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Short communication

Stability of polar pesticides on disposable solid-phase extraction precolumns

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Abstract

The stability of representatives of different groups of polar pesticides (triazines, phenylureas, carbamates, chlorinated phenols) sorbed from water samples onto a polymer sorbent and stored under different conditions was investigated. The results confirmed the stability of most of the pesticides stored on the sorbent during a seven-week period at room temperature or in the refrigerator after sorption from tap water. The differences between the stability of analytes when stored on wet or silica gel-dried sorbent were negligible. The pH value of the water sample had a significant influence on the stability of only those compounds that had acidobasic properties. The results obtained with surface water were similar to those obtained with tap water. In general, solid-phase extraction was confirmed to be a suitable technique when long-term preservation of analytes prior to analysis is required. © 1998 Elsevier Science B.V.

Keywords: Extraction methods; Pesticides; Solid-phase extraction

1. Introduction

Solid-phase extraction (SPE) has been proved to be an effective sample handling method for the analysis of organic contaminants in water [1,2]. One of its advantages is that the analytes sorbed onto the SPE column can be prevented from decomposing and, thus, can be stored for a certain period of time without a change in concentration or identity. This can be useful in the case of monitoring programmes, when the danger of alteration of the sample between in-the-field sampling and analysis in the laboratory can be minimized. Besides, transport of SPE cartridges is much more convenient than transport of bulky glass containers.

Green and LePape [3] did observe that XAD-2 macroporous resin and C_{18} had a preservative effect, which prevented a breakdown of sorbed

hydrocarbons by bacteria. Hydrocarbons stored on these solid phases for periods of up to 100 days in the presence of an oleophilic bacterial population showed no evidence of bacterial degradation. Recently, the stability of nineteen organophosphorus pesticides was investigated using precolumns from Prospekt (automated on-line SPE system) packed with C_{18} and stored under different conditions [4]. Acceptable stability was observed for most of the compounds tested. The results of a study on the stability of 34 selected pesticides extracted from water onto graphitized carbon black indicated that storage on the carbon material was a far better preservation procedure than storage in water at 4°C [5]. Also, in our previous experiments, we successfully stored cyclohexanone and cyclohexanol on a C_{18} SPE column for two weeks [6].

The aim of this work was to investigate the stability of representatives of different groups of polar pesticides (triazines, phenylureas, carbamates,

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chlorinated phenols) sorbed from water samples onto a polymer sorbent and stored under different conditions. Polymer sorbent was selected since it had been proved to be a suitable material for the pre-concentration of polar pollutants [7–9]. The influence of the time of storage, temperature, the presence of water in the cartridge during storage and the real sample matrix (surface water) was studied. The evaluation of the stability of sorbed pesticides was performed by their on-line desorption by the mobile phase into a C₁₈ LC column, followed by UV diode array detection (DAD).

2. Experimental

2.1. Chemicals

Metamitron, metoxuron, hexazinone, simazine, cyanazine, carbofuran, carbaryl, atrazine, diuron, propazine, linuron, CIPC, neburon, dinoseb, 2,4,5-trichlorophenol, pentachlorophenol and trifluralin were purchased as certified standards from Dr. Ehrenstorfer (Augsburg, Germany). All solvents and reagents were of analytical grade and were obtained from Merck (Darmstadt, Germany).

2.2. Apparatus

Pesticides were sorbed onto 10×2 mm Prospekt SPE cartridges (SPARK Holland, Emmen, Netherlands) packed with 15–25 mm PLRP-S polymeric material (Polymer Labs., Church Stretton, UK).

The precolumns were stored immediately after the preconcentration step. After the storage period had passed, the cartridges were placed into an on-line SPE–high-performance liquid chromatography (HPLC) system to elute and, subsequently, to analyse the pesticides. For this purpose, an LC-SAMOS system (Hewlett–Packard, Waldbronn, Germany) comprising a Prospekt SPE unit connected on-line to a HP 1090 HPLC with DAD UV detection was used. Elution was performed in the backflush mode. The system was fully automated. Analytes were separated in 250×4 mm I.D. analytical columns packed with 5 mm Hypersil BDS-C₁₈ using acetonitrile–0.01 M phosphate buffer, pH 3, as the mobile phase, under gradient conditions. The gradient profile was 5%

acetonitrile at the start and then to 90% acetonitrile in 55 min. The flow-rate was 1.0 ml/min. All compounds were detected at 210 nm.

2.3. Procedures

For the experiments with a model matrix, a solution containing 10 ppb of metamitron, metoxuron, hexazinone, simazine, cyanazin, carbofuran, carbaryl, atrazine, diuron, propazine, linuron, CIPC, neburon, dinoseb, pentachlorophenol and trifluralin in tap water was employed. The solution was prepared from stock solutions of pesticides in methanol. Tap water was preferred over distilled or ultrapure water to obtain realistic conditions in an aqueous matrix with a low organic load. In all experiments, 100 ml of standard solution of pesticides in tap water (without adjusting the pH, which ranged from 7.2 to 7.6) was forced through the cartridge and the loaded cartridge was stored under different conditions. To test each particular storage condition, eight cartridges were loaded simultaneously and two of them were always on-line desorbed into a HPLC–DAD UV system for analysis of pesticides according to the following schedule: Desorption immediately after loading, and one, two and seven weeks after loading, respectively. The conditions of storage of a wet (i.e., not dried prior to storage) cartridge were as follows:

- At laboratory temperature in a metal box. Silica gel was added into the box to enable the cartridge to dry.
- In the refrigerator in a metal box. Silica gel was added into the box to enable the cartridge to dry.
- In the refrigerator in a plastic sack.

To examine the influence of a change in the pH value, 100 ml of a standard solution of pesticides in tap water, adjusted to pH 3, were pumped through the cartridges and the cartridges were stored in a refrigerator in a metal box in the presence of silica gel. They were on-line desorbed using the same procedure as for unadjusted water.

To verify the results obtained with tap water, a short test was performed for fifteen pesticides (hexazinone, simazine, cyanazine, carbofuran, carbaryl, atrazine, diuron, propazine, linuron, 2,4,5-trichlorophenol, CIPC, neburon, dinoseb, pentachlorophenol, trifluralin) in a surface water matrix (river Nitra).

Blank river water was analysed prior to dissolving the pesticides, to avoid possible matrix interferences. A 100-ml volume of a 10-ppb solution of pesticides in unadjusted surface water was pumped through the cartridge. Simultaneously, six cartridges were loaded and two of them was desorbed immediately after loading, two were desorbed after one week and the remainder were desorbed after being stored wet for four weeks in a refrigerator in a plastic sack. To ensure the stability of the system's response during the whole experiment, all measurements were performed under the regime of control chart diagrams.

3. Results and discussion

The aim of the experiments was to explore the influence of storage temperature (storage at 4–5°C in the refrigerator and storage at laboratory temperature) and of the presence of water in the cartridge during the storage (stored with or without silica gel). Each particular experiment was performed twice and, for the final evaluation of the stability, mean values were used. During the whole experiment, the differences in results of two parallel samples did not exceed 20%.

The results obtained with wet cartridges stored in a refrigerator in a plastic sack (i.e. without silica gel) are shown in Fig. 1. From these data, it can be seen that only the concentration of carbaryl decreased significantly, while the other changes in peak areas did not exceed 20% and could be ascribed to typical deviation in the applied concentration range. [The National Pesticide Survey (NPS) and US Environmental Protection Agency (EPA) report permissible values of recovery for samples fortified at the $\mu\text{g}/\text{l}$ level of between 70 and 130%, i.e., up to 30% deviation [4]]. A noticeable fact is the appearance of a new compound, the concentration of which increased with time and that eluted at 15.7 min. It is supposed that this compound could be related to carbaryl, the only compound that apparently degraded.

Figs. 2 and 3 show the results obtained when cartridges were stored in a refrigerator in the presence of silica gel and from the experiments performed at laboratory temperature using silica gel,

respectively. It is apparent from these figures that the stability of the analytes tested under these conditions was similar to results obtained for cartridges stored without drying. The most important difference observed was that another new peak appeared, at 23.5 min, and there was more of this compound present when the cartridge was stored at laboratory temperature.

Considering the results from all three experiments performed with unadjusted tap water, it can be concluded that no remarkable differences in behavior of a particular pesticide under different storage conditions could be observed.

Acidifying the water sample prior to preconcentration is a common step applied in the SPE procedure to promote trapping of acidic analytes and it is also often used in general water quality screening procedures for organic pollutants. Therefore, the stability of pesticides sorbed from an acidified solution was examined as well. In this case, tap water containing the analytes at the 10 ppb level was acidified to pH 3 with hydrochloric acid prior to the preconcentration step. As can be seen in Fig. 4, acidifying the water sample improved the stability of carbaryl. This can be explained by the fact that hydrolysis of it is suppressed under acidic conditions [10]. Due to protonation of the amino group in metamitron at low pH values, it was not possible to trap this analyte by hydrophobic interactions onto a polymeric sorbent. Therefore, no data were obtained for metamitron under acidic conditions. Considering the behavior of other analytes at pH 3, the dispersion of results obtained for triazine herbicides and linuron increased. The results, however, were still acceptable. For the rest of the analytes, stability was similar to that observed after preconcentration of unadjusted water samples. The most probable reason for the missing peaks at 15.7 and 23.5 min was suppressed hydrolysis of their precursors.

Finally, the effect of a real water matrix on the stability of sorbed pesticides was investigated using a spiked unadjusted water sample from the Nitra river. Keeping the loaded cartridges in a refrigerator was selected as the means of storage. The results of this experiment (Fig. 5) indicated that there was no substantial difference between tap or surface water regarding their influence on the stability of tested pesticides.

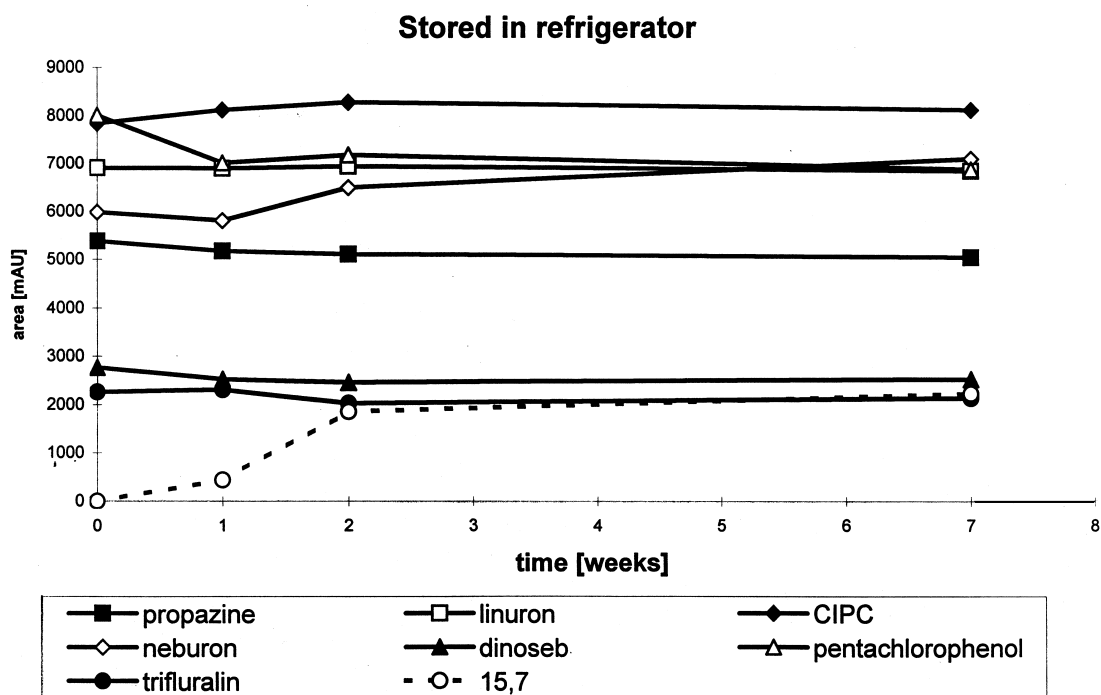
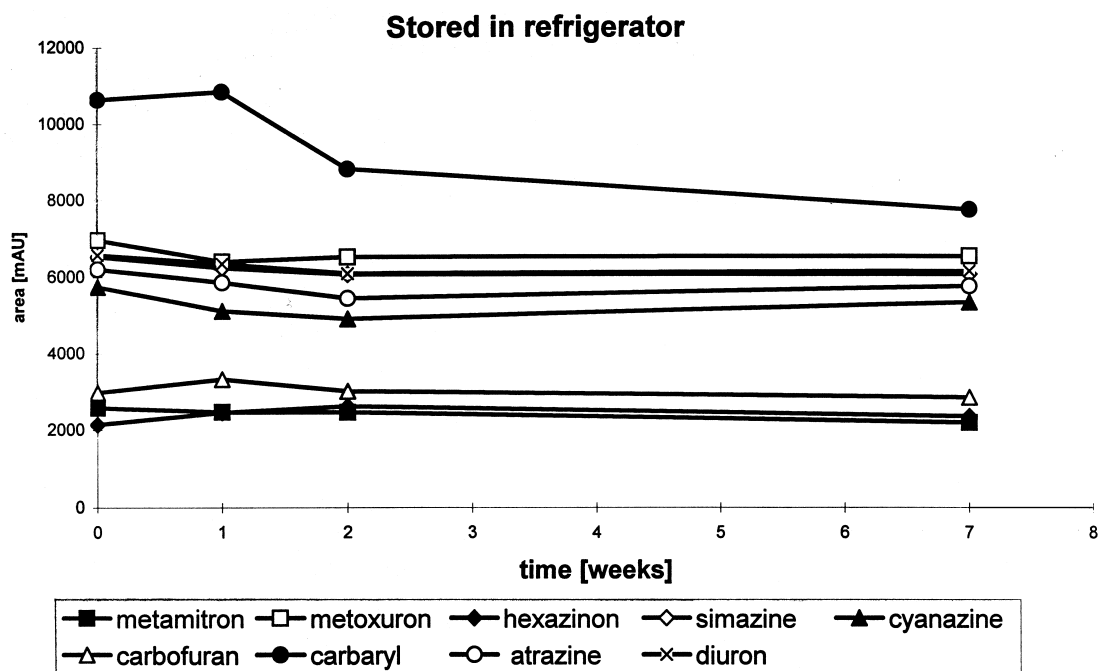
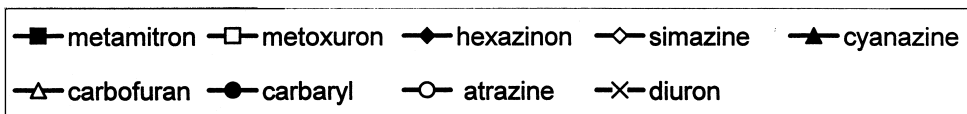
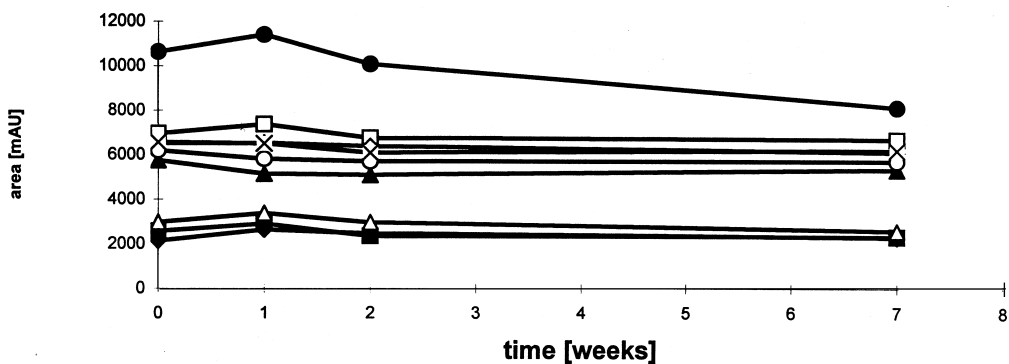


Fig. 1. Stability of pesticides sorbed onto polymer cartridges and stored wet in a refrigerator at 4–5°C. Stability is expressed as the change of chromatographic peak area vs. time.

Stored in refrigerator with silicagel



Stored in refrigerator with silicagel

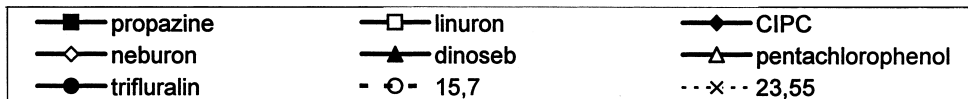
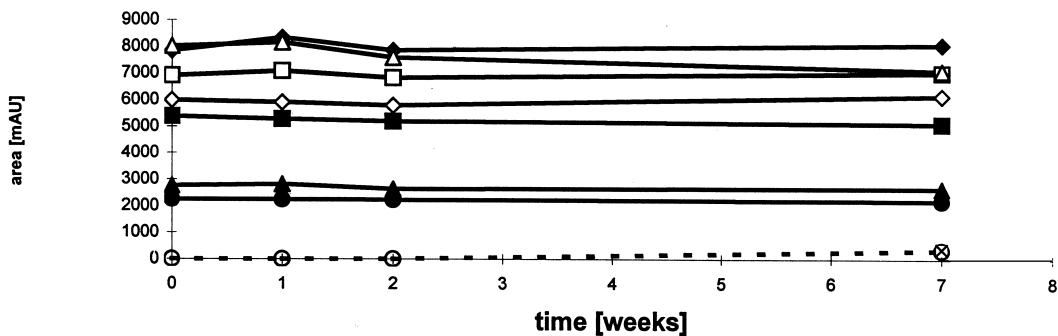
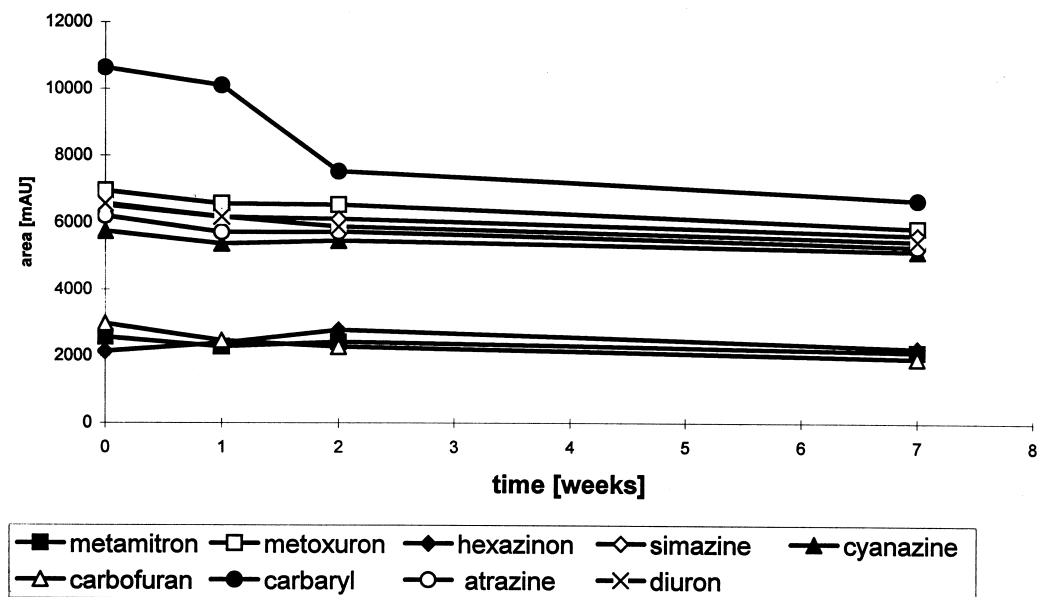


Fig. 2. Stability of pesticides sorbed onto polymer cartridges and stored in the presence of silica gel in a refrigerator at 4–5°C. Stability is expressed as the change of chromatographic peak area vs. time.

Stored in laboratory with silicagel



Stored in laboratory with silicagel

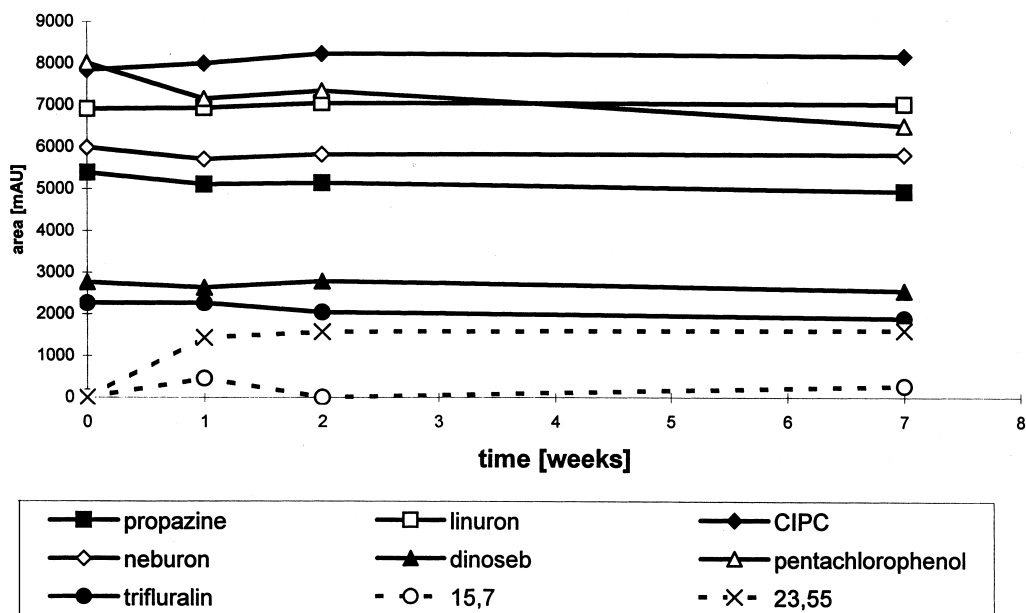


Fig. 3. Stability of pesticides sorbed onto polymer cartridges and stored in the presence of silica gel at laboratory temperature. Stability is expressed as the change of chromatographic peak area vs. time.

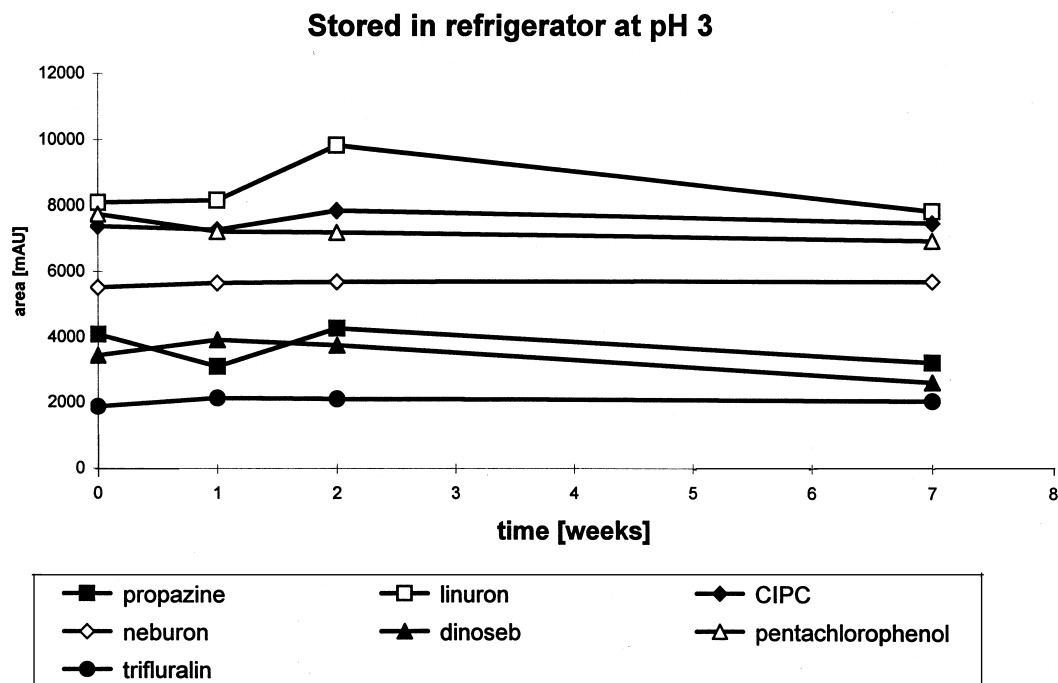
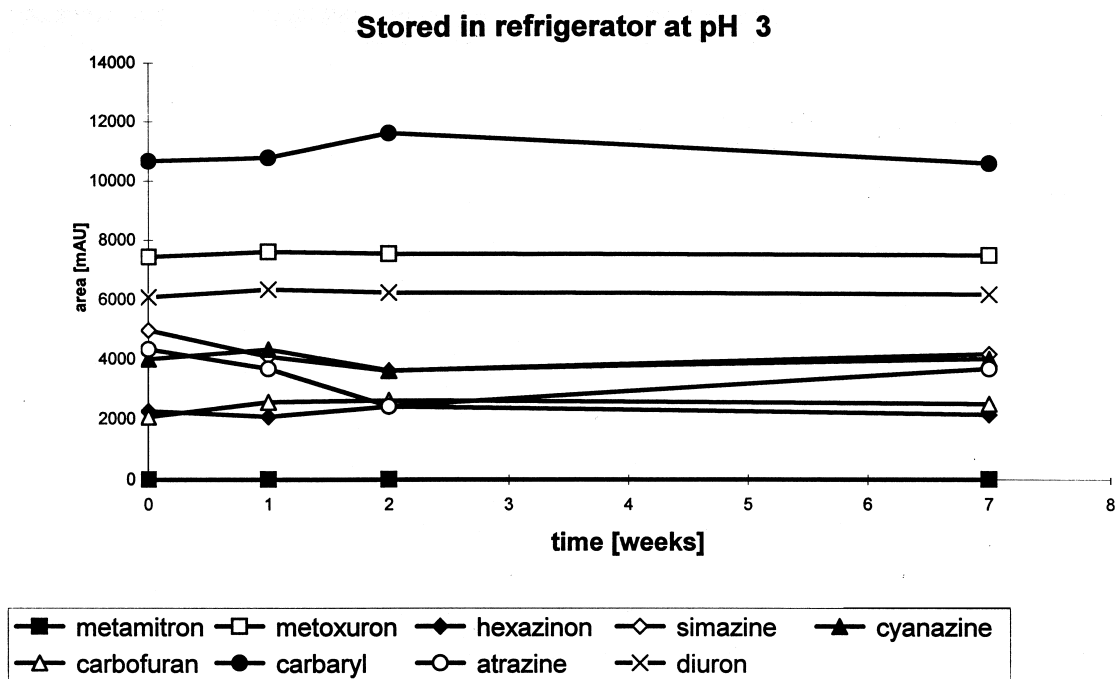


Fig. 4. Stability of pesticides sorbed from acidified water onto polymer cartridges and stored in the presence of silica gel in a refrigerator at 4–5°C. Stability is expressed as the change of chromatographic peak area vs. time.

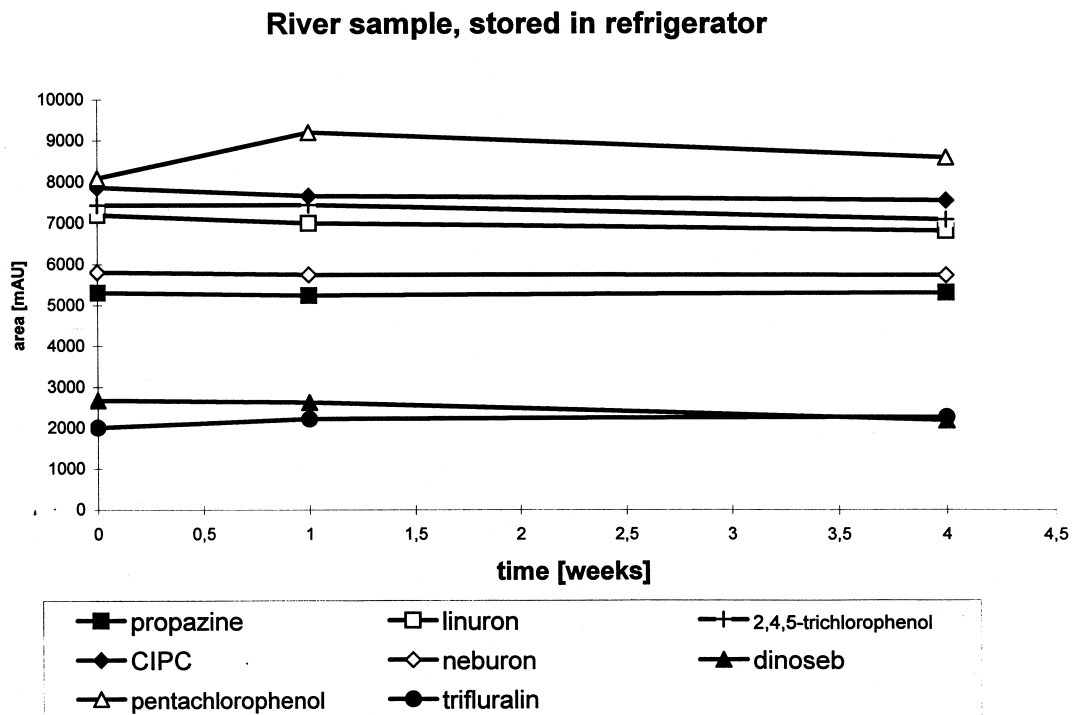
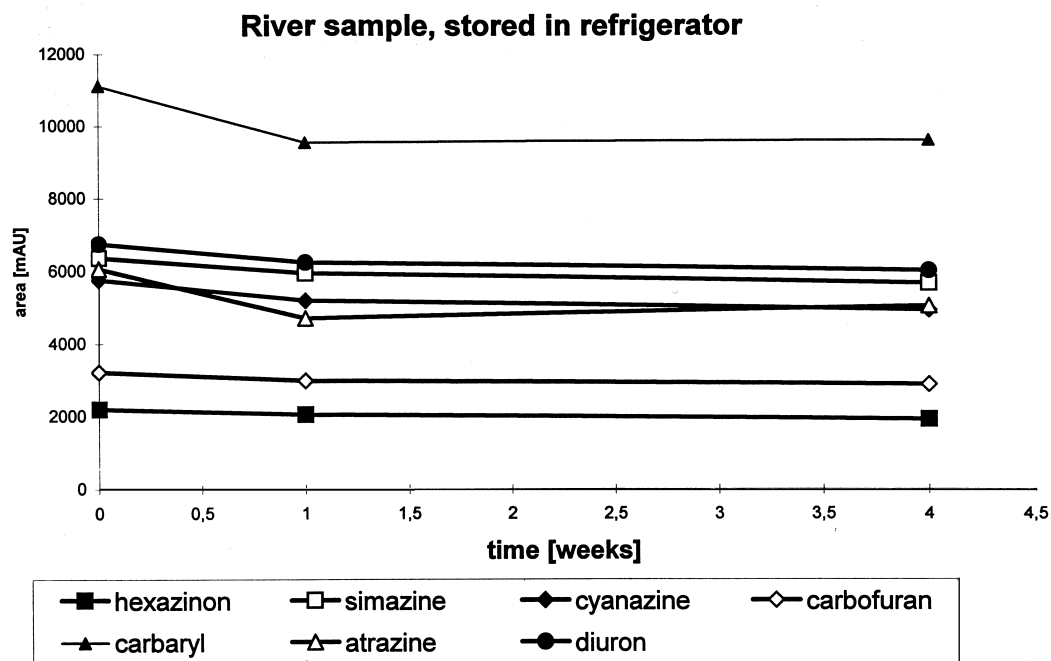


Fig. 5. Stability of pesticides sorbed from spiked surface water onto polymer cartridges and stored wet in a refrigerator at 4–5°C. Stability is expressed as the change of chromatographic peak area vs. time.

4. Conclusions

The results obtained in these experiments confirmed the stability of most of the pesticides stored for seven weeks under different conditions after their sorption onto SPE cartridges filled with polymer sorbent. The pH value of the water sample had a significant influence on the stability of compounds with acidobasic properties (e.g., met amitron, carbaryl), however, this factor is usually important for the total efficiency of the SPE procedure as well as for the chromatographic separation and, thus, it has to be considered with respect to the whole method. In general, there were no substantial differences in the stability of analytes when cartridges were stored at 4–5°C or at laboratory temperature. The presence of water in the cartridges during the storage period did not have any remarkable impact. The results obtained with surface water were similar to those obtained with tap water. Even though from the displayed line charts, the trend towards a very slight decrease in concentrations of stored pesticides within seven weeks can be observed for many analytes, these negative changes did not exceed the acceptable recovery change tolerance according to the NPS and the US EPA.

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