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Comparative study of various size-exclusion chromatographic columns for the clean-up of selected pesticides in soil samples

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Abstract

A comparative study was carried out using various types of size-exclusion chromatographic (SEC) columns (Bio-Beads SX-3, SX-8 and SX-12, Phenogel polystyrene and Zorbax PSM 60S, silica based) for the isolation of the pesticides monuron, linuron, monolinuron, isoproturon, propanil, fenitrothion, molinate, alachlor, bensulfuron, chloridazon, trifluoralin and atrazine from soil samples. Spiked soil samples (10 μg/g) were Soxhlet extracted and fractionated with SEC columns using different mobile phases. The SEC extracts were analysed either by liquid chromatography with diode-array detection or gas chromatography with nitrogen–phosphorus detection. Recoveries varying from 70 to 82% were found for all the analytes. With the low-resolution polystyrene columns better results were found using columns with a high size-exclusion range. The Phenogel column was more efficient than the Bio Beads columns for phenylurea herbicides. The method developed was applied to the determination of linuron and atrazine in a candidate reference material and was applied to investigate the decay of molinate in real soil samples at ng/g levels.

1. Introduction

Since the introduction of size-exclusion chromatography (SEC) for the isolation of organic contaminants from environmental matrices [1], its use has not been as popular as other clean-up methods such as solid-phase extraction or column chromatography. This is probably caused by the need for further equipment, such as a liquid chromatographic pump and a detector. In addition, SEC columns are not currently available as disposable cartridges, *e.g.*, Florisil and C_{18} type. SEC is a useful technique as it is not destructive, in contrast to other methods involving acid or base treatment, it can isolate a variety of compounds of different chemical types in the same fraction and it can remove a large number of interfering materials from the matrix. Moreover, SEC has been reported to give higher reproducibility than Florisil clean-up [2]. The main disadvantage is that the removal of interfering materials is not complete in many instances, especially when using low-resolution SEC columns, and so some of the samples need to be analysed twice in order to eliminate the matrix interferences completely.

In current environmental analyses, SEC is used as a clean-up procedure for organochlorine and organophosphorus pesticides, polychlorobiphenyls and herbicides, using different mobile phases in each instance, *e.g.*, cyclohexane [1,3], ethyl acetate–toluene [4,5], cyclohexane–dichloromethane [6–12] and cyclohexane–ethyl acetate [2,13–17].

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The aim of this work was to compare the performances of different SEC columns for the isolation of a group of pesticides from soil matrices. This study was accomplished by comparing the low-resolution SEC polystyrene columns Bio-Beads SX-3, SX-8 and SX-12 with a high-resolution SEC polystyrene column. The final purpose was to select the best SEC column that can eliminate the matrix interferences from the pesticides. In addition, a silica-based SEC column was also tested. This column material had a silica structure deactivated with special reagents (*e.g.*, short hydrocarbon chains containing diol groups) to prevent strong hydrophobic interactions. The main advantage of these silica-based columns is that they can withstand high pressures, flow-rates and temperatures and are compatible with a wide variety of organic and aqueous solvents.

Application to the determination of atrazine and linuron in a soil candidate reference material from the BCR (Bureau Communitaire de Référence) of the Commission of the European Communities and to study the decay of molinate in real environmental soil samples from the Ebro Delta (Tarragona, Spain) is also reported.

2. Experimental

2.1. Materials

HPLC-grade water and analytical-reagent grade cyclohexane, dichloromethane, diethyl ether, methanol and acetonitrile were obtained from Merck (Darmstadt, Germany). Hexane and tetrahydrofuran of HPLC grade were obtained from Romil Chemicals (Shepshed, Leics., UK). Ethyl acetate for residue analysis was purchased from Scharlau (Barcelona, Spain). All the solvents were passed through a 0.45-μm filter from Scharlau. Atrazine, linuron and isoproturon were obtained from Riedel-de Haën (Seelze–Hannover, Germany). Molinate, alachlor, bensulfuron, chloridazon, monuron and monolinuron were purchased from Dr. S. Ehrenstorfer Promochem (Wessel, Germany) and propanil and trifluoralin from Polyscience (Niles, IL, USA). Fenitrothion was a gift from Sumitomo Chemical (Osaka, Japan).

2.2. Sample preparation

A method developed previously in our department was used for the extraction of the pesticides from soil samples [2]. Real soil samples were collected in the Ebro delta (Tarragona, Spain). After collection, the samples were freeze-dried, sieved through a 120-μm sieve and homogenized for 2 weeks with mechanical shaking in order to obtain a homogeneous soil material that could be used as a candidate reference material. Subsequently the samples were stored at −20°C prior to carrying out the experiments. A 10-g amount of sample at room temperature was wetted and spiked with 10 μg of each pesticide with homogenization. The wet soil spiked with the pesticides was kept for 2 days and then Soxhlet extracted from 12 h with methanol. The extract was concentrated in a rotary evaporator (30°C) to *ca.* 2–3 ml. The evaporation of the solvent was carefully finished with nitrogen, and the extracts were then dissolved in 300 μl of dichloromethane or methanol depending on whether the SEC clean-up was carried out with an organic or aqueous mobile phase, respectively.

2.3. SEC clean-up

Eluent delivery was provided by a Model 64 high-pressure pump (Knauer, Hamburg, Germany) and the detection was carried out with a Vari-chrom UV–Vis detector (Varian, Sunnyvale, CA, USA). Samples were injected via a 160-μl loop (Rheodyne, Cotati, CA, USA). The columns investigated were three low-resolution columns (450 mm × 10 mm I.D.) packed with Bio-Beads SX-3, SX-8 and SX-12 with size exclusion of M_r 2000, 1000 and 400, respectively (Bio-Rad Labs., Richmond, CA, USA); a 250 mm × 6.2 mm I.D. high-resolution silica-based Zorbax PSM-60S column with a molecular mass range from 100 to 10 000 (Rockland Technologies, through Chrompack, Middelburg, Netherlands) and a 300 mm × 7.8 mm I.D. high-

resolution SEC polystyrene column (Phenogel) with a size exclusion of M_r 800 (Phenomenex, Ramuko, Palos Verdes, CA, USA). The mobile phases consisted of mixtures of dichloromethane and cyclohexane for the polystyrene columns and additionally methanol–water (70:30) for the silica-based column. A flow-rate of 1 ml/min was used throughout.

2.4. Chromatographic analysis

Liquid chromatography with diode-array detection (LC–DAD)

An HP 1090A liquid chromatograph equipped with an automatic injector and a diode-array detector was used (Hewlett-Packard, Palo Alto, CA, USA). A 20-μl volume of sample was injected into a Zorbax C_8 reversed-phase analytical column (Rockland Technologies). Elution was carried out with water–methanol–acetonitrile (60:20:20) for 3 min followed by gradient elution to 100% acetonitrile in 30 minutes at a flow-rate of 1 ml/min.

Gas chromatography with nitrogen–phosphorus detection (GC–NPD)

A GC 5300 Mega Series gas chromatograph (Carlo Erba, Milan, Italy) equipped with a nitrogen–phosphorus detector was used. The column was a 15 m × 0.15 mm I.D. fused-silica capillary column coated with chemically bonded cyanopropylphenyl DB 225 (J & W Scientific, Folsom, CA, USA). Hydrogen was the carrier gas and helium the make-up gas at 60 and 110 kPa, respectively. The temperatures of the injector and detector were held at 270°C. The column was programmed from 60 to 90°C at 10°C/min and from 90 to 220°C at 6°C/min.

Quantification

Both LC–DAD and GC–NPD quantification was performed with external standard calibration methods, except for the validation analyses, which were carried out using deethylatrazine and monuron as internal standards for atrazine and linuron, respectively. Calibration graphs were constructed for all the compounds over the concentration range 0.01–20 mg/ml for LC and 0.005–10 mg/ml for GC. The repeatability and reproducibility varied from 5 to 9% and from 7 to 12% ($n = 6$), respectively.

3. Results and discussion

3.1. SEC fractionation

Low-resolution polystyrene columns: Bio-Beads SX

The retention times of the pesticides with different columns and experimental conditions are given in Table 1 and are in the expected range found for other similar pesticides using a Bio-Beads SX-3 column [8]. As expected, the exclusion size decreased from SX-3 to SX-12 columns together with the retention times of the analytes. The dispersion observed in the retention times of the analytes could be attributed more to the existence of additional adsorption and partition interactions than to differences in the exclusion size of the pesticides. The increase in the retention time dispersion for the high exclusion size columns would be explained by the fact that the percentage of the excluded pesticide decreased when the exclusion size increased. Hence low interaction occurs in the columns with low exclusion size and consequently better peak shapes for the pesticides are obtained (Fig. 1).

It can also be observed that the trend of the matrix soil interference retention times is different, and it increases when the exclusion size decreases. This may be related to the different packing densities of the stationary phases, with a lower swelling ratio for the low exclusion size polymers. Hence when columns with the same physical dimensions are used, a higher packing density will be observed with the low exclusion size columns. Thus, when the packing density increases, the retention times of the soil matrix interferences also increase.

Another relevant parameter in SEC in the eluent. In this work a comparison was made between the performance of dichloromethane–cyclohexane and that of the ethyl acetate–cyclohexane mixture used in previous work [2].

Table 1
Elution volumes (ml) of the pesticides using four different eluents with Bio-Beads columns

Pesticide	Elution volume (ml)				
	SX-3		SX-8		SX-12
	Cyclohexane–ethyl acetate (1:1)	Cyclohexane–dichloromethane (1:1)	Cyclohexane–dichloromethane (1:1)	Cyclohexane–dichloromethane (1:3)	Cyclohexane–dichloromethane (3:1)
Monuron	22–39	18–30	17.0–24.1	14.2–19.0	13.3–12.2
Linuron	22–30	19–29	15.3–23.0	13.3–19.1	13.1–16.4
Isoproturon	21–39	18–27	15.3–22.4	n.d.	12.3–15.2
Propanil	26–38	25–35	22.1–27.3	20.0–28.1	15.1–19.3
Monolinuron	n.d.	n.d.	16.0–22.1	13.4–17.4	13.1–17.0
Fenitrothion	n.d.	n.d.	15.0–21.0	14.2–20.0	12.3–16.3
Trifluoralin	18–29	16.6–21	12.2–16.4	12.0–15.4	12.0–14.4
Alachlor	n.d.	16–27	13.1–16.1	13.0–15.2	12.0–15.0
Atrazine	n.d.	16–25	13.0–16.3	12.3–15.3	12.0–15.4
Bensulfuron	n.d.	16.6–22	12.3–17.2	11.2–19.0	11.0–11.2
Molinate	n.d.	19–26	16.0–23.0	15.3–22.0	15.1–19.4
Chloridazon	n.d.	16–25	12.1–16.1	n.d.	11.1–11.3
S.M.I.	n.d.	7–25	9.1–17.0	8.1–19.0	10.3–19.0

Chromatographic conditions: see Experimental. S.M.I. = Soil matrix interferences; n.d. = not determined.

Dichloromethane gave the best results for phenylurea herbicides, molinate, fenitrothion and propanil. The viscosities of dichloromethane and ethyl acetate are very similar (0.41 *vs.* 0.44 cP), so this parameter does not play a relevant role in the SEC separation.

The differences in the separation using the two mixtures could be explained either by using Lewis acid–base arguments or by the presence of dipoles in the molecular structure which could interact with the polystyrene via dipole–dipole interactions [18,19]. Polystyrene can be considered as a weak Lewis base so, depending on the type of mobile phase used (acidic or basic nature) different retentions can be expected. For analytes with basic groups and without important molecular dipoles in their structure, such as atrazine, alachlor and fenitrothion, a basic type of mobile phase such as ethyl acetate is recommended. Analytes such as phenylurea herbicides and propanil showed worse peak shapes using ethyl acetate as the mobile phase. When using ethyl acetate, dipole–dipole interactions between these compounds and the stationary phase become very important, giving tailing peaks. This problem does not occur when using dichloromethane (acidic character), because acid–base interactions prevent such undesirable strong dipole–dipole interaction.

Because the aim of this work was to develop a screening method that could eliminate the soil matrix interferences and monitor all the pesticides under the optimum conditions, it was decided to use dichloromethane as the eluent, as in general it gave better results than ethyl acetate. The effect of the changes in the ratio of the mobile phase components was also studied. When the proportion of dichloromethane was increased, the retention time of the analytes decreased and it was found that dichloromethane–cyclohexane (1:1) afforded the best separation. As an example, the elution profiles and the collection time from an extract of a spiked sediment sample after being processed with the Bio-Beads SX-3 and SX-8 columns are shown in Fig. 1. The Bio-Beads SX-12 column was not studied because from the retention times of the analytes and the soil matrix interferences fraction it was concluded that a good separation could not be achieved.

High-resolution SEC columns

Table 2 gives the retention times obtained for the different analytes in one of these columns.

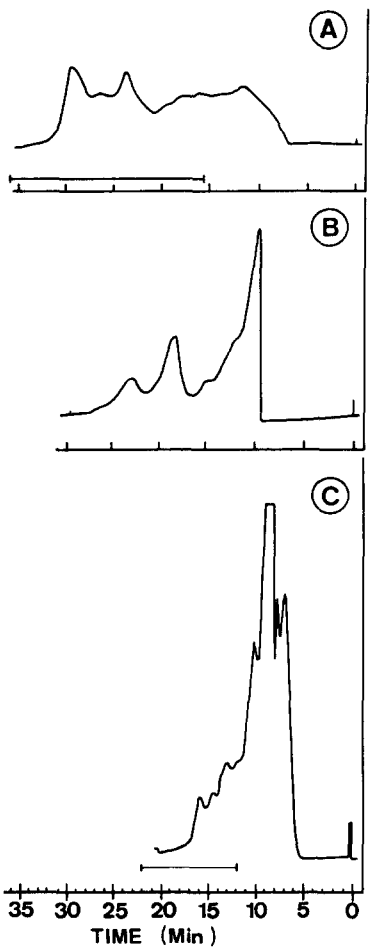

Fig. 1. SEC profiles of a soil sample spiked with all the studied pesticides (10 μg/g of each pesticide). (A) Bio-Beads SX-3; (B) Bio-Beads SX-8; (C) Phenogel high-resolution SEC. Eluent: dichloromethane–cyclohexane (1:1) (Bio-Beads columns) and dichloromethane–cyclohexane (1:3) (Phenogel high-resolution SEC). Flow-rate of eluent, 1 ml/min. Detection at 254 nm. For other chromatographic conditions, see Experimental. The sample collection intervals are indicated by the horizontal bars.

Table 2
Elution volumes (ml) of the pesticides using two different mobile phases with Phenogel column

Pesticide	Cyclohexane–dichloromethane (1:1)	Cyclohexane–dichloromethane (3:1)
Monuron	12.0	18.2–23.6
Linuron	8.6	13.6–15.6
Propanil	13.6	22.0–25.2
Monolinuron	11.4	18.2–23.2
Molinate	8.4	10.1–11.4
Alachlor	8.0	9.6–10.6
Atrazine	7.9	9.5–10.3
Trifluoralin	n.d.	9.4–10.2
Fenitrothion	8.4	10.0–12.8
Bensulfuron	n.d.	9.4–10.4
S.M.I.	n.d.	6.0–13.0
Blank	n.d.	9.4–10.2

Chromatographic conditions: see Experimental. S.M.I. = Soil matrix interferences; n.d. = not determined.

First, the conditions that were optimum for the low-resolution polystyrene columns were used, but most of the analytes co-eluted totally with the soil matrix interferences. The percentage of dichloromethane in the eluent was then reduced to 25% so the interactions of the analytes with the stationary phase increased. Even though some of the pesticides still co-eluted with the soil matrix interferences, phenylurea herbicides and propanil showed almost complete separation from the soil matrix interferences (see Fig. 1).

In Table 3, the retention times of the analytes in different mobile phases (organic and aqueous) are given. When an aqueous mobile phase was used, the samples were eluted with methanol–water (70:30). As can be seen from Table 3, the analytes were eluted in the same order as would be expected for a reversed-phase analytical column. These results were promising because in this instance the pesticides with a better separation with respect to the soil matrix interferences were less separated with the polystyrene columns (see Tables 1 and 3). The main drawback of this method is that a high percentage of water is needed. Hence in order to carry out the analytical determinations, there is the need to eliminate the water. In this operation losses of sample during the evaporation of the solvent are expected. This could be solved by connecting the SEC column on-line with an analytical LC column as reported [20], or by applying dichloromethane liquid–liquid extraction of the analytes

Table 3
Elution volumes (ml) of the pesticides using five different mobile phases from Zorbax HRSEC silica-based column

Pesticide	Methanol	Methanol–water (70:30)	Cyclohexane–dichloromethane		
			1:1 + 5% THF	1:1 + 3% THF	3:1 + 3% THF
Monuron	5.6	8.8	19.0	24.0	–[a]
Isoproturon	6	10.0	16.6	23.2	–[a]
Monolinuron	5.6	9.2	7.4	8.4	11.1
Propanil	5.8	9.8	9.2	10.6	17.0
Linuron	5.8	10.2	7.4	8.0	11.0
Alachlor	5.8	10.4	5.6	5.6	n.d.
Trifluoralin	5.8	19.0	5.6	5.6	n.d.
Atrazine	5.8	n.d.	n.d.	n.d.	n.d.
Molinate	5.7	11.6	5.8	5.9	n.d.
Fenitrothion	5.8	11.2	5.6	5.6	n.d.
Bensulfuron	5.8	5.0	5.6	5.6	n.d.
Chloridazon	5.8	10.1	5.4	5.6	n.d.
Blank sample	5.7	2.4	5.5	5.6	n.d.
S.M.I.	5.7	2.5	n.d.	5.6	5.5

Chromatographic conditions: see Experimental. S.M.I. = Soil matrix interferences; n.d. = not determined.
[a] Irreversible adsorption in the elution conditions.

from the SEC eluent. As specific on-line connection was not available in our laboratory, the latter option was performed and good results (recoveries up to 80%) for all the analytes were obtained.

It should be noted that the performance of the column is more like that of a reversed-phase column than an SEC column. When using 100% methanol most of the analytes were eluted in the solvent front (see Table 3). Hence in this instance the size exclusion contribution to the separation was minimal.

When an organic mobile phase was used, experiments were started using the same conditions as with the polystyrene columns. However, in this instance the performance of the system was more like that of an adsorption chromatographic column with large molecules (soil matrix interferences) being retained together with the pesticides. This can be attributed to a combined effect of adsorption of the diol groups of the bonded reagent and the active silanol groups left uncovered by incomplete silanization. We solved this problem by adding a small percentage of tetrahydrofuran to the mobile phase to compete for these active sites as suggested [21]. In this instance a good separation of the phenylurea herbicides and propanil was found but the other analytes were eluted with the solvent front. Similarly to the use of an aqueous mobile phase, the contribution of size exclusion to the separation process was minimal.

In spite of the good results obtained for the phenylurea herbicides and propanil, the method had the drawback that the retention time of the analytes was too dependent on the proportion of THF used (see Table 3). In this instance the possibility of making errors during the collection of the analytes is very high. Additionally, there was also a problem with optimizing the proportion of THF because it differed for the different phenylureas. For instance, 3% is optimum for monolinuron and linuron, but this was too low for monuron and isoproturon (see Table 3). Further work in this direction was therefore abandoned.

The aqueous and organic mobile phase profile of an extract of a spiked sample are shown in

Fig. 2. High band broadening for monuron and isoproturon using an organic mobile phase was observed.

3.2. Comparison between low- and high-resolution SEC columns: environmental applications

Fig. 3 shows the liquid chromatograms of the extracts obtained from pesticides added to Ebro Delta soil samples purified with the SEC columns Bio-Beads SX-3 and SX-8 and Phenogel. No significant differences were found between the Bio-Beads columns, but excellent results were achieved with the high-resolution SEC column, with a chromatogram exhibiting no interferences.

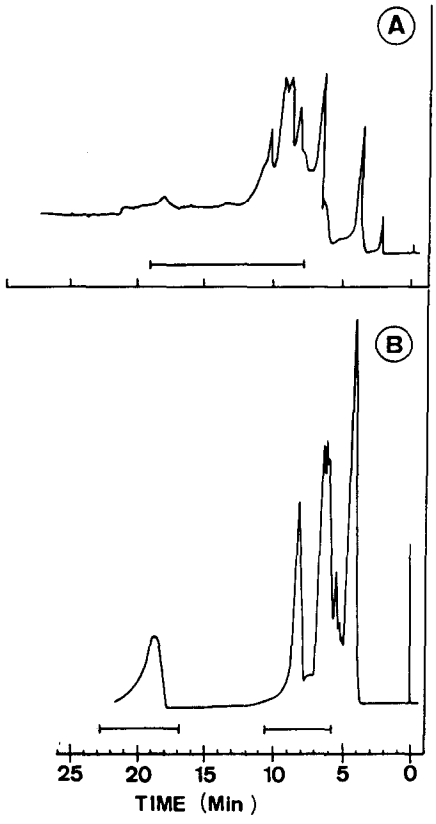

Fig. 2. SEC profiles of a soil sample spiked with all the studied pesticides (10 μg/g of each pesticide) eluted from the Zorbax silica-based column with (A) an aqueous eluent [methanol–water (70:30)] and (B) an organic eluent [dichloromethane–cyclohexane (1:1) + 5% THF]. Flow-rate of eluent, 1 ml/min. Detection at 254 nm. For other chromatographic conditions, see Experimental. The sample collection intervals are indicated by the horizontal bars.

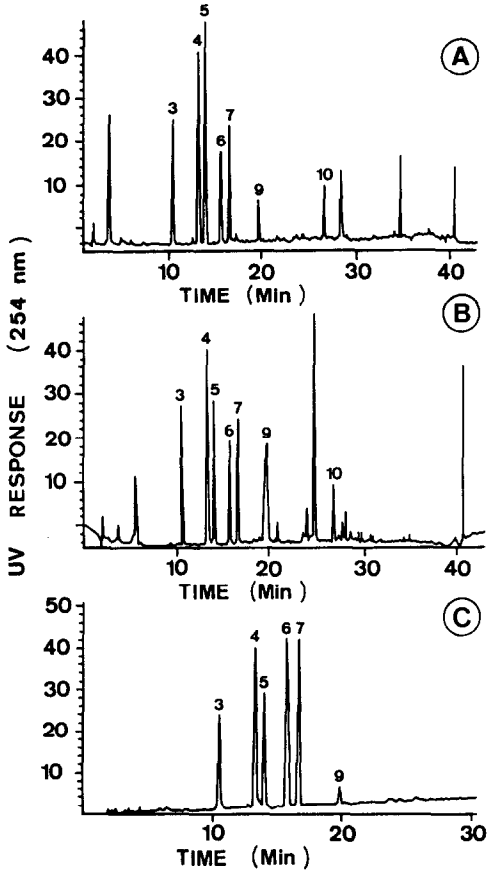

Fig. 3. Reversed-phase LC profiles of spiked samples (10 μg/g) after SEC clean-up with (A) Bio-Beads SX-3, (B) Bio-Beads SX-8 and (C) Phenogel polystyrene columns. Peaks: 3 = monuron; 4 = isoproturon; 5 = monolinuron; 6 = linuron; 7 = propanil; 8 = molinate; 9 = alachlor + fenitrothion; 10 = trifluoralin. For chromatographic conditions, see Experimental.

The results of GC–NPD of the extracts obtained from pesticides added to Ebro Delta soil samples purified with the SEC columns Bio-Beads SX-3 and SX-8 and Zorbax with an aqueous phase are shown in Fig. 4. For the less

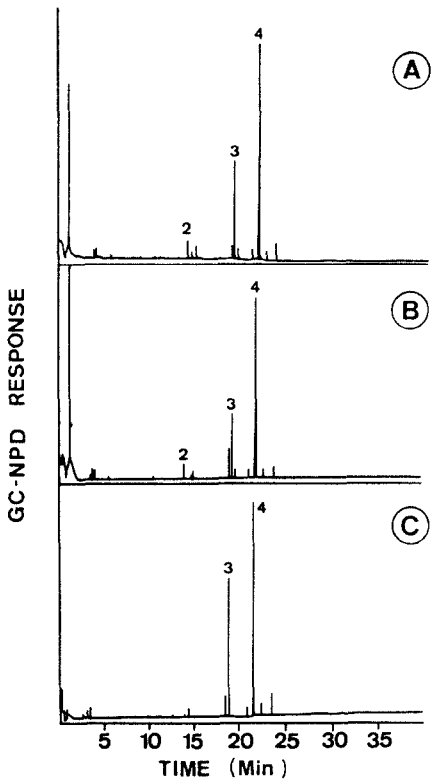

Fig. 4. GC–NPD profiles of a spiked sample (10 μg/g) after SEC clean-up with (A) Bio-Beads SX-3, (B) Bio-Beads SX-8 and (C) Zorbax silica-based columns using an aqueous mobile phase. Peaks: 2 = trifluoralin; 3 = alachlor; 4 = fenitrothion. For chromatographic conditions, see Experimental.

polar analytes good results with the Zorbax column were obtained. In general, the powerful clean-up effect of high-resolution SEC in combination with a selective analytical determination method such as GC–NPD should be emphasized.

The recoveries for the analytes after their addition to soil samples (10 μg/g) are given in Table 4. Recoveries of up to 70% for all the analytes were found. The slightly high standard deviation found with the Zorbax column can be attributed to the additional liquid–liquid extraction step, which was performed manually.

To conclude the comparative study between low- and high-resolution SEC columns, for the determination of phenylurea herbicides the use of high-resolution SEC columns (*e.g.*, Phenogel) offers the best solution. When it is required to determine volatile pesticide residues, *e.g.*, atrazine and fenitrothion, in a soil sample, the method of choice will be GC–NPD, as it offers the best sensitivity and selectivity. However, for pesticides such as isoproturon and linuron, a final determination by LC–DAD is recommended, otherwise, if it is still desired to use GC, derivatization will be required.

In order to evaluate the performance of the developed method, a candidate reference material containing atrazine and linuron was analysed. The real sediment, previously collected in the Ebro Delta area, has been treated as described

Table 4
Average recoveries from spiked soil samples (10 μg/g) ($n = 6$)

Method	Pesticide	SX-3		Phenogel		Zorbax	
		Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)	Recovery (%)	R.S.D. (%)
LC–DAD	Monuron	76	5	80	5	n.d.	
	Linuron	77	6	79	5	n.d.	
	Monolinuron	76	5	80	4	n.d.	
	Isoproturon	75	4	82	5	n.d.	
	Propanil	75	7	79	6	n.d.	
GC–NPD	Alachlor	77	4	n.d.		80	8
	Trifluoralin	77	5	n.d.		79	8
	Atrazine	69	4	n.d.		75	9

SEC eluents: dichloromethane–cyclohexane (1:1) (Bio-Beads SX-3), dichloromethane–cyclohexane (1:3) (Phenogel HRSEC) and methanol–water (70:30) (Zorbax HRSEC). Other chromatographic conditions: see Experimental.

under Experimental. The amounts of each pesticide were determined with the proposed method, using selected SEC columns, and also with another method based on clean-up with Florisil columns [2]. The values obtained for atrazine using Bio-Beads SX-3 and Phenogel were 106 ± 4 and 104 ± 4 ng/g, respectively (111 ± 10 ng/g with Florisil) and for linuron the values were 238 ± 6 and 239 ± 5 ng/g, respectively (250 ± 10 ng/g with Florisil).

The determination of the degradation profile of the pesticide molinate under real environmental conditions was carried out. This herbicide, usually applied in rice crop fields in the Ebro delta area, was found at low residue levels (below 0.1 μg/l) in earlier water analyses [22]. It was therefore decided to carry out study of its behaviour in real soil samples. Samples were collected in from rice crop fields in the Ebro Delta area with an interval of *ca.* 3 months between samples, the first sample being collected a few days after herbicide application. The analyses were carried out using the Bio-Beads SX-3 SEC column under the conditions given above.

It was found that under the Delta Ebro area conditions molinate had a half-life of *ca.* 20–25 days. This result is in agreement with others reported previously [23]. This value is lower than those for other pesticides, such as atrazine (28–30 days) and linuron (1–2 months) studied previously [24]. This may be due to the rapid oxidation of the molinate to sulphoxide by chemical and microbiological processes and also to its higher vapour pressure, which increases its volatility. Nevertheless, the sulphoxide metabolites have superior water solubility and slower degradation kinetics and are even more toxic than the parent compound [25].

4. Conclusions

A study of the use of different SEC columns as a clean-up method for analyses for pesticide residues in soil samples was undertaken.

With the Bio-Beads packings, better results were found when using columns with higher exclusion size range. Even though the efficiency of the peaks is increased by using a smaller pore diameter column, high co-elution with interferences was also observed. The benefit of the existence of weak adsorption phenomena was also confirmed. Therefore, a comparison between two different mobile phases (dichloromethane–cyclohexane and ethyl acetate–cyclohexane) was undertaken, and showed that dichloromethane–cyclohexane generally provided better results for all the compounds studied.

The excellent performance of the high-resolution SEC columns was demonstrated. The efficiency of the clean-up process was improved owing to the higher resolution and these columns are particularly appropriate for the isolation of propanil and phenylurea herbicides from soil matrix interferences. In general, high-resolution SEC is to be preferred over low-resolution SEC in order to eliminate the soil matrix interferences more effectively. Nevertheless, one of the major drawbacks is still the cost of such high-resolution SEC columns. In general, high-resolution SEC columns cost three times more than the low-solution SEC columns, which can be a serious problem for the implementation of high-resolution SEC columns in routine environmental analyses for pesticides in soil samples.

The difficulty of carrying out a clean-up process with the silica-based columns without a high degree of adsorption, owing to their wide exclusion range, was demonstrated. Further studies to obtain silica packings with narrow exclusion ranges would be desirable.

In a comparison of GC–NPD and LC–DAD, fewer interferences were found in GC–NPD owing to the superior detector selectivity, but LC–DAD offered the possibility of monitoring a larger number of compounds, their sensitivity being sufficient at the level required in soil analyses.

The method developed in this work was validated by determining linuron and atrazine herbicides in a reference candidate material of the BCR and was applied to the determination of the decay of molinate in real soil samples.

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