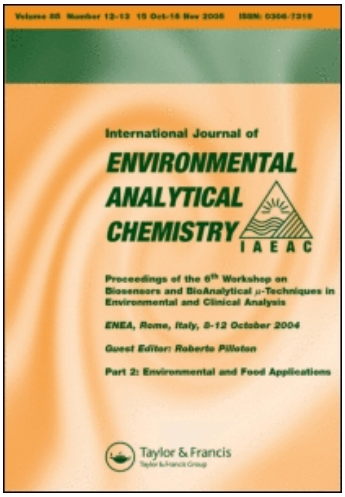

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STABILITY OF PARATHION-METHYL, METHIOCARB, DDT AND 2,4-D IN SOLID-PHASE EXTRACTION PRECOLUMNS PACKED WITH A POLYMERIC REVERSED PHASE

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The stability of parathion-methyl, methiocarb, DDT and 2,4-D, adsorbed on the polymeric PLRP-S phase packed in small stainless steel precolumns was examined, with a view to propose the use of these precolumns as alternative means for the transport of water samples. First, water samples spiked with the studied pesticide at low μg/l concentration levels were extracted and preconcentrated in the precolumns, using appropriate conditions for a total recovery. Then, the precolumns were stored at room temperature (15–20°C) or at 35°C for different time periods. At the end of the respective period each precolumn was coupled to an HPLC column via a switching valve and was on-line analyzed by reversed phase chromatography with UV detection. The four pesticide recoveries after one week in the precolumn at room temperature were higher than 90%. The same was true at 35°C except for DDT, which suffered a 30% degradation in one week. Further studies showed that DDT and parathion-methyl were stable at least for five weeks in precolumns stored at room temperature. Methiocarb also was stable for this period but storing the precolumns at 4°C.

Keywords: Pesticide stability; solid phase extraction; polymeric precolumn

INTRODUCTION

The solid-phase extraction (SPE) of organic pollutants from aqueous matrices using reversed phase (RP) adsorbents, packed in plastic cartridges, stainless steel precolumns or Empore disks, has become one of the more efficient and simple

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sample preparation techniques for environmental water analysis. This is particularly true for the on-line SPE version, which can indeed be completely automated. In this technique, one or more precolumns are coupled to an HPLC column via switching valves, allowing the on-line extraction, sample cleanup, final separation and quantitation of the compounds of interest. A great number of on-line SPE methods for the determination of a wide variety of organic pollutants (polyaromatic hydrocarbons, phenols, pesticides, aromatic amines, etc.) at very low concentration levels in water have been reported[1–6].

On the other hand, the use of SPE disks and columns as alternative means for the transport of water samples is another interesting, but not sufficiently explored, application. Indeed, the problem of the transport and adequate preservation of water samples sometimes hinders the establishment of more ambitious and serious monitoring programs for natural waters, particularly when they come from remote regions of difficult accessibility. In 1986, Green *et al*[7] reported the use of submersible instrumentation for the *in situ* SPE of aqueous samples, avoiding the collection of the water itself and thereby eliminating many contamination and handling problems. However, in order to generalize the use of SPE materials for the collection and transport of water samples, a previous study of stability of the target analytes, adsorbed on the packing phase, is necessary. Some work has been done in this area during the last years. For example, it has been reported[8] that crude oil hydrocarbons stored for 100 days on Amberlite XAD-2 or C-18 silica, in the presence of oleophilic bacteria, showed no evidence of biological degradation. In other studies[9–10] it was demonstrated that pesticides adsorbed on Empore disks had an equivalent or greater stability compared to their storage in water at 4°C; the storage of the loaded disks at −20°C seemed to be the most favorable option for analyte preservation. SPE precolumns packed with octadecyl silica had also been used to establish the storage stability of organophosphorous pesticides, which generally offer degradation problems in water; with the exception of three pesticides, complete recovery was observed in precolumns kept at −20°C for eight months[11].

In this work we chose to examine the stability of pesticides from four different families in polymeric (PLRP-S) precolumns. Due to their strong retention properties, polymeric phases are often used for the SPE extraction and preconcentration of polar and medium polarity compounds from water. However, to our knowledge, only one previous study of pesticide stability in modern polymeric phases has been reported[12]. One advantage of using stainless steel precolumns instead of disks or plastic cartridges for the transport of samples is that the former are easily inserted in the HPLC apparatus and can be directly on-line analyzed. On the other hand, the four chosen pesticides, parathion-methyl (organophosphorous), methiocarb (carbamate), DDT (organochlorine) and 2,4-D

(phenoxy acid), are of environmental concern in our country and there is a need for a more continuous and careful monitoring of these compounds in river, dam and spring waters.

EXPERIMENTAL

Chemicals

HPLC-grade acetonitrile and methanol were from Prolabo and Merck respectively. Perchloric acid from Aldrich and sodium hydroxide from Baker were both analytical-grade reagents. Type 1 reagent water was obtained from a Nanopure deionizer (Barnstead Thermolyne). The pesticides, parathion-methyl, methiocarb, 4,4′-DDT and 2,4-D were purchased from Chem Service with certified degree of purity >99%. Stock solutions of the pesticides (1000 mg/l) were prepared by weighting and dissolving each compound in acetonitrile. Individual standards, also in acetonitrile, were prepared from the stock solutions at concentrations of 4 mg/l for 2,4-D and 3 mg/l for parathion-methyl, methiocarb and DDT. The standards were used to spike the aqueous samples and for direct loop injection to calculate solute recoveries.

Chromatographic analysis

HPLC-analyses were carried out with a Varian 5000 binary gradient system equipped with a 3200 variable wavelength detector from Thermolyne Separations, an Altex 210 A injector with an *in situ* 22 µl calibrated loop[1] and a reversed phase analytical column (150 × 4.6 mm I.D.) prepacked with 5 µm Hypersil ODS from Thermoquest. Chromatograms were recorded and integrated by a Hewlett-Packard 3396 Series II integrator. A 7000 Rheodyne valve was inserted between the injector and the HPLC column for the on-line elution of precolumns.

Solute recoveries were calculated by comparing the peak area obtained from the analysis of the precolumn with that obtained from a loop injection of the corresponding standard, which contained the same amount of pesticide as the preconcentrated sample (88 ng for 2,4-D and 66 ng for parathion-methyl, methiocarb and DDT). The standards were always injected with the precolumn coupled to the analytical column because both of them participate in solute retention and peak shape. The mobile phase was adjusted for each pesticide to have retention times of about 10 min at a flow-rate of 1 ml/min; this allowed the com-

plete elution of the sample matrix peak before the elution of the compound of interest. Mobile phases were acetonitrile-water mixtures in the following respective proportions: 50:50 (v/v) for parathion-methyl, 45:55 (v/v) for methiocarb, 75:25 (v/v) for DDT and 38:62 (v/v), with the aqueous fraction acidified to pH 1.3 with perchloric acid, for 2,4-D. Detection was performed at 230 nm except for parathion-methyl that was detected at 272 nm.

We chose to study the four pesticides individually because, as it will be shown later, the optimal conditions for their quantitative recovery during the extraction step are not the same. Besides, this gives the possibility to ameliorate or adapt the proposed analytical method for one pesticide in a particular sample, by including further cleanup and/or derivatization procedures in order to increase the selectivity or the sensitivity.

Sample preparation

Stainless-steel precolumns (20 × 2 mm I.D.) homepacked with 10 μm PLRP-S from Polymer Laboratories were used for the SPE of water samples. Before use, the precolumns were activated and conditioned with the following series of solvents (25 ml each): ethanol, reagent water, NaOH solution (pH 12), reagent water, $HClO_4$ solution (pH 1) and reagent water.

The sample preparation procedure was optimized to achieve complete recovery of the pesticides when the precolumns were analyzed immediately after loading. It was considered that in-field sample collection is usually carried out in glass containers and that sample filtration is often necessary to avoid the blockage of precolumn frits by suspended solids present in the water. In previous works[1,3,5], it has been demonstrated that organic compounds in aqueous solutions may easily remain adsorbed on the walls of glass recipients and on the surface of filters, especially when the solutes are highly hydrophobic. Therefore, to recover the adsorbed analytes, all the materials that have been in contact with the aqueous sample must be rinsed with an organic solvent (usually methanol or acetonitrile) and the latter must be added to the water sample before the SPE step. This also prevents the adsorption of the analytes on the walls of the final recipient. However, the breakthrough volume of a compound in an RP-precolumn decreases as the content of organic solvent in the sample increases. Therefore, it is very important to carefully optimize the volume of solvent used for rinsing, according to the hydrophobicity of the compound(s) of interest.

The following procedure was used to determine the appropriate content of organic solvent in the sample for each pesticide. Reagent water samples containing between 3 and 10% (v/v) of methanol were spiked with the pesticide (at 13.2 μg/l for parathion-methyl, methiocarb or DDT; at 17.6 μg/l and acidifying

the sample to pH 1 for 2,4-D) and 5 ml of this sample were loaded in the precolumn by means of an Eldex CC-30-S isocratic pump. The precolumn was inserted in the switching valve of the chromatographic system and was on-line analyzed using the established mobile phase for the particular compound. The sample with the minimum methanol content that gave a ~100% recovery was considered the optimal one for that compound. In the case of DDT, the obtained recoveries were always very low; therefore, a new set of experiments was carried out using between 5 and 30% (v/v) of acetonitrile in the sample instead of methanol.

Breakthrough volumes

Different volumes (10, 25 and 50 ml) of a sample of optimal composition, according to the previous experiments, containing a fixed amount of the studied pesticide in the volume assayed (88 ng for 2,4-D and 66 ng for the other) were loaded in the PLRP-S precolumn by means of the Eldex pump. The precolumn was further on-line analyzed and solute recoveries were calculated.

Stability experiments

From the results of the preceding experiments, water samples with the adequate content of methanol or acetonitrile were spiked at 2.64 μg/l for parathion-methyl, methiocarb or DDT, or at 3.52 μg/l and acidifying the sample to pH 1 with perchloric acid for 2,4-D. The PLRP-S precolumns were loaded with 25 ml of the sample, rinsed with 1 ml of reagent water, plugged at both ends without previous drying and stored at room temperature (15–20°C) or at 35°C in a column heather (Eppendorf CH-30). For each pesticide, duplicate on-line analysis of precolumns were performed immediately after loading and at various intermediate days during the one-week storage period. To compare the stability of the adsorbed pesticides with their stability in solution, the aqueous samples used to load the precolumns were also stored in a closed glass flask kept at room temperature and duplicate analysis were carried out the same days as the stored precolumns.

Reagent water was used to prepare the samples for the initial stability studies. Afterwards, a surface water from a dam (Necaxa Dam in the state of Puebla) without any treatment except filtering was used. Some characteristics of this water are, pH: 7.12–7.16, alkalinity: 30.9 mg of $CaCO_3$/l, chlorides: 1.73 mg of Cl/l, sulfates: 18.2 mg of SO_4/l, total hardness: 56.6 mg of $CaCO_3$/l. In order to observe the effect of a recommended preservative agent, additional studies were carried out with dam water containing 40 mg/l of sodium sulfite. The samples

were prepared as before and the stability of the pesticides in solution and adsorbed on the polymeric phase in the precolumn was compared.

Finally, the long-term stability (5 weeks) of parathion-methyl, methiocarb and DDT in precolumns stored at room temperature and at 4°C (only methiocarb) was examined. The samples for these experiments were prepared from dam water.

RESULTS AND DISCUSSION

Analytical method

Although the establishment of an analytical method for the studied pesticides was not the aim of this work, it was considered that the stability experiments should have to be performed under a set of conditions that were appropriate for a good analysis of the aqueous sample. Therefore, the composition and volume of the samples loaded in the precolumns were optimized for complete recovery of the analytes.

It was found that the minimum organic solvent content in the sample to avoid losses by adsorption of the pesticides on the walls of the recipient was: 4% (v/v) of methanol for methiocarb and 2,4-D (molecular solute; sample acidified to pH 1), 8% (v/v) of methanol for parathion-methyl and 25% (v/v) of acetonitrile for DDT. As expected, the required organic solvent content in the water sample is in direct relation with the compound hydrophobicity. From these results, the maximum volume of solvent that can be used to rinse the sampling bottle and the filter during the first stages of the sample preparation procedure can be deduced.

TABLE I Pesticide recoveries as a function of the sample volume loaded in the precolumn. Precolumn: 20 × 2 mm I.D. packed with 10 μm PLRP-S. Samples: reagent water with different proportions of methanol or acetonitrile, depending on the pesticide (see text), containing 88 ng of 2,4 D or 66 ng of parathion-methyl, methiocarb or DDT in the loaded volume

Volume (ml)	*Recoveries (%)*[a]			
	Parathion-methyl	*Methiocarb*	*DDT*	*2,4-D*[b]
10	100.5	100.5	100.6	100.1
25	99.7	99.8	100.1	99.9
50	76.2	71.0	75.1	94.3

a. Mean from duplicate experiments.
b. Sample acidified to pH 1 with perchloric acid.

On the other hand, Table I shows the results obtained from the breakthrough experiments for each pesticide in the PLRP-S precolumn. It can be observed that, with the sample composition used for each analyte, the breakthrough volume of the four pesticides is larger than 25 ml but lower than 50 ml. Therefore, for all the stability experiments, 25-ml volumes of the fortified sample containing the appropriate organic solvent proportion for the particular compound were loaded in the precolumns.

It is interesting to remark that the breakthrough volumes of the four pesticides are similar, despite the high hydrophobicity of DDT. This is of course due to the different content of organic solvent in the samples, but it means that a higher hydrophobicity is not a guarantee of higher sensitivity when SPE is used for the extraction and preconcentration of solutes from water samples. In fact, as the hydrophobicity of the solute increases, more organic solvent has to be added to the water sample in order to reduce losses by adsorption of the compound on the surface of all the materials that are in contact with the sample (vessels, filters, pump tubing, etc.). However, the latter provokes a parallel reduction of solute retention in the adsorbent of the SPE precolumn or cartridge and limits the volume of sample that can be preconcentrated.

Stability study

The stability of the four pesticides was evaluated from the recoveries determined at the end of each storage period. The reported results are the mean from duplicate experiments and the difference between recoveries obtained from two parallel experiments never exceeded 2%. The latter is an indication of the high precision of the analytical method.

TABLE II Pesticide recoveries after seven days of storage in the precolumn (room temperature or 35°C) or in the aqueous sample (room temperature). Samples prepared from reagent water

Compound	*Recoveries (%)*[a]		
	In Precolumn		*In solution*
	15–20°C	*35°C*	*15–20°C*
Parathion-methyl	97	94	92
Methiocarb	96	91	73
DDT	100	69	98
2,4-D	94	94	92

a. Mean from duplicate experiments.

The results of the experiments performed with fortified reagent water samples (Figure 1 and Table II) show that, in general, these pesticides are well preserved at least for 7 days either in the solution at room temperature or in the precolumns stored at room temperature and at 35°C. Only two exceptions were observed. The first one corresponded to methiocarb, which was slowly but continuously degraded in the aqueous sample, arriving to a loss of 27% after seven days. On the contrary, the stability of methiocarb adsorbed on the polymeric phase was very good (recoveries >90% after one week), even at 35°C and despite the fact that the precolumn void volume was filled with water. This indicates a lower reactivity for the adsorbed molecules, which may possibly be protected from reactive agents by the organic solvent layer that presumably covers the surface of activated reversed phases. The second exception observed in these experiments was for DDT in the precolumns stored at 35°C. Figure 1 shows that this pesticide remains relatively stable until the fourth day at this temperature, but at the seventh day its recovery has decreased to about 70%. This result was surprising considering the known high persistency of this pesticide in the environment. However, it has been reported[13] that the activity of DDT decreases at high temperatures, which in a certain way is consistent with the observed degradation. On the other hand, at room temperature DDT was the most stable of the four examined pesticides, either in solution or in the precolumn. Finally, it must be remarked that the good stability of parathion-methyl, DDT and 2,4-D in solution may be due, at least in part, to the presence of organic solvent in the prepared samples. The addition of small amounts of methanol or acetonitrile to aqueous samples is sometimes recommended for solute preservation.

In the experiments carried out with samples prepared from dam water (Figure 2 and Table III) the obtained results for parathion-methyl and DDT were similar to the previous ones. Both pesticides showed a good stability in the precolumns or in the solution kept at room temperature for seven days. Parathion-methyl also was stable in the precolumns at 35°C, but DDT again presented a loss of about 30% after one week at this temperature. On the contrary, the behavior of 2,4-D was completely different; this pesticide suffered a very rapid initial degradation in the dam water. Indeed, the analysis of the fortified sample performed only 30 min after its preparation gave a herbicide recovery of 79%. However, after the fast initial loss of 2,4-D in the sample, the degradation rate considerably decreased and the pesticide recovery after one week in the precolumns at both temperatures or in solution was over 60%. We cannot propose an explanation to this phenomenon, which only occurred with 2,4-D, a relatively stable pesticide known to persist more than 25 weeks in natural waters[14]. The last pesticide, methiocarb, again remained fairly stable in the precolumns at both temperatures during the seven-day period, but its degradation

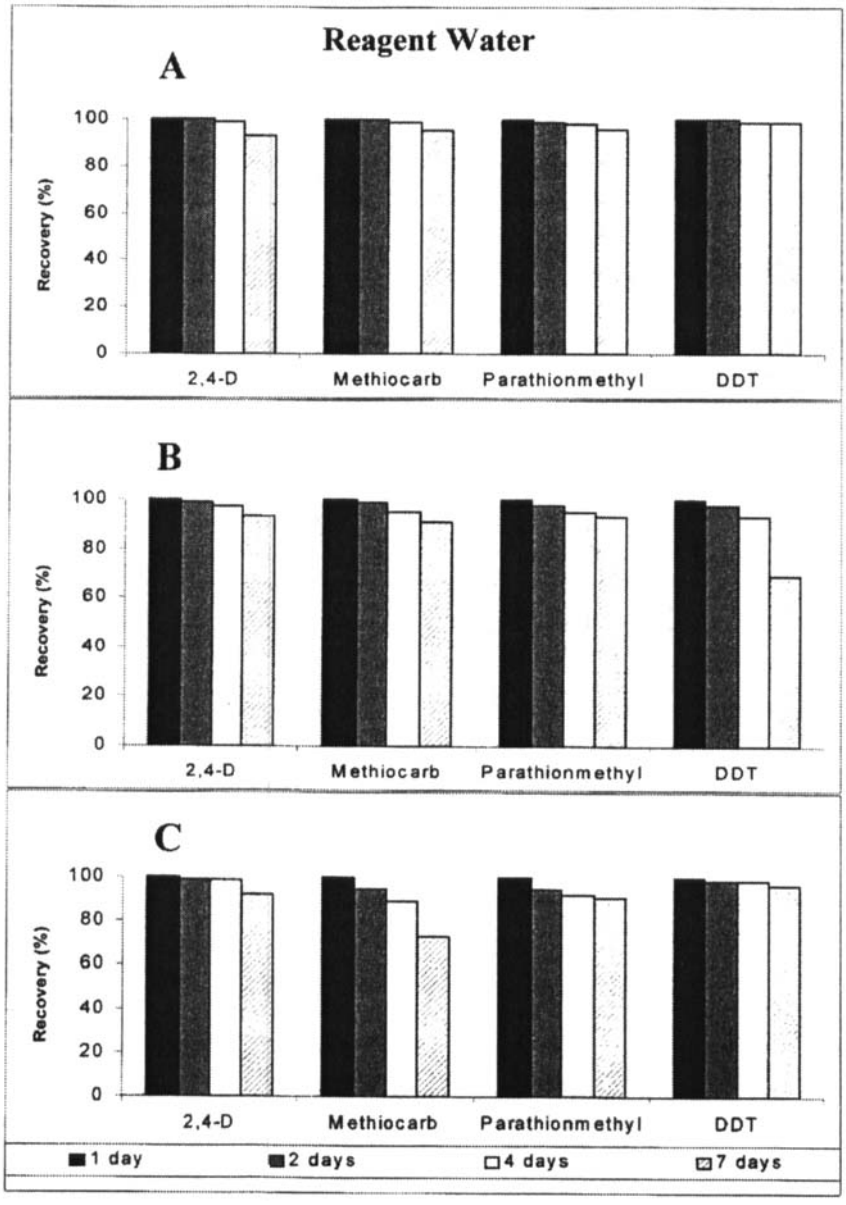

FIGURE 1 Stability of pesticides in (A) Precolumns stored at room temperature, (B) Precolumns stored at 35°C and (C) Aqueous sample kept at room temperature. Reagent water samples containing methanol or acetonitrile (experimental section) were spiked at 3.52 μg/l of 2,4-D or at 2.64 μg/l of methiocarb, parathion-methyl or DDT. The PLRP-S precolumns (20 × 2 mm I.D.) were loaded with 25 ml of a fortified sample

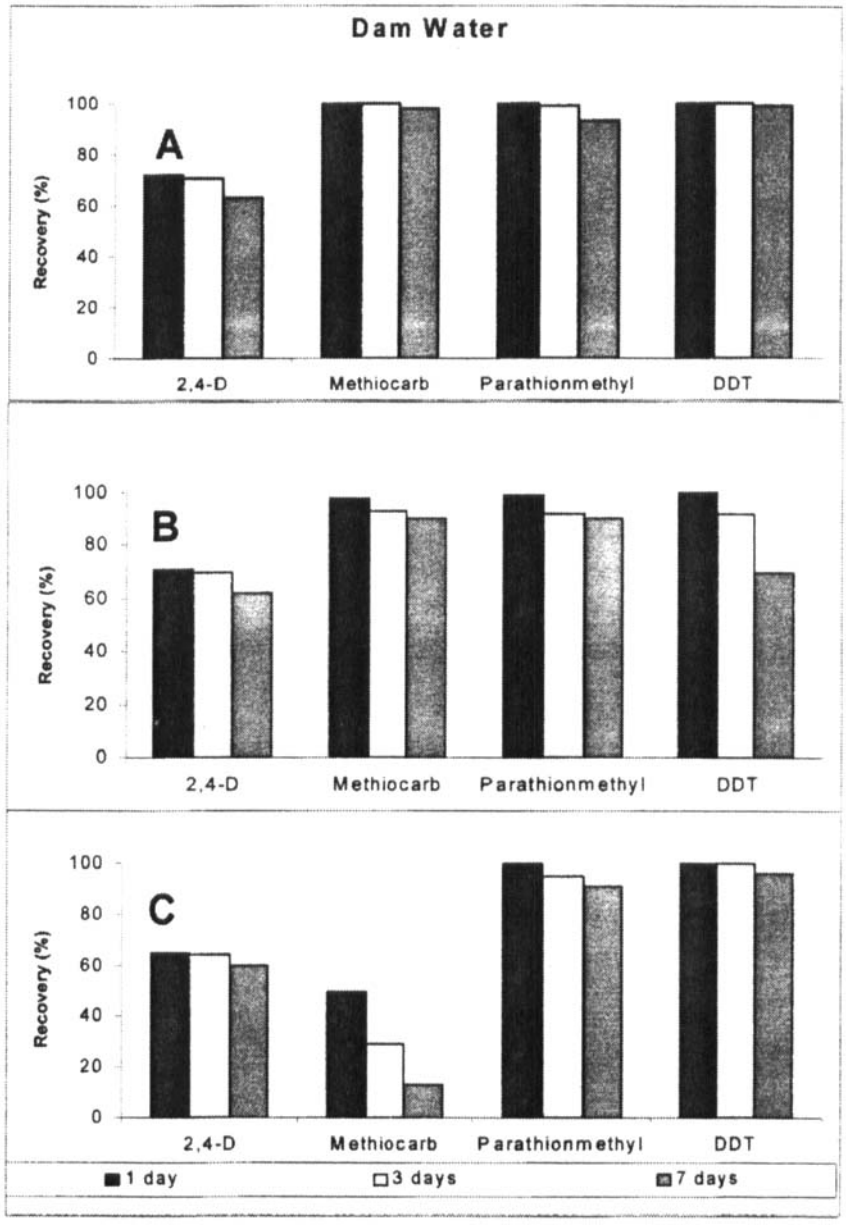

FIGURE 2 Stability of pesticides in (A) Precolumns stored at room temperature, (B) Precolumns stored at 35°C and (C) Aqueous sample kept at room temperature. Other conditions as in Fig. 1, except that the fortified samples were prepared from surface water of the Necaxa Dam (Puebla, Mexico)

in the dam water sample was more rapid than in the reagent water sample. Besides, the chromatograms obtained from the analysis of the fortified dam water in different days showed a new peak that progressively increased with time as the methiocarb peak decreased (Figure 3). The retention of the new peak was about 1.4 min lower than the methiocarb retention, indicating the formation of a metabolite more polar than the parent compound. Probably, methiocarb was hydrolyzed to its alcohol metabolite in this water. It is interesting to mention that this metabolite peak was never observed in the previous experiments with reagent water, although the methiocarb degradation after one week in that sample was almost 30%. This means that not only the speed, but also the metabolic route for the degradation of this pesticide in water are highly dependent on the aqueous matrix composition.

TABLE III Pesticide recoveries after seven days of storage in the precolumn (room temperature or 35°C) or in the aqueous sample (room temperature). Samples prepared from dam water

Compund	*Recoveries (%)*[a]		
	In Precolumn		*In Solution*
	15–20°C	*35°C*	*15–20°C*
Parathion-methyl	93	90	91
Methiocarb	92	90	13
DDT	99	73	97
2,4-D	64	63	61

a. Mean from duplicate experiments.

The addition of sodium sulfite to water samples is a common practice for analyte preservation. Table IV shows the results obtained in the experiments carried out with dam water containing 40 mg/l of sodium sulfite. The preservative agent provoked a slight decrease of the initial 2,4-D degradation in this water; as a result, the herbicide recoveries after seven days in the precolumns or in solution were 10% higher than in the previous experiments. Again, there was not a significant difference between the two media, or between the two storage temperatures. A similar result was observed for the stability of methiocarb after one week in the aqueous solution; its recovery was 10% higher than in the dam water without sodium sulfite, but it still remained too low (23% instead of 13%). The most interesting observed effect in this set of experiments was a remarkable increase of the DDT stability in the precolumns stored at high (35°C) tempera-

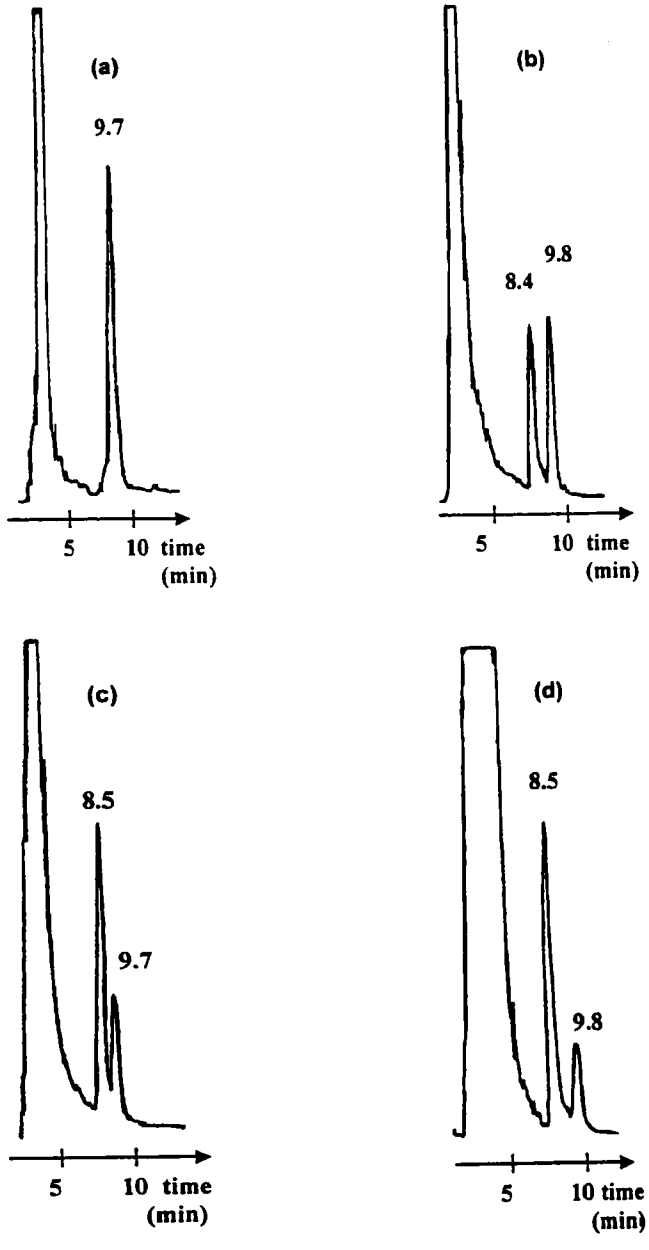

FIGURE 3 Chromatograms obtained from the on-line SPE-HPLC analysis of dam water spiked at 2.64 μg/l of methiocarb. The sample was analyzed after (a) 0 days (initial chromatogram), (b) 1 day, (c) 3 days and (d) 7 days of storage at room temperature. Chromatographic conditions described in the experimental section

ture. This was unexpected because, to our knowledge, sodium sulfite is not adsorbed on the polymeric reversed phase; neither could it be present in the precolumn void volume that was rinsed with reagent water after loading the sample. A deeper research should have to be done to understand the action of this salt on DDT.

TABLE IV Pesticide recoveries after seven days of storage in the precolumn (room temperature or 35°C) or in the aqueous sample (room temperature). Samples prepared from dam water containing 40 mg/l of sodium sulfite

Compound	*Recoveries (%)*[a]		
	In Precolumn		*In Solution*
	15–20°	*35°C*	*15–20°C*
Parathion-methyl	95	91	91
Methiocarb	99	92	23
DDT	97	93	98
2,4-D	74	75	73

a. Mean from duplicate experiments.

Finally, Table V shows the excellent long-term stability of parathion-methyl and DDT in precolumns stored at room temperature. The precolumns were loaded with the fortified dam water sample, without sodium sulfite, and were analyzed after five weeks of storage. The stability of methiocarb in the same conditions was not so good, a loss of 28% was observed after five weeks. However, in additional experiments where the precolumns were stored in a refrigerator (4°C) for the same period, methiocarb was completely recovered.

TABLE V Long-term stability. Pesticide recoverics after five weeks of storage in the precolumn. Samples prepared from dam water

Compound	*Recoveries (%)*[a]	
	15–20°C	*4°C*
Parathion-methyl	91	--
Methiocarb	72	99
DDT	98	--

a. Mean from duplicate experiments.

CONCLUSION

This study has demonstrated that the stability of parathion-methyl, methiocarb, DDT and 2,4-D adsorbed on a PLRP-S phase packed in a stainless steel precolumn is generally better or at least as good as their stability in the aqueous sample, even if the latter contains preservative agents.

If the ambient temperature is ≤ 35°C, the loaded precolumns can be stored at least for seven days without any significant degradation of the pesticides. The only exception is DDT, which requires a lower storage temperature (15–20°C) for a good stability. Indeed, at temperatures ≤20°C, parathion-methyl and DDT can remain stable in the precolumns for at least five weeks.

From these results, PLRP-S precolumns seem to be an excellent option for the transport of water samples containing the studied pesticides or similar ones. The pesticides are very well preserved in the precolumns during a time that should be sufficient in most cases to carry the samples to the analytical laboratory. The loaded precolumns do not need to be refrigerated and their small size and robustness allows the easy transport of many samples in one expedition.

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