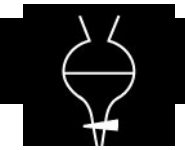
PESTICIDES



Extraction from Water

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Introduction

Pesticides and their metabolites have received particular attention in the last few years in environmental trace organic analysis because they are regularly detected in surface and ground waters especially throughout Europe and North America as a consequence of their widespread use for agricultural and nonagricultural purposes. Several priority lists have been published to protect the quality of drinking and surface waters.

Pesticides, as organic compounds, are usually determined by chromatographic and related techniques. However, they are present in the environment at trace levels and despite advances in separation and quantification, no sample can be directly analysed and an extraction and concentration step is required, whatever the matrix. The detection levels required for monitoring pesticides in drinking water at a regulatory level depend on the particular country. In the USA, a priority list has been established on the basis of the toxicity of the analytes which contains about 25 pesticides and metabolites with a health advisory level in the range 1–700 $\mu g\,L^{-1}$. Europe has more drastic regulations since the concentration of each pesticide should be lower than 0.1 $\mu g\,L^{-1}$, and quantification at this level requires detection limits of 0.01 $\mu g\,L^{-1}$ for the analytical procedure. For the monitoring of ground and surface water, several parameters have been taken into account such as quantities used, water solubility, hydrolysis half-life and soil adsorption coefficient. In surface water, in the USA, the recent National Pesticide Survey (NPS) list includes almost 150 pesticides with many degradation products; in Europe, a priority list was published in 1992 which contained 55 compounds.

Therefore, in order to reduce the price and time of environmental monitoring, it is relevant to perform multiresidue analysis which includes modern polar pesticides and their degradation products. Sample preparation remains the weakest link and the time-determining step in the whole procedure for trace analysis of pesticides. Before implementing any strategy it is important to consider the strong interdependence of the various steps of the whole procedure, i.e. sample handling, separation and detection. There is no unique strategy for the sample handling step, because it depends on the nature of the pesticides to be determined (e.g. volatility and polarity), on the nature of the matrix and on the degree of preconcentration necessary. Interference removal is a critical step which is strongly related to the concentration of the analyte of interest and of the matrix. It is evident that the strategy for determining pesticide below the micrograms per litre level in drinking water may be different from that used in a very polluted river.

The methods for extraction and concentration of pesticides are mainly liquid–liquid extraction and solid-phase extraction. One key problem in pesticide analysis comes from the diversity of their chemical functional groups with varying polarity and physicochemical properties.

Liquid–Liquid Extraction

Liquid–liquid extraction (LLE) is the simplest extraction method and is described in US EPA (Environmental Protection Agency) official methods. The large choice of solvents which provide a wide range of solubility and selective properties, is often given as an advantage of the method. But, in fact, each solvent is not really specific for a class of compounds. Hexane and cyclohexane are typical solvents for extracting nonpolar compounds, such as organochlorine and some organophosphorus pesticides, whereas dichloromethane and chloroform are the common solvents used for the extraction of medium-polarity pesticides. EPA method 507 allows the determination of 46-nitrogen- and phosphorus-containing pesticides in water, with an extraction of a 1 L sample of water with 200 mL of dichloromethane, followed by an evaporation step, a reconcentration in 5 mL of methyl t-butyl ether (MTBE) and an analysis step using GC with a nitrogen–phosphorus detector (NPD). Detection limits are estimated in the range 0.1–4.5 $\mu g\,L^{-1}$, depending on the analyte. EPA method 508 uses a similar extraction step for chlorinated pesticides in ground water using GC electron capture detector (ECD) with detection limits in the range 0.02–1.3 $\mu g\,L^{-1}$. The detection limits of these two methods are in agreement with Health Advisory

Levels in the USA. Many European laboratories use LLE methods which are derived from the EPA methods; the enrichment factor can be easily increased by greatly reducing the final volume which allows detection limits closer to the EU regulatory level of 0.1 $\mu g\,L^{-1}$ for each pesticide.

However, due to the trend shown by the EPA for reducing the consumption of organic solvents, new methods involve micro-LLE extraction. As an example, EPA method 504 for the determination of organochlorine pesticides in water requires only 2 mL of dichloromethane or hexane for a 35 mL aqueous sample volume with detection limits in the range 0.08–7 $\mu g\,L^{-1}$. Micro-LLE of this sort cannot be adapted to meet the EU detection limits.

LLE allows a fractionation into acidic pesticides and basic/neutral fraction with successive extractions at different pH values. However, extraction of relatively polar and water-soluble organic compounds is difficult. The recovery obtained from 1 L of water using dichloromethane is 90% for atrazine but only 16% and 46% for deisopropyl- and deethylatrazine. When using a mixture of dichloromethane and ethyl acetate with 2 M ammonium formate these metabolites of atrazine are extracted with recoveries of 62% and 87% respectively.

The main advantages of LLE are its simplicity and requirements for simple equipment, but the glassware must be carefully washed and stored under rigorous conditions. LLE is not free from practical problems (such as formation of emulsion) which are difficult to break. The disposal, use and evaporation of large volumes of solvent, often toxic and flammable, are the main drawbacks. These organic solvents should be of pesticide grade which makes them rather expensive. Automation requires the use of robots and LLE is typically an offline procedure, with risks of loss and contamination during transfer and evaporation steps. Therefore, the trends in reducing the use of organic solvents in analytical laboratories and the low performances in extracting polar compounds explain the increasing replacement of LLE by solid-phase extraction.

Solid-Phase Extraction

Recent Developments of SPE Formats

Offline SPE materials are mainly disposable cartridges and disc membranes. The recent developments tend to increase the sample throughput and to use solid-phase sorbents able to broaden the polarity range of analytes.

Limitations of packed SPE conventional cartridges and discs include restricted flow rates and plugging of the top frit when handling water containing suspended solids, such as surface water. Therefore, the percolation of natural samples can take a long time for a typical 500 mL volume unless the sample has been carefully filtered beforehand. Various approaches have been developed to solve this problem. One consists in depth filters which can be placed above the cartridge or membrane extraction disc, or which are now integrated in some SPE cartridges providing fast flow rates. Empore discs have recently become available with sorbent trapped in a PTFE matrix. These discs are also included in cartridges, known as disc cartridges. New discs, which consist of a thin bed of microparticles supported in a laminar structure, allow the percolation of 1 L of surface water without any previous filtration in less than 5 min.

With regard to sorbent technology, many are now specified as specially made for broadening the polarity range of analytes. These include not-end-capped C_{18} silicas and monofunctional C_{18} silicas, the aim being to increase the number of unmodified silanol groups on the bonded silica surface in order to provide secondary polar interactions with basic polar solutes. Cross-linked styrene-divinylbenzene (SDVB) copolymers with high specific areas in the range 500–1200 $m^2\,g^{-1}$ are now available from all manufacturers in cartridges and/or discs. Typical amounts of sorbent are 100–200 mg and the cartridge designs have been optimized for rapidly processing large volumes of water. Carbonaceous sorbents have also been shown to extract very polar analytes.

Automation

A typical SPE sequence includes four steps: (i) conditioning of the sorbent; (ii) application of the sample; (iii) rinsing and clean up of the sample; and (iv) desorption of the analytes to be separated. These steps can be performed sequentially for up to 24 cartridges at the same time using extraction units working under positive or negative pressure. The whole sequence can also be easily automated using devices which can accept any commercial cartridges or extraction discs. Examples are the ASPEC from Gilson, Microlab from Hamilton, AutoTrace and RapidTrace from Zymark. The possibility exists with some of these devices for automatic injection of an aliquot of the final extract into the chromatographic system. Complete automation also exists which couples SPE directly with online LC analysis (ASPEC XL from Gilson; Prospekt from Spark Holland; OSP-2 from Merck). These last two pieces of equipment improve productivity since the next sample is automatically prepared while the previous sample is being analysed.

Selection of the Sorbent for Multiresidue Extraction

LC has been shown to be suitable for multiresidue separation of many compounds over a wide range of polarity without previous derivatization and examples can be found in the literature, the most impressive one being the multiresidue separation of 72 pesticides in one run published by Di Corcia and Marchetti. Identification of compounds is widely performed with UV diode array detectors which can provide the whole spectrum of the analytes. Fluorescence is also used because of its sensitivity for the detection of n-methyl carbamates, following a post-column derivatization reaction. LC with mass spectrometry is also increasingly used in environmental laboratories.

The extraction of analytes from water requires the selection of an extraction sorbent which will provide a 90–100% recovery with the sample volume required for the necessary quantification. According to the detection limits obtained with conventional LC-UV diode array detectors or MS interfaces, typical sample volumes using offline extraction procedures are in the range 300–500 mL in order to provide detection limits in drinking water as low as 0.01–0.03 $\mu g\,L^{-1}$ and 0.1 $\mu g\,L^{-1}$ in surface waters for transport and fate studies.

The same sorbents as those used in reversed-phase LC are utilized and there is an analogy between the SPE processes and classical elution chromatography. Processes involved in SPE are a frontal chromatographic process during the extraction step and displacement chromatography during the desorption step. It is then possible to predict and optimize the main SPE parameters from data generated by LC. Among the various tools for selecting the sorbent and predicting the recovery according to the percolated sample volume, the most important is the retention factor of the analyte in water, k_w. Therefore, developing a SPE method only requires knowledge of the retention behaviour of the analytes with the extraction sorbent in LC with water as mobile phase, as measured by k_w. Both breakthrough curves and recovery curves have been modelled according to the sample volume. With an amount of sorbent of 500 mg, a recovery in the range 90–100% will require a sorbent providing $\log k_w > 3$ for the analytes. Whatever the SPE format, disc or cartridge, the process is the same and the criteria for the selection of the sorbets are similar. It is just necessary to know the amount of sorbent.

A good stability has been observed for analytes on SPE sorbents which allows the percolation of samples on site and further analysis in the laboratory.

Multiresidue Extractions Using n-Octadecyl Silicas

Prediction from the water–octanol partition coefficient of the compound Octadecyl- and octyl-bonded silicas have been the universal extraction sorbents for many years. Since the retention mechanism is primarily governed by hydrophobic interactions between the analyte and the carbonaceous moieties of the alkyl chains grafted to the silica surface, a relation has been observed between the retention factors of the analytes and their water–octanol partition coefficient (K_{ow}). Therefore, k_w values can be approximated without any additional measurements from K_{ow} values which were reported in a recent edition of the *Pesticide Manual*.

Limitation for the extraction of polar pesticides in a multiresidue mixture For LC purposes, trifunctional silanes are preferred over monochlorosilanes for the bonding synthesis because a layer or multiple carbon–siloxane covalent bonds on the silica surface is formed. The objective in SPE is to increase to a maximum hydrophobic interactions and the surface coverage so that rather highly porous silica is usually selected, with an average surface area above $500\,m^2\,g^{-1}$ and with average carbon content of 17–18% for n-alkyl silicas. These C_{18} silicas will provide the highest retention for the more polar analytes. Like LC phases, the SPE alkyl silicas were first end-capped but, in order to enhance secondary interactions, the number of residual silanol groups has been increased by eliminating end-capping procedures, or by using monofunctional silane and no end-capping. Hydrogen bonding interactions and, especially, ionic interactions with polar basic compounds after pH adjustment can be increased and that is the reason for the broader range of polarity which can be achieved by these silicas specially designed for polar analytes. However, even if an increase of recoveries for some polar basic analytes has been observed, the increase in $\log k_w$ values is small at 0.2–0.5 in log units.

The limitation in using C_{18} silicas is in the extraction of polar pesticides and/or metabolites, which are characterized by $\log K_{ow}$ below 2. To give an example, recoveries of deisopropylatrazine and phenol ($\log K_{ow}$ values of 1.2 and 1.5 respectively) are lower than 20% with a sample volume of 500 mL and using an extraction disc containing 450 mg of C_{18} silica. Increasing the amount of sorbent to 1 g in the cartridge, gives a recovery of deisopropylatrazine of 52% and 44% from a sample volume of 1 L using respectively C_{18} Polar Plus from J.T Baker and LiChrolut RP-18 from Merck.

Application to drinking water samples **Figure 1** illustrates the potential of C_{18} silica for determining many pesticides over a wide range of polarity in drinking water at $0.1\ \mu g\ L^{-1}$. The triazines and phenylureas have been selected because they include some polar analytes such as the degradation products

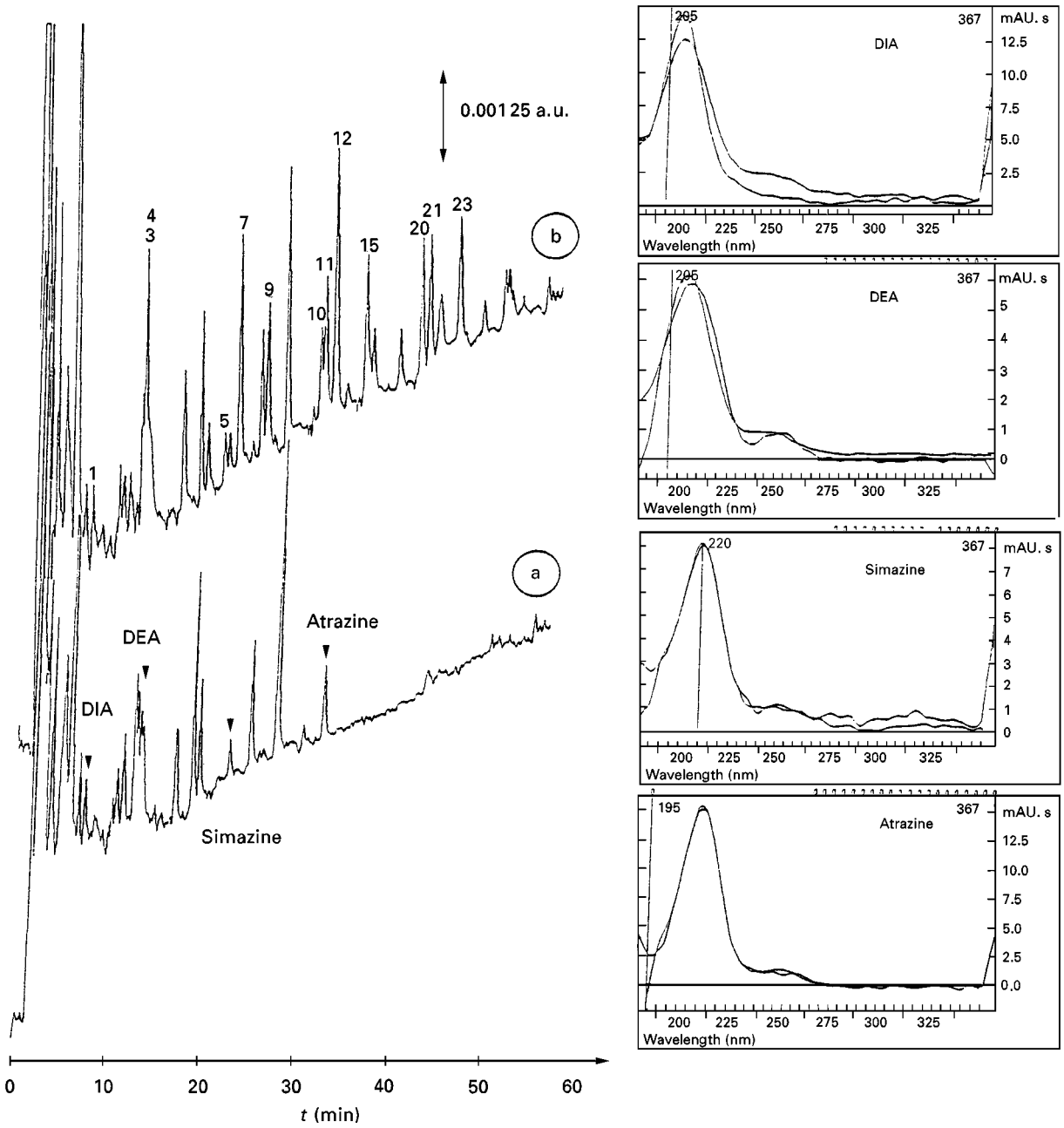

Figure 1 Chromatogram corresponding to the preconcentration of 500 mL of drinking water and spectra of the peaks identified using the UV DAD software: (a) non-spiked and (b) spiked with $0.1\ \mu g\ L^{-1}$ of each analyte.

Preconcentration using a 500 mg C_{18} silica cartridge, desorption with 4 mL of methanol, evaporation to dryness, and addition of 500 μL of an acetonitrile/water mixture (20/80, v/v). Injection of 50 μL. Analytical column: Supelcosil LC-18-DB 25 cm × 4.6 mm i.d.; acetonitrile gradient with 0.005 M phosphate buffer at pH 7; UV detection at 220 nm. Peaks: 1, DIA; 2, fenuron; 3, OHA; 4, DEA; 5, hexazinone; 6, metoxuron; 7, simazine; 8, monuron; 9, cyanazine; 10, metabenzthiazuron; 11, simetryne; 12, atrazine; 13, chlortoluron; 14, fluometuron; 15, prometon; 16, monolinuron; 17, isoproturon; 18, diuron; 19, difenoxuron; 20, sebutylazine; 21, propazine; 22, buturon; 23, terbutylazine; 24, linuron; 25, chlorbromuron; 26, chloroxuron; 27, difluzbenzuron; 28, neburon. (Reproduced from *International Journal of Environmental and Analytical Chemistry* 65, Pichon V, Cau Dit Coumes C, Chen L and Hennion M-C, Solid-phase extraction, clean-up and LC for routine multiresidue analysis of neutal and acidic pesticides in natural waters in one run, pp. 11–25, Copyright (1996), with permission from Gordon and Breach, Science Publishers.)

of atrazine, i.e. deisopropylatrazine (DIA), hydroxyatrazine (OHA) and deethylatrazine (DEA), and fenuron or metoxuron (with log k_w around 2.5 or lower), many moderately polar compounds and rather apolar pesticides such as neburon (log K_{ow}4.3). The separation was not optimized because the occurrence of each compound in the same sample is unlikely. Co-eluted analytes do not belong to the same group and can easily be differentiated by the UV diode array detector. The chromatogram in **Figure 1**b represents the chromatogram obtained for an extract from 500 mL of drinking water spiked with 0.1 μg L^{-1} of each pesticide. Recoveries were above 85–90% for each analyte, except the early eluted peaks 1 to 4 for which recoveries were 26, 51, 68 and 68%. Recoveries of peaks 7 and 12 were higher, due to the presence of these compounds in the sample, as shown in Figure 1a where a nonspiked sample was analysed under the same experimental conditions. The occurrence of simazine (peak 7) and atrazine (peak 12) was confirmed by comparison of retention times and of UV spectra from the library of the DAD at concentrations of 0.016 ± 0.003 μg L^{-1} and 0.12 ± 0.02 μg L^{-1} respectively. The match between the retention times and the two UV spectra was excellent so that no further confirmation was required. The peaks which showed up at 7.9 and at 13.3 min may be deisopropylatrazine and deethylatrazine, but the match was not good and another method is required for confirmation.

Multiresidue extraction including acidic pesticides: pH and matrix effects Acidic herbicides are very slightly retained by C_{18} silica in their ionic form so that they can be extracted using a C_{18} silica cartridge provided the sample has been previously acidified before percolation. **Table 1** shows the low extraction recoveries measured for some acidic herbicides when percolating 500 mL of spiked drinking water at pH 7 and the much better results when acidified at pH 2 or 3 with perchloric acid. When natural water samples are acidified at pH 2, there is an interfering peak due to humic and fulvic acids as shown when comparing the chromatograms of **Figure 2**a and b. The strong acidity of humic and fulvic acids (pK_a around 3) explains why interferences are only detected at acidic pH. This co-extraction of humic and fulvic acids requires an optimization of the mobile phase gradient in order to elute the first compounds after the interfering peak, so that most of the pesticides can still be determined at the 0.1 μg L^{-1} level in drinking water samples. In **Figure 2**b, only the very polar ones will show up in the interfering peak if the mobile phase gradient is adjusted in order that most of the peaks are eluted after 20 min. Surface water contains higher amounts of humic and fulvic acids and determination of pesticides at the 0.1 μg L^{-1} level becomes impossible, as shown in **Figure 2**c. An additional clean-up step using a Florisil cartridge was applied to the extract obtained after desorption from the C_{18} cartridge and detection limits could be improved as shown in **Figure 3**b. However setting up the analytical conditions for this step is not straightforward but laborious, time-consuming and generates additional losses in recovery.

Table 1 Recoveries (%) of acidic herbicides at different pH used for the preconcentration of samples (500 mL) of drinking water spiked with 0.5 μg L^{-1} of each analyte using a 500 mg C_{18} cartridge

Compound	*pK_a*	*pH2*	*pH3*	*pH7*
Dicamba	1.94	89	46	2
Bentazone	3.2	100	100	6
Ioxynil	3.96	98	83	31
MCPP	3.07	104	108	27
2,4-DB	4.8	98	92	38
2,4,5-TP		100	78	10
Dinoterb	5.0	72	49	30

Multiresidue Extractions Using Apolar Styrene-Divinylbenzene (SDVB) Copolymers

Potential for extraction of very polar analytes as compared with C_{18} silicas In recent years, ultraclean highly cross-linked styrene-divinylbenzene (SDVB) polymers with relatively high specific surface areas have been introduced by most manufacturers of disposable cartridges and have shown high capability for the extraction of polar analytes. This is demonstrated by 100% recoveries for phenol and deisopropylatrazine from a sample volume of 1 L and using 200 mg of SDVB sorbents. **Table 2** compares the retention factors in water, which have been measured or estimated for a C_{18} silica and SDVB with different specific surface areas. The higher retention of SDVB sorbents over C_{18} silicas is due to strong π–π interactions between analytes and the SDVB matrix in addition to common hydrophobic interactions. The effect of the surface area is very important and an increase in retention by a factor of 20 to 100 may be observed when the specific area of the SDVB sorbent increases from 400 to 1000 $m^2 g^{-1}$.

Therefore, highly cross-linked SDVBs are the sorbents of choice for multiresidue extraction of a mixture containing highly polar analytes.

Application to the determination of acidic, neutral and basic pesticides in the same run with removal of humic and fulvic acid interferences The retention of acidic pesticides was studied at neutral pH in order to

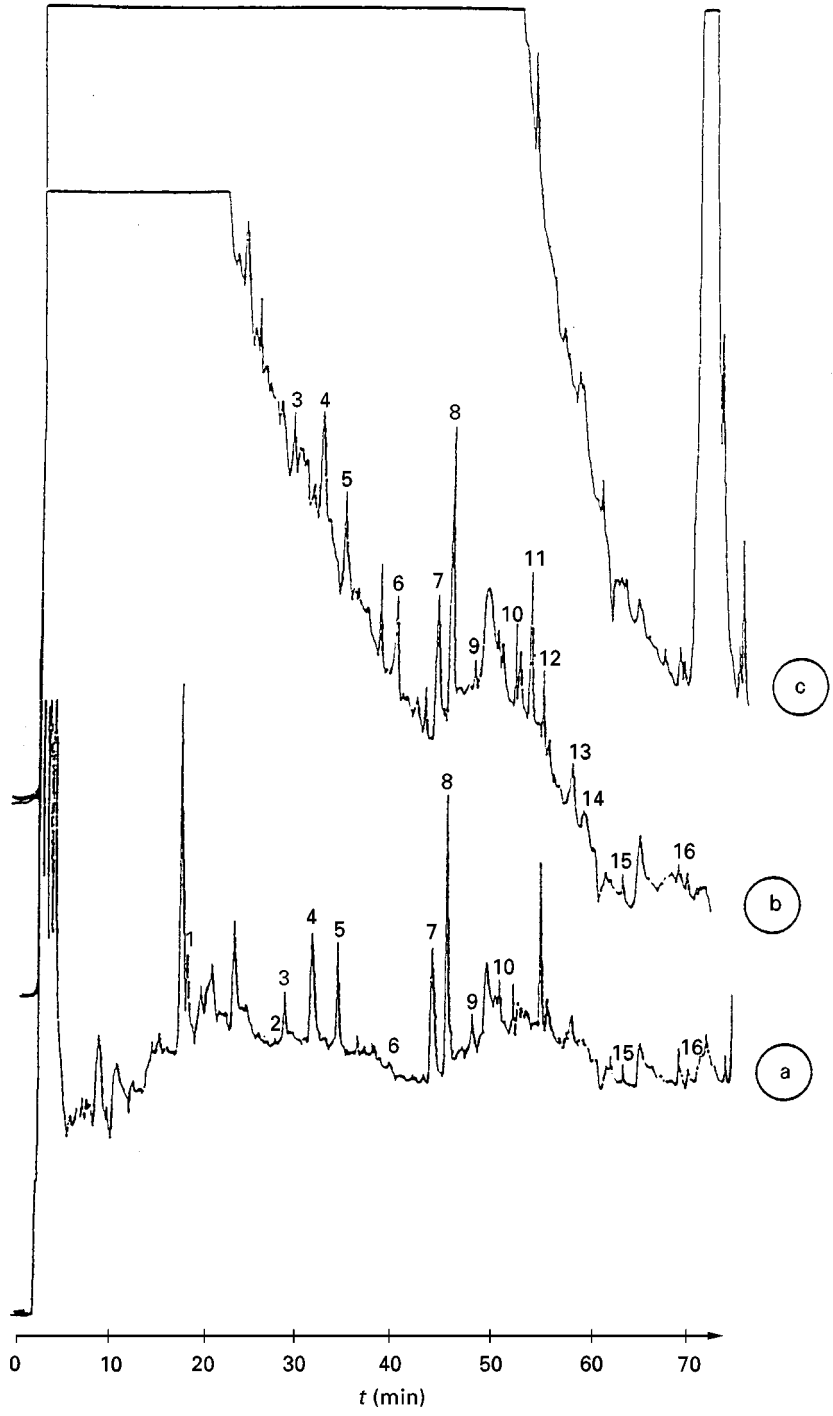

Figure 2 Effect of sample pH and of the sample matrix on the preconcentration of 500 mL of (a) drinking water spiked with 0.1 μg L^{-1} of each analyte at pH 7; (b) drinking water spiked with 0.1 μg L^{-1} of each analyte at pH 2; and (c) River Seine water spiked with 0.1 μg L^{-1} of each analyte at pH 2.

Preconcentration using a 500 mg C_{18} silica cartridge, desorption with 3 mL of methanol, evaporation to dryness, and addition of 500 μL of a dichloromethane/water mixture (20/80, v/v). Analytical column: Bakerbond narrow pore C_{18} silica, 25 cm × 4.6 mm i.d.; acetonitrile gradient with 0.005 M phosphate buffer at pH 3. UV detection at 220 nm. Peaks: 1, chloridazon; 2, aldicarb; 3, metoxuron; 4, simazine; 5, cyanazine; 6, bentazone; 7, atrazine; 8, carbaryl; 9, isoproturon; 10, difenoxuron; 11, ioxynil; 12, MCPP; 13, 2,4-DB; 14, 2,4,5-TP; 15, metolachlor; 16, dinoterb. (Adapted from *International Journal of Environmental and Analytical Chemistry* 65, Pichon V, Cau Dit Coumes C, Chen L and Hennion M-C, Solid-phase extraction, clean-up and LC for routine multiresidue analysis of neutral and acidic pesticides in natural waters in one run, pp. 11–25, Copyright (1996), with permission from Gordon and Breach, Science Publishers.)

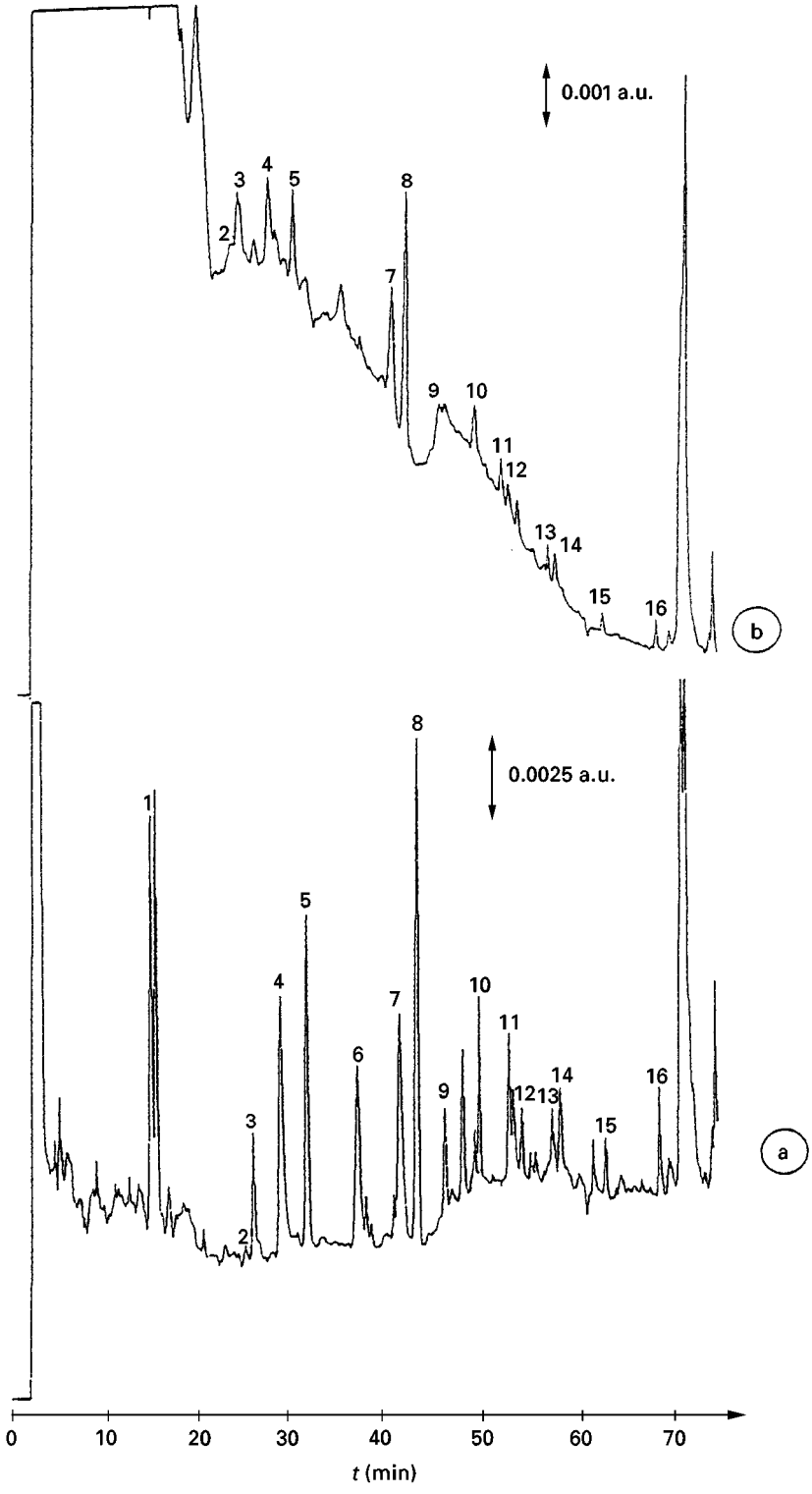

Figure 3 Preconcentration of 500 mL of Seine River water spiked at 0.5 $\mu g\,L^{-1}$ and acidified at pH 2 (b) without and (a) with a clean-up step on Florisil. Analytical conditions and numbering of peaks as in Figure 2. (Reproduced from *International Journal of Environmental and Analytical Chemistry* 65, Pichon V, Cau Dit Coumes C, Chen L and Hennion M-C, Solid-phase extraction, clean-up and LC for routine multiresidue analysis and neutral and acidic pesticides in natural waters in one run, pp 11–25, Copyright (1996), with permission from Gordon and Breach, Science Publishers.)

decrease the amount of co-extracted humic and fulvic acids in surface waters. The recoveries of the acidic pesticides reported in Table 1 using a C_{18} silica cartridge were also measured using a 200 mg SDVB cartridge and a sample volume of 500 mL of drinking water spiked with 0.1 μg L^{-1} of the acidic analytes and adjusted to pH 7. The recoveries of dicamba which was lower than 3% on a 500 mg C_{18} cartridge under the same extraction conditions was increased to 78% on SDVB and the recoveries of all other acidic compounds were found to be higher than 85–90%. As on C_{18} silicas, humic and fulvic interferences were shown to be co-extracted at pH 3 whereas they are not at pH 7 as shown by **Figure 4**. The fact they are

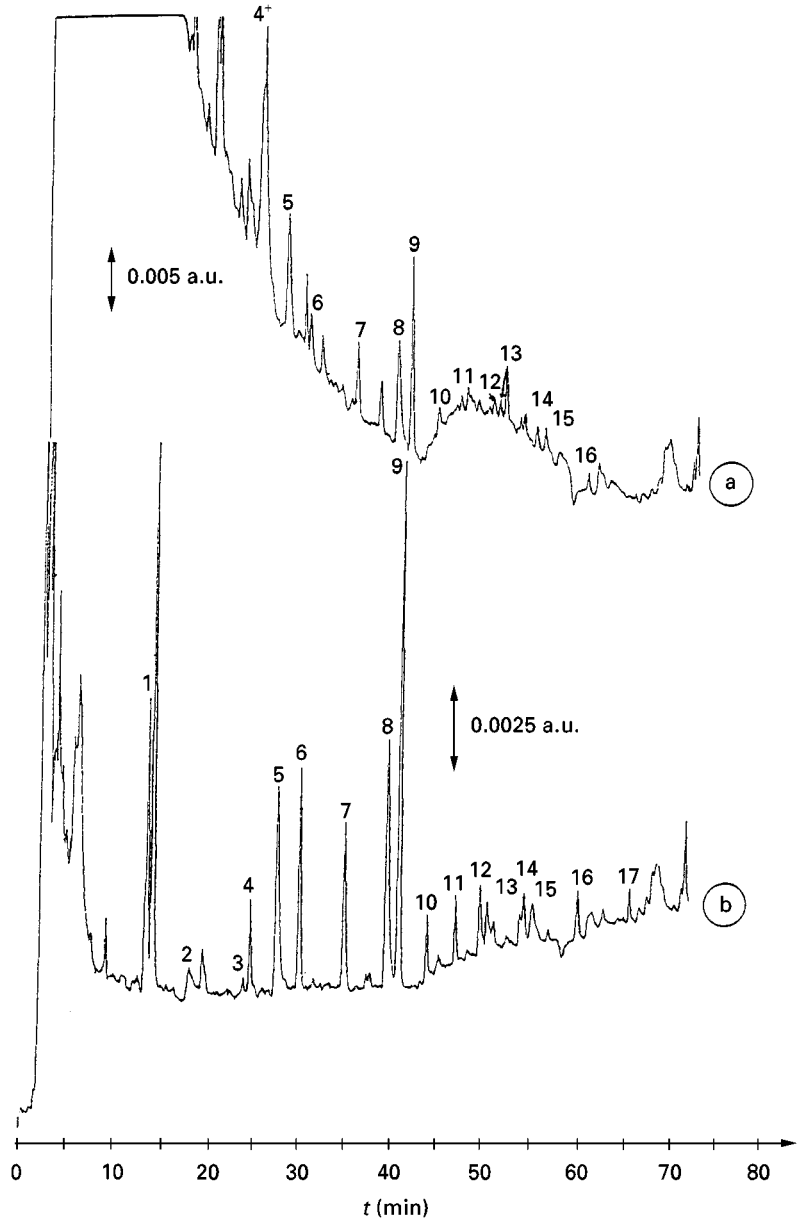

Figure 4 Effect of pH of the sample on the preconcentration of 500 mL of drinking water spiked at 0.1 μg L^{-1} with various acidic, neutral and basic pesticides: (a) pH 3 and (b) pH 7 using a 200 mg SDB cartridge.

Desorption with 4 mL of methanol, evaporation to dryness, and addition of 200 μL of an acetonitrile/water mixture (20/80, v/v). Analytical column: Bakerbond narrow pore C_{18} silica, 25 cm × 4.6 mm i.d.; acetonitrile gradient with 0.005 M phosphate buffer at pH 3. UV detection at 220 nm. Peaks: 1, chloridazon; 2, dicamba; 3, aldicarb; 4, metoxuron; 5, simazine; 6, cyanazine; 7, bentazone; 8, atrazine; 9, carbaryl; 10, isoproturon; 11, ioxynil; 12, MCPP; 13, difenoxuran; 14,2,4-DB; 15, 2,4,5-TP; 16, metolachlor; 17, dinoterb. (Reprinted from *Journal of Chromatography A* 737 Pichon V, Cau Dit Coumes C, Chen L, Guenu S and Hennion M-C. Simple removal of humic and fulvic acid interferences using polymeric sorbents for the simultaneous solid-phase extraction of polar acidic, neutral and basic pesticides, pp. 25–35, Copyright (1996), with permission from Elsevier Science.)

Table 2 Comparison of log k_w obtained for various sorbents and polar analytes and measured or estimated from LC data

Analytes	log K_{ow}	log k_w			
		C_{18} silica[a]	*PRP-1 (415 m^2 g^{-1})*	*SDVB (350 m^2 g^{-1})*	*SDVB (1060 m^2 g^{-1})*
Oxamyl	0.3	1.7 ± 0.1	nd	2.8 ± 0.1	4.1 ± 0.2
Chloridazon	1.2	2.3 ± 0.1	nd	3.8 ± 0.2	nd
Deisopropylatrazine	1.2	2.3 ± 0.1	3.1 ± 0.1	3.2 ± 0.2	4.4 ± 0.2
Phenol	1.5	1.9 ± 0.1	nd	3.0 ± 0.1	nd
Aldicarb	1.4	2.5 ± 0.1	nd	4.0 ± 0.2	5.3 ± 0.2
Deethylatrazine	1.5	2.7 ± 0.1	3.5 ± 0.3	3.5 ± 0.2	4.8 ± 0.3
Simazine	2.3	3.4 ± 0.1	> 4	4.1 ± 0.2	5.9 ± 0.3
2-Chlorophenol	2.4	2.9 ± 0.1	> 4	3.6 ± 0.2	nd

[a]C_{18} silica in Empore disc from J. T. Baker, specific surface area 510 m^2 g^{-1}, carbon loading 17–18% C, end-capped; nd, not determined.

still not retained at pH 7 is due to their high polarity because of the numerous ionized groups and/or to their different configuration at pH 7 and their possible occurrence in the colloidal fraction. However, the consequence of a high retention of acidic pesticides in their ionic form together with the absence of retention of humic and fulvic interferences gives the remarkable possibility of determining acidic and neutral pesticides in surface water samples without any clean-up at the low 0.1 μg L^{-1} concentration level as shown in **Figure 5**.

Use of Porous Graphic Carbon for the Extraction of very Polar Metabolites

The most commonly used carbonaceous sorbents are graphitized carbon blacks (GCB). Their higher efficiency over C_{18} silica for trapping polar pesticides has been extensively shown by the group of Di Corcia *et al*. GCB is not pressure resistant enough to be used in LC so that no data indicating the LC behaviour of solutes are available. In recent years, a porous graphitic carbon (PGC) has been available in SPE cartridges. It has been derived from that made for LC (under the trade mark Hypercarb). PGC has been shown to be particularly efficient for the extraction of some very polar analytes which cannot be extracted by the SDB polymers, such as for instance di- and tri-hydroxyphenols, aminophenols, and other aromatic derivatives containing several polar functional substituents. They have been shown to extract the highly polar degradation products of atrazine including cyanuric acid. As an example **Figure 6** shows the determination of the degradation products of atrazine, DEA and DIA as well as the didealkylated metabolite deethyl-deisopropylatrazine (DDA) in ground water. Recoveries were in the range 90–95% for each analyte using a SPE cartridge packed with 200 mg of Hypercarb and a sample volume of 500 mL. DDA is a very polar metabolite, with a log K_{ow} value of 0, and its occurrence in ground water has never been shown, due to the difficulty of extraction and analysis. It was shown that in soil DEA is stable whereas DIA is rapidly transformed into DDA. Our results have confirmed this hypothesis because DEA is detected in high amounts, DIA at

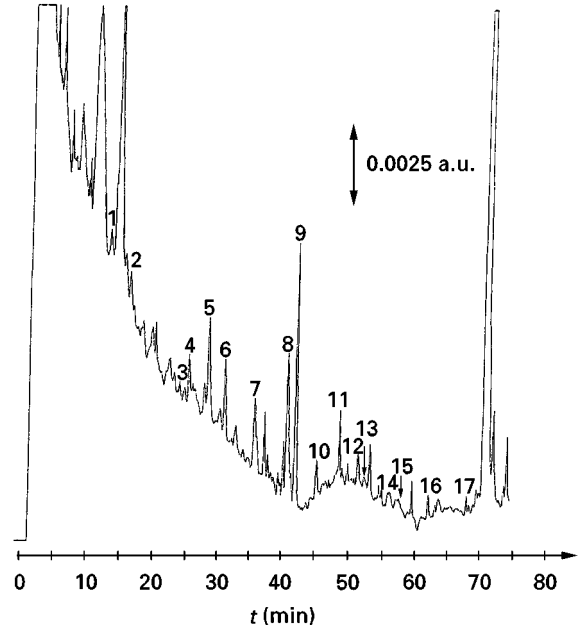

Figure 5 Preconcentration of 500 mL of River Seine water spiked with 0.1 μg L^{-1} of herbicides at pH 7. Experimental conditions as in Figure 4b. (Reprinted from *Journal of Chromatography A* 737 Pichon V, Cau Dit Coumes C, Chen L, Guenu S and Hennion M-C. Simple removal of humic and fulvic acid interferences using polymeric sorbents for the simultaneous solid-phase extraction of polar acidic, neutral and basic pesticides, pp. 25–35, Copyright (1996), with permission from Elsevier Science.)

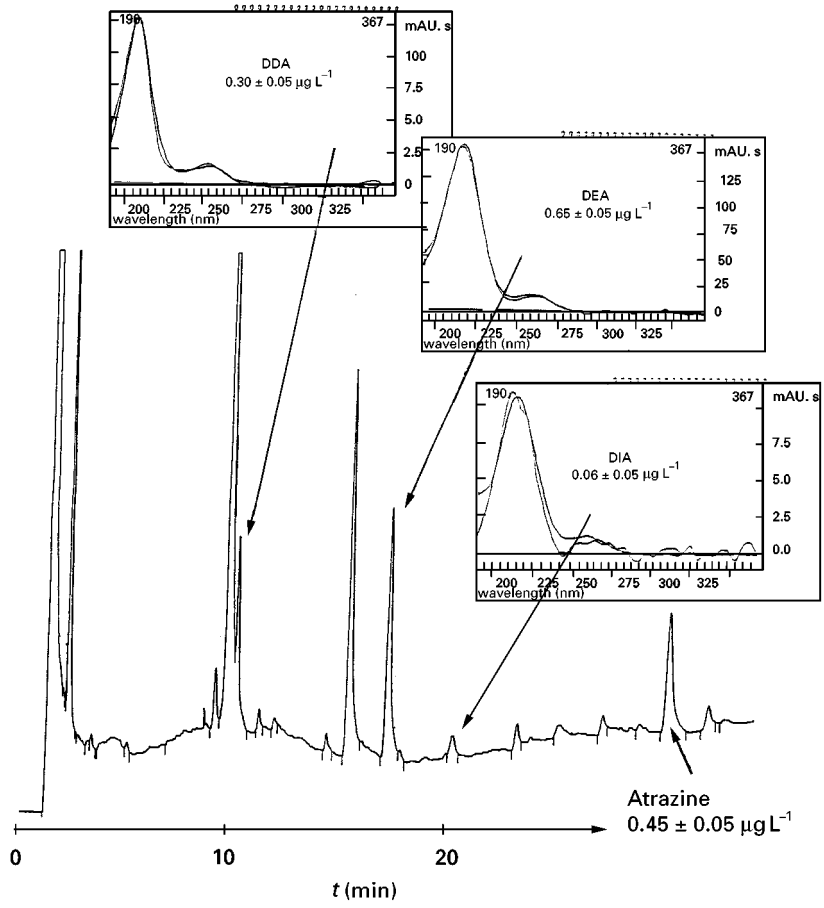

Figure 6 Preconcentration of 500 mL of ground water and spectra of the peaks identified using the UV DAD software. Preconcentration using a 200 mg Hypercarb cartridge. Analytical column: Hypercarb, 10 cm × 4.6 mm i.d.; acetonitrile gradient with 0.005 M phosphate buffer at pH 7. UV detection at 220 nm.

trace level and DDA has half the concentration of DEA. This last figure illustrates the persistence and importance of the degradation products in ground water, since the sum of the concentration of metabolites is twice the concentration of the parent compound atrazine.

Further Trends

Research for sample preparation is a very active area at the moment, partly explained by the need for reducing as much as possible the use, disposal and release in the environment of toxic solvents, together with a reduction of the total analysis cost. In Europe, chemists are faced with the drastic drinking water regulatory level of 0.1 µg L^{-1} for each pesticide. Therefore, trends are for setting up multiresidue analysis.

Trends are also for simplifying the labour of sample preparation, increasing its reliability and eliminating the clean-up step of aqueous samples by decreasing as much as possible the amount of interfering components extracted from complex matrices. Regarding these last two aspects, the new polymeric extraction sorbents have a remarkable potential. Sorbents based on immunaffinity extraction are also promising for their high selectivity, and extraction, concentration and clean-up are performed in the same step.

See also: **II/Extraction:** Analytical Extractions: Solid-Phase Extraction. **III/Porous Graphitic Carbon: Liquid Chromatography: Solid Phase Extraction with Discs.**

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Gas Chromatography

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Introduction

A pesticide is usually defined as any organism or substance that is manufactured for direct or indirect control or prevention of any pest. Pesticides often alter the growth, development or characteristics of insects and plants. Most pesticides are synthetic chemicals that can be classified into six classes, according to their chemical type: organochlorine compounds, organophosphorus compounds, carbamates, phenoxyalkanoic acid derivatives, substituted ureas and triazines. Currently, several hundred pesticides are widely applied to a broad variety of crops to reduce losses from weeds, insects and diseases. Herbicides are employed in agriculture for pre- and post-emergent weed control of corn, wheat, barley and sorghum; they are also used on railways and roadside verges. In general, organochlorine compounds are resistant to hydrolysis, and those that undergo photochemical reaction tend to form compounds with a persistence comparable to, or greater than, their parent compounds. Some organochlorine pesticides have been banned due to their toxicity, persistence and bioaccumulation in environmental matrices. Owing to the environmental impact of pesticides, several priority lists, also called 'black' or 'red' lists, have been published to protect the quality of surface and tap water. Thirty-nine pesticides are listed in priority order in the 76/464 EEC (European Economic Community) Council Directive on pollution caused by certain dangerous substances discharged into the aquatic environment of the community. The US Environmental Protection Agency (EPA) has established drinking water regulations and health advisory levels for individual pesticides.

Since the publication of Rachel Carson's book *Silent Spring* in 1962, many countries have legislated for public health protection. Such regulations have ultimately focused on protecting the general public