Environ Monit Assess (2012) 184:2017–2029
DOI 10.1007/s10661-011-2096-5

Application of physicochemical data for water-quality assessment of watercourses in the Gdansk Municipality (South Baltic coast)

Monika Cieszynska · Marek Wesolowski · Maria Bartoszewicz · Malgorzata Michalska · Jacek Nowacki

Received: 7 April 2010 / Accepted: 25 April 2011 / Published online: 8 June 2011

Abstract The paper presents water-quality evaluation based on an 8-year monitoring programme in the Gdansk Municipality region, on the Southern coast of the Baltic Sea. The studies were carried out from 2000 to 2007 by surface water analysis at 15 various sites within eight watercourses. Sampling sites included rather urbanized or developed lands, farming fields and non-polluted city recreational areas such as parks and forests. Most of the watercourses were sampled monthly at two locations, one within the upper course of the watercourse and the other near its mouth. In all samples, eight parameters of water quality were determined: total suspended solids, dissolved oxygen, water temperature, oxygen saturation, 5-day biochemical oxygen demand, chemical oxygen demand, total phosphorus and total nitrogen concentration. Interpretation of the obtained results revealed that examination of those basic physicochemical parameters permits to discriminate initially watercourses with respect to level of water contamination. During the research, a large dataset was obtained and it was described by both basic statistical parameters and chemometric method of cluster analysis. The paper presents relations between analysed parameters and influence of land exploitation mode on water quality and describes variation of the results both in space and time.

Keywords Cluster analysis · Gdansk Municipality · Monitoring · Physicochemical parameters · River water quality

M. Cieszynska (✉) · M. Bartoszewicz · M. Michalska · J. Nowacki
Department of Environmental Protection and Hygiene of Transport,
Medical University of Gdansk, Powstania Styczniowego 9B str., 81-519 Gdynia, Poland
e-mail: Cieszynskam@gumed.edu.pl

M. Wesolowski
Department of Analytical Chemistry,
Medical University of Gdansk,
Al. Gen. J. Hallera 107, 80-416 Gdansk, Poland

Introduction

Water is the most common and widespread chemical compound in nature which is a major constituent of all living creatures. It is essential for metabolism and many accompanying processes in cells, and what is more, for many organisms, it constitutes the only habitat for life. Natural surface waters are a solution of many non-organic and organic compounds, colloids, suspensions of natural or anthropogenic origin (Dojlido 1987).

The quality of water is of great importance also for human lives as it is commonly consumed and used by households. In industry, it serves as a solvent, substrate or catalyst of chemical reactions (Goncharuk 2008; Holt 2000; Van Leeuwen 2000; Petraccia et al. 2006). To minimise health hazards, an extensive monitoring programme of surface water quality within limits of Gdansk Municipality, located on the southern shore of the Baltic Sea, was introduced. The examined watercourses flow through areas that significantly differ, not only with regard to natural landscape but also to the type of the surrounding land development. The watercourses have also different hydrological characteristics. The performed monitoring programme generated a large database of results which was assessed by basic statistical parameters in order to describe variation of analysed parameters in particular years and determine pollution levels of water from respective watercourses, taking into consideration land exploitation mode.

Agglomerative hierarchical cluster analysis (CA) was applied for a detailed interpretation of the results. CA is an extremely useful tool which supports interpretation of large and multidimensional sets of environmental data. In this paper CA for the results explanation was selected because contrary to other pattern recognition techniques (e.g. principal components analysis) it accounts for the whole variation in the data and no simplification of the information is necessary (Hill and Lewicki 2006; Otto 1999; Vega et al. 1998).

The utility of CA is confirmed in many papers regarding quality of surface waters (Zhang et al. 2009). CA can assist in classification of sampling stations in accordance with similarity of chemical composition of water (Giridharan et al. 2009). When applied for different watercourses, it supports recognition of regions with similar physicochemical properties of water and enables detection of factors controlling water quality. Examples of CA application are included in papers concerning rivers in Northern Italy (Reisenhofer et al. 1998) and Northern Greece (Simeonov et al. 2003). In both cases, analysed samples of water were grouped into four distinct clusters collected from various watercourses and with different water quality.

In this paper, CA was applied to describe variation among samples collected from each watercourse in the whole study period. In such case, CA permits to determine whether water quality can be modified with the watercourse flow and allows identification of areas with specific properties of water. Samples collected from one watercourse can be grouped into two—clean and polluted, or three—clean, highly and medium polluted clusters representing similar water properties (Brogueira and Cabeçadas 2006; Chang 2005; Kannel et al. 2007; Reghunath et al. 2002). Marengo et al. (1995) mentions application of CA for samples from Lagoon of Venice collected from various sites and at different seasons of the year. In this instance, it was concluded that location of sampling point rather than a season of sample collection determines clustering of the results.

Experimental

The Gdansk Municipality lies on the southern coast of the Baltic Sea, in Northern Poland. It is characterized by a temperate climate with four clearly differentiated seasons. Winters are moderately severe with mean daily temperatures of −3.4°C in January; summers are mild with mean temperature of 21.3°C in August and frequent

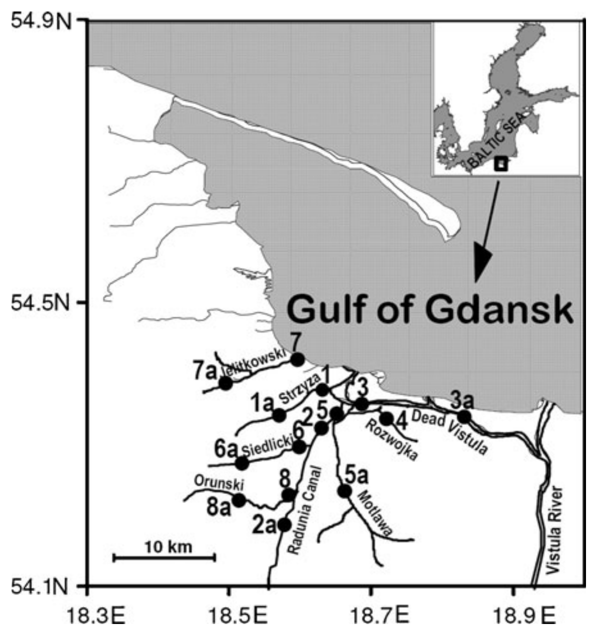


Fig. 1 Map of the study area and locations of the monitoring stations that provided data for the present study

rain or thunderstorms. Monthly rainfall varies from 17.9 to 66.7 mm.

Figure 1 shows map of the study area with monitoring stations used to provide the study data. All watercourses in the study area enter the Gulf of Gdansk via Dead Vistula River, only Jelitkowski Stream flows directly into the Gulf of Gdansk in the Jelitkowski Park. Table 1 presents names of eight watercourses covered by this study, their general characteristics as well as geographical coordinates of the sampling stations.

The sampling points were selected in such a way that one of them was situated farthest upstream (labelled by adding letter “a”), the other point was near the mouth. The exception was Rozwojka Canal sampled only at one point. The water samples were collected from 2000 to 2007. From each watercourse, with the exception of Rozwojka Canal, two samples were taken monthly from the mainstream, at the depth about 20 cm using plastic scoop. On rare occasions, when it was not possible to collect samples from the mainstream of the watercourse (Dead Vistula River and Motlawa River), the samples were taken at the distance equal to maximum length of the scoop arm, (about 3 m) from the river bank.

In all samples, eight parameters characterising the quality of water were analysed: total

Table 1 General characteristics of the watercourses studied in the Gdansk Municipality area, details of the area surrounding the sampling stations and their locations

Watercourse	Notation of sampling site	Geographical coordinates Longitude (E)	Latitude (N)	Average depth [m]	Length [km]	Average flow [$m^3 \cdot s^{-1}$]	Site description
Strzyza Stream	1	18.6°	54.4°	0.4	13.3	0.23	Shipyard, power station (industrial and urban area)
	1a	18.6°	54.4°				Forest
Radunia Canal	2	18.6°	54.3°	0.4	13.5	1.50	City centre (urban area)
	2a	18.6°	54.2°				Area with heavy vehicle traffic nearby (urban area)
Dead Vistula River	3	18.7°	54.4°	5.0–8.0	27.0	600.00 to 1200.00	City centre (urban area)
	3a	18.8°	54.3°				Mounds of phosphogypsum wastes and ashes from a power station (industrial area)
Rozwojka Canal	4	18.7°	54.3°	1.0	4.6	controlled by inflow of wastewater	Oil refinery, heavy vehicle traffic nearby (industrial area)
Motlawa River	5	18.7°	54.4°	2.0	65.0	6.80	City centre (urban area)
	5a	18.7°	54.3°				Fields (rural area)
Siedlicki Stream	6	18.6°	54.3°	0.2	6.9	0.06	Park in a city centre (recreational area)
	6a	18.5°	54.3°				Privately owned rural, suburban lands, wastelands (rural area)
Jelitkowski Stream	7	18.6°	54.4°	0.3	9.7	0.25	Park, beach—mouth to the Gulf of Gdansk (recreational area)
	7a	18.5°	54.4°				Forest, park
Orunski Stream	8	18.6°	54.3°	0.2	7.5	0.03	Park in a city centre (recreational area)
	8a	18.5°	54.3°				Fields, privately owned rural, suburban lands and wastelands (rural area)

suspended solids (TSS), dissolved oxygen (DO), water temperature (T), oxygen saturation (OS), 5-day biochemical oxygen demand (BOD), chemical oxygen demand (COD), total phosphorus (TP) and total nitrogen (TN). Determinations were performed using the procedures recommended in APHA (2005). List of examined parameters with their units, used abbreviations and applied analytical methods is shown in Table 2. All the analytical reagents were supplied by the POCH Joint-Stock Company, Poland, and by Merck Poland. Thermometer (model HI 145-20) was provided by HANNA instruments Inc., Woonsocket, RI, USA. 'Spectronic Genesys 5' spectrophotometer used for colorimetric determinations of TN and TP was produced by Milton Roy Company, Rochester, NY, USA. For TSS determination, Millipore filtration system was used (Millipore Sp. z o. o., Warsaw, Poland).

All physicochemical parameters of water were determined immediately upon arrival of the samples at the laboratory. Sample storage was avoided because it might have changed the chemical composition of water.

All dendrograms in cluster analysis were plotted using Ward's method (Hill and Lewicki 2006; Otto 1999). Euclidean distance was applied for clustering of water samples (Fig. 5); for clustering of variables (Fig. 4), 1-r Pearson distance was used. All data were initially standardized through *z*-score transformation (Marengo et al. 1995), and then statistical and mathematical calculations were performed using version 8.0 of the Statistica software (StatSoft Inc., Cracow, Poland) and Microsoft Office Excel 2003 spreadsheet (Microsoft Corporation, Warsaw, Poland). For dendrograms shown in Fig. 5, the number of significant clusters was determined using the more restrictive Sneath's index criterion, at 1/3 of the maximum distance D_{max} (Astel et al. 2007).

Results and discussion

Physicochemical characteristics of the studied watercourses

A statistical description of eight physicochemical parameters determined in Gdansk Municipality region for consecutive years of study from 2000 to 2007 is presented in Fig. 2a–f, whereas for different watercourses in the whole study period in Fig. 3a–f. In the study, over 1,300 samples of water were collected and analysed, what produced a large database of more than 10,500 results. Figures 2 and 3 are whisker plots which present

Table 2 List of physicochemical parameters measured for the river water, their units and abbreviations used

Parameter	Units	Abbreviation used in the text	Applied analytical techniques
Water temperature	°C	T	Thermometer
5-day biochemical oxygen demand	mg O_2/L	BOD	Incubation, Winkler titration
Chemical oxygen demand	mg O_2/L	COD	Permanganate titration
Total nitrogen concentration	mg/L	TN	Peroxydisulfate oxidation, cadmium–copper reduction, spectrophotometry
Total phosphorus concentration	mg/L	TP	Peroxydisulfate oxidation, spectrophotometry
Oxygen saturation	%	OS	Calculated based on the DO values after accounting for T, atmospheric pressure, and water salinity.
Dissolved oxygen concentration	mg O_2/L	DO	Winkler titration
Total suspended solids	mg/L	TSS	Filtration and drying

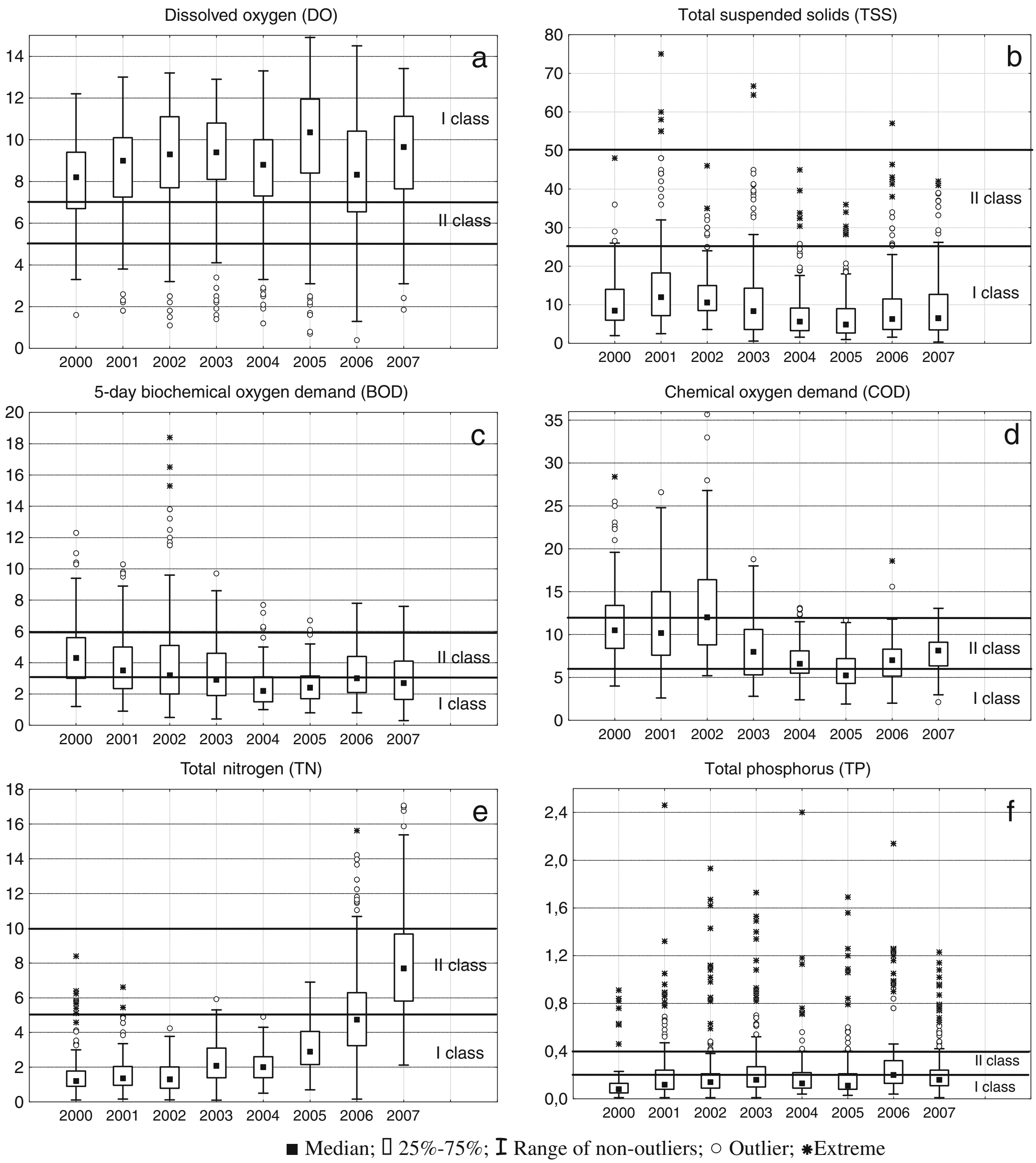
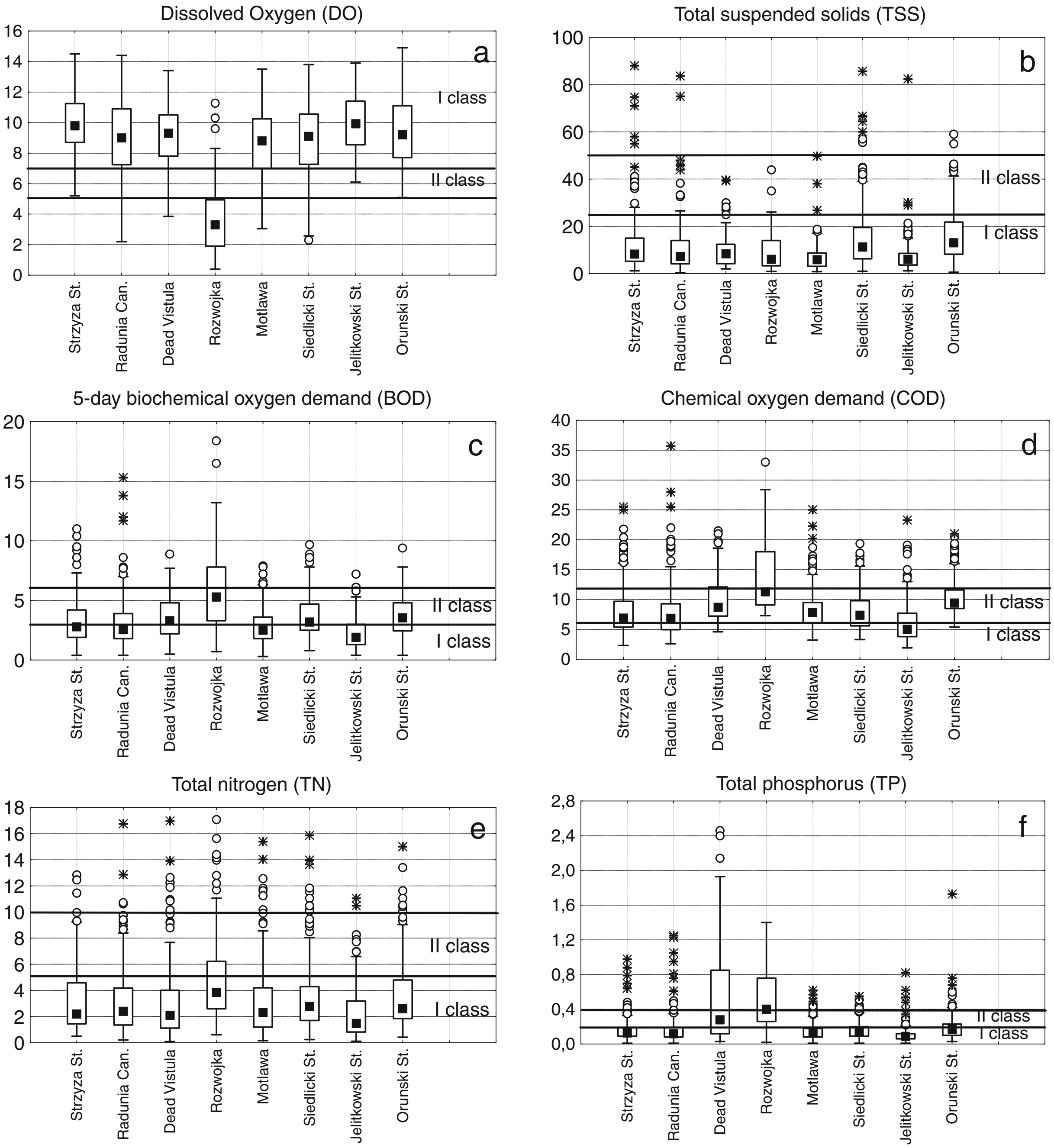


Fig. 2 **a**–**f** Whisker plots of the results for years 2000–2007 covered by this study, eight studied watercourses are listed in Table 1, units are given in Table 2

minimal, maximal and median values of investigated parameters and indicate outliers and extremes. Median values were used instead of mean values because they are less dependent on the extremes and therefore better characterise environmental data



■ Median; ▯ 25%-75%; I Range of non-outliers; ○ Outlier; ✱Extreme

Fig. 3 **a**–**f** Whisker plots for the studied watercourses (listed in Table 1), results from years 2000–2007; units are given in Table 2

The assessment of water quality is based on standards established by the Polish Minister of the Environment (Dz. U. Nr 162, poz. 1008 2008), which implement guidelines of the Directive 2000/60/EC of the European Parliament known as Water Framework Directive (WFD 2000) into Polish legal system. WFD mainly highlights on biotic components of the European Waters; however, chemical monitoring is also taken into account as an effective source of information (Ocampo-Duque et al. 2006). The values for the first and second class of water had been marked in the whisker plots; inferior water quality classes had not been assigned.

From Figs. 2a–f and 3a–f, it can be concluded that the quality of examined waters is relatively good. They are well-oxygenated, with median DO values in the first class of water quality; median TSS content is also within the first class according to Polish standards, below 10 mg/L for most years and majority of watercourses. The nutrient (TN, TP) concentrations are within the limits for the first class of water quality; however, since 2006, a significant increase in the TN content should alarm the local authorities. In Fig. 3e, elevated concentrations of TN rather do not refer to Strzyza Stream and Jelitkowski Stream. The results for TP concentration in consecutive years are quite variable, with many extreme and outlying values (Fig. 2f). This is for the most part caused by elevated TP concentrations detected for the two watercourses: Dead Vistula (site 3a) and Rozwojka (site 4). In case of Rozwojka, high TP values might be attributed to low flow conditions and urban run-off. For site 3a on the Dead Vistula River, high TP concentrations are caused by a release of phosphorus to the water from the phosphogypsum waste dump in Wislinka district, situated near station 3a. Considering the rapid water flow in Dead Vistula River (from 600 to 1,200 $m^3\ s^{-1}$) and its depth of more than 5 m, it can be concluded that the amount of phosphates delivered to water from the waste dump in Wislinka cannot be neglected.

The analysed waters are characterised by rather high organic matter content. It refers to both organic matter biodegraded by organisms in biochemical processes (BOD) or oxidised by a strong chemical oxidant such as permanganate (COD) (Xia et al. 2005). BOD and COD values for the examined waters were in the second or close to the second class of water quality; some improvement can be observed from year 2004. Elevated organic matter content was observed in the warm season; therefore it may be concluded that intensive organic matter production and a high rate of photosynthesis are the main causes of elevated BOD and COD values.

Figure 3a–f shows that physicochemical properties of water from the two watercourses—Jelitkowski Stream and Rozwojka Canal, noticeably differ from the others in the area of Gdansk Municipality. The Jelitkowski Stream (sites 7, 7a) can be distinguished from all watercourses by the lowest load of pollution. In the whole study period, this watercourse had the lowest levels of organic pollution (BOD and COD). Moreover, in Jelitkowski Stream, the lowest concentrations of TN and TP were determined. Jelitkowski Stream contained the least TSS content; water from this watercourse was also well saturated with oxygen (high DO). Good quality of water in case of Jelitkowski Stream can be attributed to the fact that it flows through protected area of a Tricity Landscape Park and a few recreational parks. The second watercourse with an outstanding water quality is Rozwojka Canal. In the whole study period, most physicochemical parameters of its waters had median values in the second class of water quality or below, the only exception was noticed for TSS and TN values. This refers especially to DO concentration and organic matter content (BOD, COD) and may indicate considerable contamination of water (Olajire and Imeokparia 2001). Pollution of water in Rozwojka Canal (site 4) and the highest median value of water temperature (T) might be caused by an inflow of drainage waters or treated wastewater from the nearby oil refinery or the refinery's wastewater treatment plant. Effluents from the oil refinery cannot be easily flushed away because of a relatively low or at times even no flow of water.

Radunia Canal, Motlawa River and Strzyza Stream belong to rather clean watercourses, with similar physicochemical properties. Examination of water quality in those watercourses allows concluding that in the investigated area fields and farming areas (Radunia Canal, Motlawa River) do not contribute to increase in water pollution or higher concentrations of biogenic substances. In case of Strzyza Stream, vicinity of shipyard, power station and storage place for ashes from the power station also does not remarkably worsen the water quality.

More polluted seem to be the three remaining watercourses: Dead Vistula River, Siedlicki Stream and Orunski Stream. Deteriorated water quality in the Dead Vistula can be caused by the fact that it is an artificial canal that intersects Vistula River, the largest River in Poland, which flows through the whole country and accumulates vast quantities of various origins pollution (sewage, wastewater, urban and agricultural runoff). Both Siedlicki Stream and Orunski Stream have similar hydrological properties with rather low flow of water (0.06 and 0.03 m^3 s^{-1}, respectively) and average depth of only 0.2 m. In case of both streams, one sampling point, close to mouth, was situated in the city centre park; however, such a poor quality of water in those watercourses is attributed to their flow through wastelands or privately owned rural or suburban lands, often developed for gardening or used as a second home. Because these lands are not served by a sewage system and are often managed agriculturally, water quality is at higher risk.

Relations between physicochemical parameters of water

Relations between the physicochemical parameters measured in all water samples in the whole study period are explained on the basis of the values of linear Pearson's correlation coefficients presented in Table 3. Analysis of correlation coefficients ($p = 0.05$) shows that some common relations only for variables describing oxygen conditions of water can be noticed. The value of correlation coefficient equals –0.66 for the pair DO and T, and 0.83 for DO with OS. It can be explained by the fact that OS is calculated based on DO, taking into consideration the values of temperature, atmospheric pressure and water salinity (Chang 2005; Yunus and Nakagoshi 2004). It is though not surprising that the relation between DO and water temperature (T) is inversely proportional; with the increase of temperature the value of DO decreases (correlation –0.66). DO and OS depletion occurs also with an increase of BOD and COD values, another pair of intercorrelated variables. The COD with BOD correlation can be explained by the fact that BOD represents labile organic matter which undergoes biotic decomposition and is a part of COD. COD describes total organic matter content, which is oxidised by a strong oxidant (Almeida et al. 2007). A positive correlation of 0.70 between BOD and COD might suggest that regardless the season of sampling relation between these two variables is constant.

The values of correlation coefficients between the other physicochemical parameters of water are statistically non-significant ($p = 0.05$). However, it is worth to point out that the values of correlation coefficients were calculated on the basis of a huge number of pairs of the results (>1,300), what considerably increases the their level of significance. Moreover, the studies carried out through the long period of 8 years, are of environmental character and are described by high variability, with frequently observed extreme and outline values, what also significantly influences the correlation coefficients.

Application of CA, a chemometric method of data exploration, broadened and confirmed information about relations between investigated variables. Figure 4 shows dendrogram presenting the clustering of the analysed variables. It can be observed that the lowest agglomeration distance,

Table 3 Correlation matrix for studied parameters, data from the whole study

	TSS	DO	T	OS	BOD	COD	TP
DO	−0.03						
T	0.05	**−0.66**					
OS	0.00	**0.83**	−0.14				
BOD	0.19	−0.35	0.25	−0.27			
COD	0.23	−0.32	0.14	−0.31	**0.70**		
TP	0.00	−0.18	0.03	−0.22	0.24	0.19	
TN	−0.03	−0.08	−0.14	−0.22	−0.03	−0.11	0.15

$n > 10\,500$. Boldfaced values represent significant correlation ($p = 0.05$)

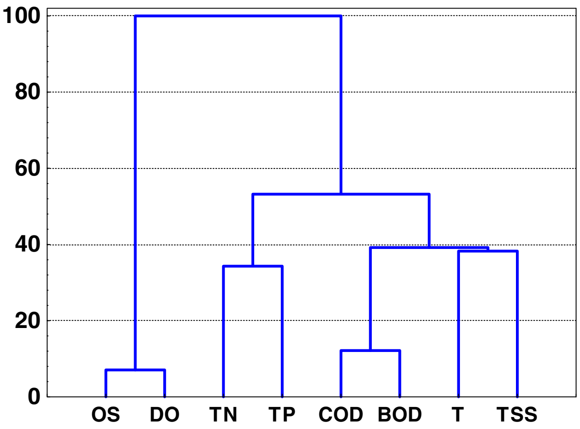


Fig. 4 Dendrogram showing clustering of 8 variables (listed in Table 2) plotted for samples collected from all monitoring sites from 2000 to 2007

less than 15% of the maximum distance D_{max} is noticed for the two pairs of variables: DO with OS, and COD with BOD. For these two pairs of the results, also the highest positive values of correlation coefficients were noted.

Different results variation was observed for the pair of DO and OS. Both variables attach the other physicochemical parameters of water at the maximum distance D_{max}. It was also reflected in the values of their linear correlation coefficients. DO as well as OS are negatively correlated to all other variables, and this is why they form a separate cluster on the left side of the dendrogram.

The remaining variables are found on the right side of the dendrogram. COD and BOD were grouped in a common cluster at a distance less than 40% of the maximum with the TSS and T. This means that TSS to some extent is made up of organic compounds, and also that the values of COD, BOD and TSS can change seasonally accompanied by the change of T.

OS and DO concentration are found in a different cluster than BOD and COD, what can be explained by the fact that high values of OS and DO are usually associated with low values of COD and BOD in case of clean natural waters, opposite situation for polluted waters occurs (Ekpo and Inyang 2000).

Separate cluster for the pair of TN and TP was also formed. This cluster at the distance of 55% of the maximum D_{max} is attached to cluster created by the variables: COD, BOD, T and TSS.

The fact that TN, TP, COD, BOD, T and TSS were included in a common cluster on the right side of the dendrogram may imply that those variables are involved in the processes of production and mineralization of organic matter. In this cluster, variables with low values of Pearson's linear correlation coefficients are present, what indicates that some relations of a non-linear character can be noted.

CA of water samples originating from particular watercourses

CA was also applied to provide a visual presentation of clustering of all samples collected from a particular watercourse. CA supports detection of regularities or inner relations in the whole studied database.

The way of samples from particular watercourses (Radunia Canal and Rozwojka Canal, Dead Vistula River and Motlawa River as well as Strzyza, Siedlicki, Jelitkowski and Orunski streams) grouping considering eight studied variables (TSS, DO, T, OS, BOD, COD, TP, TN) in a simplified form is shown in Table 4. The detailed analysis of these data revealed that two watercourses Rozwojka Canal and Strzyza Stream exhibit the lowest variability of the results because only two and three clusters were formed respectively. The highest number of five clusters was detected for the samples collected from Jelitkowski and Orunski Stream. The results obtained for the other four watercourses: Radunia Canal, Dead Vistula River, Motlawa River and Siedlicki Stream, enabled discrimination of four clusters with different physicochemical water properties. The dendrograms of results from a particular watercourse permitted to observe differences in physicochemical properties of water between two, sampling sites within one watercourse. The data presented in Table 4 suggest that the least differences were noticed for the samples from two stations (5, 5a) on a Motlawa River. In each cluster, there are a similar number of samples collected from both stations situated in the upper (5a) and lower (5) course of the river. Also for the Dead Vistula

Table 4 Composition of the clusters detected by the cluster analysis of water samples collected from 2000 to 2007

Watercourse	Clusters	Year								Total
		2000	2001	2002	2003	2004	2005	2006	2007	
Strzyza Stream	I	1								1 (1a)
1, 1a	II	1	2	1					1	4 (1), 1 (1a)
	III	13	22	23	24	18	24	24	23	83 (1), 88 (1a)
Radunia Canal	I	7	3	10	3	1	2	10	7	13 (2), 30 (2a)
2, 2a	II	5	6	2	3	3		1	4	18 (2), 6 (2a)
	III	4	6	7	8	7	4	4	7	18 (2), 29 (2a)
	IV	2	5	4	7	7	18	9	6	40 (2), 18 (2a)
Dead Vistula River	I	3	10	11	11	4	10	13	12	40 (3), 34 (3a)
3, 3a	II	1	2	4	3	8	4	7	3	19 (3), 13 (3a)
	III	2	4			2	1	3	2	9 (3), 5 (3a)
	IV	3	5	9	9	4	9	1	7	21 (3), 26 (3a)
Rozwojka Canal	I	2	5	7	6	6	12	10	2	50 (4)
4	II	7	7	5	3	3		2	10	37 (4)
Motlawa River	I	6	5		5	3	2	11	6	20 (5), 18 (5a)
5, 5a	II	2	8	6	10	3	4	9	9	25 (5), 26 (5a)
	III	7	6	8	3	8	7	1	4	24 (5), 20 (5a)
	IV	3	5	10	5	4	11	3	5	23 (5), 23 (5a)
Siedlicki Stream	I	2								1 (6), 1 (6a)
6, 6a	II	4	5	12	10	9	18	10	5	28 (6), 45 (6a)
	III		3		4	1	1	4	6	13 (6), 6 (6a)
	IV	12	11	12	9	8	5	10	13	43 (6), 37 (6a)
Jelitkowski Stream	I	1	2	6	4	6	10	8	6	15 (7), 28 (7a)
7, 7a	II	1	4		3	1	3			9 (7), 3 (7a)
	III	10	8	4	5	6		6	8	31 (7), 16 (7a)
	IV		7	5	10	5	11	8	8	23 (7), 31 (7a)
	V	6	3	9	2			2	2	12 (7), 12 (7a)
Orunski Stream	I	1				1				1 (8), 1 (8a)
8, 8a	II	1								1 (8)
	III	1	11	8	4	5	3	7	4	19 (8), 24 (8a)
	IV	8	8	14	14	10	17	7	15	48 (8), 45 (8a)
	V	7	5	2	6	2	4	10	5	21 (8), 20 (8a)

Eight water parameters listed in Table 2 were determined at each sampling site. Site locations and characteristics are described in Table 1. Data in the table represent the number of samples that were grouped into a given cluster

River (sites 3 and 3a) and Orunski Stream (sites 8 and 8a) samples differences in water composition from the two sampling sites were not significant. Therefore, it can be concluded that rivers transferring considerable amounts of water (Motlawa, Dead Vistula) have more stable composition due to higher ability for self-purification and are more resistant to inflow of pollutants or more polluted water from other watercourses. The highest diversity of results between two stations 2 and 2a was detected for Radunia Canal. Most of the samples collected from station 2 were arranged in cluster IV, while samples from the site 2a were found mainly in clusters I and III. In contrast to the samples originating from the station 2, the samples from the station 2a, located in the upper course of the canal were characterised by lower concentration of TSS and DO, smaller degree of organic matter pollution (COD, BOD) and biogenic compounds (TN, TP). It was attributed not only to seasonal small flow or low water level in the Radunia Canal but also inflow of water from Orunski Stream and Siedlicki Stream, what can modify water properties of Radunia Canal at its mouth to the Motlawa River.

Analysis of dendrograms in Fig. 5a–d plotted for samples collected from the particular watercourses indicated that a month of sample collection may influence the arrangement of samples into clusters. Grouping of samples in two periods was observed: warm, spring–summer, approximately from May to September, and cool, autumn–winter, more or less from October to April. Seasonal patterns were detected mainly for DO and OS with maximal values in cool season, accompanied by minimal values of COD and BOD. Similar observations were made by Simeonov et al. (2001). The exception was year 2005, for which most of the samples were grouped into one cluster. In dendrograms plotted for the watercourses Rozwojka Canal, Radunia Canal and Jelitkowski Stream, the samples collected in cool period of the year were located in the right side of the plots (example on Fig. 5a). In case of Orunski Stream and Dead Vistula River the opposite situation was noticed with the samples from the colder period of the year on the left side of the dendrograms (Fig. 5b). The samples collected from three watercourses: Strzyza Stream, Siedlicki Stream and Motlawa River, have also tendency to cluster in accordance with the period of their collection. This can take place either within certain clusters (Strzyza Stream, Siedlicki Stream; Fig. 5c), or alternately, when clusters I and III group samples from warmer period, whereas II and IV from cool period (Motlawa River; Fig. 5d).

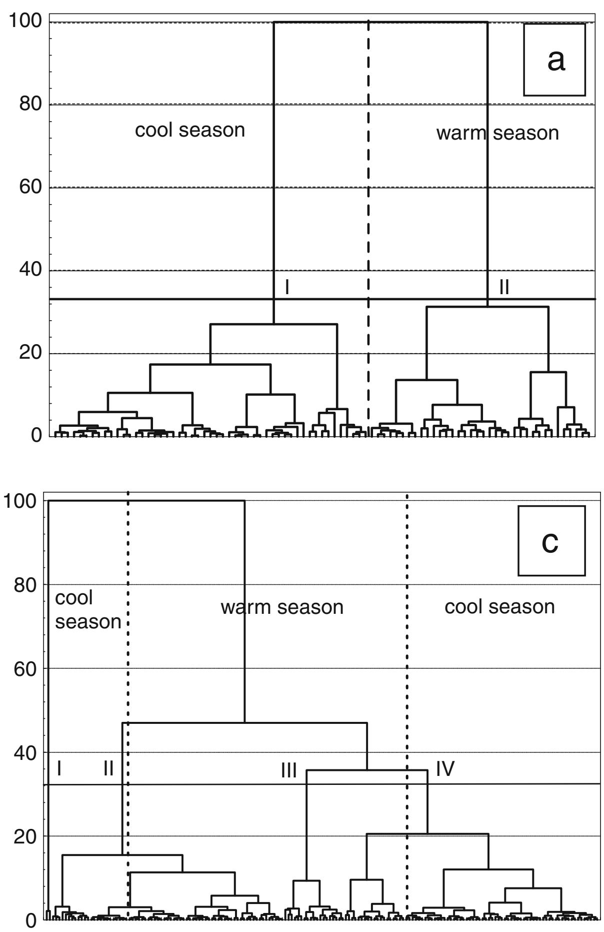


Fig. 5 a–d Dendrograms illustrate clustering (eight parameters listed in Table 2) of samples collected from Rozwojka—site 4 (**a**); Orunski Stream—sites 8, 8a (**b**); Siedlicki Stream—sites 6, 6a (**c**) and Motlawa River—sites 5, 5a (**d**) from 2000 to 2007. The two seasons of sampling (warm, cool) with different water properties are separated with a *vertical dashed line*

Conclusions

Interpretation of the monitoring results revealed that eight analysed water quality parameters: TSS, DO, T, OS, BOD, COD, TP and TN allow to differentiate watercourses according to water quality.

It can be also concluded that the quality of examined waters is relatively good with respect to Polish standards of water quality which implement EU Water Framework Directive. Distinctive physicochemical properties of water were noted for two watercourses Jelitkowski Stream and Rozwojka Canal. It confirms that water quality of the watercourses in the region of Gdansk Municipality depends on their location. Jelitkowski Stream flows through forests, Tricity Landscape Park and recreational areas, whereas Rozwojka on her way passes oil refinery and receives inflow of treated sewage and drainage water. Heap of phosphogypsum dump is another source of pollution, releasing phosphorus to water. However, this contamination regards Dead Vistula River – a large river with high flow of water and considerable depth.

Application of cluster analysis revealed that common clusters were formed for the two pairs of variables: DO concentration with OS, and COD with BOD. Moreover, DO and OS are found in separate cluster than other variables. CA showed also that Rozwojka Canal and Strzyza Stream exhibit the least difference of results, while the highest number of five clusters was observed for Jelitkowski Stream and Orunski Stream. In addition, CA demonstrated that the least differences for samples collected from two sampling sites were for the Dead Vistula River, Motlawa River and Orunski Stream. The largest diversity of results between the two stations on one watercourse in case of Radunia Canal was detected. CA also indicated that samples of water are clustered in two periods warm and cool, as a month of sample collection may determine their arrangement into clusters.

References

Almeida, C. A., Quintar, S., Gonzalez, P., & Mallea, M. A. (2007). Influence of urbanization and tourist activities on the water quality of the Potrero de los Funes River (San Luis–Argentina). *Environmental Monitoring and Assessment, 133*, 459–465.

APHA (2005). *Standard methods for the examination of water & wastewater* (21st ed.). Washington. D.C: American Public Health Association.

Astel, A., Tsakovski, S., Barbieri, P., & Simeonov, V. (2007). Comparison of self-organizing maps classification approach with cluster and principal components analysis for large environmental data sets. *Water Research, 41*(19), 4566–4578.

Brogueira, M. J., & Cabeçadas, G. (2006). Identification of similar environmental areas in Tagus estuary by using multivariate anlysis. *Ecological Indicators, 6*(3), 508–515.

Chang, H. (2005). Spatial and temporal variations of water quality in the Han River and its tributaries, Seoul, Korea, 1993–2002. *Water Air & Soil Pollution, 161*, 267–284.

Dojlido, J. (1987). *Chemia wody (chemistry of water)*. Warsaw: Arkady.

Dz. U. Nr 162, poz. 1008 (2008). Rozporządzenie Ministra Środowiska z dnia 20 sierpnia 2008 roku w sprawie sposobu klasyfikacji stanu jednolitych części wód powierzchniowych (Regulation of the Polish Minister of Environment of 20 August 2008 on the classification of the surface water bodies), 8654–8681. http://static1.money.pl/d/akty_prawne/pdf/DU/2008/162/DU20081621008.pdf. Accessed 20 March 2010.

Ekpo, N. M., & Inyang, L. E. D. (2000). Radioactivity, physical and chemical parameters of underground and surface waters in Qua Iboe River estuary, Nigeria. *Environmental Monitoring and Assessment, 60*, 47–55.

Giridharan, L., Venugopal, T., & Jayaprakash, M. (2009). Assessment of water quality using chemometric tools: A case study of river Cooum, South India. *Archives of Environmental Contamination and Toxicology, 56*, 654–669.

Goncharuk, V. V. (2008). A new concept of supplying the population with a quality drinking water. *Journal of Water Chemistry and Technology, 30*, 129–136.

Hill, Y., & Lewicki, P. (2006). *Statistics, methods and applications: A comprehensive reference for science, industry, and data mining*. Tulsa: StatSoft.

Holt, M. S. (2000). Sources of chemical contaminants and routes into the freshwater environment. *Food Chemistry and Toxicology, 38*, S21–S27.

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

Marengo, E., Gennaro, M. C., Giacosa, D., Abrigo, C., Saini, G., & Avignone, M. T. (1995). How chemometrics can helpfully assist in evaluating environmental data. Lagoon water. *Analytica Chimica Acta, 317*, 53–63.

Ocampo-Duque, W., Ferré-Huguet, N., Domingo, J. L., & Schuhmacher, M. (2006). Assessing water quality in rivers with fuzzy inference systems: A case study. *Environment International, 32*(6), 733–742.

Olajire, A. A., & Imeokparia, F. E. (2001). Water quality assessment of Osun River: Studies on inorganic nutrients. *Environmental Monitoring and Assessment, 69*, 17–28.

Otto, M. (1999). *Chemometrics: Statistics and computer application in analytical chemistry*. New York: Wiley.

Petraccia, L., Liberati, G., Masciullo, S. G., Grassi, M., & Fraioli, A. (2006). Water, mineral waters and health. *Clinical Nutrition, 25*, 377–385.

Reghunath, R., Sreedhara Murthy, T. R., & Raghavan, B. R. (2002). The utility of multivariate statistical techniques in hydrogeochemical studies: An example from Karnataka, India. *Water Research, 36*, 2437–2442.

Reisenhofer, E., Adami, G., & Barbieri, P. (1998). Using chemical and physical parameters to define the quality of karstic freshwaters (Timavo River, North-Eastern Italy): A chemometric approach. *Water Research, 32*, 1193–1203.

Simeonov, V., Sarbu, C., Massart, D. L., & Tsakovski, S. (2001). Danube River water data modelling by multivariate data analysis. *Mikrochimica Acta, 137*, 243–248.

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.

Van Leeuwen F. X. R. (2000). Safe drinking water: The toxicologist's approach. *Food Chemistry and Toxicology, 38*, S51–S58.

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

WFD (2000). Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy. http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:32000L0060:EN:NOT. Accessed 20 March 2010.

Xia, X., Yang, Z., Wang, R., & Meng, L. (2005). Contamination of oxygen-consuming organics in the Yellow River of China. *Environmental Monitoring and Assessment, 110*, 185–202.

Yunus, A. J. M., & Nakagoshi, N. (2004). Effects of seasonality on streamflow and water quality of the Pinang River in Penang Island, Malaysia. *Chinese Geographical Science, 14*, 153–161.

Zhang, Y., Guo, F., Meng, W., & Wang, X.-Q. (2009). Water quality assessment and source identification of Daliao river basin using multivariate statistical methods. *Environmental Monitoring and Assessment, 152*, 105–121.