Application of multivariate statistical techniques to evaluation of water quality in the Mała Wełna River (Western Poland)

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Abstract The paper presents the results of determinations of physico-chemical parameters of the Mała Wełna waters, a river situated in Wielkopolska voivodeship (Western Poland). Samples for the physico-chemical analysis were taken in eight gauging cross-sections once a month between May and November 2006. To assess the physico-chemical composition of surface water, use was made of multivariate statistical methods of data analysis, viz. cluster analysis (CA), factor analysis (FA), principal components analysis (PCA), and discriminant analysis (DA). They made it possible to observe similarities and differences in the physico-chemical composition of water in the gauging cross-sections, to identify water quality indicators suitable for characterising its temporal and spatial variability, to uncover hidden factors accounting for the structure of the data, and to assess the impact of man-made sources of water pollution.

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Introduction

In the recent years, an ever wider use has been made in the analysis of environmental data of multivariate statistical methods known as chemometric techniques. Cluster analysis (CA), factor analysis (FA), principal components analysis (PCA), and discriminant analysis (DA) help in the interpretation and evaluation of multivariate data sets coming from environmental monitoring. Chemometric techniques are a useful instrument in characterising the quality of water and its temporal and spatial variability caused by natural and man-made factors (Singh et al. 2004). There have been many studies confirming the usefulness of those techniques in the analysis of large, complex sets of measurement data and in the planning of measuring networks for efficient control of sources of surface

water pollution (Simeonov et al. 2003). The literature provides many examples of the application of chemometric techniques in the interpretation of physico-chemical results of river water (Einax et al. 1998; Vega et al. 1998; Simeonov et al. 2000, 2001, 2002; Marques da Silva and Sacomani 2001; Brodnjak-Voncina et al. 2002; Mendiguchia et al. 2004; Singh et al. 2004, 2005a,b; Ouyang 2005; Ouyang et al. 2006; Panda et al. 2006; Charkhabi and Sakizadeh 2006; Kowalkowski et al. 2006; Sundaray et al. 2006; Tarrado et al. 2006; Zeilhofer et al. 2006; Kannel et al. 2007; Shrestha and Kazama 2007; Sotelo et al. 2007).

The aim of the present research was to use chemometric techniques (CA, PCA, FA and DA) in order to: (1) discover similarities and differences in the physico-chemical composition of water in the gauging cross-sections on the Mała Wełna river under study, (2) identify water quality indicators suited to its temporal and spatial variability, (3) expose hidden factors accounting for the structure of the data, and (4) identify man-made sources of water pollution.

Material and methods

Study area

In terms of Kondracki's (2000) physical-geographic division of Poland, the catchment of the Mała Wełna river is situated in the central part of the Wielkopolska–Kujawy Plain, in the Wielkopolska Lakeland macroregion and the Gniezno Lakeland mesoregion. In accordance with the European Union's coding system for hydrographic units, the Mała Wełna catchment has been assigned the code 1866 (Czarnecka 2005). In abiotic typological terms, the Mała Wełna has been classified as a small river whose ecological functioning is independent of the eco-regions established in Europe. It is a left-bank tributary of the Wełna river, which in turn empties into the Warta. The total area of the Mała Wełna catchment equals 688 km^2, while the part up to the Kiszkowo cross-section, which closes the study area, occupies 342 km^2. On its course from the headwaters to the Kiszkowo cross-section, the Mała Wełna passes through eight lakes with a total area of 392.8 ha. Nineteen more lakes are located in its

catchment and a complex of fish ponds with a total area of 780.5 ha, which gives the catchment area a lake percentage of 2.3%.

The catchment is agricultural in character: the proportion of agricultural land is high here, at 82.7%, of which arable land accounts for 75.2%, grassland for 7.2%, and orchards for 0.3%. Its afforestation level is low, at about 6% of the area. It is covered with mineral deposits formed mostly from loamy sands and tills, with a predominance of lessivé soils.
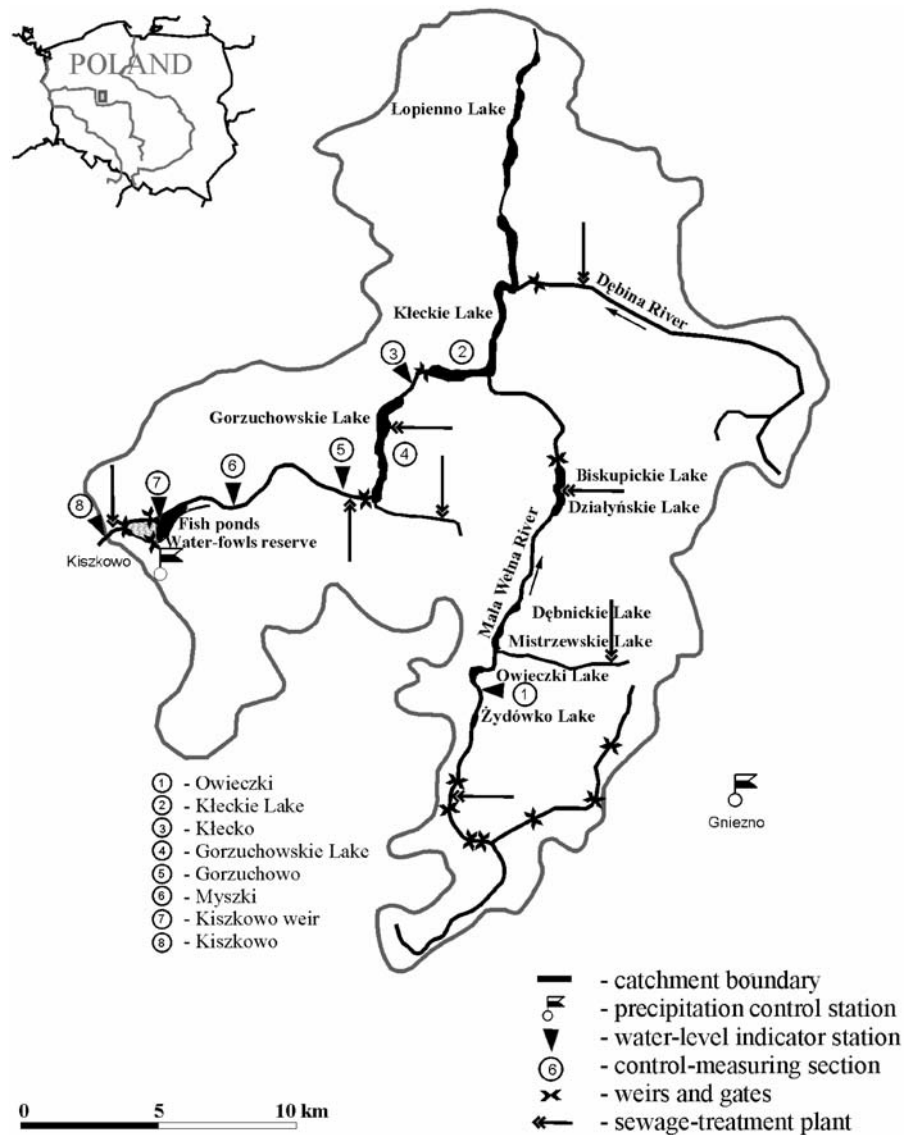
In the hydrological year 2006, the mean annual air temperature was 9.2°C while rainfall amounted to 565 mm. In the summer half-year, rainfall was 298 mm, 13 mm lower than the 1989–2006 average, and the mean air temperature was 17.1°C, or 2.2°C higher than the multi-year average. The mean discharge in the Kiszkowo cross-section equalled 0.302 m^3 s^{-1}, which was 0.122 m^3 s^{-1} lower than the multi-year average. In the summer half-year, the mean discharge was 0.447 m^3 s^{-1}, up by 0.080 m^3 s^{-1} from the multi-year average. The discharges in the individual cross-sections along the river course varied on sampling days: the highest flows were recorded in May, from 0.128 m^3 s^{-1} in cross-section no 1 to 0.857 m^3 s^{-1} in no 8, and the lowest in July, under 0.109 m^3 s^{-1} (Fig. 1).

Sample collection

Surface water was sampled for physico-chemical analysis from May to November 2006 in six gauging cross-sections situated along the Mała Wełna river and in two lakes through which it passes (Fig. 1). Measurements taken directly in the field included the temperature, pH reaction and electrolytic conductivity of the water with the help of a multifunctional measuring device, Multi 197, made by the firm WTW (Weilheim, Germany). The samples were collected in polyethylene (PE) bottles using a Toń 2 sampler (Mera Błonie, Gdańsk). The samples were then fixed in accordance with the PN-EN ISO 5667-3 (2005) standard in force.

In each gauging cross-section hydrometric measurements were performed, which included depth and width of the cross-section, as well as the water flow velocity. This was done using a Valeport BMF002 model of hydrometric current meter (Devon, United Kingdom).

Fig. 1 Catchment of the Mała Wełna River down to the Kiszkowo cross-section

1 - Owieczki
2 - Kłeckie Lake
3 - Kłecko
4 - Gorzuchowskie Lake
5 - Gorzuchowo
6 - Myszki
7 - Kiszkowo weir
8 - Kiszkowo

— - catchment boundary
— - precipitation control station
▼ - water-level indicator station
⑥ - control-measuring section
✕ - weirs and gates
← - sewage-treatment plant

Chemical analysis

Determinations of Cl^- were performed using argentometric titration, and SO_4^{2-}, the gravimetric method. Total water hardness and Ca^{2+} concentration were determined by the versenate method, while Mg^{2+} concentration was calculated from the difference between total hardness and the concentration of Ca^{2+} ions. NH_4^+ was determined by the spectrophotometric method with Nessler's reagent; NO_2^-, with sulphanilic acid and 1-naphthylamine; NO_3^-, by the salicylate method; and PO_4^{3-} was determined by the molybdate method with ascorbic acid as a reducer, using a Merck Nova 60 apparatus (Merck KGaA, Darmstadt, Germany). The dissolved oxygen content (DO) and biochemical oxygen demand (BOD_5) were determined using Winkler's method, and chemical oxygen demand (COD), the dichromate method. Determinations of $Fe_{(tot.)}$ and Mn^{2+} were made using atomic absorption spectrometry with flame atomisation (F-AAS), and those of K^+ and Na^+ (with $CsCl_2$ as modifier), using atomic emission spectrometry (F-AES) on a two-beam Perkin Elmer instrument, the AAnalyst 300 model (Perkin Elmer,

Table 1 Mean, median values and ranges of physical and chemical properties of water in the monitoring sites during the research period

Parameters	Abbreviations	Units	Sampling location								
			1			2			3		
			Range	Mean	Median	Range	Mean	Median	Range	Mean	Median
Discharge	Q	$m^3\,s^{-1}$	0 0.128	0.037	0.022				0 0.579	0.160	0.091
Water temperature	WT	°C	7.5 22.0	16.3	18.0	8.5 23.0	16.6	18.0	8.0 23.0	16.2	17.0
pH	pH	pH unit	7.4 7.9	7.7	7.7	7.5 8.1	7.9	7.9	7.2 8.1	7.5	7.4
Dissolved oxygen	DO	$mg\cdot dm^{-3}$	1.8 12.4	4.7	2.8	6.8 13.2	9.8	9.0	2.8 9.2	5.6	5.0
Biochemical oxygen demand	BOD	$mgO_2\cdot dm^{-3}$	4.0 13.0	9.0	9.4	3.8 7.6	5.7	5.9	3.8 7.6	5.0	4.65
Chemical oxygen demand (Cr)	COD_{Cr}	$mgO_2\cdot dm^{-3}$	68.0 84.0	75.3	75.0	37.0 63.0	51.7	53.5	34.0 47.0	42.3	42.5
Electrical conductivity	EC	$\mu S\cdot cm^{-1}$	1.029 1.133	1.084	1.090	721 774	741	735	735 817	760	752
Nitrate nitrogen	$N\text{–}NO_3$	$mg\,dm^{-3}$	0.3 5.5	1.5	0.8	0.2 3.0	1.4	1.1	LOD 2.8	1.3	1.1
Nitrite nitrogen	$N\text{–}NO_2$	$mg\cdot dm^{-3}$	LOD 0.10	0.03	0.01	0.01 0.08	0.04	0.03	0.02 0.07	0.04	0.04
Ammonium nitrogen	$N\text{–}NH_4$	$mg\cdot dm^{-3}$	0.05 1.91	0.66	0.36	0.03 1.32	0.37	0.11	0.01 1.07	0.40	0.22
Phosphates	PO_4	$mg\cdot dm^{-3}$	LOD 3.3	1.7	1.8	LOD 0.2	0.1	0.1	LOD 0.2	0.1	0.1
Sulfates	SO_4	$mg\cdot dm^{-3}$	137.8 197.1	168.4	172.8	139.9 167.5	152.4	151.0	134.5 152.2	142.8	142.6
Chlorides	Cl	$mg\cdot dm^{-3}$	95 100	99	100	75 85	82	83	80 90	83	80
Hardness	Hard	$mgCaCO_3\cdot dm^{-3}$	520 600	548	540	330 350	340	340	340 380	355	350
Sodium	Na	$mg\cdot dm^{-3}$	25.9 58.6	38.7	37.8	18.8 23.2	21.8	22.7	19.2 25.1	22.5	23.5
Potassium	K	$mg\cdot dm^{-3}$	7.6 27.5	12.3	9.6	8.0 9.5	9.0	9.4	7.8 9.5	8.6	8.4
Calcium	Ca	$mg\cdot dm^{-3}$	160 200	179	184	68 96	84	84	68 108	92	96
Magnesium	Mg	$mg\cdot dm^{-3}$	17.0 28.2	24.0	24.3	17.0 38.4	28.1	27.5	24.3 43.8	30.4	26.7
Iron	$Fe_{(Tot.)}$	$mg\cdot dm^{-3}$	0.16 1.55	0.49	0.29	0.05 0.43	0.16	0.10	0.04 1.51	0.46	0.31
Manganese	Mn	$mg\cdot dm^{-3}$	0.06 0.13	0.09	0.08	0.01 0.06	0.03	0.02	0.01 0.22	0.09	0.07

LOD (Limit of detection) for $N\text{–}NO_3 - 0.1\ mg\cdot dm^{-3}$, $N\text{–}NO_2 - 0.01\ mg\cdot dm^{-3}$, $PO_4 - 0.1\ mg\cdot dm^{-3}$

Table 1 (continued)

Parameters	Sampling location														
	4			5			6			7			8		
	Range	Mean	Median	Range	Mean	Median	Range	Mean	Median	Range	Mean	Median	Range	Mean	Median
Discharge				0.070 0.686	0.229	0.155	0.075 0.699	0.247	0.177	0.005 0.548	0.137	0.072	0.109 0.857	0.370	0.228
Water temperature	8.5 23.0	16.3	17.5	8.0 23.0	15.8	16.0	8.0 24.0	16.1	16.5	7.5 23.0	15.8	15.5	8.0 23.0	15.5	15.0
pH	7.4 8.2	7.7	7.6	7.2 7.5	7.4	7.4	7.0 7.3	7.2	7.3	7.0 7.5	7.3	7.3	7.2 7.6	7.4	7.3
Dissolved oxygen	8.4 13.6	9.9	9.4	1.6 11.2	5.1	4.1	0.3 4.8	2.3	2.0	0.1 8.4	3.7	3.8	1.0 6.8	3.8	3.5
Biochemical oxygen demand	4.4 8.0	6.4	6.6	2.2 11.2	5.4	5.15	1.6 5.8	3.6	4.0	2.0 9.4	5.2	4.0	3.8 15.0	7.5	7.15
Chemical oxygen demand (Cr)	26.0 64.0	47.8	53.5	36.0 65.0	48.0	46.5	38.0 54.0	44.0	43.0	38.0 62.0	47.8	47.5	30.0 69.0	44.5	42.0
Electrical conductivity	726 848	778	773	745 867	809	812	749 849	802	810	749 822	780	772	738 912	834	843
Nitrate nitrogen	0.1 1.7	1.1	1.1	LOD 1.4	0.8	1.0	0.8 1.7	1.1	0.9	0.2 1.2	0.8	0.9	0.7 1.5	1.1	1.1
Nitrite nitrogen	LOD 0.05	0.02	0.02	0.01 0.10	0.03	0.02	0.01 0.11	0.03	0.02	LOD 0.05	0.02	0.01	0.02 0.05	0.03	0.03
Ammonium nitrogen	0.06 0.27	0.13	0.12	0.08 1.71	0.95	0.95	0.08 1.25	0.63	0.69	0.06 0.78	0.31	0.18	0.01 3.25	1.19	0.81
Phosphates	LOD 0.2	0.1	0.1	0.1 0.9	0.5	0.6	0.1 0.5	0.3	0.4	LOD 1.4	0.5	0.2	0.1 0.9	0.6	0.6
Sulfates	143.6 156.6	150.1	151.0	135.0 154.3	144.9	144.9	140.7 153.9	149.3	150.4	108.6 164.2	138.0	140.9	91.8 134.1	115.6	114.4
Chlorides	80 85	83	85	85 90	87	85	80 85	84	85	85 90	86	85	75 85	82	82.5
Hardness	330 395	365	360	330 390	367	370	340 400	378	385	350 390	370	370	380 470	435	445
Sodium	19.9 25.2	23.6	24.9	20.5 30.4	26.4	28.2	20.4 27.3	25.0	26.9	21.0 27.1	24.0	24.2	18.8 26.7	24.0	26.3
Potassium	7.9 10.4	9.5	10.1	7.67 11.6	10.1	10.85	8.0 10.7	9.7	10.5	7.3 11.2	9.5	9.9	6.1 11.1	8.6	8.8
Calcium	80 96	86	82	80 116	99	100	96 120	107	106	92 140	109	106	112 148	133	138
Magnesium	17.0 38.4	30.3	34.0	21.9 43.8	28.4	24.3	21.9 38.4	27.3	25.5	24.3 28.2	25.4	24.3	24.3 26.7	24.7	24.3
Iron	0.03 0.30	0.12	0.09	0.04 0.93	0.30	0.20	0.08 0.52	0.22	0.14	0.08 0.59	0.28	0.24	0.12 0.85	0.42	0.29
Manganese	0.02 0.06	0.04	0.05	0.02 0.16	0.06	0.03	0.02 0.36	0.10	0.04	0.02 0.59	0.19	0.10	0.01 0.38	0.17	0.14

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Fig. 2 Dendrogram showing clustering of the sampling sites on the Mała Wełna River down to Kiszkowo
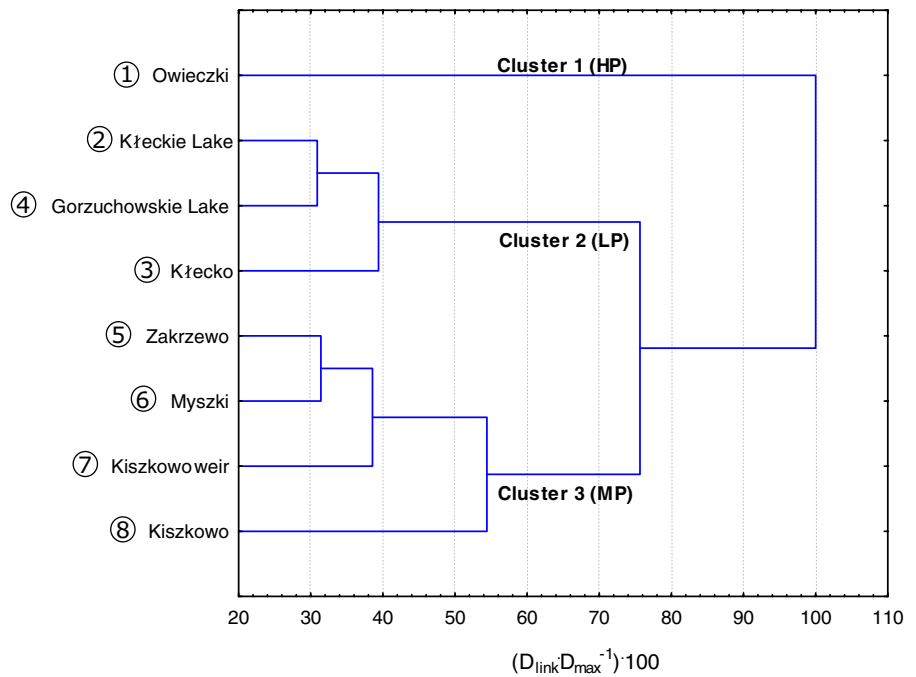

Norwalk, CT, USA). This instrument was equipped with a Perkin Elmer AS 90 autosampler (Perkin Elmer, Norwalk, CT, USA). Hollow cathode lamps (HCL) were used for the determinations (Perkin Elmer, Norwalk, CT, USA).

Reagents

All the reagents used were of analytical grade, water was deionised and of resistivity >18 MΩ in a Milli Q-RG apparatus (Millipore, France). The reference standard

Fig. 3 Principal components scores for all monitoring sites located on the Mała Welna river down to Kiszkowo
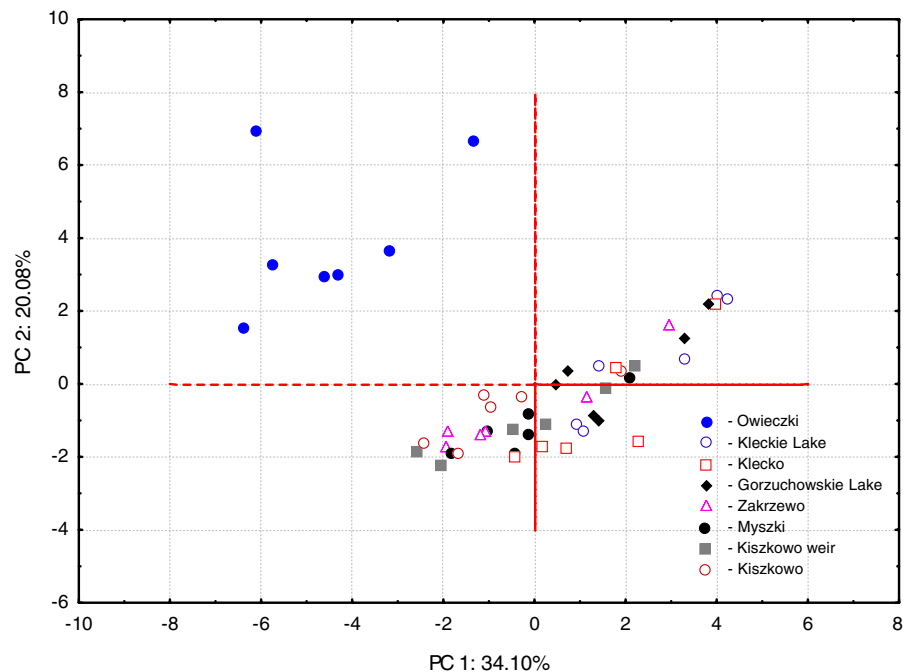
solutions were made of commercial standards for AAS analysis made by Merck (Merck, Darmstadt, Germany).

Data treatment and statistical analysis

The evaluation of the physico-chemical composition of water in the Mała Wełna catchment rested on a set of data embracing 19 parameters of water quality determined in the eight gauging cross-sections between May and November 2006. Before performing the statistical analysis, preliminary work was done on the data matrix which included the assembling and transformation of the data. At the assembling stage, the levels of nitrate nitrogen, nitrite nitrogen and phosphates, which were below detection limit, were complemented with values equal to half the detection limit. Then, with the help of the W (Shapiro–Wilk) test, the agreement of the distribution of the physico-chemical parameters of water with the normal distribution was checked. Variables with a distribution other than normal were subjected to a transformation (Mazerski 2000). In the case of water temperature as well as chloride and magnesium concentrations, their post-transformation distribution differed significantly from the normal one, hence those parameters were not taken into consideration when making the chemometric analyses. The data set embracing 16 parameters of water quality was standardised and finally analysed using three multivariate statistical methods: CA, PCA and FA. CA was performed to highlight similarities and differences among the gauging cross-sections using Ward's method. The PCA and FA techniques were used to accentuate the components/factors characterising the temporal and spatial variability of water quality. Discriminant analysis was made using the data which had not been subjected to transformation (Kowalkowski et al. 2006; Singh et al. 2005a, b; Shrestha and Kazama 2007). Its chief aim was to employ the water quality parameters to build a model (a discriminant function) that would allow an assessment of the temporal and spatial variability of water quality.

To evaluate the temporal and spatial variability of concentrations of the parameters under study, use was made of the analysis of variance (ANOVA).

All the statistical and mathematical calculations were performed using the Microsoft Office – Excel 2000 spreadsheet (Microsoft Corporation, Poland) and the Statistica 7.1 software (StatSoft, Poland).

Results and discussion

General characteristics of water quality in the Mała Wełna River over the study period

Over the study period, the water in the Mała Wełna catchment showed an alkaline reaction ranging from pH 7.0 to 8.3. The concentrations of nitrate nitrogen were found to be low, from <0.1 to 5.5 mg dm^{-3}, while those of nitrite nitrogen, from <0.01 to 0.11 mg dm^{-3}. Sulphates were found to vary from 91.8 to 197.1 mg dm^{-3}, calcium from 68 to 200 mg dm^{-3}, iron from 0.03 to 1.55 mg dm^{-3}, and manganese from 0.01 to 0.59 mg dm^{-3}. Elevated concentrations were observed of biochemical oxygen demand (BOD$_5$), from 1.6 to 15.0 mg dm^{-3}, chemical oxygen demand (COD$_{Cr}$), from 26.0 to 84.0 mg dm^{-3}, ammonia nitrogen, from 0.01 to 3.25 mg dm^{-3}, and phosphates, from <0.1 to 3.3 mg dm^{-3}. In the first cross-section the highest concentrations of COD$_{Cr}$ were recorded, up to 84.0 mg O$_2$ dm^{-3}, of phosphates

Table 2 Matrix of factor loadings calculated on the basis of water quality parameters measured in the period from May to November 2006 in the Mała Wełna river down to Kiszkowo (except the Owieczki cross-section)

Parameter	VF1	VF2	VF3	VF4
pH	−0.39	−0.32	0.00	−0.60[a]
DO	−0.43	−0.30	−0.24	−0.66[a]
BOD	0.12	−0.15	−0.80[b]	0.18
COD$_{Cr}$	−0.18	−0.06	−0.74[a]	−0.32
EC	0.54[a]	0.28	0.33	0.17
N–NO$_3$	−0.05	−0.29	−0.03	−0.11
N–NO$_2$	0.24	−0.66[a]	−0.17	−0.36
N–NH$_4$	0.50[a]	0.35	0.05	0.36
PO$_4$	0.73[a]	0.44	0.06	0.28
SO$_4$	0.81[b]	−0.08	−0.35	0.13
Hard	0.56[a]	0.08	0.44	0.36
Na	0.26	0.87[b]	0.09	0.11
K	0.11	0.92[b]	0.07	0.02
Ca	0.82[b]	−0.02	0.24	0.19
Fe	0.07	0.13	0.06	0.75[b]
Mn	0.23	0.01	−0.01	0.89[b]
Eigenvalue	6.74	2.19	1.41	1.29
Variance %	42.16	13.72	8.83	8.08
Cumulative variance %	42.16	55.87	64.71	72.78

[a] Medium correlated factor loadings

[b] Strongly correlated factor loadings

up to 3.3 mg dm^{-3}, the highest electrolytic conductivity, at 1.133 µS cm^{-1}, and very low concentrations of DO, below 3.6 mg dm^{-3}, which can also be associated with a very low discharge here, at 27 dm^3 s^{-1}. The statistical parameters of the water quality indicators under study are listed in Table 1.

The analysis of variance showed there to be temporal variations over the study period in the concentrations of dissolved oxygen and the compounds of nitrogen, sodium and potassium, as well as spatial variations in the levels of dissolved oxygen, biochemical oxygen demand, chemical oxygen demand, phosphates, sulphates, chlorides, sodium, and calcium, and in the hardness, electrolytic conductivity and pH reaction of water (statistically significant differences at the Pα=0.05 level).

Assessment of the temporal and spatial variability of water using multivariate statistical methods

The results of cluster analysis CA are presented in a dendrogram (Fig. 2). The gauging cross-sections were grouped into three statistically significant clusters (D_{link}/D_{max})×100<60. The first (HP, highly polluted) embraced the cross-section at Owieczki (1) located in the upper course of the river, with the most polluted water; the second (MP, medium polluted), the cross-sections at Zakrzewo (5), Myszki (6), the Kiszkowo weir (7) and Kiszkowo (8) with a moderate level of water pollution; and the third (LP, low-polluted), the sites on lakes Kłeckie (2) and Gorzuchowskie (4) as well as the Kłecko cross-section (3) located between them. The lakes in the
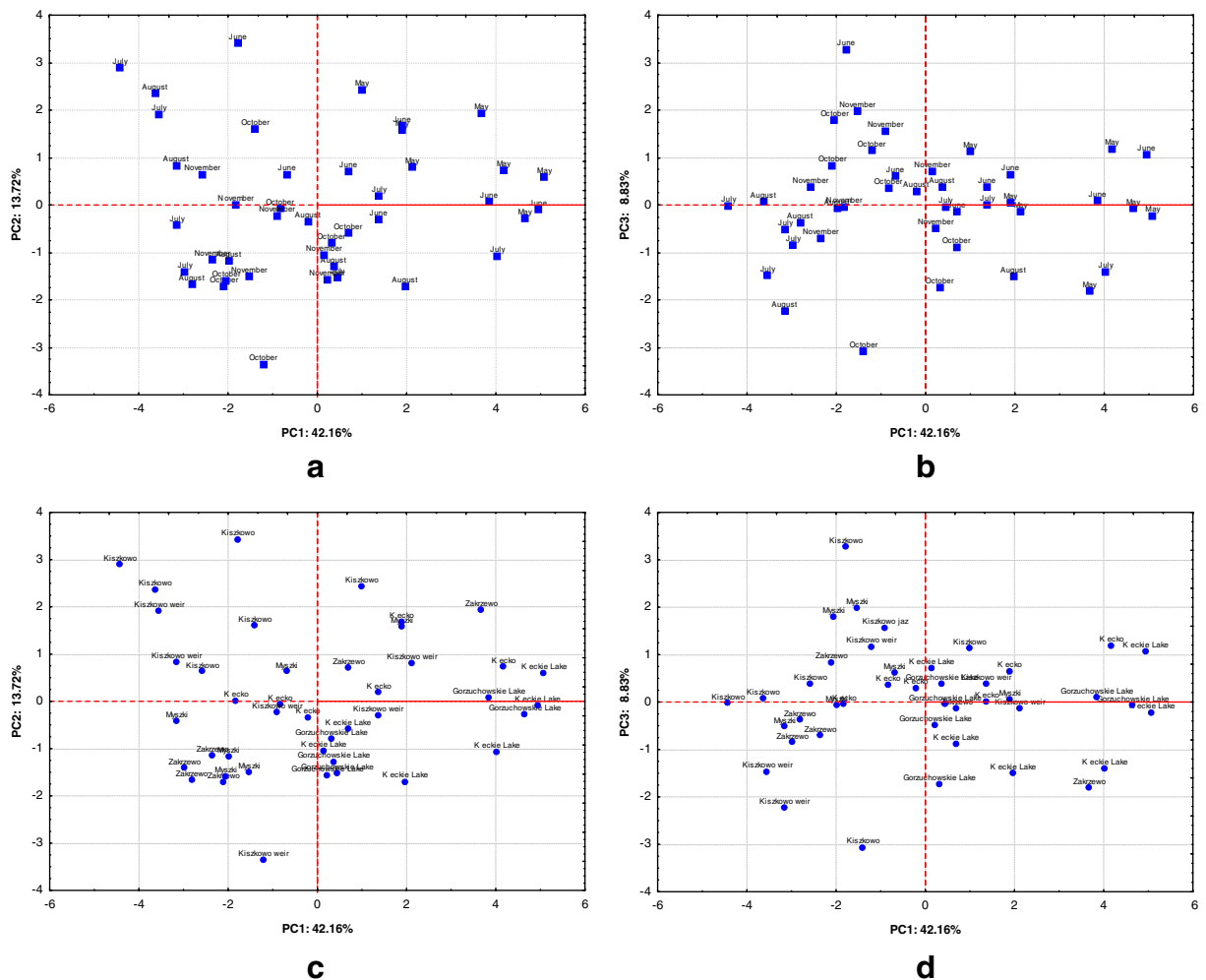

Fig. 4 Results of principal components analysis (PCA) for months of sample collection (a, b) and monitoring cross-sections (c, d)

stream–lake system of the studied catchment have a high capacity for stopping and immobilising chemical compounds, whether dissolved or adsorbed to suspension, hence the composition of water and its quality in the Kłecko cross-section (3) are determined by the impact of Lake Kłeckie (2). The reason the Zakrzewo site (5) was not classed in group three (LP) was the discharge of waste from a treatment plant located below Lake Gorzuchowskie (4) – Fig. 1.

Principal components analysis (PCA) confirmed the significant differences in the composition of the analysed physico-chemical parameters of water in the Owieczki cross-section (1), which is clearly affected by point pollution sources (domestic and agricultural waste) – Fig. 3. The cumulative variance for the first two principal components (PC1 and PC2) was only 54.18%, which caused the results of PCA analysis to diverge from those of cluster analysis (CA). The measuring points formerly placed in groups two (MP) and three (LP) did not show under PCA. In the next stage of the calculations, the Owieczki cross-section (1) was eliminated from the PCA, FA and DA analyses in order to ensure a correct interpretation of the results.

Factor analysis made it possible to reduce the set of 16 parameters used initially to characterise water

quality in the catchment to four factors (VF – varifactors) necessary to identify sources of the elements in the river and to describe water quality (Table 2). The factors account for about 73% of the structure of the parameters analysed, each having an eigenvalue higher than 1. By the criterion proposed by Liu et al. (2003), when factor loadings between the water quality parameters and the VF factors are equal to 0.75–1.00, 0.50–0.75 and 0.30–0.50, the values are strongly, medium and weakly correlated, respectively. The first factor, VF1 (accounting for as much as 42.16% of total variance), was strongly correlated with the concentrations of sulphates and calcium, which can imply a natural origin of those components in the water of the Mała Wełna catchment: they may have been released from carbonate tills. The next three factors with a cumulative variance amounting to 30.62% were strongly correlated with the levels of sodium and potassium (VF2), BOD_5 and COD_{Cr} (VF3), and iron and manganese (VF4), which is indicative an inflow of organic pollutants. The negative correlation of the fourth factor, VF4, with the concentrations of dissolved oxygen and the pH reaction shows that at low values of those two parameters iron and manganese can be released from bottom deposits into the body of water.

Table 3 Results of discriminant analysis calculated on the basis of water quality parameters measured in the period from May to November 2006 in the Mała Wełna river down to Kiszkowo (except the Owieczki cross-section)

Monitoring sites				Months			
Parameter	Wilks' lambda	Partial Wilks' lambda	Tolerance	Parameter	Wilks' lambda	Partial Wilks' lambda	Tolerance
Ca	0.0023	0.685	0.509	Na	0.0033[a]	0.574[a]	0.198[a]
DO	0.0028[a]	0.550[a]	0.197[a]	$N–NO_3$	0.0046[a]	0.410[a]	0.481[a]
$N–NO_2$	0.0025	0.633	0.391	Mn	0.0026	0.722	0.319
$N–NH_4$	0.0027[a]	0.572[a]	0.218[a]	Fe	0.0031[a]	0.599[a]	0.413[a]
Hard	0.0041[a]	0.381[a]	0.217[a]	EC	0.0024	0.780	0.355
SO_4	0.0026	0.600	0.397	$N–NO_2$	0.0026	0.732	0.643
pH	0.0034[a]	0.458[a]	0.222[a]	COD_{Cr}	0.0025	0.744	0.647
BOD	0.0025	0.615	0.411	K	0.0027	0.701	0.252
Fe	0.0030[a]	0.521[a]	0.305[a]	$N–NH_4$	0.0025	0.740	0.307
EC	0.0025	0.627	0.220	SO_4	0.0032[a]	0.582[a]	0.301[a]
$N–NO_3$	0.0021	0.734	0.326	pH	0.0028	0.663	0.195
Mn	0.0022	0.707	0.329	BOD	0.0032[a]	0.590[a]	0.325[a]
K	0.0023	0.684	0.074	DO	0.0030[a]	0.628[a]	0.130[a]
Na	0.0022	0.716	0.061	PO_4	0.0025	0.763	0.238

[a] The greatest discriminant power in the model created

Principal components analysis performed with the help of the VARIMAX method with rotation did not allow an unequivocal assessment of the temporal and spatial variability of the composition

of water in the catchment and its quality (Fig. 4). This is probably due to the fact that the first and second components, PC1 and PC2, and the first and third ones, PC1 and PC3, jointly account for a mere

Fig. 5 Results of discriminant analysis (DA) for months of sample collection (**a**) and monitoring cross-sections (**b**)
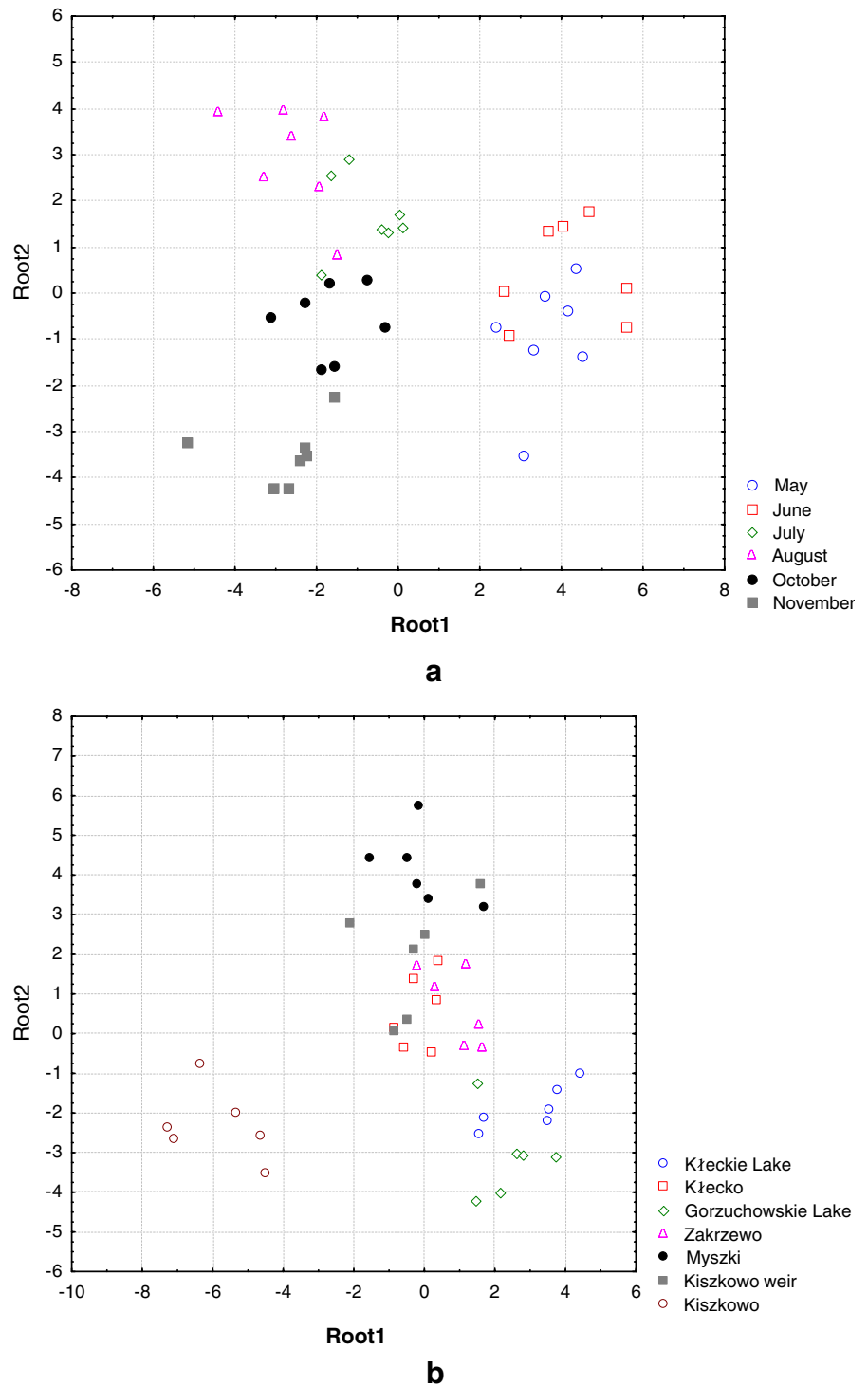
55.88 and 50.99%, respectively, of the internal structure of the analysed parameters of water quality.

In the final stage of calculations, discriminant analysis was performed on the preliminarily processed data using a forward stepwise method. This allowed the building of two models (functions) containing 14 parameters of water quality, which were used to characterise the temporal and spatial variability of the physico-chemical composition of water in the catchment (Table 3).

The discriminant functions were created with an exclusion of two parameters, viz. the levels of phosphates and COD_{Cr} (the first function), and the levels of calcium and hardness (the second function), because partial Wilks' lambdas were higher than 0.75 (Kowalkowski et al. 2006). The discriminant analysis made it possible to build four orthogonal functions with a cumulative variance of 98.55% in the case of temporal changes and 97.75% in the case of spatial ones. The first two were employed in characterising the temporal and spatial variability of water quality in the Mała Wełna catchment (Fig. 5). The partial Wilks' lambdas presented in Table 3 show that the concentrations of DO, ammonia nitrogen and iron, as well as the pH reaction and water hardness were the most influential in discriminating the gauging cross-sections. In turn, the parameters most crucial for the model of the temporal variability of the physico-chemical composition of water were the levels of nitrate nitrogen, iron, sulphates, DO and BOD. The discriminant analysis allowed the gauging cross-sections to be divided into four groups. Group I – Lakes Kłeckie (2) and Gorzuchowskie (4): lacustrine ecosystems with their physico-chemical composition of water differentiating them from the other measuring sites; group II – Kłecko (3) and Zakrzewo (5): cross-sections located below weirs raising the water levels of Lakes Kłeckie and Gorzuchowskie; group III – Myszki (6) and the Kiszkowo weir (7): cross-sections located above a weir which impounds water to fill fish ponds; and group IV – Kiszkowo (8): the cross-section situated below the Kiszkowo weirs, markedly affected by fish-pond water management and a treatment plant. The other discriminant model allowed a division of the successive observation months into three periods: group I – May and June; group II – July and August; and group III – October and November.

Conclusions

The results of the determination and analysis of the parameters of water quality in the period from May to November 2006 permit the following conclusions:

1. In the study period the following were observed:

    – A temporal variability in the concentrations of DO and the nitrogen, sodium and potassium compounds,
    – A spatial variability in the levels of dissolved oxygen, biochemical oxygen demand, chemical oxygen demand, phosphates, sulphates, chlorides, sodium, calcium, and the hardness, electrolytic conductivity and pH reaction of water; this is undoubtedly a result of the agricultural nature of the Mała Wełna catchment and discharges from point pollution sources.

2. A special impact of point pollution sources is visible in the gauging cross-section no 1 (Owieczki), in the period from June to October at very low discharges, under 27 dm^3 s^{-1}.

3. Cluster analysis allowed a division of the gauging cross-sections into three groups characterised by various levels of pollution (HP, MP and LP).

4. Principal components analysis and factor analysis did not corroborate unequivocally the division of the measuring sites obtained on the basis of cluster analysis.

5. Discriminant analysis permitted the building of two models, which made it possible to classify the seven measuring points into four groups following from the interaction between the hydraulic structures and local pollution sources, and a division of the research months into three periods displaying a similar composition and variability of water quality.

References

Brodnjak-Voncina, D., Dobcnik, D., Novic, M., & Zupan, J. (2002). Chemometrics characterisation of the quality of river water. *Analytica Chimica Acta*, *462*, 87–100.

Charkhabi, A. H., & Sakizadeh, M. (2006). Assessment of spatial variation of water quality parameters in the most polluted branch of the Anzali wetland, Northern Iran. *Polish Journal of Environmental Studies*, *15*, 395–403.

Czarnecka, H. (2005). Hydrographic division of Poland, vols 1 and 2. Warsaw IMGW (in Polish).

Einax, J. W., Truckenbrodt, D., & Kampe, O. (1998). River pollution data interpreted by means of chemometric methods. *Microchemical Journal*, *58*, 315–324.

Kannel, R. P., Lee, S., Kanel, S. R., & Kahn, S. P. (2007). Chemometric application in classification and assessment of monitoring location of an urban river system. *Analytical Chimica Acta*, *582*, 390–399.

Kondracki, J. (2000). Geography, geographic and physical mesoregions, Warsaw, Wydawnictwo Naukowe (in Polish).

Kowalkowski, T., Zbytniewski, R., Szpejna, J., & Buszewski, B. (2006). Application of chemometrics in river water classification. *Water Research*, *40*, 744–752.

Liu, C. W., Lin, K. H., & Kuo, Y. M. (2003). Application of factor analysis in the assessment of groundwater quality in blackfoot disease in Taiwan. *The Science of the Total Environment*, *313*, 77–89.

Marques da Silva, A. M., & Sacomani, L. B. (2001). Using chemical and physical parameters to define the quality of Pardo river water (Botucatu – SP-Brazil). *Water Research*, *35*, 1609–1616.

Mazerski, J. (2000). Fundamentals of chemometrics, Gdańsk, Wydawnictwo Politechniki Gdańskiej (in Polish).

Mendiguchia, C., Moreno, C., Galindo-Riano, M. D., & Garcia-Vargas, M. (2004). Using chemometric tools to assess anthropogenic effect in river water, a case study: Guadalquivir River (Spain). *Analytical Chimica Acta*, *515*, 143–149.

Ouyang, Y. (2005). Evaluation of river water quality monitoring stations by principal component analysis. *Water Research*, *39*, 2621–2635.

Ouyang, Y., Nkedi-Kizza, P., Wu, Q. T., Shinde, D., & Huang, C. H. (2006). Assessment of seasonal variations in surface water quality. *Water Research*, *40*, 3800–3810.

Panda, U. C., Sundary, S. K., Rath, P., Nayak, B. B., & Bhatta, D. (2006). Application of factor and cluster analysis for characterization of river and estuarine water system – A case study: Mahanadi River (India). *Journal of Hydrology*, *331*, 434–445.

PN-EN ISO 5667-3 (2005). Water quality. Part 3: Guidelines for the fixing and treatment of water samples (in Polish).

Shrestha, S., & Kazama, F. (2007). Assessment of surface water quality using multivariate statistical techniques: A case study of the Fuji river basin, Japan. *Environmental Modeling and Assessment*, *22*, 464–475.

Simeonov, V., Einax, J. W., Stanimirova, I., & Kraft, J. (2002). Environmetric modeling and interpretation of river water monitoring data. *Analytical and Bioanalytical Chemistry*, *374*, 898–905.

Simeonov, V., Sarbu, C., Massart, D. L., & Tasakovski, S. (2001). Danube river water data modeling by multivariate data analysis. *Microchimica Acta*, *137*, 243–248.

Simeonov, V., Stefanov, S., & Tasakovski, S. (2000). Environmetrical treatment of water quality survey data from Yantra Rive, Bulgaria. *Microchimica Acta*, *134*, 15–21.

Simeonov, V., Stratis, J. A., Samara, C., Zachariadis, G., Voutsa, D., Anthemidis, A., et al. (2003). Assessment of the surface water quality in Northern Greece. *Water Research*, *37*, 4119–4124.

Singh, K. P., Malik, A., Mohan, D., & Sinha, S. (2004). Multivariate statistical techniques for the evaluation of spatial and temporal variations in water quality of Gomti River (India) – A case study. *Water Research*, *38*, 3980–3992.

Singh, K. P., Malik, A., & Singh, V. K. (2005a). Chemometric analysis of hydro-chemical data of an alluvial river – A case study. *Water, Air and Soil Pollution*, *170*, 383–404.

Singh, K. P., Malik, A., & Sinha, S. (2005b). Water quality assessment and apportionment of pollution sources of Gomti river (India) using multivariate statistical techniques– A case study. *Analytical Chimica Acta*, *538*, 355–374.

Sotelo, F. M., Andrade, J. M., Carlosena, A., & Tauler, R. (2007). Temporal characterization of river waters in urban and semi-urban areas using physico-chemical parameters and chemometrics methods. *Analytical Chimica Acta*, *583*, 128–137.

Sundaray, S. K., Panda, U. C., Nayak, B. B., & Bhatta, D. (2006). Multivariate statistical techniques for the evaluation of the Mahanadi river-estuarine system (India) – A case study. *Environmental Geochemistry and Health*, *28*, 317–330.

Tarrado, M., Barcelo, D., & Tauler, R. (2006). Identification and distribution of contamination sources in the Erbo river basin by chemometrics modeling coupled to geographical information systems. *Talanta*, *70*, 691–704.

Vega, M., Pardo, R., Barrado, E., & Deban, L. (1998). Assessment of seasonal and polluting effects on the quality of river water by exploratory data analysis. *Water Research*, *32*, 3581–3592.

Zeilhofer, P., Lima, E. B. N. R., & Lima, G. A. R. (2006). Spatial patterns of water quality in the Cuiaba river basin, Central Brazil. *Environmental Monitoring and Assessment*, *123*, 41–62.