59,61–63]
	H	MCPP (mecoprop)	620	[34,53–56,58,59,61–63,122]
	H	2,4-D	600	[34,53–56,58,61–63,78,122]
	H	2,4-DB	46	[34,54–56,58,61,63,78]
	H	2,4-DP (dichlorprop)	350	[53,55,56,58,61,122]
	H	2,4,5-T	278	[34,53,55,58,59,61,63,78]
	H	2,4,5-TB		[58,122]
	H	2,4,5-TP (fenoprop)	176	[34,53,55,58,61]
Pyrethroids	I	Esfenvalerate		[90]
Triazines	H	Ametryn	185	[30,32,38,46,113]
	H	Atraton	1800	[30]
	H	Atrazine	70	[2,3,5–9,28,30,32–34,37,40,46,65,77,90,113,119]
	H	Cyanazine	171	[30,31,34,40,65,96]
	H	Prometon	750	[30–32,38,113]
	H	Prometryn	48	[30,32,38,40,46,113]
	H	Propazine	8.6	[30–32,38,40,77,113]
	H	Simazine	5	[2,3,9,30–33,36,38–40,46,65,77,113,119,121]
	H	Terbuthylazine	8.5	[3,31,40,46,77,96]
	H	Terbutyrn	58	[32,38,40,46,77,113]
Triazinones	H	Metamitron	1820	[35,40,77]
	H	Metribuzine	1220	[34,35,40,46,77,90]
Uracils	H	Bromacil	815	[22,34,35,121]
	H	Lenacil	6	[22]
	H	Terbacil	710	[22]

[a] H = herbicide; I = insecticide; F = fungicide; A = acaricide; N = nematicide.
[b] Taken from Ref. [27].

2.1. Triazine herbicides

Triazines represent an important group of pesticides. They can be divided into the three groups (chloro-, methoxy- and methylthiotrizines). Metribuzin and metamitron are non-symmetric triazines known as triazinones.

Symmetrical triazines are well chromatographed by GC and give good responses with NPD, owing to the five nitrogen atoms in their molecules. Non-symmetric triazines are more polar than symmetrical triazines.

Classical extraction of triazines from water samples with dichloromethane and sample clean-up on Florisil [28–30] give sufficient recoveries. Pichon et al. [31] reported the on-line preconcentration of some triazines on PLRP-S precolumns. On PLRP-S polymer sorbent, the breakthrough volumes of simazine, atrazine and cyanazine (at $\mu g\ l^{-1}$ concentration levels) were ca. five times higher than on C_{18} silica. Determination limits were less then 0.1 $\mu g\ l^{-1}$. LSE of triazine residues on C_{18} cartridges [32,33], GCB [34,35] or C_8 or C_{18} membrane extraction discs [36,37] were described. Land [38] described the selective isolation of triazines with a cation exchanger (sulfonic acid type) prior to LC–UV with a determination limit of less than 0.1 $\mu g\ l^{-1}$. Generally there are no problems with the effective isolation of triazines from water samples. Capillary GC with selective NPD [9,28,30,33] seems to be a very suitable method for the determination of triazines (owing to the five nitrogen atoms in their molecule). More than one order of magnitude lower sensitivity of LC–DAD determination compared with GC–NPD was reported by Durand et al. [9]. ITD was used for confirmation of triazine residues in water [28]. HPLC with UV detection at the absorption maxima has been routinely employed [34,38,39].

2.2. Phenylurea herbicides

The use of phenylurea herbicides is growing partially because they are replacing more persistent triazine herbicides.

Dichloromethane [40,41] and a mixture of *n*-pentane and diethyl ether (1:1, v/v) [42] have been used for the LLE of phenylurea residues from water samples. The water was extracted under neutral (pH 6.5–7) or slightly alkaline conditions (pH 7–8). LSE on Carbopack B cartridges has been used for the isolation of parent compounds in the presence of their degradation products (substituted anilines) [34]. No pH adjustment of environmental water was necessary. The detection limits by this method were between 0.03 and 0.06 $\mu g\ l^{-1}$. Hatrík et al. [43] employed on-line preconcentration on a short C_{18} precolumn prior to the LC determination of monolinuron, metobromuron, linuron and their anilines in surface water. Compounds were detected by UV and amperometric detection operated in tandem at the low-ppt concentration level. The determination of five phenylurea herbicides by microcolumn HPLC with UV and electrochemical detection was reported by Boussenadji et al. [41]. The sensitivities of both detection methods for the studied phenylureas were comparable. De Kok et al. [44] described GC–ECD/NPD and LC–UV/ECD determination of phenylurea herbicides after their catalytic hydrolysis on silica and derivatization of anilines with HFBA. Herbicides and anilines were detected by ECD at the 0.01–0.1 $\mu g\ l^{-1}$ level in surface water. GC–ECD turned out to be 20–100 times more sensitive than GC–NPD.

The determination of phenylureas with a GC method is difficult because of their thermal instability. Therefore, mostly derivatization before GC analysis is required. The most frequently used derivatization agents are HFBA [45], TMAH or TMSH [42] and methyl iodide [10]. Derivatives are thermally stable and can be chromatographed by GC–ECD/NPD/MS [42, 46]. Tekel' et al. [47] described a GC–NPD method for the determination of four phenylurea herbicides and their corresponding substituted anilines in water without derivatization.

2.3. Organophosphorus pesticides

Organophosphorus pesticides were isolated from water by LLE with dichloromethane [47],

SPE on C_{18} cartridges [33,48,49] and on C_8 membrane extraction discs [47]. De la Colina et al. [48] reported how recoveries of some polar organophosphorus pesticides (dimethoate, fenthion, fonofos) on a conventional C_{18} cartridge. Better results were obtained with the more universal sorbent GCB [34] and the polymer resin Amberlite XAD-2. All the above methods provided recoveries of 75–95%.

GC with NPD [47–49], ECD [47–49], or FPD-P [50] has frequently been the instrumental technique of choice for the determination of volatile organophosphorus pesticides for reasons of selectivity and sensitivity. Mass spectrometric detection [36,50,51] were employed as a confirmatory characterization technique.

The LC–UV determination of organophosphorus pesticides residues was reported by Pichon and Hennion [31] and Di Corcia and Marchetti [34].

2.4. Phenoxy acid herbicides

Phenoxy acid herbicides are the oldest group of synthetic herbicides, introduced in agriculture in the 1940s. It was reported [52] that the acidic herbicides (2,4-D, MCPA, MCPP, TCA) are being used in Europe in amounts of over 500 tons per year. Most of them are transient and leachers through the soil. The use of 2,4,5-T has been prohibited in Sweden since 1977 owing to the toxic contaminant 2,3,7,8-tetrachlorodibenzo-*p*-dioxin [53].

The residues of phenoxy acids were extracted from water samples with dichloromethane [54–56] and diethyl ether [57]. Phenoxy acids and their ethyl esters were extracted with benzene prior to extraction with Et–Ac–*n*-hexane (4:1, v/v) [58]. Extraction was effective only after acidification of sample (pH 2). Extracts from heavily polluted water samples can be cleaned on Florisil. Mering et al. [59] described the isolation of some phenoxy acids by phase-transfer catalysed derivatization with fluorobenzyl bromide dissolved in dichloromethane prior to GC–MS with LOD around 0.05 $\mu g\ l^{-1}$. Solid-phase extraction on C_{18} silica [58,60] gives a satisfactory recovery only for acidified water samples (pH 2). The ionic character of phenoxy acid herbicides allows their isolation on anion exchangers, e.g., QEA Sephadex A-25 [53] or a strong silica-based anion exchanger (SAX) [60]. With Carbopak B high recoveries (minimum 95%) of pyenoxy acids were obtained [34,60]. In this way an LOD of 0.1 $\mu g\ l^{-1}$ was obtained when using LC–UV detection. Geerdink et al. [61] reported off-line preconcentration of some phenoxy acids on a polymeric precolumn (PLRP-S).

Because of their highly polar nature and low volatility, they cannot be directly determined by GC and they have to be derivatized to esters (usually with diazomethane [55], TFE [53] and PFBB [84]). The residues in the form of esters have been determined by GC–ECD. Chlorophenoxy acid herbicides can easily be derivatized with CEDMSDEA reagent prior to GC–NPD [54].

HPLC methods for phenoxy acids are now generally preferred over GC methods. HPLC with UV [61] or DAD [56,62] detection has been routinely used. After derivatization with ADAM [57,58], derivatives can be detected with a fluorescence detector (excitation, 365 nm; emission, 412 nm) at very low levels (0.2 $\mu g\ l^{-1}$). De Ruiter et al. [63] applied on-line postcolumn ion-pair extraction with a fluorescent counter ion, after trace enrichment by SPE on PLRP-S, for the determination of 2,4-D, MCPA, MCPB, MCPP and 2,4,5-T. The detection limits were as low as 0.05–0.1 $\mu g\ l^{-1}$. TSP-MS [62] has been recommended for the identification of acidic herbicides.

2.5. Carbamates

The majority of pesticides in the carbamate group are insecticides. Desmedipham and phenmedipham are the most important herbicides in this group [22]. They are usually used for the protection of sugar beet. TLC on silica gel with chronometric detection (inhibition of Hill reaction) was employed as a screening method for the determination of their residues [22].

Sample preservation of carbamates is very important. Carbamates are very unstable under

both neutral and alkaline conditions at room temperature and they are also thermolabile. N-Methylcarbamates are thermally decomposed into the corresponding phenols and methyl isocyanate [64]. Müller and Stan [64] studied the conditions of the GC sampling technique for four carbamates (aminocarb, bendiocarb, carbaryl and dioxacarb) and reported that the thermolabile pesticides are best analysed using on-column injection. Carbamates were extracted from water samples using dichloromethane [22,40], GCB [34,35] or a C_{18} cartridge [40]. Alzaga et al. [65] isolated carbaryl from freeze-dried water by SFE. The hydrolytical instability of N-methylcarbamates (degradation to substituted anilines) has been utilized in the post-column derivatization method with HFBA prior to GC–ECD or LC–ECD [44].

HPLC methods for N-methylcarbamates are now preferred over GC methods. For HPLC, no derivatization is required and the water samples can be analysed either directly or after trace enrichment. Marvin and co-workers [66,67] reported on-line preconcentration on a C_{18} precolumn with LODs between 0.01 and 0.07 $\mu g\ l^{-1}$. The HPLC method for the determination of carbamates is based on postcolumn hydrolysis, reaction with OPA/MERC and fluorescence detection. De Kok et al. [68] described a multiresidue method for twelve N-methylcarbamates and their important transformation products sulfoxides and sulfones. The combination of SPE with HPLC separation and fluorescence detection after solid-phase-catalysed hydrolysis and derivatization of methylamine with OPA reagent allowed carbamates to be determined at levels below 0.1 $\mu g\ l^{-1}$.

2.6. Other classes of herbicides

Bentazone and chloridazone are the most significant representatives of diazinone herbicides. Sometimes also bromacil, lenacil and terbacil are inserted into this group (normally these are listed in the group of uracils).

Diazinone herbicide residues were isolated from water by LLE with dichloromethane [9]. In the case of bentazone the sample was acidified to pH 2. GCB cartridges were used for the isolation of diazinones from the water sample without pH adjustment [34]. Bentazone was extracted using C_{18} and SDB membrane extraction discs [62] and on a PLRP-S polymeric precolumn at pH 3 [61]. The most frequently used method for the determination of diazinones is LC–UV [34] and LC–DAD [9]. Bentazone [62] was determined by LC–FD and/or LC–TSP-MS.

Paraquat and diquat are very polar bipyridyl cations. Both paraquat and diquat are toxic to man, the former being implicated in many deaths. The extraction of paraquat and diquat is complicated by their high water solubilities. Their isolation on a 100-mg silica column prior to LC–DAD [69] with an LOD of 0.1 $\mu g\ l^{-1}$ was reported. LC–DAD and postcolumn reaction with sodium hydrosulfide were employed to confirm diquat and paraquat in water samples. The use of electrodialytic sample treatment coupled on-line with LC–UV for environmental water was described by Debets et al. [70]. The detection limit for paraquat was 0.5 $\mu g\ l^{-1}$

Sulfonylurea herbicides are soil acting and normally applied at levels from 10 to 20 g ha^{-1}. They can be phytotoxic to susceptible species at levels as low as 0.1 g ha^{-1} [22]. The sulfonylurea herbicides chlorsulfuron and metsulfuron-methyl were isolated with LSE on a C_{18} column [71] and on a membrane extraction disc [72] or by LLE with dichloromethane [73,74]. The water sample was acidified with acetic acid before LLE and the extract was cleaned using a Florisil column. The method of cGC–ECD/NPD after derivatization with PFBB [71] has been reported. Residues were confirmed by GC–MS using selected-ion monitoring (SIM).

Pesticides of the nitroaniline group are herbicides extensively used in ornamental nurseries for control of weeds both in and around containers. These herbicides could by phytotoxic when runoff water is used in irrigation and have an adverse environmental impact. Riley and co-workers [12,75,76] used SPE on C_{18} silica and LC–UV for the determination of pendimethalin in pond water from container plant nurseries. Davi et al. [46] isolated nitroanilines from water using LLE. Two extractions (2×100 ml) with

dichloromethane were performed on a 1-l sample of water. The first extraction was performed on water as such and the second on water previously adjusted to basic pH with NaOH. The purity of the extracts obtained by using C_8 membrane extraction discs was better than that obtained by LLE. Vitali et al. [77] preconcentrated nitroanilines on a C_{18} cartridge prior to LC–UV. Dinitroaniline recoveries were between 66 and 78%. cGC–NPD [28] and cGC–ECD [47] methods were used for the determination of nitroanilines in water samples. A GCB cartridge was employed for the isolation of bromoxynil [34] and ioxynil [78] prior to LC–UV from water with high recoveries.

Anilides were extracted using dichloromethane [9], a C_{18} cartridge [40] or a GCB cartridge [34]. The recoveries with these methods were generally higher than 90%. LC–UV/DAD [9,34,40] and cGC–NPD/ITD [9,28] or cGC–ECD [47] are mainly used.

3. Pesticide transformation products

Analytical methods for the determination of pesticide residues concentrate on the toxicologically important transformation products of pesticides (metabolites, degradation products).

Atrazine is the most significant representative of triazine herbicides. Its important metabolites are often determined together with its residues. Hydroxy derivatives are the possible metabolites of chlorotriazines. Dealkylation of triazines leads to dealkyltriazines (deethylatrazine and deisopropylatrazine from atrazine). The basic information about some transformation products of pesticides and methods of their determination is given in Table 6. Chromatographic methods are suitable for the determination of pesticide residues in the presence of their transformation products. Methods for the determination of atrazine residues in the presence of hydroxyatrazine [79–81] or dealkylatrazines [6,28,29, 35,80–82] have been reported.

Some herbicide metabolites, such as deethylatrazine, are also phytotoxic and persist over the corn harvest [83]. Therefore, the determination of these compounds in water and soil is of interest to obtain information about environmental contamination and possible phytotoxicity problems in crop rotation.

SPE on C_{18} cartridges [35] and classical LLE with dichloromethane [29,79,82] or dichloromethane–ethyl acetate (50:50, v/v) containing 0.2 *M* ammonium acetate [80] were used for the extraction of metabolites. Confirmation of the identity of dealkyltriazines was achieved by derivatization with TFAA [82].

Substituted anilines are widespread environmental pollutants, owing to their relatively high water solubilities. They can be present in the aquatic environment as a result of industrial discharges from industrial processes using substituted anilines as reagents for synthesis (pharmaceutical, dye and pesticide industries). They also occur as the degradation products (microbial degradation) of some herbicides (phenylureas, carbonates, anilides). For example aniline originates from the degradation of fenuron, desmedipham, propham, 4-chloroaniline from the degradation of monuron, buturon and monolinuron, 3,4-dichloroaniline from the degradation of diuron, neburon, linuron and propanil and 4-bromoaniline (metobromuron), 4-methyl-3-chloroaniline (chlortoluron, solan), 3-methylaniline (phenmedipham), 3-chloro-aniline (chlorpropham) and other substituted anilines are formed by the degradation of phenylureas, carbamates and anilides. Methods for the determination of substituted anilines have been partly discussed with phenylurea herbicides. A summary of methods with references is given in Table 6.

Chlorophenols represent a major class of contaminants that are released into the environment through many industrial processes and also as a result of the degradation of phenoxyalkanoic acids. Their presence in water is monitored. Even small amounts of chlorophenols have adverse effects on the taste and odour of drinking water. Chlorophenols are strongly toxic. Owing to the polar nature and low volatility of chlorophenols, their conversion into less polar derivatives prior to GC is usually employed. Esterification of chlorophenols with acetic anhydride,

Table 6
List of some important pesticide transformation products and their chromatographic methods

Transformation product	Parent pesticide	Method	Ref.
Hydroxyatrazine	Atrazine	LC–UV, GC–MS	[31,79,80,96]
Deethylatrazine	Atrazine	LC–DAD	[31,35,40,42,53,80,96]
		GC–NPD(AFID)	[6,28,29,82]
		LC–MS	[37]
Deisopropylatrazine	Atrazine, cyanazine, simazine	LC–DAD	[31,35,40,53,80,81,96]
		GC–NPD(AFID)	[6,29,82]
		LC–MS	[37]
Deethyldeisopropylatrazine	Atrazine, cyanazine, simazine	GC–NPD(AFID)	[29]
Hydroxydeethylatrazine	Atrazine	LC–UV, GC–MS	[79]
Hydroxysimazine	Simazine	LC–UV, GC–MS	[79]
Hydroxypropazine	Propazine	LC–UV, GC–MS	[79]
Hydroxyterbuthylazine	Terbuthylazine	LC–UV, GC–MS	[79]
Aniline	Desmedipham, fenuron, propham	LC–UV	[98,101,112]
		LC–ECD	[44,99]
		GC–NPD	[115]
4-Bromoaniline	Metobromuron	LC–ECD	[43,44]
		GC–NPD	[115]
		LC–UV	[101,112]
4-Bromo-3-chloroaniline	Chlorbromuron	LC–ECD	[44]
		LC–UV	[101]
4-Chloroaniline	Buturon, diflubenzuron, monuron, monolinuron	LC–UV	[43,98,101,114]
		LC–ECD	[44]
		GC–NPD	[115]
		LC–FD	[97]
3-Chloroaniline	Chlorpropham	LC–UV	[114]
		LC–ECD	[44,99]
		GC–NPD	[115]
		LC–FD	[97]
3-Chloro-4-methylaniline	Chlortoluron	LC–ECD	[44]
		GC–NPD	[115]
		LC–UV	[101]
3-Chloro-4-methoxyaniline	Metoxuron	LC–ECD	[44]
		GC–NPD	[115]
		LC–UV	[101,118]
3,4-Dichloroaniline	Diuron, linuron, neburon, propanil	LC–ECD	[43,44]
		LC–UV	[101,112,114,117]
		GC–NPD	[115]
		LC–FD	[97]
3-Methylaniline	Phenmedipham	LC–ECD	[44]
		GC–NPD	[115]
		LC–FD	[97]
4-Isopropylaniline	Isoproturon	LC–ECD	[44]
		GC–NPD	[115]
		LC–UV	[101]
2-Methyl-4-chlorophenol	MCPA	GC–ECD	[84]
2,4-Dichlorophenol	2,4-D	LC–UV, GC–ECD	[84,87,123,124]
2,4,5-Trichlorophenol	2,4,5-T	GC–ECD	[84,123,124]
ETU	EBDC	GC–AFID	[89]
		LC–UV	[120]

treatment with alkylating reagents such as diazomethane or methyl iodide and with PFBB or HFBA improves peak shape and detectability. Chlorphenols were extracted from acidified water samples with a slightly polar organic phase, *n*-hexane–diethyl ether (1:1, v/v) [84]. Alternatively, various sorbents have been examined for the SPE of phenols from water: resin [85], silica-bonded reversed phase [86] and GCB [34,78,87]. Turnes et al. [88] studied the capability of very selective GC–AED to determine chlorophenols in drinking waters after preconcentration on GCB. The LOD was below 0.5 $\mu g\ l^{-1}$. The GC conditions as used for the determination of chlorophenols are very often suitable for the determination of phenoxy acid herbicides.

Ethylenethiourea (ETU) is the transformation product of fungicides from the group of ethylenebisdithiocarbamates (EBDC) such as maneb, zineb and mancozeb. Although EBDC toxicities are relatively low, ETU has shown mutagenic, teratogenic, carcinogenic and goitrogenic characteristics [18]. ETU is a relatively stable and very polar metabolite and in the areas where EBDC fungicides are used, its possible occurrence in ground and river water is a major concern for the safety of drinking water. Direct extraction of ETU with dichloromethane or ethyl acetate is not feasible. A GC method [89] with AFID and MS confirmation of ETU in water was reported. The method is based on the extraction of ETU with dichloromethane in the presence of thiourea and sodium L-ascorbate. The LOD was less than 0.1 $\mu g\ l^{-1}$ and the average recovery was around 71%.

4. Conclusion

The choice of the method for the isolation of various types of pesticides and transformation products from water samples depends on the analyte characteristics (polarity, ionic character, stability). Liquid–liquid extraction with traditional solvents (dichloromethane, diethyl ether, ethyl acetate, etc.) is still used for the isolation of some pesticide classes. Liquid–liquid extraction tends to consume large volumes of high-purity solvents which may have significant health hazards and disposal costs associated with their use. It is frequently plagued by problems, such as emulsion formation. For more polar pesticides (e.g., phenoxy acids) and especially their metabolites, LLE is not the best choice. SPE (off-line, on-line or solid-phase microextraction) on the various types of silica-bonded, polymeric or carbon-type phases is now generally preferred over LLE. Computer-assisted optimization of an SPE method for the isolation and preconcentration of various pesticides was investigated by Wells [90]. Five parameters (pH, elution solvent strength, ionic strength of the sample, content of the organic modifier in the sample and type of elution—gravity, vacuum) were optimized in order to maximize the extraction efficiency. A progressive technique in SPE uses polymer membranes containing the enmeshed sorbent particles in a web of polymer microfibrils, so-called membrane extraction discs (MED). A high flow-rate of the sample through the membrane allows the concentration of pesticides from a relatively large volume (1–2 l) in a short time (10 min) [36,37,51,91]. Barceló et al. [92] discussed various aspects of SPE using C_{18} and styrene–divinylbenzene Empore extraction discs. The influence of the water type and of matrix interferences in the determination of various pesticides (including acidic herbicides) at the low $\mu g\ l^{-1}$ level were investigated.

The most popular C_{18} and C_8 bonded silicas were used for the isolation and preconcentration of a wide range of pesticides and their transformation products from water samples (triazines [32], organophosphorus insecticides [33], phenylureas [10,45], sulfonylureas [71], phenoxy acid herbicides [58], anilines [43], dinitroanilines [77] and hydroxytriazines [79]). These apolar phases are suitable for the isolation of non-polar compounds. Extraction of polar compounds is often very difficult and coupled with their low breakthrough volumes. The use of C_{18} silica for the simultaneous analysis of a mixture of pesticides with a wide range of polarities appears to be impracticable. For complex mixtures, GCB

Table 7
Evaluation of GCB as a selective adsorbent for the extraction of pesticide residues and transformation products from water

Pesticide group	Contamination level ($\mu g\ l^{-1}$)	Recovery (%)	Elution system	Ref.
35 pesticides: carbamates (6), pyridazine (1), phenylureas (5), uracils (1) triazines (3), organophosphates (6), anilides (2), bentazone, phenoxy acids (6), phenols (4)	0.25–1.50	92–101	CH_2Cl_2–MeOH (80:20, v/v)	[34]
14 acidic organic compounds: nitrophenols (4), chlorophenols (2), dicamba, bentazone, phenoxy acids (4), ioxynil, warfarin	0.25–2.00	95–101	CH_2Cl_2–MeOH (90:10, v/v) basified with TMAOH (20 mmol l^{-1})	[78]
26 polar pesticides: carbamates (7), uracils (1), phenylureas (2), triazinones (2), dealkylated trazines (2), pyridazines (1), other compounds (11)	0.3–1.2	72–102	CH_2Cl_2–MeOH (80:20, v/v)	[78]
Phenylureas (14), chloroanilines (2)	0.03–3.0	>92	CH_2Cl_2–MeOH (95:5, v/v)	[103]
Phenol pollutants: phenol, nitrophenols (5), chlorophenols (5)	0.2–0.4	95–102	CH_2Cl_2–MeOH (80:20, v/v) acidified with TFA (10 mmol l^{-1})	[87]
11 phenol pollutants (according to EPA)	0.07–0.48	70–100	0.25 mol l^{-1} formic acid in CH_2Cl_2–MeOH (90:10, v/v)	[88]
Phenoxy acid herbicides (8), dicamba	0.10–0.50	95–100	CH_2Cl_2–MeOH (90:10, v/v) basified with NaOH (1 mmol l^{-1})	[60]
Chloroanilines (14)	0.20–2.00	88–102	AcCn acidified with HCl (10 mmol l^{-1})	[114]
Triazine herbicides (8)	0.015–2.00	95–100	CH_2Cl_2–AcCN (60:40, v/v)	[113]

seems to be more suitable (see Table 7). In comparison with C_{18} silica, GCB has a far better extraction efficiency for highly soluble phenols [34,87], anilines and other polar compounds [93]. Because of the porous character of GCB, the extraction in comparison with a C_{18} cartridge is about seven times faster and no pH adjustment of environmental water samples is necessary for acidic compounds [34,60]. For a 250-mg GCB (Carbopack B) cartridge, a flow-rate of 150–160 ml min^{-1} can be used. Guenu and Hennion [94] investigated the potential of a porous graphitized sorbent for extracting very polar degradation products of some widely used triazine herbicides, e.g., cyanuric acid. This analyte was very slightly retained by C_{18} silica and not at all by the polymeric sorbent PRP-1, but it was highly retained by porous graphitized carbon. De Kok and co-workers [68,95] compared C_8, C_{18} and low-carbon C_{18}/OH silica sorbents for the SPE of polar N-methylcarbamates and their degradation products. C_{18}/OH had a special selectivity for the polar carbamates. It concentrated the polar compounds better than did C_8 with a shorter alkyl chain.

The styrene–divinylbenzene copolymer sorbent PLRP-S seems to be universal for the isolation of a wide range of pesticides

[11,31,39,94–96]. PLRP-S appears to be very suitable for moderately polar compounds.

Ion exchangers can be used in two ways in pesticide residue analysis. They can be directly applied for the isolation of some ionizable pesticides (phenoxy acids [53], trizines and triazinones [38], substituted anilines [97–99]). The main problem is connected with ions naturally occurring in environmental waters. They can decrease the capacity of the ion-exchange column and often must be removed, e.g., with a chelating agent [99]. Because the extraction efficiency depends on the pH of the sample and the compounds within a certain group often have similar acidic–basic properties, ion exchangers allow selective extraction [100]. Ion exchangers can also be employed for the selective filtering of interfering compounds, e.g. substituted anilines in the presence of their parent phenylureas [101,102].

The majority of the literature published on the supercritical fluid extraction (SFE) of pesticides is concerned with SFE of solid matrices with little or no water content. Only a few workers [91,103,104] have reported the direct extraction of pesticides from aqueous samples. The main problem is the relatively high solubility of water in supercritical carbon dioxide. Alzaga et al. [65] compared SFE and LLE of selected pesticides (simazine, carbaryl, atrazine, fenithrothion, fenamiphos) in a freeze-dried water sample. With SFE higher recoveries and better selectivity were obtained. A more effective utilization of SFE is the combination of SFE and SPE. Pesticides trapped on, e.g., a membrane extraction disc can be eluted by a supercritical fluid. This type of isolation method combines the advantages of both SPE and SFE [51,91,105].

GC and LC are currently the major techniques for the trace determination of pesticide residues. GC with capillary columns coated with non-polar or semi-polar stationary phases (SE-30, SE-54, OV-1, DB-1, DB-5, DB-17 [49]) dominates. Most LC work on pesticide residues has been done on C_{18} or C_8 reversed phases. Amino- and cyano-bonded stationary phases are less common. Both isocratic and gradient elution are employed. Different GC detection methods used for pesticide residue analysis have been reviewed by Westmoreland and Rhodes [106]. NPD and ECD are most frequently used. NPD predominates in the determination of triazine residues and is often used for phenylureas and uracils. ECD is the choice for the determination of phenoxy acid herbicides and chlorophenols. Both can be used either for direct detection (not requiring derivatization) or after conversion of the analytes into suitable derivatives. Derivatization is essential for thermolabile pesticides (phenylureas, sulfonylureas, N-methylcarbamates) or very polar pesticides (phenoxy acids). GC–MS is routinely used in the confirmation of pesticide residues [111].

HPLC is a non-destructive method especially suited to non-volatile, thermally labile and polar pesticides. DAD in combination with SPE can be employed for both the determination and confirmation of pesticide residues at $\mu g\ l^{-1}$ concentration levels. Two groups [31,96] reported a powerful combination of DAD and a chemometric method (multi-component analysis) that allowed the quantification of co-eluting peaks with determination limits as low as 0.01 $\mu g\ l^{-1}$. In some cases UV detection is not the best choice. Hatrík et al. [43] reported a ca. 100 times higher sensitivity of ED for substituted anilines. Fluorescence detection is highly sensitive but pre- or postcolumn derivatization of pesticides is often necessary. McGarvey [107] reviewed the literature dealing with HPLC methods for pesticides employing derivatization reactions. According to that review, OPA–MERC is the single most widely used derivatization reagent for pesticide determination by HPLC. It is used in postcolumn reaction systems for fluorescence detection of phenylurea herbicides, EBDC or N-methylcarbamates. Nowadays LC–MS is also widely used [37,39,93,105,108]. Volmer et al. [108] described an LC–TSP-MS method for the determination of 128 polar pesticides in water samples. In combination with SPE this method reaches the EEC drinking water guidelines of $\mu g\ l^{-1}$ for most pesticides. Chiron et al. [37] observed higher sensitivity and selectivity of TSP-MS in comparison with DAD for 34 pesticides and their transformation products.

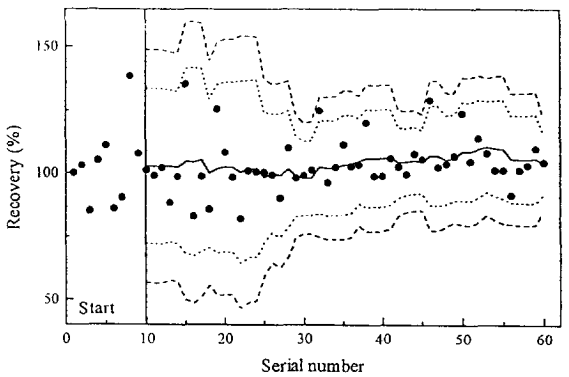

Fig. 1. Dynamic quality control chart [110] for the recovery of 0.1 $\mu g\ l^{-1}$ of atrazine in drinking water. Start = starting period of tex experiments. Reproduced with permission of *Fresenius' J. Anal. Chem.*

The results of routine pesticide analyses vary widely. A fortification experiment carried out with every series of samples represents the performance of the analytical system at the moment of analysis. The principles of analytical quality assurance were reviewed by Mesley et al. [109]. Sometimes the information about intra-laboratory variations, which are a very important part of analytical quality, may be very useful. Vogelgesang [110] applied the quality control chart principle to the determination of very low concentrations of pesticide residues in drinking water. Dynamic quality control charts provided a valuable and reliable view of routine analytical performance. The starting period included the results of ten experiments (recoveries) and displayed analytical performance in terms of the mean and of the ±3 standard deviations confidence band. The period of ten results is moved with every new result. The example of dynamic QCC is shown in Fig. 1. Narrowing confidence band or a mean joining the 100% recovery level reported an improvement in laboratory performance.

List of abbreviations

AcCn	Acetonitrile
ADAM	9-Anthryldiazomethane
AFID	Alkali flame ionization detection
CEDMSDEA	2-Cyanoethyldimethyl(diethyl)-aminosilane
DAD	Diode-array detection
2,4-D	(2,4-Dichlorophenoxy)acetic acid
2,4-DB	4-(2,4-Dichlorophenoxy)butyric acid
2,4-DP	2-(2,4-Dichlorophenoxy)-propionic acid
EBCD	Ethylenebisdithiocarbamate
ECD	Electron-capture detection
ED	Electrochemical detection
EEC	European Economic Community
EPA	Environmental Protection Agency (US)
EPTC	S-Ethyl-N,N-dipropyl-thiocarbamate
EtAc	Ethyl acetate
ETU	2-Imidazolinethiourea (ethylenethiourea)
FD	Fluorescence detection
FPD	Flame photometric detection
cGC–NPD	Capillary gas chromatography with nitrogen–phosphorus detection
cGC–ECD	Capillary gas chromatography with electron-capture detection
GC	Gas chromatography
GCB	Graphitized carbon black
GUS	Groundwater ubiquity score
HFBA	Heptafluorobutyric acid anhydride
ITD	Ion-trap detection
LC	Liquid chromatography
LLE	Liquid–liquid extraction
LOD	Limit of detection
LOQ	Limit of quantification
LSE	Liquid–solid extraction
MED	Membrane extraction disc
MeOH	Methanol
MERC	2-Mercaptoethanol
MPCA	(4-Chloro-2-methyl)-phenoxyacetic acid
MPCB	4-(4-Chloro-2-methyl-phenoxy)butyric acid

MPCP	2-(4-Chloro-2-methylphenoxy)propionic acid
NPD	Nitrogen–phosphorus detection
OPA	*o*-Phthalaldehyde
PFBB	Pentafluorobenzyl bromide
QCC	Quality control chart
SDB	Styrene–divinylbenzene
SFE	Supercritical fluid extraction
SPE	Solid-phase extraction
2,4,5-T	2,4,5-Trichlorophenoxy acid
2,4,5-TB	2,4,5-Trichlorophenoxybutyric acid
2,4,5-TP	2-(2,4,5-Trichlorophenoxy)-propionic acid
TFA	Trifluoroacetic acid
TFAA	Trifluoroacetic anhydride
TFE	2,2,2-Trifluoroethanol
TLC	Thin-layer chromatography
TMAH	Trimethylanilinium hydroxide
TMAOH	Tetramethylammonium hydroxide
TMSH	Trimethylsulfonium hydroxide
TSP-MS	Thermospray mass spectrometry
WHO	World Health Organization

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