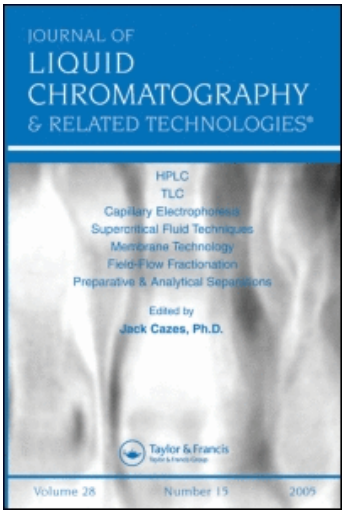

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Abstract: The objective of this work is to present a new procedure for the analysis of pesticides in water samples with use of solid phase extraction (SPE) and high performance chromatography with diode array detection (HPLC-DAD) and thin layer chromatography with diode array scanning (TLC-DAD). Pesticides were enriched from lakes water samples by solid phase extraction (SPE) on C18/SDB-1, C18, C18 Polar Plus, and CN cartridges. SPE was used not only for preconcentration of analytes but also for their fractionation. The analytes were eluted with methanol, and next with dichloromethane. Methanol eluates were analysed by HPLC-DAD, the dichloromethane eluates with TLC-DAD. The method was validated for precision, repeatability, and accuracy. The calibration plots were linear between 0.1 and 50.0 μg mL^{-1} for all pesticides, the correlation coefficients, *r*, were between 0.9992 and 1.000, as determined by HPLC-DAD. In the TLC experiments, the best fit for the calibration lines was found when the calibration data were analyzed using a second degree polynomial regression. Calibration plots lay between 0.1 and 17 μg $spot^{-1}$ for all pesticides, the correlation coefficients, *r*, were between 0.9974 and 0.9997, as determined by TLC-DAD. The limit of detection (LOD) was between 0.04 and 0.65 μg $spot^{-1}$ (TLC-DAD) and between 0.02 and 1.56 μg mL^{-1} (HPLC-DAD).

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Keywords: Environmental analysis, HPLC-DAD, Pesticides, SPE, TLC-DAD, Water analysis

INTRODUCTION

Thin layer chromatography (TLC) is a very useful and rapid chromatographic method. TLC in connection with modern videoscanning and densitometry provides the possibility of quantitative analysis. The last decade has seen strong growth in the use of TLC, especially in technically less advanced countries, where the latest technology for column chromatography with mass spectrometry is often too expensive for the solution of a local problem. Compared with high performance liquid chromatography (HPLC), thin layer chromatography is most effective for low cost analysis of samples requiring minimal cleanup, saving both time and expense. TLC and HPLC methods are separation techniques with high separation power. TLC coupled with a scanner with a diode array detector (TLC-DAD) and HPLC-DAD method can be successfully applied for more credible, repeatability, of correct identification of the analytes and their quantitative analysis in the environmental samples.

Analysis of environmental samples requires good extraction methods for sample preparation. Solid phase extraction can be used in water analysis, owing to the fact that it provides high concentration ratios. It also enables satisfactory cleanup of dirty samples. Huge amounts of water can be extracted with barely any effort, and eluted with small quantities of organic solvent. If analyzed substances represent different classes there is also the possibility to use SPE not only to preconcentrate, but also to partially fractionate the complex mixtures. The concentration of the pesticides in original samples is very low and a preconcentration method should be applied. Current methods to screen pesticides from environmental water matrices require an enrichment step, usually solid phase extraction (SPE), prior to analysis by high performance liquid chromatography (HPLC)[1–5] or gas chromatography methods.[6] TLC is the analytical method of choice for non-volatile and thermally labile pesticides. Application of modern diode array TLC scanners have several advantages;[7–9] a modern TLC scanner can measure thin layer chromatography plates simultaneously at different wavelengths, without destroying the plate surface and permits parallel recording of chromatograms and in situ UV spectra in the range of 191–1033 nm, so that it is possible for a more credible and correct identification of the compounds on a chromatogram. The TLC scanner DAD permits analysis of each compound at its optimum wavelength, thus offering

optimum sensitivity for detection of each component; the TLC scanner DAD allows obtaining a three dimensional chromatogram $A = f(\lambda, t)$; the TLC-scanner DAD enables comparison of parallel UV spectra of a compound with spectrum of its standard from the library of spectra; software is available which allows the user access to all common parameters used in HPLC-DAD: peak purity, resolution, identification via spectral library match etc.; the TLC scanner DAD is especially useful in correct identification of components, which occur in difficult, complicated mixtures, e.g., in plants extract and toxicological analysis.

At present, only a limited number of papers describe fibre optical scanning in thin layer chromatography, especially of pesticides. An application of fibre optical scanning densitometry for identification and quantitative analysis of fenitrothion in fresh apple juice was demonstrated.[10] In other papers an application of fibre optical scanning densitometry (TLC-DAD) and HPLC-DAD for identification and quantitative analysis of pesticides in water samples was demonstrated.[11,12]

Southeastern Poland, particulary Łęczyńsko-Włodawskie Lake District, is a region where intensive agricultural activity takes place. Farmers utilize large quantities of chemicals (e.g., pesticides). The objective of analysis is as a rule separation and identification of the composition of pesticides mixtures and quantitative analysis. The purpose of the present work is to demonstrate an application by HPLC-DAD and TLC-DAD for identification and quantitative analysis of pesticides in water samples.

EXPERIMENTAL

Standards of Pesticides

The standards of investigated pesticides were obtained from the Institute of Organic Industry (IPO, Warsaw, Poland). All standards were dissolved in methanol. The purity of standards of investigated pesticides were in the range of 98.6 to 99.7%.

Solvents and Mobile Phase Solutions

Acetonitrile, dichloromethane, methanol, *n*-heptane, and tetrahydrofuran were prochromatography grade from Merck (E. Merck, Darmstadt, Germany); ethyl acetate was proanalysis grade from Polish Reagents (POCh, Gliwice, Poland). Bidistilled water was used.

Adsorbents

In planar chromatography experiments, precoated HPTLC glass backed plates with Silica gel 60 F_{254}, 10 cm × 20 cm, 0.25 mm, No. 1.05729 (E. Merck, Darmstadt, Germany) were used.

SPE Cartridges

C18/SDB-1 (C18 500 mg on top +SDB 200 mg on bottom/6 mL), C18 (2000 mg/6 mL), C18 Polar Plus (3000 mg/6 mL), and CN (1000 mg/6 mL) Bakerbond SPE cartridges (J.T. Baker, Deventer, The Netherlands) were used.

Sample Preparation–Water Samples

Samples were collected in one liter (1 L) glass bottles, sampling at 20–50 cm below the surface of water. Just after collection, water samples were passed through 0.45 μm membrane filters (Milipore, Bedford, MA, USA). They were brought to the laboratory the same day of sampling and were stored at 4°C in the dark until solid phase extraction, which was carried out in seven days or less after sampling. Dates of acquisition: April, May, June, July, August 2007.

Procedures

Solid-Phase Extraction

For SPE assays, each cartridge was conditioned with 3 × 2 mL CH_2Cl_2, 3 × 2 mL methanol, and 3 × 2 mL water. After being loaded with the water samples (1 L; flow rate 10 mL min^{-1}; over pressure 75 mm Hg), the SPE column was washed with methanol-H_2O (5:95, v/v), followed by vacuum drying for 1 min and eluted with 5 mL methanol, followed by vacuum drying for 10 min, and next eluted with 5 mL CH_2Cl_2. Dichloromethane eluates were evaporated to dryness, redissolved in 1 mL dichloromethane, and analysed by TLC-DAD. The use of adsorbents other than silica, e.g., octadecyl silica, wettable with water (RP-18 W) decreased the time of vacuum drying in the described procedure and reduced the time of experiments, since the need for elimination of the excess of water after the elution step could be reduced.

HPLC Experiments and Calibration Procedure (HPLC)

After SPE, the methanol eluates were analysed at at $22 \pm 1°C$ using an Agilent Technologies 1200 Series chromatograph equipped with quaternary gradient pump with degasser set at a flow-rate 1 mL min^{-1}, and with diode array detection (DAD). Methanol eluates were injected into the eluent with a Rheodyne 20 μL injector. The HPLC apparatus was equipped with a ZORBAX Eclipse XDB-C18 150×4.6 mm column, $d_p = 5$ μm (Agilent Technologies, USA). The gradient applied was: start −30% B, 0–30 min – linear to 76% B, 30–35 min – linear to 100% B, 35–45 min: isocratic 100% B (A – H_2O; B – acetonitrile).

The calibration procedure was performed based on the peak areas of standards of pesticides, prepared as methanol solutions at nine concentration levels ($0.1 - 50$ μg mL^{-1}), with triplicate injection on the ZORBAX Eclipse XDB-C18 column at the same chromatographic conditions (Table 1).

TLC Experiments and Calibration Procedure (TLC)

The plates were developed to a distance of 9 cm in horizontal, Teflon DS chamber (Chromdes, Lublin, Poland). The plates were developed with ethyl acetate – *n*-heptane (20:80, *v*/v), (30:70, *v*/v), (40:60, *v*/v), or (70:30, *v*/v) as mobile phases. Next, the plates were scanned by the TLC scanner, diode-array spectrophotometer (J&M Aalen, Germany) working in the range $\lambda = 200$ to 600 nm with average optical resolution better than 2.0 nm.[7–9]

The calibration procedure was carried out based on the peak areas of standards of pesticides prepared as methanol solutions at nine concentration levels (0.1–17 μg $spot^{-1}$), triplicate automated application as 1 cm bands (AS 30, Desaga, Heidelberg, Germany) on $10\,cm \times 20\,cm$ glass backed silica gel TLC $60\,F_{254}$ plates (E. Merck; # 1.05729.0001). The plates were developed with ethyl acetate – *n*-heptane (20:80, *v*/v) or (30:70, *v*/v) as mobile phase. The peak area was plotted against the concentration of applied solutions, and the recorded relationship was quadratic (Table 2).

Validation of the TLC and HPLC Methods

The method was validated for precision, repeatability, and accuracy (Table 2). Instrumental precision was checked by repeated scanning of all pesticides (400 μg L^{-1}) 5 times and was expressed as coefficient of variation (CV). The repeatability of the method was confirmed by analyzing 400 μg L^{-1} samples of standard solution of all pesticides after

Table 1. Method validation parameters for the quantification of pesticides by the proposed SPE/HPLC-DAD method

Pesticide	t_r (min^{-1})	222 nm LOD ($\mu g\ mL^{-1}$)	222 nm LOQ ($\mu g\ mL^{-1}$)	Range ($\mu g\ mL^{-1}$)	r
Alachlor	19.542–19.736	0.39	1.17	1.8–50	0.9999
Atrazine	9.249–9.343	0.13	0.39	0.1–50	1.0000
Aziprotryne	15.764–15.858	0.44	1.35	0.3–50	0.9999
Bitertanol	18.391–18.528	0.22	0.65	1.8–50	1.0000
Buturon	13.201–13.269	0.02	0.08	1.2–100	1.0000
Chlorfenvinphos	20.805–21.028	0.02	0.06	0.6–33	1.0000
Clofentezine	24.683–25.111	0.34	1.04	0.5–15	0.9996
Flufenoxuron	30.991–31.083	0.05	0.15	0.3–50	1.0000
Hexaflumuron	25.303–25.392	0.10	0.29	0.3–50	1.0000
Hexazinon	4.696–4.843	0.05	0.15	0.3–50	1.0000
Isoproturon	9.501–9.575	0.03	0.10	0.6–100	1.0000
Lenacil	6.582–6.635	0.06	0.19	0.3–50	1.0000
Lufenuron	29.033–29.189	0.09	0.28	0.15–3.6	0.9995
Methabenzthiazuron	7.618–7.966	0.10	0.31	0.1–100	1.0000
Metamitron	2.927–2.986	0.25	0.75	0.3–50	1.0000
Metribuzin	7.546–7.602	0.03	0.08	0.3–50	1.0000
Neburon	20.393–20.469	0.10	0.30	0.3–50	1.0000
Procymidone	19.060–19.540	0.03	0.10	0.3–100	1.0000
Propaquizafop	26.081–27.405	0.05	0.16	0.3–50	1.0000
Quizalofop-p-Et	27.080–27.340	0.09	0.27	0.3–100	1.0000
Terbutryne	17.281–17.623	0.02	0.05	0.1–50	1.0000
Terbuthylazine	14.050–14.096	0.02	0.06	0.1–50	1.0000
Thiram	9.714–9.750	0.07	0.22	0.15–50	1.0000
Trifluralin	31.758–31.892	0.03	0.11	0.3–50	1.0000
α-cypermethrin	34.826–34.942	0.09	0.28	0.15–100	1.0000
Flufenoxuron (*270 nm)	30.991–31.083	0.06*	0.18*	0.3–50*	1.0000*
Tralkoxydim (*280 nm)	30.340–30.380	1.56*	4.72*	1.2–50*	0.9992*
Dinoseb (*370 nm)	13.334–13.480	0.41*	1.25*	0.6–50*	1.0000*

application on the HPTLC plate (n = 5) and was expressed as CV. Limits of detection (LOD) and limits of quantitation (LOQ) were also calculated according to the formulas: LOD = 3.3 (SD/S) and LOQ = 10 (SD/S), respectively; where SD was standard deviation of the response and S the slope of the calibration curve. The HPLC method was validated also (Table 1). Accuracy of the method was tested by performing recovery studies at 3 different levels. The average recoveries were calculated also.

Table 2. Method validation parameters for the quantification of pesticides by the proposed SPE/HPTLC-DAD method

Parameters	Clofentezine	Neburon	Chlorfen-vinphos	Lenacyl	Trifluralin	Thiram	Procymidone	Flufenoxuron	Tralkoxy-dim	Propaquiz-afop	Dinoseb
Instrumental precision (CV%, $n=5$)	0.84	0.76	0.88	0.98	0.86	0.72	0.99	0.77	0.87	0.74	0.77
Repeatability of standards (CV%, $n=5$)	1.01	1.19	0.98	1.26	0.94	1.21	1.31	1.18	0.97	1.23	1.22
Repeatability of sample (CV%, $n=5$)	0.23	0.18	0.45	0.14	0.4	0.19	0.17	0.16	0.46	0.17	0.18
Optimal λ (nm)	278.25	249.42	246.95	273.31	277.43	280.73	208.21	268.37	284.02	244.47	366.42
Limit of detection (μg spot^{-1})	0.23	0.06	0.16	0.04	0.06	0.16	0.65	0.1	0.07	0.06	0.08
Limit of quantification (μg spot^{-1})	0.7	0.18	0.49	0.12	0.18	0.49	1.92	0.31	0.22	0.17	0.24
Specificity	Specific	Specific	Specific	Specific	Specific	Specific	Specific	Specific	Specific	Specific	Specific
Linearity											
r (correlation coefficient)	0.9899	0.9979	0.9921	0.9987	0.9979	0.9785	0.9861	0.9962	0.9988	0.9973	0.9951
Range (μg spot^{-1})	0.1–1.5	0.2–1.0	0.5–1.0	0.2–1.0	0.3–0.9	0.1–1.0	2.0–11	0.1–2.0	0.3–1.0	0.1–1.0	0.2–1.0
Second-degree polynomial regression											
r (correlation coefficient)	0.9987	0.9995	0.9981	0.9996	0.9988	0.9988	0.9974	0.9977	0.9984	0.9992	0.9997
Range (μg spot^{-1})	0.1–10	0.2–11	0.5–17	0.2–5	0.3–17	0.1–17	2.0–17	0.1–17	0.3–17	0.1–17	0.2–17

RESULTS AND DISCUSSION

Fractionation of complex mixtures of analytes by solid phase extraction (SPE) combined with HPLC-DAD and TLC-DAD for identification of pesticides in water is presented. Analytes were eluted with methanol,

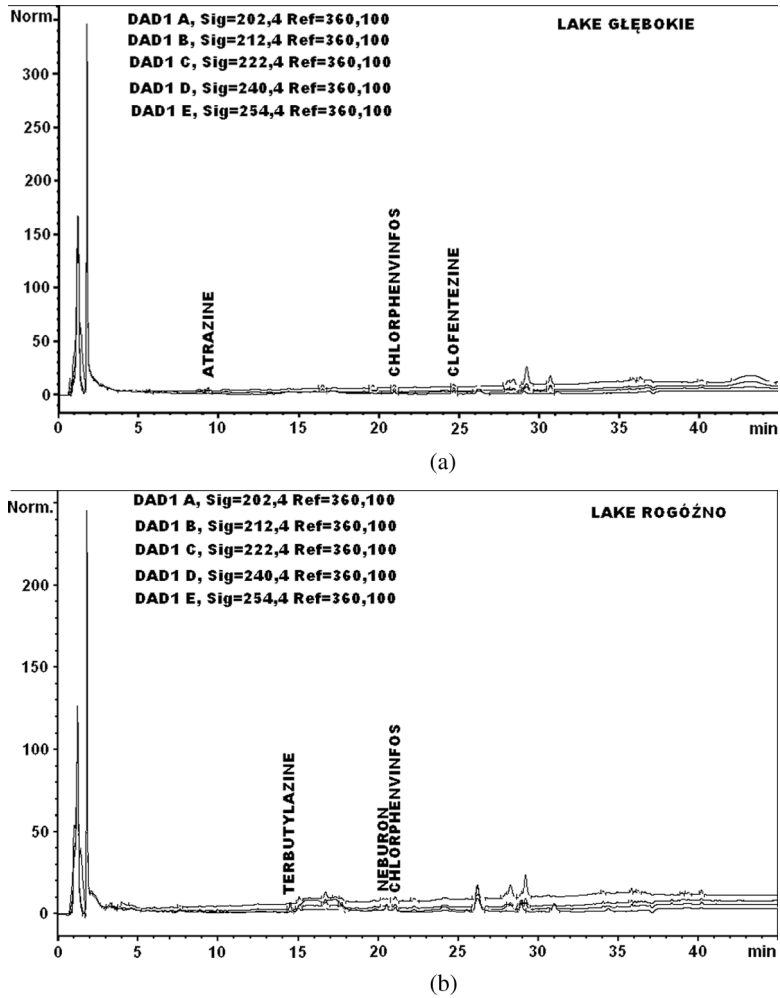

Figure 1. Chromatograms obtained: (a) after SPE with C18 Polar Plus cartridge of 1 L water from lake Głębokie sample (August 2007) showing three detected and quantified pesticides; (b) after SPE with Octadecyl cartridge of 1 L water from Lake Rogóźno sample (June 2007) showing three detected and quantified pesticides. Conditions are the same as in section HPLC experiments and calibrations procedure.

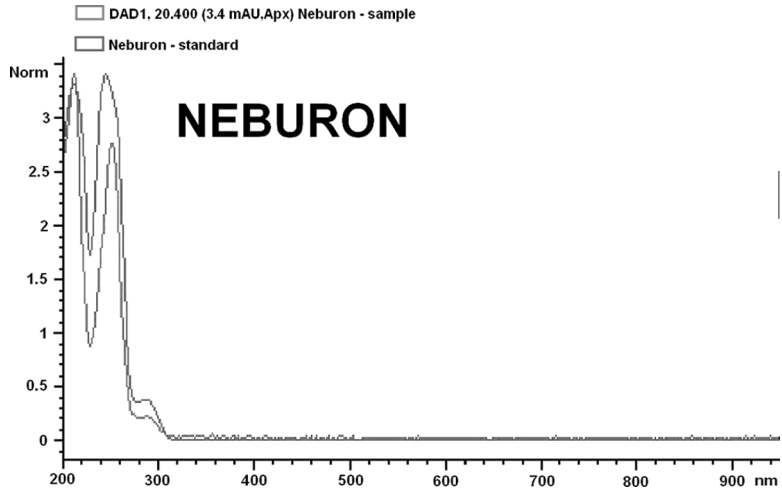

Figure 2. Comparison of UV spectrum of neburon found in surface water from Lake Rogóźno (June 2007) with UV spectrum of pesticide standard from library for neburon. Conditions are the same as in HPLC experiments and calibration procedure (HPLC).

and next with dichloromethane. Methanol eluates were analyzed by HPLC-DAD (Figure 1 a, b). Analyte identification was accomplished on the basis of the retention times of the analytes (Table 1) and by comparison between the UV spectrum of the reference compound in the library and the UV spectrum of the detected peak in the sample (Figure 2). Purity of peaks was determined also. A match equal or higher than 990 was fixed to confirm identification between both spectra for all the pesticides determined and the purity of the peaks (Figure 3). Dichloromethane eluates were analysed by planar chromatography with diode array scanning (TLC-DAD). Chromatograms were obtained at optimal wavelength for the pesticides determined (Figure 4). The identities of the bands of analytes in the water samples were confirmed by comparing their UV absorption spectra with those of the standards of these compounds (Figure 5). The peak purity index is a numeral measure of the quality of coincidence between two datasets. The peak purity index is a numerical index for the quality of the coincidence between to datasets. It is given by the least squares fit coefficient calculated for all intensity pairs in the two datasets under consideration. The following equation is applied:[10]

$$P = \frac{\sum_i (s_i - \bar{s})(r_i - \bar{r})}{\sqrt{\sum_i (s_i - \bar{s})^2 \sum (r_i - \bar{r})^2}} \quad (1)$$

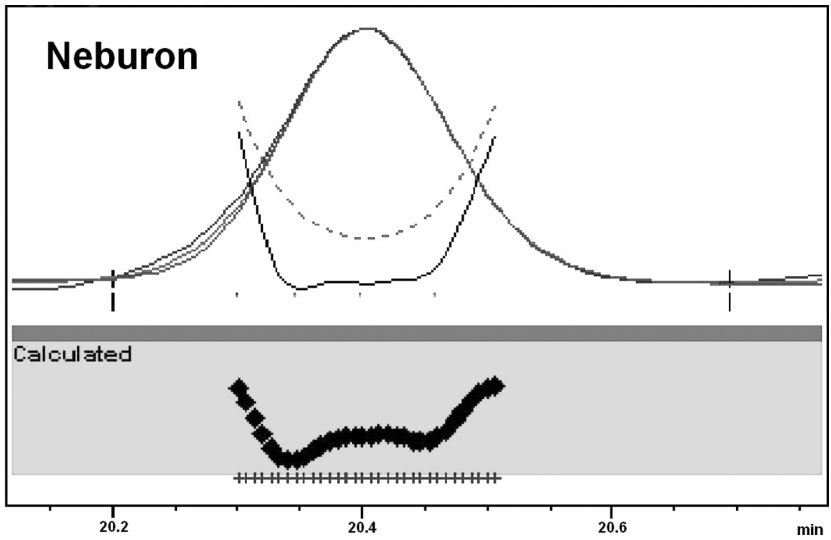

Figure 3. Purity of peak of neburon found in surface water from Lake Rogóźno (June 2007). Conditions are the same as in HPLC experiments and calibration procedure (HPLC).

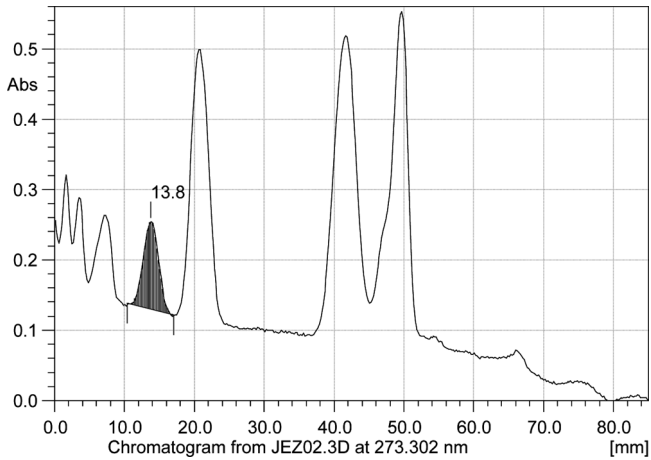

Figure 4. Chromatogram obtained of 1 L fortified water sample after SPE with C18/SDB-1 cartridge and TLC-DAD for optimal wavelength ($\lambda = 273.302$ nm) for flufenoxuron. Conditions: The silica plate was developed with ethyl acetate – *n*-heptane (30:70, *v*/v) as mobile phase. Other conditions are the same as in TLC experiments and calibration procedure (TLC).

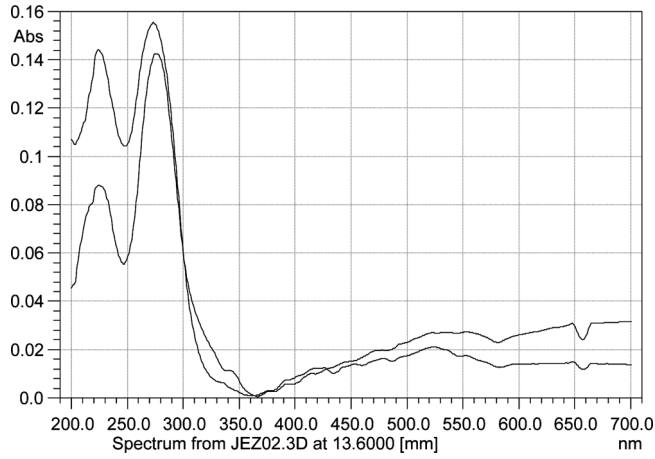

Figure 5. Comparison of UV spectrum of flufenoxuron standard with in-situ spectrum of fortified water sample after SPE and TLC-DAD. Conditions: The silica plate was developed with ethyl acetate – *n*-heptane (30:70, *v*/v) as mobile phase. Other conditions are the same as in TLC experiments and calibration procedure (TLC).

where s_i and r_i are the respective intensities for the same abscissa value, i is the number of data points, and $\bar{s}$ and $\bar{r}$ are the average intensities of the first and second dataset. A peak-purity index of 1 indicates that the compared spectra are identical. Least squares fit value (obtained by cross correlation) of spectrum from a fortified sample of water and spectrum from a tralkoxydim standard are presented also (Figure 6). Purity index (Pearson's r) for compared spectra was between 0.9326 and 0.9955.

The main purpose of the research was to find a combination of sorbents for the SPE method that would permit the determination of many classes of pesticides. Pesticides were determined on four types of SPE sorbents: octadecyl (C_{18}), C_{18} Polar Plus, cyanopropyl (CN), and combinations of them (C_{18}/SDB-1). Pesticides from water were extracted (concentrated and fractionated) by use of two different organic solvents and the extraction efficiency was checked by recovery experiments (Figure 7). Recovery rates were between 51% and 132% for both octadecyl (C_{18}) and C_{18} Polar Plus extraction materials, except for flufenoxuron, lufenuron, and isoproturon (39%, 17%, and 12% on octadecyl (C_{18}) and 40%, 17%, and 12% on C_{18} Polar Plus sorbents, respectively). The lowest recoveries were obtained on cartridges with cyanopropyl adsorbent, especially for buturon, isoproturon, metamitron, metribuzin, lenacil, and atrazine (1%, 1%, 2%, 2%, 6%, and 7%, respectively). The C_{18} and C_{18} Polar Plus sorbents are strongly recommended for

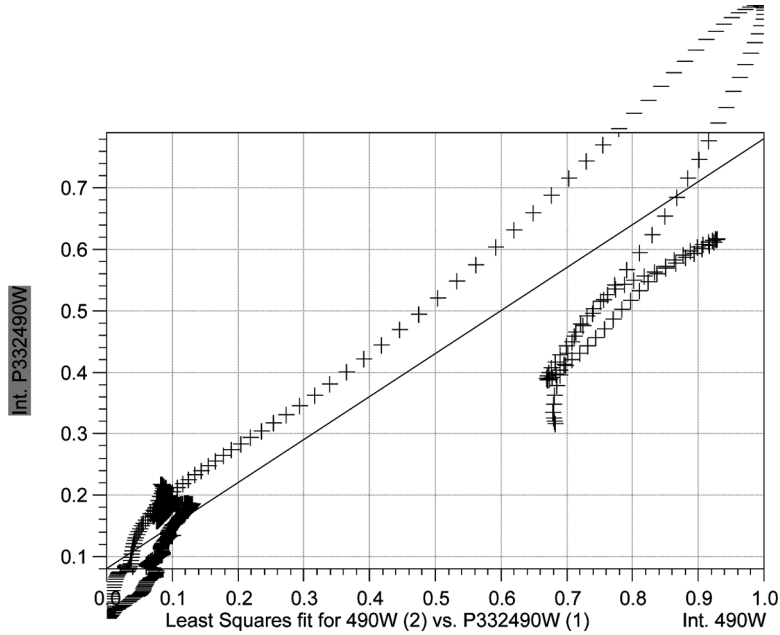

Figure 6. Least squares fit value (obtained by cross-correlation) of spectrum of flufenoxuron from fortified sample of water and spectrum from flufenoxuron standard. Purity index (Pearson's r) for compared spectra was 0.9326.

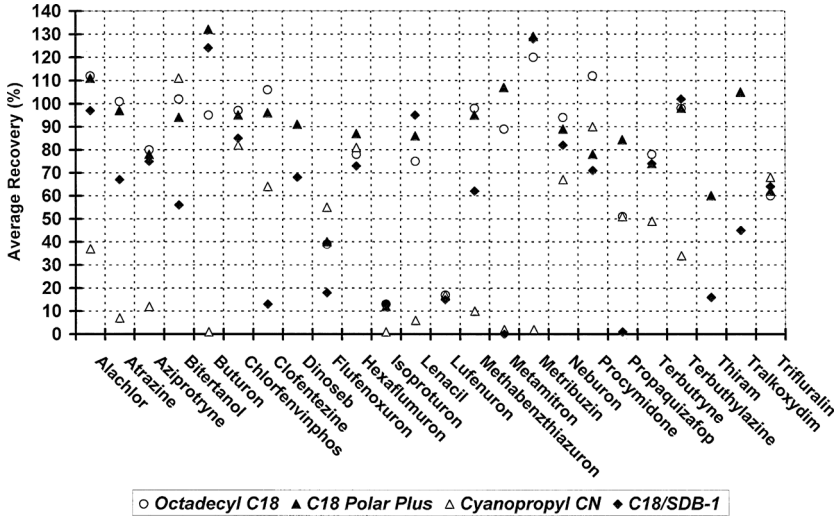

Figure 7. Average recovery (%) on four different cartridges—study of pesticides by the proposed SPE/HPLC-DAD method.

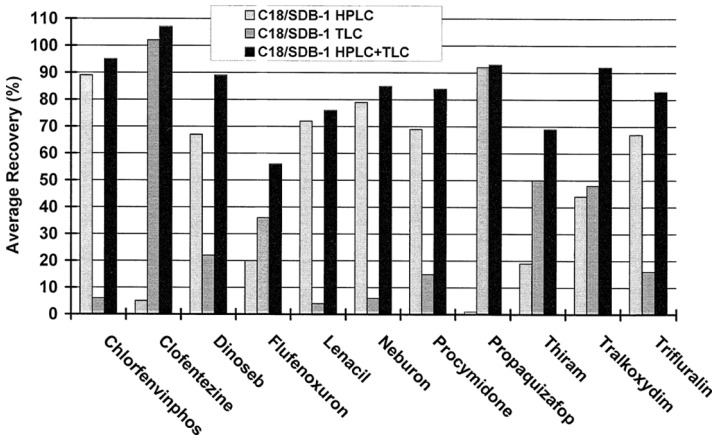

Figure 8. Recovery study of pesticides by the proposed SPE/HPLC-DAD and HPTLC-DAD methods (for water samples fortified 400 $\mu g\,L^{-1}$ of all pesticides).

concentration of analytes from water samples from the chemical classes of pesticides such as chlorotriazine herbicides (e.g., atrazine, terbuthylazine), methylthiotriazine herbicides (e.g., aziprotryne, terbutryne) and triazinone herbicides (e.g., metamitron, metribuzin). High recoveries for chlorotriazine and methylthiotriazine herbicides were obtained on cartridges with combined two sorbents: C_{18} and SDB-1 (C_{18}/SDB-1) also. Similar values of recoveries were obtained on four sorbents (C_{18}, C_{18} Polar Plus, CN, C_{18}/SDB-1) for the next classes of pesticides: chloroacetanilide herbicides (e.g., alachlor) and urea herbicides (e.g., methabenzthiazuron).

The sum of recoveries obtained on the cartridge with combined two sorbents: C_{18} and SDB-1 (C_{18}/SDB-1) and on C_{18} Polar Plus after HPLC and TLC experiments was also partially presented in Figure 8. Nonpolar pesticides e.g., trifluralin and clofentezine are strongly retained on C_{18} Polar Plus material and partially eluted with methanol and finally, with dichloromethane. Extraction with C_{18}/SDB-1 cartridges leads to a very satisfactory sum of recoveries, between 69% and 107%, with a relative standard deviation (RSD) of $\pm 0.8 - 3.8\%$. For flufenoxuron the sum of recoveries was lower. Clofentezine and propaquizafop are strongly retained in C_{18}/SDB-1 cartridges and pesticides were finally eluted by dichloromethane. Average recoveries for propaquzafop on C_{18}/SDB-1 cartridges were 1% and 92% for the methanol eluate, which were analysed by HPLC-DAD, and the dichloromethane eluate analysed by TLC-DAD, respectively. The sum of recoveries for propaquizafop obtained on C_{18}/SDB-1 cartridge was 93%. Average recoveries for clofentezine on C_{18}/SDB-1 cartridges were 5% and 102% for the methanol and

Table 3. Results obtained for the analysis of pesticides in lakes from the Łęczyńsko-Włodawskie Lake District (southeastern Poland)

Sorbent (SPE)	Dates of aquisition	Pesticide	Concentration (μg L^{-1}) $\lambda = 222$ nm					
			Lake Głębokie	Lake Krasne	Lake Rogóźno	Lake Majdan Zahorodyński	Lake Zagłębocze	Fajsławice pond
C18 POLAR PLUS	May 2007	Chlorphenvinfos	—	5.89	2.64	—	—	—
		Atrazine	1.13	—	—	—	—	0.85
		Trifluralin	—	—	—	—	—	1.43
		Procymidone	—	—	—	—	—	2.78
		Benomyl	0.54	0.45	—	—	—	—
	June 2007	α-Cypermethrin	1.25	—	—	—	—	—
		Methabenzthiazuron	0.55	—	—	—	—	—
		Procymidone	0.89	—	—	—	—	—
		Propaquizafop	1.26	—	—	—	—	—
	July 2007	Clofentezine	—	6.21	1.79	31.44	2.24	2.69
		Hexaflumuron	—	—	0.86	1.49	—	—
	August 2007	Lenacyl	—	—	—	2.26	—	1.97
		Atrazine	0.99	—	—	—	—	—
		Clofentezine	1.30	—	—	—	—	—
		Chlorphenvinfos	1.52	—	—	1.89	—	—
Octadecyl	May 2007	Chlorphenvinfos	—	2.34	—	—	—	—
		Procymidone	—	—	2.92	—	—	—
		Trifluralin	—	—	1.49	—	—	—
	June 2007	Chlorphenvinfos	—	—	1.14	—	—	—
		Terbutylazine	—	—	0.71	—	—	—
		α-Cypermethrin	—	—	—	0.81	—	—

		Methabenzthiazuron	—	—	—	0.33	—	—
		Neburon	—	—	1.25	2.85	—	—
		Propaquizafop	—	—	—	0.76	—	—
	July 2007	Clofentezine	18.68	10.60	—	—	9.21	—
		Flufenoxuron	1.70	—	—	—	—	—
		Hexaflumuron	1.22	2.79	—	—	1.54	—
CN	May 2007	Procymidone	—	—	1.43	—	—	1.78
		Trifluralin	—	—	2.03	—	—	—
		Chlorphenvinfos	—	3.65	—	—	3.41	—
	July 2007	Atrazine	—	—	1.04	—	—	—
		Alachlor	—	—	—	—	—	—
		Clofentezine	7.06	6.29	—	—	8.23	4.07
		Hexaflumuron	1.04	—	—	—	—	—
	August 2007	Chlorphenvinfos	—	—	5.39	—	—	—
		Lufenuron	—	—	—	—	4.56	—
C18/SDB	May 2007	Trifluralin	—	—	1.42	—	—	—
		Atrazine	—	—	—	—	—	1.16
		Chlorphenvinfos	—	2.24	—	—	—	1.94
		Alachlor	5.26	—	—	—	—	—
	July 2007	Bitertanol	—	—	—	—	—	—
		Clofentezine	—	—	1.65	—	—	—
		Terbutylazine	—	—	—	—	1.59	—
	August 2007	Atrazine	3.56	—	—	—	—	—
		Chlorphenvinfos	8.34	—	—	—	—	—
		Lenacyl	—	1.25	—	—	—	—

dichloromethane eluates, which were analysed by HPLC-DAD and TLC-DAD, respectively. The sum of recoveries for clofentezine obtained on C_{18}/SDB-1 cartridge was 107%. The C_{18}/SDB-1 cartridge with combined two sorbents: C_{18} and SDB-1 connect the properties of two adsorbents. The obtained results – recoveries, the fractionation experiments, and determination of analytes by two chromatographic techniques HPLC-DAD and TLC-DAD can be used for the selection of the most suitable eluents and SPE cartridges for selected analytes or the whole group of the analysed compounds.

The efficiency of the cleanup method and SPE procedure was evaluated using real water samples from lakes from Łęczyńsko-Włodawskie Lake District (Southeastern Poland). The results obtained from May to August 2007 are presented in Table 3. Chlorphenvinfos and trifluralin were detected with the highest frequency in water samples. Chlorphenvinfos was detected in the highest amounts also. Clofentezine was detected also in methylene chloride eluates of samples determined by SPE and TLC-DAD, but below the level of quantitation and above the level of detection.

Summing up, the described procedure can be used for correct identification of pesticides in environmental samples. Levels of pesticide residues in drinking water and surface waters is of public concern and according to the European Union directive on water quality (98/83/CE), the maximum concentration admissible for pesticides is 0.1 μg/L for individual compounds and 0.50 μg/L for their sum.[13] The described method can be used to screen pesticides in water on lower levels than presented above, after loading much larger samples of water and concentration of analytes. Then, eluates should be combined and evaporated to dryness and redissolved in a very small quantity of solvents.

CONCLUSIONS

The described methods enable monitoring of popular pesticides of different classes, ureas, triazines, amides, and others, widely used in the Łęczyńsko-Włodawskie Lake District in Poland and other locations worldwide. The present methodology proved to be a reproducible and suitable alternative to the conventional methods and to other chromatographic techniques, used to screen different classes of pesticides in water samples.

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