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# Resolution by polarographic techniques of atrazine–simazine and terbutryn–prometryn binary mixtures by using PLS calibration and artificial neural networks

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The simultaneous polarographic determination of atrazine–simazine and terbutryn–prometryn binary mixtures is reported. The polarographic signals of these compounds show high overlap, and for this reason different multicomponent approaches such as partial least squares (PLS) and artificial neural networks (ANNs) were utilized to determine each compound in their respective mixtures. Calibration models were made from solutions containing river water and known concentration of the pesticides. The results obtained for synthetic samples and river water samples spiked with known amount of these pesticides were satisfactory. For terbutryn–prometryn mixtures the lowest standard deviations and the best results in the prediction were achieved with ANN.

## Introduction

Atrazine, simazine, terbutryn and prometryn are pesticides which belong to the 1,3,5-triazine family, and they are used extensively in agriculture as herbicides. The properties of the 1,3,5-triazines derivatives are determined by the substituent at position 2, which is usually chlorine (atrazine and simazine), methoxy (prometryn) or thiomethyl (terbutryn). On the other hand, aminoalkyl groups in positions 4 and 6 have a less marked effect. It has been demonstrated that 1,3.5-triazines have mutagenic and sometimes pathogenic effects on living organisms.[1] They have a long persistence, which leads to an accumulation in soil and crops that have been treated directly.[2] Moreover, they can be present as pollutants, *e.g.*, in water[3,4] and fruits.[5]

Chromatographic techniques have been used widely in the determination of these pesticides. In HPLC, UV and electrochemical detectors are utilized in the analysis of water samples of different origin, soils and oils. Similar kinds of samples are analysed by using GC techniques. The four analytes mentioned above have been determined together but more frequently the studied mixture is atrazine–simazine. In general, a preconcentration step is needed to determine ppb levels.

Polarography, which is less expensive than chromatographic techniques, is another possibility in the analysis of these mixtures. In the literature, exhaustive studies of the polarographic behaviour of the atrazine, simazine, terbutryn and prometryn can be found, and different techniques such as dc (direct current), DPP (differential pulse polarography) and AdSV (adsorptive stripping voltammetry) have been used. The methods proposed have been applied to their determination in waters,[6–14] soils[13,15] and pears,[10] in different media such as methanol, 50% v/v water–ethanol, micellar and emulsified media. Taking into account the proximity of the potential values of atrazine and simazine and of terbutryn and prometryn, the simultaneous analysis of the respective binary mixtures by direct measurements, is not possible. For this reason, the resolution of the binary mixtures by polarographic techniques through the utilization of chemometric methods [partial least squares (PLS) and artificial neural networks (ANNs)] was investigated in this work. Previously, a basic polarographic study was accomplished to select the optimum chemical and instrumental conditions, where the differences between each compound in the respective mixtures would be maximal.

## Experimental

### Apparatus

Two systems of electrochemical equipment were used. The first was an Autolab (Eco Chemie, The Netherlands) PSTAT10 computer controlled potentiostat with a Metrohm (Herisau, Switzerland) 663 VA stand. The system was controlled *via* a Tystar PC 486 microcomputer equipped with the General Purpose Electrochemical System (GPES), version 3.0, software package. The second system was a Metrohm 693 VA processor with a Metrohm 694 VA stand connected to a Tystar PC 486 microcomputer equipped with the 693 VA Backup Version 2.2 software package. Both stands include a three-electrode cell with an Ag/AgCl(s)/KCl reference electrode, a platinum wire auxiliary electrode and a dropping mercury working electrode. The Grams 386 (Galactic Industries, USA) Level 1 Version 2.0 software package with the PLS Plus Version 2.1G application software[16] was used for the application of the PCR and PLS factor analysis based multivariate calibration methods. Neural Unscrambler software version 1.02 from CAMO (Trondheim, Norway) was also used.

### Reagents

Pesticides were obtained from Riedel-de Haën (Seelze, Germany) (atrazine and simazine) or from Chem Service (West Chester, PA, USA) (terbutryn and prometryn) and were used without further purification. Stock standard solutions in ethanol (100 ppm) were prepared by weighing. More dilute working standard solutions containing 10% ethanol were prepared by

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suitable dilution. A stock Britton–Robinson buffer solution was also prepared. Diethyl ether and ethanol were of HPLC grade and all other chemicals were of analytical-reagent grade.

### General procedure for the simultaneous determination of atrazine–simazine and terbutryn–prometryn binary mixtures in river water

In order to achieve a lower detection limit, preconcentration of the samples is proposed. In a separating funnel, 100 mL of river water (previously filtered) with $1.5 \times 10^{-7}$ M of the pesticides or more are placed and HCl is added to obtain a pH value around 5.8. Subsequently, extraction with 25 mL of diethyl ether is made, shaking the mixture vigorously for 5 min. The organic phase is separated and collected in a 25 mL calibrated flask where it is evaporated by a flow of nitrogen. This extraction step is repeated once more on the aqueous phase remaining, collecting also the organic phase in the same 25 mL calibrated flask.

Ethanol (10% v/v) and 5.0 mL of Britton–Robinson buffer (pH 2.0) are added to this 25 mL calibrated flask, then the mixture is diluted to volume with Milli-Q grade water (Millipore, Bedford, MA, USA), deoxygenated by passing nitrogen through the solution for 8 min, and the DPP polarogram is recorded between −0.75 and 1.05 V with a scan rate of 6 mV $s^{-1}$ and a pulse amplitude of −100 mV.

The polarogram, suitably converted, is used to determine the concentration of each pesticide by using the respective optimised calibration matrices for each mixture. The calibration matrices are calculated by the application of the PLS or PCR methods or an artificial neural network. These calibration matrices are constructed from the polarograms of samples containing between $5 \times 10^{-7}$ and $2 \times 10^{-6}$ M of atrazine–simazine or terbutryn–prometryn, prepared in the medium already mentioned and in the presence of 5 mL of river water (taken from different locations along the river).

## Results and discussion

The polarographic study of these pesticides was carried out in an ethanol–water medium (10% v/v) in order to ensure the solubilization of the compounds, by using sampled dc, DPP and cyclic voltammetric (CV) techniques. The objective was to select the optimum chemical and instrumental conditions for the determination of the pesticides in their respective mixtures, where the differences between the polarographic signals will be greater.

### Influence of pH

The study of the influence of pH was carried out by using a Britton–Robinson buffer in the pH range 2.2–6. Atrazine and simazine exhibit two waves (dc sampled) at pH < 3 [Fig. 1(A)]. The $I_{lim}$ of these waves (for both compounds) remains constant at pH < 3 whereas at higher pH just one wave is observed with an $I_{lim}$ value resulting of the sum of the two waves. For pH > 5, disappearance of the waves is observed. The $E_{1/2}$ values of these waves are shifted towards more negative potentials as the pH is increased [Fig. 1(B)].

Similar information is obtained by using DPP and CV, but in this case just one peak (even in CV) with a shoulder (DPP) appears throughout the pH range (Fig. 2). $E_p$ changes linearly with pH ($E_p$ = −0.0664pH −0.785 for simazine and $E_p$ = −0.0661pH −0.787 for atrazine). The $I_p$ remains constant in the pH range 2.2–3.2 and decreases at higher pH. CV demonstrates the total irreversibility of the overall process for these compounds.

With respect to terbutryn and prometryn, just one wave is observed by sampled dc in the pH range studied (2.0–7.0), showing a maximum. $I_{lim}$ remains constant in the pH range 2–6.5 and it disappears at higher pH. $E_{1/2}$ changes with pH. By DPP only one peak is observed (Fig. 3), but in this case the intensity value increases until pH 3.7 (probably owing to the appearance of the above indicated maximum) and decreases at higher pH. $E_p$ changes linearly with pH ($E_p$ = −0.0570pH

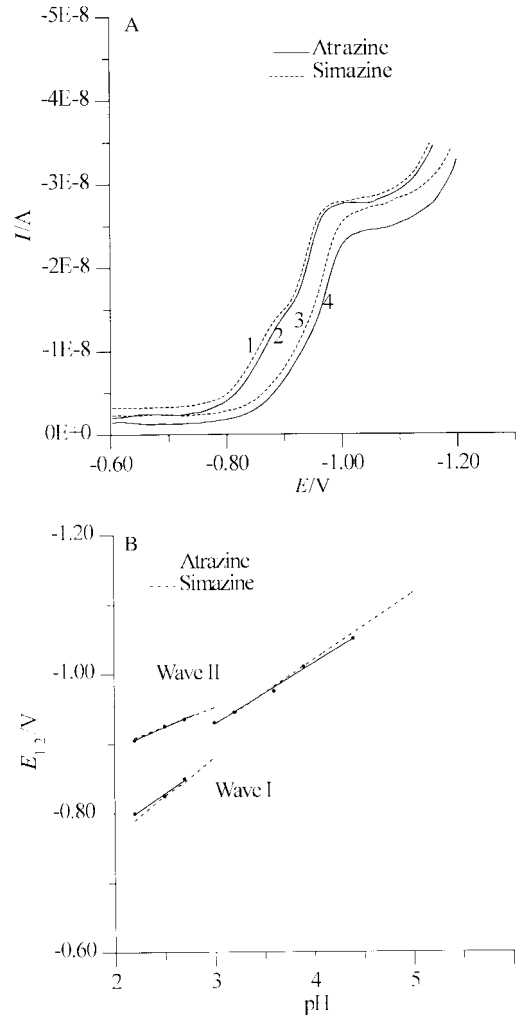


**Fig. 1** (A) Sampled dc polarograms, simazine and atrazine (2 ppm). 1 and 2, pH 2.7; 3 and 4, pH 3.2. (B) Influence of pH on $E_{1/2}$.

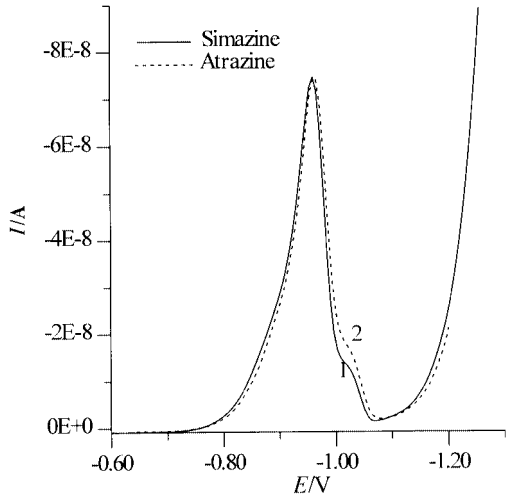


**Fig. 2** DPP polarograms, simazine and atrazine (2 ppm), pH 2.7 ($\Delta E$ = −50 mV).

$-0.888$ for terbutryn and $E_p = -0.570\text{pH} - 0.879$ for prometryn). Similar results are obtained by CV: just one wave throughout the pH range studied is observed and the process is also irreversible. On the other hand, the symmetrical shape of the waves probably indicates adsorption phenomena, as mentioned in the literature.

Based on the above results, a pH of 2.5 was selected for subsequent work.

### Influence of other variables

The study of the influence of instrumental variables such as pulse amplitude and drop time was made by DPP at pH 2.5 (Britton–Robinson buffer), with solutions containing 2 ppm of pesticide. The variation of $I_p$ with pulse amplitude is linear in the range $-10$ to $-100$ mV for atrazine and simazine. A $-100$ mV pulse amplitude was selected based on the maximum difference between their polarograms (with respect to the shoulder). For terbutryn and prometryn there are two linear stretches in the variation of $I_p$ *vs.* pulse amplitude with an intersection point at $-40$ mV. However, a $-100$ mV pulse amplitude was selected because the difference between the $I_p$ for these compounds is higher.

The influence of temperature in the range 10–40 °C was studied by using sampled dc polarography. One initial (prior to heating) and other final polarograms were recorded, the last ones after cooling the sample to the initial temperature, in order to demonstrate the stability of the compounds against heating. The $I_{lim}$ of the waves of these compounds increased with increases in temperature, with temperature coefficients for the first wave of atrazine and simazine of 1.5 and 1.7% $°C^{-1}$ and for the second wave 2.8 and 3.2% $°C^{-1}$, respectively. The temperature coefficients for terbutryn and prometryn are 2.0 and 2.8% $°C^{-1}$, respectively. This behaviour indicates the participation of adsorption processes. The adsorptive character of the reduction processes of these compounds is also demonstrated by the linear relationship observed between the currents and the scan rate in CV (scan rates between 10 and 500 mV $s^{-1}$).

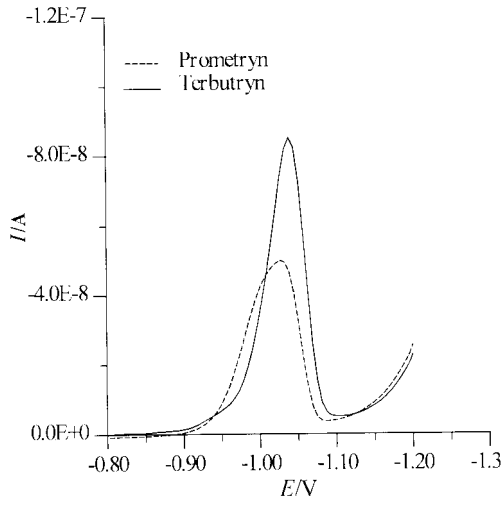


**Fig. 3** DPP polarograms, terbutryn and prometryn (2 ppm), pH 2.6 ($\Delta E = -50$ mV).

### Influence of concentration. Analytical figures of merit

The proportion of ethanol was fixed at 10% for the determination of atrazine, simazine, terbutryn and prometryn. Samples with different concentrations of each compound were prepared in triplicate and the DPP current was plotted against concentration. Good linearity was obtained for all the indicated waves, as shown in Table 1, which also gives the statistical parameters corresponding to the univariate regression analysis. The analytical sensitivities were calculated as the ratio between the standard deviation of the regression of $y$ to $x$ (signal to

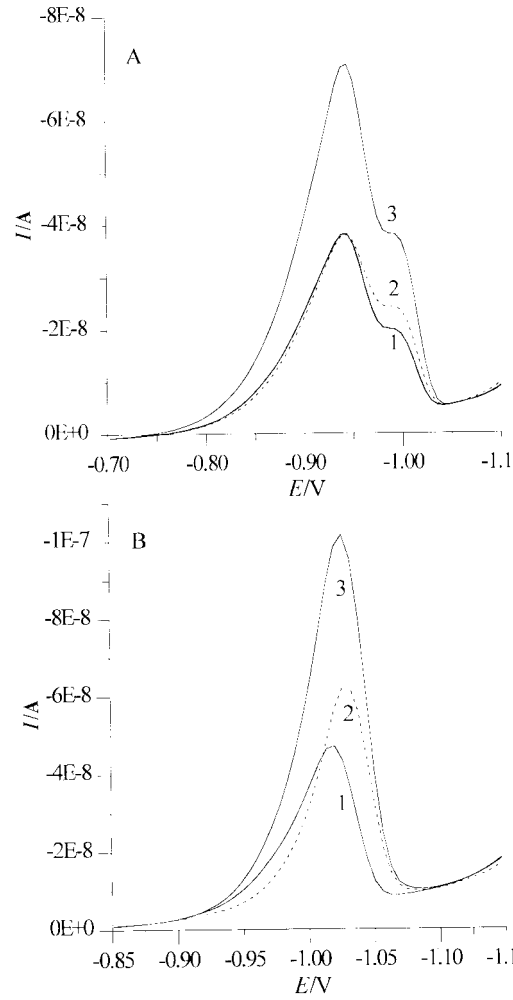


**Fig. 4** DPP polarograms for (A) (1) simazine, $1.98 \times 10^{-6}$ M; (2) atrazine, $1.86 \times 10^{-6}$ M; (3) atrazine, $1.86 \times 10^{-6}$ M + simazine, $1.98 \times 10^{-6}$ M and (B) (1) prometryn, $1.99 \times 10^{-6}$ M; (2) terbutryn, $1.99 \times 10^{-6}$ M; (3) prometryn + terbutryn, $1.99 \times 10^{-6}$ M, respectively.

**Table 1** Influence of concentration on the DPP currents (10% ethanol, pH 2.4, $\Delta E = -100$ mV)

| Compound | Range studied/ $10^7$ M | Equation[a] | $r^2$ | Analytical sensitivity ($\times 10^{-8}$) | DL/$10^8$ M |
|---|---|---|---|---|---|
| Atrazine | 5–50 | $I = 1.81 \times 10^{-2} C + (3.60 \times 10^{-10})$ | 0.9996 | 3.48 | 9.4 |
| Simazine | 5–50 | $I = 1.71 \times 10^{-2} C + (4.03 \times 10^{-10})$ | 0.9998 | 2.13 | 5.2 |
| Terbutryn | 5–50 | $I = 3.02 \times 10^{-2} C - (2.79 \times 10^{-9})$ | 0.9998 | 2.77 | 7.2 |
| Prometryn | 5–50 | $I = 2.07 \times 10^{-2} C - (1.03 \times 10^{-9})$ | 0.9999 | 1.70 | 4.4 |

[a] $I$ is the intensity in nA and $C$ is the molar concentration.

concentration) and the slope of the straight lines;[17] the detection limits (DLs) were obtained by Clayton *et al.*'s method,[18] selecting false-positive and false-negative probabilities of 0.05.

### Determination of atrazine–simazine and terbutryn–prometryn binary mixtures by application of PLS methods

The polarograms of these pesticides (Fig. 4) show a high degree of overlap and for this reason it is not possible to determine the concentration of each of them in the respective mixtures by measuring the intensity at their peak potential values. This problem can be solved by using chemometric techniques.

**Atrazine–simazine binary mixture.** For atrazine and simazine a training set (calibration matrix) of 20 samples in the concentration range $5 \times 10^{-7}$–$5 \times 10^{-6}$ M was prepared and their DPP signals were subjected to the PLS algorithms. The potential region used for the analysis of data was from −0.75 to −1.05 V, which implies 51 experimental points.

To select the number of factors for PLS methods, Haaland and Thomas's criterion[19] was used. The statistical parameters found are given in Table 2.

The ability of the optimized models using the PLS-1 and PLS-2 mathematical algorithms was examined in the resolution of synthetic binary samples. Recoveries of 79–116% for atrazine and 86–110% for simazine were obtained for both methods.

**Terbutryn–prometryn binary mixture.** For terbutryn and prometryn, the training set consisted of 18 samples in the concentration range $5 \times 10^{-7}$–$5 \times 10^{-6}$ M. The potential region used for the analysis of data was from −0.86 to −1.10 V, which implies 41 experimental points. Haaland and Thomas's criterion was also used for the selection of the number of factors. Statistical parameters of the selected calibration matrices are given in Table 2. Recoveries of 95–102% for terbutryn and 95–105% for prometryn were obtained in the prediction step.

The developed methods for the analysis of the atrazine–simazine and terbutryn–prometryn mixtures were also applied to the determination of these compounds in river water. In order to achieve a lower detection limit, preconcentration is proposed, based on extraction into diethyl ether according to the procedure described above. However, in the analysis of spiked river waters samples, the recoveries obtained for the pesticides ranged from 50 to 125%.

These unsatisfactory results are due to the matrix effect, since it produces a signal distortion which involves a non-linear behaviour of the system. A general way to decrease the matrix effects is to use samples with features similar to those of real samples instead of performing a calibration with pure solutions.[20–22] On the other hand, although PCR and PLS methods have been essentially devised to model linear information, they can also describe non-linear systems by incorporating more latent variables than those necessary to describe linear systems[23,24] or by using new non-linear versions of PCR and PLS algorithms.[25–29] Together with these methods, widely used as the large number of reports in the literature demonstrate,[25,30–35] new techniques, such as the ANN, have been particularly developed to model non-linear information, which is important in electrochemical measurements in which the electrode response can behave in a non-linear way[36,37] in addition to the other sources responsible for this behaviour.

In this work we considered two ways to deal with non-linearity: decrease of the matrix effect through the preparation of the samples in a medium similar to that for the real samples and subsequent PCR or PLS analysis using their linear versions, and ANN modelling using the same calibration samples.

**Table 2** Number of factors for calibration and statistical parameters

| Component | Method | Number of factors | $r^2$ | RMSD |
|---|---|---|---|---|
| Atrazine | PLS-1 | 3 | 0.9962 | 0.1074 |
| Simazine | | 3 | 0.9928 | 0.1505 |
| Atrazine | PLS-2 | 3 | 0.9962 | 0.1070 |
| Simazine | | | 0.9928 | 0.1500 |
| Terbutryn | PLS-1 | 6 | 0.9982 | 0.674 |
| Prometryn | | 6 | 0.9971 | 0.828 |
| Terbutryn | PLS-2 | 6 | 0.9982 | 0.675 |
| Prometryn | | | 0.9969 | 0.855 |

### Calibration matrices using pesticide standard concentrations in samples containing river water. PCR and PLS analysis

New calibration matrices (matrix 1 for atrazine–simazine mixture and matrix 2 for terbutryn–prometryn mixture in Table 3) containing different concentrations of the binary mixtures of the pesticides prepared in the presence of 5 mL of river water (taken from different locations along the river) in a final volume of 25 mL was attempted. Samples of river water were previously analysed using DPP to determine if they contained the pesticides or not. In this case we examined the application of different multivariate methods, PCR, PLS-1 and PLS-2. In all cases the tested pre-processing algorithms were mean centering of the data, variance scaling, and baseline correction of the polarogram signals and their first derivative. The regions used for analysis were −0.75 to −1.00 V for the atrazine–simazine mixture and −0.85 to −1.10 V for the terbutryn–prometryn mixtures and each measurement was made at 2.4 mV, which implies 104 experimental points. The statistical parameters $R^2$ and root mean square deviation (RMSD) (corresponding to the calibration matrices from raw or processed signals) did not show any significative difference. Subsequently all calibration matrices used were constructed from original signals with baseline correction. The analysis of samples of 100 mL of spiked river water, treated as indicated in the proposed

**Table 3** Composition of the samples of matrix 1 (atrazine–simazine binary mixture) and matrix 2 (terbutryn–prometryn binary mixture)

| Matrix 1 | | | Matrix 2 | | |
|---|---|---|---|---|---|
| Sample No. | Atrazine/ $10^6$ M | Simazine/ $10^6$ M | Sample No. | Terbutryn/ $10^6$ M | Prometryn/ $10^6$ M |
| 1M | 0 | 0 | M1 | 0 | 0 |
| 2M | 5 | 0 | M2 | 5 | 0 |
| 3M | 74 | 0 | M3 | 74 | 0 |
| 4M | 99 | 0 | M4 | 99 | 0 |
| 5M | 148 | 0 | M5 | 148 | 0 |
| 6M | 0 | 0 | M6 | 186 | 0 |
| 7M | 0 | 50 | M7 | 0 | 50 |
| 8M | 0 | 74 | M8 | 0 | 74 |
| 9M | 0 | 99 | M9 | 0 | 99 |
| 10M | 0 | 148 | M10 | 0 | 148 |
| 11M | 0 | 186 | M11 | 0 | 186 |
| 12M | 186 | 186 | M12 | 186 | 186 |
| 13M | 99 | 186 | M13 | 99 | 186 |
| 14M | 186 | 99 | M14 | 186 | 99 |
| 15M | 50 | 50 | M15 | 50 | 50 |
| 16M | 74 | 148 | M16 | 74 | 148 |
| 17M | 148 | 74 | M17 | 148 | 74 |
| 18M | 99 | 99 | M18 | 99 | 99 |
| 19M | 186 | 148 | M19 | 186 | 148 |
| 20M | 50 | 99 | M20 | 50 | 99 |
| | | | M21 | 148 | 186 |

procedure, provided the results given in Table 4. The recoveries are now better than those obtained from calibration matrices constructed from pure solutions of the pesticides in Milli-Q water, but they have large deviations (high RSDs).

## Artificial neural networks

ANNs are non-parametric calibration methods specially created to model non-linear information, although they are able to deal with a linear behaviour and often they can improve the results in comparison with the linear mode. The so-called multilayer feed-forward networks[38] are often used for prediction as to classification. The unscramble multilayer feed-forward network (MLFU) consists of four layers of neurons or nodes which are the basic computing unit: the input layer with the number of active neurons (up to 16) corresponding to the predictor variables in regression, two hidden layers with a number of active neurons (up to 16 in the first and three in the second hidden layer) which is optimized during the training and the output layer with just one unit (Fig. 5).

The neurons are connected in a hierarchical manner. That is, the outputs of one layer of nodes are used as inputs for the next layer and so on. Direct connections from the input layer to the output layer are also available. In a neural network which use direct connections, the weighted input data are directly added to the output neuron and it increases the training speed, but its use is inadvisable for modelling systems with strong non-linearity.

In the hidden layer the sigmoid function $f(x) = 4/(1 + e^{-x}) - 2$ is used, and the output of the hidden neuron $j$, $O_j$, is calculated as

$$O_j = f\left[\sum_{i=1}^{i}(s_i w_{ij} + w_{bj})\right]$$

where $s_i$ is the input from the neuron $i$ in the layer above to the neuron $j$ in the hidden layer, $w_{ij}$ are the connection weights between each neuron $i$ and neuron $j$ and $w_{bj}$ is a bias to neuron $j$. In the input and output layers linear functions are used. In the UMLF the learning is carried out through the back-propagation rule.[39]

In this work, the inputs to the network were the unit-variance scaled scores of a PCR model obtained from the calibration matrices composed of samples that contain a portion of river water (using scores instead of raw data permits the dimensionality reduction and, therefore, a decrease in the risk of overfitting). Sometimes a PLS model can be used, but PLS components conserve more information linearly correlated than PCR components and, therefore, this treatment of raw data is generally preferable.

The network architecture describes the pattern in which the net is used and indicates the number of neurons in each layer and also whether direct connections are used or not. An architecture as (6, 2, 0, 1)+ direct symbolizes a net with six inputs, two nodes in the first hidden layer, one output neuron and direct connections. To optimize the net architecture we start with activating a number of neurons in the input layer corresponding to the optimum number of PCs in the PCR or PLS model and we try to reduce the number of neurons with which we started. In the first hidden layer we start with just one activated neuron and we increase this number if necessary. Quantitative predictions, as in our case, does not usually need the second hidden layer which is generally required for classification proposes. The general applied rule was to try the simplest possible architecture.

The fitness of the model was measured by the RMSEC (root mean square error of calibration) and the prediction ability was measured by the RMSEP (root mean square error of prediction):

$$\mathrm{RMSEC} = \sqrt{\{\Sigma[\hat{y}_i(\mathrm{cal}) - y_i(\mathrm{cal})]^2\} / N(\mathrm{cal})}$$

$$\mathrm{RMSEP} = \sqrt{\{\Sigma[\hat{y}_i(\mathrm{val}) - y_i(\mathrm{val})]^2\} / N(\mathrm{val})}$$

where $\hat{y}_i$ and $y_i$ are the measured and the predicted values for the $N$ samples of the training set (cal) and the test set (val).

UMLF was applied to simultaneous determination of terbutryn–prometryn and atrazine–simazine. For terbutryn–prometryn in their binary mixtures the same samples with river water as in PCR and PLS analysis were used. A separated and randomized five sample set was used as a test set for validation. The numbers of neurons in the input and first hidden layers were optimized and, in each case, the learning rate and the update parameters were also optimized. The activation of neurons from the second hidden layer does not improve the net resolution and increases the risk of overfitting. On the other hand, the different nets tested were very stable in the learning rate and the update parameter changes. For terbutryn–prometryn mixtures the selected architectures (numbers of neurons in input, first hidden, second hidden and output layers) were (3, 1, 0, 1) for prometryn and (3, 3, 0, 1) for terbutryn. For atrazine–simazine mixtures the network architectures were (6, 4, 0, 1) for atrazine and (5, 4, 0, 1) for simazine. Direct connections were not employed. The results are given in Table 4.

**Table 4** Recoveries of the pesticides in the analysis of spiked river waters samples

| Sample No.[a] | Pesticide | Added/ $10^7$ M | Recovery ± RSD (%) PLS1 | ANN |
|---|---|---|---|---|
| P2 | Terbutryn | 2.00 | 94 ± 29 | 99 ± 6 |
| P3 | Terbutryn | 3.23 | 97 ± 17 | 98 ± 1 |
| P4 | Terbutryn | 2.23 | 31 ± 47 | 97 ± 2 |
| P5 | Terbutryn | 1.48 | 78 ± 41 | 99 ± 6 |
| P1 | Prometryn | 2.23 | 122 ± 24 | 92 ± 5 |
| P2 | Prometryn | 3.23 | 93 ± 28 | 101 ± 1 |
| P3 | Prometryn | 1.48 | 92 ± 52 | 104 ± 4 |
| P5 | Prometryn | 2.00 | 110 ± 31 | 105 ± 15 |
| P7 | Atrazine | 2.23 | 98 ± 23 | 107 ± 22 |
| P8 | Atrazine | 4.08 | 97 ± 17 | 100 ± 16 |
| P9 | Atrazine | 2.23 | 96 ± 6 | 92 ± 5 |
| P6 | Simazine | 2.23 | 91 ± 10 | 85 ± 12 |
| P7 | Simazine | 4.08 | 90 ± 20 | 92 ± 15 |
| P8 | Simazine | 1.48 | 89 ± 45 | 109 ± 36 |

[a] Samples P1, P4, P6 and P9 have just one component. All samples analysed in triplicate.

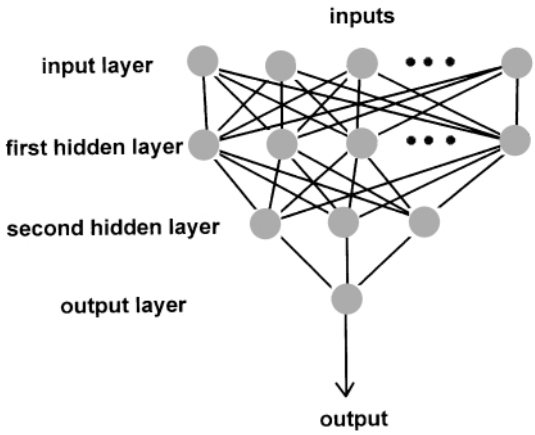


**Fig. 5** Schematic representation of the UMLF network without direct connection.

## Conclusions

It is possible to determine the pesticides in both mixtures by subjecting DPP data to PCR or PLS. Extraction of river water samples with diethyl ether allows the determination of concentrations as low as $2.00 \times 10^{-7}$ M for terbutryn and prometryn and $1.48 \times 10^{-7}$ M for atrazine and simazine. In spite of the satisfactory results, the RSDs are large. The neural network calibration method notably improves the results for terbutryn and prometryn and yields a significant decrease in the RSD. For atrazine and simazine an insignificant slight decrease in the RSD is found.


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