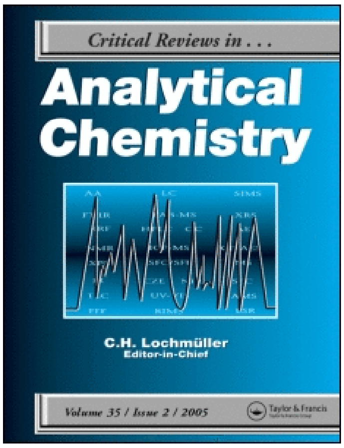

Critical Reviews in Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713400837

Chemometric Estimation of Natural Water Samples Using Toxicity Tests and Physicochemical Parameters

Vasil Simeonov[a]; Lidia Wolska[b]; Agnieszka Kuczyńska[b]; Jacek Gurwin[c]; Stefan Tsakovski[a]; Jacek Namieśnik[b]

[a] Faculty of Chemistry, University of Sofia, Bulgaria [b] Department of Analytical Chemistry, Chemical Faculty, Gdansk University of Technology, Gdansk, Poland [c] Department of Applied Hydrogeology, Institute of Geological Sciences, Wrocław University, Wrocław, Poland

To cite this Article Simeonov, Vasil , Wolska, Lidia , Kuczyńska, Agnieszka , Gurwin, Jacek , Tsakovski, Stefan and Namieśnik, Jacek(2007) 'Chemometric Estimation of Natural Water Samples Using Toxicity Tests and Physicochemical Parameters', Critical Reviews in Analytical Chemistry, 37: 2, 81 — 90

To link to this Article: DOI: 10.1080/10408340601107821

URL: http://dx.doi.org/10.1080/10408340601107821

Critical Reviews in Analytical Chemistry, 37:81–90, 2007
Copyright © Taylor and Francis Group, LLC
ISSN: 1040-8347 print / 1547-6510 online
DOI: 10.1080/10408340601107821

Chemometric Estimation of Natural Water Samples Using Toxicity Tests and Physicochemical Parameters

Vasil Simeonov
Faculty of Chemistry, University of Sofia "St. Kl. Okhridski," Bulgaria

Lidia Wolska and Agnieszka Kuczyńska
Department of Analytical Chemistry, Chemical Faculty, Gdansk University of Technology, Gdansk, Poland

Jacek Gurwin
Department of Applied Hydrogeology, Institute of Geological Sciences, Wrocław University, Wrocław, Poland

Stefan Tsakovski
Faculty of Chemistry, University of Sofia "St. Kl. Okhridski," Bulgaria

Jacek Namieśnik
Department of Analytical Chemistry, Chemical Faculty, Gdansk University of Technology, Gdansk, Poland

The present study deals with the assessment of the quality of natural waters by the use of chemometric interpretation of monitoring data from physicochemical parameters and toxicity tests. The data set consists from data originating from the Turawa reservoir (surface water, sediment core water and groundwater). All 154 samples were analysed for 33 physicochemical parameters as well as for acute and chronic toxicity by respective biotests. The monitoring results were considered both separately (chemical and toxicity data) and simultaneous in order to identify pollution sources in the region and to detect correlation between chemical and toxicity tests. The chemometric methods applied were cluster and principal components analysis. The identified latent factors responsible for the data structure resemble the impact of sources like marine influence, water hardness, turbidity, nutrition etc. It is quite interesting to detect that there is no direct high correlation between chemical and toxicity data, which is an important indication that the water quality has to be assessed by both groups of parameters. Still, some indications for the formation of acute and chronic toxicity by some chemical parameters are found and discussed.

Keywords multivariate statistics, natural waters, sediments, toxicity, water quality

INTRODUCTION

The careful monitoring of natural water systems like river streams, lakes, wells, and underground sources is a very responsible task. Usually, a set of chemical and physicochemical parameters reflecting the surface or underground water quality are carefully analysed and the results obtained are compared to certain threshold values in order to decide if the water quality meets the quality desired. The choice of quality parameters is normally standardized and described in various instructions and directives for individual countries or unions like the EU (1–4). Recently, a very specific attention requires a different type of water quality parameter called "toxicity" ("ecotoxicity") (5–10). It is well known that biological tests are already often applied to environmental samples, especially water for drinking purposes but in the case of testing toxicity, the aim is to determine the level of pollution in the systems of interest.

Address correspondence to Vasil Simeonov, Faculty of Chemistry, University of Sofia "St. Kl. Okhridski," 1164 Sofia, 1, J. Bourchier Blvd., Bulgaria. E-mail: vsimeonov@chem.uni-sofia.bg

Chemical analysis enables the detection, quantitative determination and identification of organic and inorganic pollutants, but does not provide information about the potential negative impact of environmental compounds on particular components of ecosystems. This is because chemical analysis does not consider (11–13):

- all the compounds present in the environment,
- the bioavailability of their different forms, or
- their different biological activities.

A complementary approach, taking into account the above-mentioned facts, can include the application of biotests. Moreover, usage of biotests enables the detection of toxic effects of the combination of many different pollutants in a sample. Synergistic as well as antagonistic effects can be observed (14–16).

Bioassays provide data about the effect, without pinpointing the substances and the potential source. Therefore, a tool is necessary for providing toxicity data as well as an identification of the compounds causing the effects. An integrated approach based on parallel application of bioassays and chemical analysis is the most powerful tool for the assessment of environmental pollution (17, 18).

Very often, however, the monitoring data are considered in a "univariate" way—each parameter separately. In reality, the state of an ecosystem depends simultaneously on many factors and parameters. Therefore, these systems are multivariate in nature. That is why the classification, modeling and interpretation of the monitoring data sets have to be performed by the use of the chemometrics and environmetrics (19–28), where the references given are only a tiny part of many environmetric studies. The specific point in this particular study of natural waters and bottom sediments is that there is a lack of intelligent data analysis of monitoring sets with simultaneous estimation of both chemical (physicochemical) and toxicity parameters.

The aim of the present study is to interpret monitoring data from the region of Turawa Lake (Poland) where water and sediment samples were chemometrically tested for both chemical and toxic content. The final assessment of the quality of the ecosystem and the possible pollution sources will make it possible to reveal various relationships between the quality parameters and the systems studied.

MATERIALS AND METHODS

Description of Region

The Turawa Lake is located in southwest Poland within the Opole voivodship and belongs to municipalities of Turawa and Ozimek. This artificial reservoir was built on Mała Panew River, which together with two other rivers, the Libawa and the Rosa, flow directly into the lake. The area of the lake is approx. 20 km^2, and the volume of retention equals 106 million m^3, whereas the total area of the lake catchment occupies 1424 km^2. An average annual temperature equals to 8.2°C and average negative temperatures from –4.7 to –0.6°C occur in December, January and February with 32 frosty days. The warmest months are July and August with temperature 18.4°C and 17.6°C, respectively. An average annual precipitation in this region fluctuates from 651 mm (the Siedlec station) to 788 mm (the Góra Świętej Anny station), whereas calculated values of evapotranspiration ranges from 390 mm to 540 mm. The forest cover occupies approx. 67% of the catchment. The potential sources of pollution in the Mała Panew watershed are mainly: agriculture activity, urban and domestic sewage. The 68 dumping sewage locations are documented within the watershed. An excessive algae growth and eutrophication process appear, primarily due to phosphorous compound. Besides the biogenic content a toxic contamination is present including heavy metals, especially extremely high cadmium concentrations in sediments.

The sampling region was Turawa Impoundment Lake where lake water, groundwater and bottom sediments were collected as samples. Surface and groundwater samples were taken also from the entire Mala Panew River basin. This region was selected for a pilot project among other 14 objects from the Odra river catchment within the large-scale program called "The ecological state of barrier lakes in the Odra river basin and conducted works towards its improvement." Such a multidisciplinary research project for assessing ecological conditions of the reservoir was carried out thanks to the Government Coordinator of the Odra Programme 2006. The 10 working teams representing scientific institutes and companies from Poland and abroad were involved in complex explorations of the lake (29, 30). The aim of the studies is the evaluation of the Turawa Lake ecosystem in order to design and manage the remediation procedures (31). The investigations of surface and groundwater conditions (water sampling, water flow and water level measurements) were developed among several other tasks that were made in the project.

The necessity of carrying out a full monitoring campaign results from the lack of any official information on pollution, influence of specific pollutants or their combination during eutrophication processes. By the way this is a similar situation with many Bulgarian catchments and the active participation of scientists from both countries (Poland and Bulgaria) in this particular project is of vital importance for many ecosystems in both countries.

Sampling and Sample Testing

The water samples from the region were separated between surface water samples, sediment core water samples and groundwater samples. Altogether 154 samples were tested (62 surface water samples, 58 groundwater samples and 34 sediment samples; in the latter case the samples were the core water collected from the sediment). Two water sampling campaigns were conducted, the first one in November 2003 and the second one in May 2004 (32). The major drilling campaign in the bottom of the lake was carried out in the period between June and September 2004.

Thirty-three chemical and physicochemical parameters were analysed (pH, conductivity, dissolved oxygen, biological oxygen demand BOD_5, chemical oxygen demand COD, chloride, sulfate, dissolved silica, ammonia nitrogen, nitrate nitrogen, nitrite nitrogen, Kjeldahl nitrogen, phenols, anionic detergents, total iron, mercury, lead, copper, nickel, zinc, cadmium, manganese, total chromium, chromium (VI), magnesium, sodium, potassium, calcium, alkalinity, total hardness, turbidity, total content of solutes, and suspended matter). As seen the chemical analysis includes the standard water quality parameters, heavy metals, some organic components. The analytical methods used were potentiometry (pH, dissolved oxygen, BOD_5), conductometry (conductivity), titrimetry (COD_{Mn}, chloride, Ca, alkalinity, total hardness), gravimetry (sulfate, total content of solutes, suspended matter), colorimetry (dissolved silica, ammonia nitrogen, nitrate nitrogen, nitrite nitrogen, Kjeldahl nitrogen, phenols, anionic detergents, total Fe), flame atomic absorption spectrometry (Cu, Ni, Zn, Mn, total Cr, Cr (VI), Mg, K), flame atomic emission spectrometry (Na), electrothermal atomic absorption spectrometry (Pb, Cd), cold vapour atomic absorption spectrometry (Hg), absorption spectrophotometry (turbidity). No special description of the analytical methods and their parameters is given since they are well known and widely used as standard procedures in water analysis.

The next step in the sample testing was the performance of a series of measurements allowing for an assessment of acute and chronic toxicity of all samples taken. Acute toxicity was determined by the use of *ToxAlert 100* (33) and *Microtox Model 500* (34). As bioindicator organisms the bioluminescent bacteria from the comma bacillus group (*Vibrio fischeri* class) were applied. Toxicity measurements were conducted in accordance with the requirements of PN-EN ISO 11348 standards (35, 36). Additionally, the determination of the toxicity of water samples included microbiotests performed by application of *Daphna magna* crustacean in order to determine the acute toxicity (*Daphtoxkit F magna*) according to PN-EN ISO 6341 (37) as well as chronic toxicity, tested in accordance with ISO 10706 norms (38).

The numerical measures of the toxicity test for acute or chronic toxicity and for both types of organisms were the experimental values for:

- Bioluminescent inhibition (high values are indication for higher toxicity);
- Mobility inhibition (same as above);
- Reproduction inhibition (same as above);
- Mortality (same as above);
- $EC_{20(50)}$—the concentration of a sample that causes 20% or 50% of the maximal biological response, e.g., inhibition of bioluminescence, mobility or reproduction; low values indicate high toxicity and high values–lack of toxicity.

Two sets of monitoring results were constructed: the first one containing only chemical and physicochemical parameters for assessment of the water quality, and the second one with addition of the sample acute and chronic toxicity data. These sets were then subject to chemometric analysis.

Chemometric Methods

Cluster analysis (CA) and principal components analysis (PCA) were used for multivariate statistical modeling of the input data (39, 40). The main goal of the hierarchical agglomerative cluster analysis is to spontaneously classify the data into groups of similarity (clusters) searching objects in the n-dimensional space located in the closest neighborhood and to separate a stable cluster from other clusters. Usually, the sampling sites are considered as objects for classification, each one determined by a set of variables (chemical concentrations). It is also possible to search for links between the variables turned to objects of classification. In order to achieve this a series of procedures is necessary:

1. Normalization of the raw input data to dimensionless units in order to avoid the influence of the different range of chemical dimensions (concentration);
2. Determination of the distance between the objects of classification by application of some similarity measure, e.g., Euclidean distance or correlation coefficient;
3. Performing appropriate linkage between the objects by some of the cluster algorithms like single, average or centroid linkage;
4. Plotting the results as a dendrogram;
5. Determination of the cluster significance by 0.33 D_{max} or 0.66 D_{max} criterion;
6. Interpretation of the clusters both for objects and variables.

Using cluster analysis one could display the object similarity in a reliable way to make the initial interpretation of the data set structure. But a more reliable display method proves to be PCA. It enables the reduction of the dimensionality of the space of the variables in the direction of the highest variance of the system, new variables being linear combinations of the previous variables, replacing the old coordinates of the factor space. The new coordinates are called latent factors or principal components. The interpretation of the new factors is the main goal of the chemists since they deliver useful information about latent relationships within the data set. The results are indicated by two sets—factor scores giving the new coordinates of the factor space with the location of the objects and factor loadings providing information on the relationship between the variables. Only statistically significant loadings (>0.70) are important for the modeling procedure.

The new principal components (latent factors) explain a substantial part of the total variance of the system for an adequate statistical model. Usually, the first principal component (PC1) explains the maximal part of the system variation and each additional PC has a respective contribution to the variance explanation but with less significance.

A reliable model requires normally such a number of PCs, so that over 75% of the total variation can be explained. In our modeling we have applied the Varimax rotation mode of PCA that allows a better explanation of the system in consideration since it strengthens the role of the latent factors with higher impact on the variation explanation and diminishes the role of PCs with lower impact.

In order to understand the contribution of each latent factor to the total mass of the chemical components in the surface water, an apportioning model is offered. The source apportioning follows the approach of Thurston and Spengler (41) that uses multiple regression of the total mass on the absolute principal components scores (APCS) obtained by the performance of PCA.

All calculations were performed by the use of the software package STATISTICA 6.0.

RESULTS AND DISCUSSION

Physicochemical Quality Parameters

The input data of the monitoring of the three different water systems were at first treated separately: surface water samples; sediment core water sample; groundwater samples. The application of principal components analysis (PCA) to these three data subsets aimed the identification of latent factors responsible for the data structure and, possibly, representing the emission sources for each subset. A Varimax-normalized mode of PCA was used in the chemometric treatment. In Tables 1–3, the factor loadings are shown for each type of sampling. The statistically significant loadings are marked for better interpretation. It is important to note that not all variables were involved in the chemometric analysis. Some of them indicate almost or constant level throughout the monitoring period and for all monitoring sites, for others there is serious lack of information (missing data). That is why a careful selection of significant variables for each type of samples was undertaken and only the chosen ones were included in PCA.

Surface Water Phase. Five latent factors are found to explain 83.5% of the total variance of the system (62 samples were interpreted with 22 variables; from the set the variables with almost constant concentration were eliminated; also variables with many missing results were not involved). It is readily seen that the latent factors are as follows:

PC1 (explained variance 25.1%) includes the following strong correlated variables:

Conductivity (COND), sulfate (SO$_4$), calcium (Ca), alkalinity (ALK), total hardness (THARD), total dissolved solutes (TDS);

PC2 (explained variance 24.3%) includes the following strong correlated variables:

TABLE 1
Factor loadings for surface water samples (all significant loadings are marked)

Parameter	PC 1	PC 2	PC 3	PC 4	PC 5
pH	0.124	−0.095	0.092	**−0.817**	0.190
COND	**0.861**	0.495	0.009	0.045	0.038
BOD	0.094	**0.635**	0.322	−0.294	0.100
COD	−0.027	0.197	**0.886**	−0.146	0.052
CL	0.169	**0.872**	0.068	0.026	−0.043
SO4	**0.899**	0.039	0.049	−0.112	0.137
DIS_SI	0.046	0.148	−0.010	**0.863**	0.179
NH4_N	0.227	**0.864**	0.053	0.228	−0.001
NO3_N	0.284	−0.183	−0.145	0.012	**0.811**
NO2_N	−0.122	0.156	0.116	−0.083	**0.838**
KJEL_N	0.251	**0.855**	0.203	0.180	0.015
TOT_FE	−0.038	0.047	**0.795**	0.542	−0.019
MN	0.006	0.303	0.424	**0.713**	−0.128
MG	0.312	**0.750**	0.053	−0.038	−0.035
NA	0.172	**0.881**	0.016	0.233	−0.108
K	−0.078	**0.836**	−0.106	0.205	0.108
CA	**0.967**	0.101	0.032	−0.061	−0.020
ALKAL	**0.896**	0.295	0.067	0.046	−0.168
TOT_HARD	**0.981**	0.073	0.055	−0.038	0.001
TURB	0.055	0.092	**0.836**	−0.097	0.103
TOT_SOL	**0.910**	0.272	0.063	0.062	0.182
SUSP_MAT	0.205	−0.065	**0.905**	0.168	−0.055
Expl. var (%)	**25.1**	**24.3**	**15.2**	**11.7**	**7.2**

TABLE 2
Factor loadings for sediment core water samples (all significant loadings are marked)

Parameter	PC 1	PC 2	PC 3	PC 5	PC 4	PC 6	PC 7
pH	−0.177	0.067	−0.546	−0.013	−0.138	**0.639**	0.098
COND	0.200	**0.872**	0.062	0.069	0.336	0.050	−0.123
BOD	0.378	0.347	**0.687**	0.043	0.241	−0.159	0.145
COD	**0.882**	−0.059	0.040	0.127	0.030	0.087	0.236
CL	0.162	−0.022	0.129	−0.043	**0.871**	−0.018	−0.079
SO4	−0.139	**0.806**	−0.170	0.030	−0.333	0.214	−0.117
DIS_SI	0.180	−0.169	−0.017	0.096	−0.058	0.063	**0.885**
NH4_N	**0.823**	0.174	0.204	−0.008	0.351	0.044	−0.015
NO3_N	0.597	−0.077	**0.636**	0.104	−0.019	0.023	−0.185
NO2_N	**0.936**	0.015	−0.025	−0.047	−0.052	−0.084	−0.061
KJEL_N	**0.905**	−0.129	0.115	0.052	0.054	0.036	0.133
PHEN	0.280	***−0.446***	0.152	0.266	−0.080	0.079	−0.166
TOT_FE	0.163	−0.006	**0.753**	−0.393	0.197	−0.110	0.107
PB	**0.869**	0.142	0.361	−0.038	0.034	0.008	0.009
CU	**0.758**	0.081	0.173	−0.398	−0.063	0.030	0.313
NI	0.121	−0.101	0.048	−0.913	−0.086	0.012	0.043
ZN	**0.693**	0.489	0.250	0.048	−0.006	0.129	−0.007
CD	−0.071	0.020	−0.079	0.099	−0.028	**−0.879**	0.043
MN	−0.012	0.018	0.048	**−0.898**	0.101	0.109	−0.068
MG	0.162	**0.906**	0.025	0.018	0.181	−0.043	−0.179
NA	0.019	0.146	−0.076	−0.072	**0.912**	0.080	−0.040
K	**0.580**	0.366	−0.007	0.147	0.386	−0.197	−0.138
CA	**0.892**	0.121	0.128	−0.285	0.054	−0.175	0.075
ALK	−0.053	0.412	0.177	0.124	**0.674**	−0.168	0.057
TOT_HARD	**0.723**	0.160	0.050	−0.230	0.079	-0.505	0.153
TURB	0.241	−0.188	0.181	-0.500	−0.090	−0.318	**0.661**
TOT_SOL	0.339	**0.791**	0.162	0.097	0.206	−0.172	−0.018
SUSP_MAT	0.070	−0.039	**0.862**	−0.010	−0.060	0.091	0.015
Expl. var (%)	**27.1**	**14.1**	**10.6**	**9.0**	**10.0**	**6.5**	**5.8**

Ammonia nitrogen (NH_4), Kjeldahl nitrogen (Kjel N), magnesium (Mg), sodium (Na), potassium (K), biological oxygen demand (BOD), chloride (Cl);

PC3 (explained variance 15.2%) includes the following strong correlated variables:

Chemical oxygen demand (COD), total iron (TOT Fe), turbidity (TURB), suspended matter (SUSP);

PC4 (explained variance 11.7%) includes the following strong correlated variables:

pH, dissociated silica (Dis Si), manganese (Mn);

PC5 (explained variance 7.2%) includes the following strong correlated variables:

Nitrate nitrogen (NO_3), nitrite nitrogen (NO_2).

In the first latent factor, predominantly chemical components responsible for the formation of the water hardness are included with high factor loadings. We assume that this factor has a major impact on this important quality parameter and its conditional name is *"water hardness."* The significance of the factor loadings for parameters related to the biological processes in the surface water phase in PC2 allows the assumption that this is a *"biological"* factor. Further, PC3 could be conditionally named the *"water turbidity"* factor, due to the strong correlation between the quality parameters turbidity, suspended matter and total iron content. The fourth latent factor is conditionally named *"acidic"* and the last one—*"anthropogenic."* In general, natural factors, which are related to the water quality, are PC1 and PC3, since the other three indicate an anthropogenic impact. The low and constant concentration of heavy metals does not allow selecting of tracers for more specific types of pollution.

Sediment Core Water Phase. Seven latent factors are found to explain 85.1% of the total variance of the system (34 samples were interpreted with 27 variables; it is important to note that in this case many heavy metals are included since they have different concentrations for different sites and monitoring periods). They could be presented as follows:

TABLE 3
Factor loadings for underground water samples (all significant loadings are marked)

Parameter	PC 1	PC 2	PC 3	PC 4	PC 5	PC 5
COND	0.277	**0.938**	0.051	0.005	0.087	−0.017
BOD	**0.821**	0.196	0.372	−0.081	0.019	0.177
COD	**0.925**	0.104	0.276	0.109	−0.013	0.019
CL	0.048	**0.848**	0.040	0.051	0.157	0.169
SO4	0.085	**0.786**	0.221	0.063	−0.061	−0.274
DIS_SI	−0.221	0.090	−0.207	0.464	0.236	**−0.561**
NH4_N	0.289	**0.471**	0.051	0.456	−0.149	0.164
NO3_N	0.010	0.140	−0.113	**−0.856**	−0.017	0.009
NO2_N	−0.017	0.092	**0.772**	0.179	−0.059	0.095
KJEL_N	**0.951**	0.128	0.173	0.084	−0.027	0.015
PHEN	**0.704**	−0.036	0.074	0.015	−0.076	0.553
TOT_FE	0.649	0.081	**0.666**	−0.131	0.165	−0.010
PB	0.169	0.033	**0.814**	−0.074	−0.015	−0.011
ZN	0.088	0.027	−0.004	0.134	**0.928**	−0.005
MN	**0.586**	0.113	0.430	−0.351	0.063	−0.052
MG	0.264	**0.859**	0.007	−0.140	0.060	−0.099
NA	0.032	**0.850**	−0.049	−0.016	0.111	0.117
K	−0.032	0.366	−0.030	−0.159	**0.703**	0.123
CA	**0.927**	0.180	0.085	0.071	0.079	0.048
ALK	0.258	**0.523**	−0.140	0.389	0.036	0.035
TOT_HARD	0.052	0.018	0.013	0.094	0.171	**0.819**
TURB	0.459	0.040	**0.847**	−0.005	−0.057	0.053
TOT_SOL	−0.188	**0.828**	0.236	−0.155	0.094	−0.086
SUSP_MAT	0.484	0.069	**0.831**	0.023	0.025	0.018
Expl. var (%)	**22.6**	**21.5**	**15.6**	**6.7**	**6.6**	**6.3**

PC1 (explained variance 27.1%) includes the following strong correlated variables:

COD, NH_4, NO_3, NO_2, Kjel N, K, Pb, Cu, Zn, Ca, THARD. The interpretation of this particular latent factor is not simple since it includes many variables with high factor loadings. It is obvious that anthropogenic (Pb, Cu, Zn, NO_3, NO_2) impacts are mixed with biological (NH_4, Kjel N) and even natural (Ca, THARD). The conditional name could be *"mixed factor."*

PC2 (explained variance 14.1%) includes the following strong correlated variables:

COND, SO_4, Mg, PHEN. It is interesting that the high factor loading for phenols (PHEN) is negative, so the phenol concentration is contrasting the other three concentration levels. This is probably an indication for the different way of absorption of organic and inorganic compounds on the bottom sediments. The conditional name offered is *"organic and inorganic salt factor."*

PC3 (explained variance 10.6%) includes the following strong correlated variables:

TOT Fe, SUSP MAT, BOD.

PC4 (explained variance 10.0%) includes the following strong correlated variables:

Na, Cl, ALK.

PC5 (explained variance 9.0%) includes the following strong correlated variables:

Mn, Ni.

The last three factors (PC3, PC4, and PC5) need a common interpretation. It is clear that they reflect the influence of the bottom sediment constitution (major components Fe, Mn, Ni) and, probably, a marine impact (Na, Cl). Moreover, the factor loading for total iron in PC 5 is also relative high. Therefore, this group of latent factors could be considered as one possible source for determination of the sediment core water state and may be conditionally named *"sediment bulk impact."*

Additional proof to this assumption is the very close percentage of explained variance by each one of the group members.

PC6 (explained variance 6.5%) includes the following strong correlated variables:

pH, Cd.

PC7 (explained variance 5.8%) includes the following strong correlated variables:

Dis Si, TURB.

The last two latent factors describe a small part of the total variance but are still sufficient in order to be taken into account. They indicate the role of the acidity and turbidity of the sediment core water samples and could be conditionally named *"acidic"* and *"turbidity"* factor, respectively.

Underground Water Phase. Six latent factors are found to explain 79.0% of the total variance of the system (58 samples were interpreted with 25 variables). They could be presented as follows:

PC1 (explained variance 22.6%) includes the following strong correlated variables:
BOD, COD, Kjel N, PHEN, Ca, Mn
PC2 (explained variance 21.5%) includes the following strong correlated variables:
COND, Cl, SO_4, Mg, Na, Tot Sol, NH_4, ALK
PC3 (explained variance 15.6%) includes the following strong correlated variables:
NO2, Pb, TURB, Susp Mat, Tot Fe
PC4 (explained variance 6.7%) includes the following strong correlated variables:
NO3
PC5 (explained variance 6.6%) includes the following strong correlated variables:
Zn, K
PC6 (explained variance 6.3%) includes the following strong correlated variables:
THARD, Dis Si

In this set of underground water samples the latent factor interpretation is quite difficult. On one side, the explained variance of the system even with 6 factors is relatively low, which is an indication for the complex character of the samples. On the other hand, the relation between number of samples and number of variables on the set is not quite favorable for chemometric analysis. Besides, the natures of the factors are different compared to the other two phases. Conditionally the latent factors could be named (due to the level of factor loadings) *"biological," "soil impact," "turbidity," "nutrient," "salt," and "hardness,"* respectively.

It is evident that the three different phases reveal a different pattern of factors responsible for the data structure and, hence, different influences from the environment on their quality parameters. This assumption was proven by the application of cluster analysis. Ward's method of linkage (squared Euclidean distance as similarity measure) was applied to detect similarities or dissimilarities between all 154 samples (object of clustering) from the different water phases. The dendrogram obtained (Fig. 1) reveals clearly the three various clusters (groups of similarity).

Cluster 1 contains dominantly samples from surface water, cluster 2 from sediment core water, and cluster 3 from underground water. This clear difference between the water phases with respect to the patterns forming the water quality confirms the output from the PCA. It is expected that the addition of the results of the toxicity tests for acute and chronic toxicity may present more information about the water quality in addition to the separation by phases.

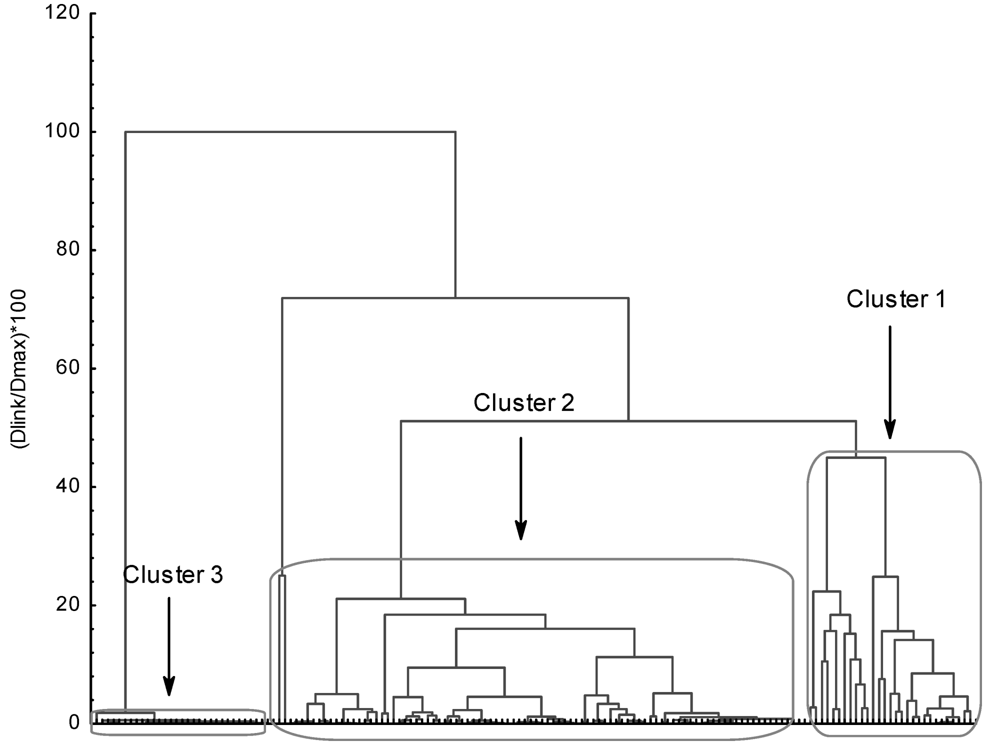

FIG. 1. Hierarchical dendrogram for all samples from Turawskie region.

TABLE 4
Apportioning (in %) for some water quality parameters

	COND	SO4	T_FE	K	CA	ALK	TURB	THARD
PC1(s)	67.2	80.9	—	—	65.4	70.2	69.1	94.3
PC2(s)	21.4	—	—	61.4	21.2	13.7	14.5	—
PC3(s)	—	—	49.3	—	—	—	—	—
PC4(s)	—	—	40.7	13.8	—	—	—	—
PC5(s)	—	7.5	—	17.1	—	—	9.2	—
Intcpt	*11.4*	*11.6*	*10.0*	*7.7*	*13.4*	*16.1*	*7.2*	*5.7*
PC1(c)	10.8	—	10.4	34.6	69.1	—	4.4	56.6
PC2(c)	54.1	68.9	—	50.3	12.9	7.8	5.3	21.2
PC3(c)	—	—	53.2	—	—	10.1	6.1	—
PC4(c)	12.6	—	-	10.2	8.4	57.3	—	9.7
PC5(c)	—	—	9.8	—	7.1	6.7	4.9	6.4
PC6(c)	-	13.7	—	—	—	—	5.7	—
PC7(c)	—	—	8.9	—	—	—	55.3	—
Intcpt	*22.5*	*17.4*	*17.7*	*4.9*	*2.5*	*18.1*	*18.3*	*6.1*
PC1(u)	10.2	—	44.3	—	59.8	12.6	10.7	—
PC2(u)	81.6	74.4	—	21.1	23.2	57.3	—	—
PC3(u)	—	16.7	46.1	—	—	—	64.5	—
PC4(u)	—	—	—	—	—	19.1	—	—
PC5(u)	—	—	4.2	65.6	—	—	—	19.5
PC6(u)	—	—	—	6.2	—	—	—	67.7
Intcpt	*8.2*	*8.9*	*5.4*	*7.1*	*16.8*	*11.0*	*24.8*	*12.8*

The final part of the chemometric assessment of the water quality includes an apportioning procedure to show the contribution of each identified latent factor to the formation of the total concentration of each physicochemical parameter. The apportioning is performed by the use of the Thurston–Spengler approach. The results (in% contribution) for selected parameters from each water phase (*s*, surface water; *c*, core sediment water; *u*, underground water) are presented in Table 4. It should be remembered that each PC in the table represents a latent factor with a conditional name.

The regression models presented are adequate, and they show a very good fit between "measured" and "calculated by the model" results ($R^2 > 0.75$). The unexplained part of the total concentration of a certain parameter is indicated by the value of the regression intercept. The results in Table 4 do not need special comments but it is readily seen that, for instance, the total concentration of calcium in surface water is explained dominantly by contribution of "water hardness" factor (65.4%) and "biological" factor (21.2%) and the unexplained part is 13.4%. For the same parameter in core sediment water samples, the main contributions have more factors—"mixed" (including a series of parameters inclusive water hardness), "organic and inorganic salt", "sediment bulk" (including sediment constitution impact and marine impact). For the third phase, underground water, the "biological" and "soil impact" factors determine the apportioning results (59.8% and 23.2%, respectively). Again, a different configuration of influences makes the calcium pattern for the underground water phase. The same interpretation scheme has to be applied to each of the parameters.

Physicochemical and Toxicity Quality Parameters

It was of substantial importance to link the chemometric results for the physicochemical parameters with data from the toxicity tests. Since for many samples the values of the toxicity are equal and indicate lack of toxic effects, a real multivariate statistical approach (combining monitoring data for physicochemical and toxicity parameters simultaneously) is not reliable due to the strongly reduced number of cases in the data set matrix. Still, a lot of important information on the toxicity of the various water phase samples could be derived by the use of correlation analysis of samples with proved high toxicity and respective chemical content.

The higher toxicity values (for the whole environmental system including surface, sediment core and underground water) for *acute toxicity* tested by *Vibrio fischeri* bacteria are correlated mainly to pH, conductivity, ammonia nitrogen, Kjeldahl nitrogen, anionic detergents and some metals (Pb, Cu, Zn, and Mn), e.g., to acidic, biological and anthropogenic latent factors identified by PCA. This is a logical output since these particular factors are obviously responsible for acute toxicity increase in some of the sampling and monitoring periods.

For the *acute toxicity* tested by *Daphna magna* crustacean, an enhanced level of correlation with pH, conductivity, chloride, phenols, alkalinity, sodium, potassium and magnesium is observed. In this case the impact of latent factors like acidity, organics and marine salts contributes to the effects of inhibition of reproduction. The increased concentrations of the chemical parameters for the period with registered high toxicity reveals their role for the formation of the new quality parameter of acute toxicity. Formally speaking, these levels of chemical concentrations are within the limits of allowable thresholds but, probably, their joint influence affects seriously the acute toxicity tested by *Daphna magna*.

It proved to be more difficult to assess the *chronic toxicity* in the environmental system of Turawskie water reservoir. Slightly enhanced correlations are observed between the chronic toxicity test values and the other water quality parameters. Still, correlation could be reported for chloride, phenols and anionic detergents. These are typical pollutants for water environment and obviously form the background of existing of long-term toxicity, although their values measured seem not to be threatening.

CONCLUSION

The water quality assessment carried out by the use of multivariate statistical methods has indicated that the monitoring data should be estimated in a multiple way in order to reveal the real situation with a certain environmental system or phase. Thus, the toxicity effects (acute or chronic) can be readily explained not only by the traditional chemical pollution impact but also as results of specific processes and phenomena in the specific environment. Obviously, the information about all possible interactions in a complex environment becomes available only in the case of multivariate assessment approach.

ACKNOWLEDGMENTS

Authors V. Simeonov and S. Tsakovski would like to express their sincere gratitude to the National Fund "Scientific Research," Ministry of Education and Science, Bulgaria for the generous financial support (Project No. VUH 02/05, 2437), which made this study possible. This scientific work was also financially supported by science in 2005–2007 as a research project (3 T09D 077 29).

REFERENCES

1. Bulgarian Drinking Water Analysis Standard (BDWS), Ministry of Environment and Water, Sofia, Bulgaria, 1990.
2. EU Instruction 80/778, Water analysis and Control, Brussels, Belgium, 1990.
3. Greek Hygiene Office Instruction (GHOI) A5/228, Standardized Methods for Potable Water Analysis, Athens, Greece, 1986.
4. Council Directive 91/692/EEC, European Union Directive (EUD), 1991.
5. U.S. Environmental Protection Agency (USEPA). Clarifications regarding toxicity reduction and identification evaluations in the national pollutant discharge elimination system program, March 2001, Washington, DC.
6. G. Goodfellow, L. Ausley, D. Burton, D. Denton, P. Dorn, D. Grothe. M. Heber, T. Norberg-King, and J. Rogers, Major ion toxicity in effluents: A review with permitting recommendations. *Environmental and Toxicological Chemistry* 19 (2000):175–182.
7. J. Gorsuch, F. Dwyer, C. Ingersoll, and T. LaPoint eds., *Environmental Toxicology and Risk Assessment.* Vol. 2. (American Society for Testing and Materials, Philadelphia, PA, 1993), p. 774.
8. D. Pillard, D. DuFresne, D. Caudle, J. Tietge, and J. Evans, Predicting the toxicity of major ions in seawater to mysid shrimp (*Mysidopis bahia*), sheepshead minnow (*Cyprinodon variegates*), and inland silverside minnow (*Menidia beryllina*). *Environmental and Toxicological Chemistry* 19 (2000):183–191.
9. USEPA, Toxicity Identification Evaluation: Characterization of Chronically Toxic Effluents. Phase 1. EPA 600-6-91-005F. National Effluent Toxicity Assessment Center, Duluth, MN, 1992.
10. USEPA, Toxicity Identification Evaluation: Toxicity Identification Procedures for Samples Exhibiting Acute and Chronic Toxicity. Phase 2. EPA 600-R-92-080. National Effluent Toxicity Assessment Center, Duluth, MN, 1993.
11. K. Zabetoglou, D. Voutsa, and C. Samara, Toxicity and heavy metal contamination of surficial sediments from the Bay of Thessaloniki (Northwestern Aegean Sea) Greece. *Chemosphere* 49 (2002):17–26.
12. I. Mantis, D. Voutsa, and C. Samara, Assessment of the environmental hazard from municipal and industrial wastewater treatment sludge by employing chemical and biological methods. *Ecotoxicological and Environmental Safety* 62 (2005):397–407.
13. A. Baun, A. Ledin, L. A. Reitzel, P. L. Bjerg, and T. H. Christensen, Xenobiotic organic compounds in leachates from ten Danish MSW landfills—Chemical analysis and toxicity tests. *Water Research* 38 (2004):3845–3858.
14. M. Salizzato, B. Pavoni, A. Volpi Ghirardini, and P. F. Ghetti, Sediment toxicity measured using *Vibrio fischeri* as related to the concentrations of organic (PCBs, PAHs) and inorganic (metals, sulphur) pollutants. *Chemosphere* 36 (1998):2949–2968.
15. R. Boluda, J. F. Quintanilla, J. A. Bonilla, E. Sáez, and M. Gamón, Application of the Microtox test and pollution indices to the study of water toxicity in the Albufera Natural Park (Valencia, Spain). *Chemosphere* 46 (2002):355–369.
16. S. Pérez, M. Farré, M. J. García, and D. Barceló, Occurrence of polycyclic aromatic hydrocarbons in sewage sludge and their contribution to its toxicity in the ToxAlert 100 bioassay. *Chemosphere* 45 (2001):705–712.
17. N. Reineke, K. Bester, H. Hühnerfuss, B. Jastorff, and S. Weigel, Bioassay-directed chemical analysis of River Elbe surface water including large volume extractions and high performance fractionation. *Chemosphere* 47 (2002):717–723.
18. W. Brack, R. Altenburger, U. Ensenbach, M. Möder, H. Segner, and G. Schüürmann, Bioassay-directed identification of organic toxicants in river sediment in the industrial region of Bitterfeld (Germany)—A contribution to hazard assessment. *Archives of Environmental Contamination and Toxicology* 37 (1999):164–174.
19. V. Simeonov, S. Stefanov, and S. Tsakovski, Environmetrical treatment of water quality survey data from Yantra River, Bulgaria. *Mikrochimica Acta* 134 (2000):15–21.
20. V. Simeonov, D. L. Massart, G. Andreev, and S. Tsakovski, Assessment of metal pollution based on multivariate statistical modeling of "hot spot" sediments from the Black Sea. *Chemosphere* 41 (2000):1411–1417.

21. V. Simeonov, C. Sarbu, D. L. Massart, and S. Tsakovski, Danube River water data modeling by multivariate data analysis. *Mikrochimica Acta* 137 (2001):243–248.
22. S. Tsakovski, H. Puxbaum, V. Simeonov, M. Kalina, H. Löffler, G. Heimburger, P. Biebl, A. Weber, and A. Damm, Trend, seasonality and multivariate modelling study of wet precipitation data from the Austrian Monitoring Network (1990–1997). *Journal of Environmental Monitoring* 2 (2000):424–431.
23. G. Mihailov, V. Simeonov, N. Nikolov, and G. Mirinchev, Environmetric approaches to estimate pollution impacts on a coastal area by sediment and river water studies. *Water Science and Technology* 46 (2002):45–52.
24. V. Simeonov, J. W. Einax, I. Stanimirova, and J. Kraft, Environmetric modeling and interpretation of river water monitoring data. *Analytical and Bioanalytical Chemistry* 374 (2002):898–905.
25. C. Samara, Th. Kouimtzis, R. Tsitoridou, G. Kanias, and V. Simeonov, Chemical mass balance source apportionment of PM_{10} in an industrialized urban area of Northern Greece. *Atmospheric Environment* 37 (2003):41–54.
26. V. Simeonov, J. Stratis, C. Samara, G. Zachariadis, D. Voutsa, A. Anthemidis, M. Sofoniou, and Th. Kouimtzis, Assessment of the surface water quality in Northern Greece. *Water Research* 37 (2003):4119–4124.
27. V. Simeonov, S. Tsakovski, T. Lavric, P. Simeonova, and H. Puxbaum, Multivariate statistical assessment of air quality. A case study. *Microchimica Acta* 148 (2004):293–298.
28. I. Stanimirova, M. Daszykowski, D. L. Massart, F. Questier, V. Simeonov, and H. Puxabaum, Chemometrical exploration of the wet precipitation chemistry from the Austrian Monitoring Network (1988–1999). *Journal of Environmental Management* 74 (2005):349–363.
29. J. Gurwin, J. Kryza, L. Poprawski, and A. Skowronek, *Zintegrowana kampania badawcza dla określenia ekologicznego stanu zbiornika retencyjnego "Jezioro Turawskie" zgodnie z zasadami zrównowaonego rozwoju*, in *Ochrona i rekultywacja terenów dorzecza Odry*, *Zeszyty Naukowe U. Ziel*. nr 131, Inynieria årodowiska 12 (Zielona Góra: Oficyna Wyd. U. Ziel., 2004), 133–140.
30. J. Gurwin, J. Kryza, L. Poprawski, and A. Skowronek, *Geoecological Research of the Turawskie Lake,* in *Zasoby wodne triasu opolskiego i ekologia Jezior Turawskich* (Opole-Strzelce Op.: NOT FSNT w Opolu, 2005), 211–222.
31. J. Gurwin and A. Skowronek, *The concept of the Turawa Lake revitalisation—In accordance with, "Assessment of ecological condition of the Turawa Lake for the planning of improvement action."* XI International Scientific and Technological Conference On Water Resources Management in the Odra River Basin (Wrocław: RWMB, 2006) (in press).
32. J. Gurwin, *The results of surface water monitoring in the watershed of the Turawskie Lake to assess ecological state of this reservoir*. XI International Scientific and Technological Conference On Water Resources Management in the Odra River Basin, (Wrocław: RWMB, 2006) (in press).
33. ToxAlert 100 Operating Manual, Version 0.09, Merck, Germany, 1999.
34. Microtox Analyzer Manual, Tigret, Poland, 2006.
35. PN-EN ISO 11348:1998. Water quality—Determination of the inhibitory effect of water samples on the light emission of Vibrio fischeri (Luminescent bacteria test)—Part 2: Method using liquid-dried bacteria. Polish Committee for Standardization, Warsaw. Poland.
36. PN-EN ISO 11348:2002. Water quality—Determination of the inhibitory effect of water samples on the light emission of Vibrio fischeri (Luminescent bacteria test)—Part 3: Method using freeze-dried bacteria. Polish Committee for Standardization, Warsaw. Poland.
37. PN-EN ISO 6341:2002. Water quality—Determination of the inhibition of the mobility of Daphnia magna Straus (Cladocera, Crustacea)—Acute toxicity test. Polish Committee for Standardization, Warsaw, Poland.
38. ISO 10706:2000. Water quality—Determination of long term toxicity of substances to Daphnia magna Straus (Cladocera, Crustacea). International Organization for Standardization, Geneva, Switzerland.
39. D. L. Massart and L. Kaufman, *The Interpretation of Analytical Chemical Data by the Use of Cluster Analysis* (Wiley, New York, 1983).
40. B. Vanderginste, D. L. Massart, L. Buydens, S. De Jong, P. Lewi, and J. Smeyers-Verbeke, *Handbook of Chemometrics and Qualimetrics* (Elsevier, Amsterdam, 1998).
41. G. Thurston and J. Spengler, A quantitative assessment of source contributions to inhalable particulate matter pollution in metropolitan Boston. *Atmospheric Environment* 19 (1985):9–25.