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Spatial distribution and temporal variation of chemical properties of drainage watercourses in rural and peri-urban areas of Novi Sad (Serbia)—a case study

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Abstract Waters are among to the most vulnerable environmental resources exposed to the impact of various point and non-point pollutants from rural/urban activities. Systematic and long-term monitoring of hydro-resources is therefore of crucial importance for sustainable water management, although such practice is lacking across many (agro-)hydro-ecosystems. In the presented study, for the first time, the spatial distribution (covering almost 9000 ha) and temporal variation (2006–2013) in certain quality parameters was characterized in drainage watercourses Tatarnica and Subic, whose catchment is rural and suburban areas close to the city of Novi Sad, Republic of Serbia. Based on majority of observed parameters, both watercourses belonged to I and II water quality classes, with occasional presence of certain parameters (e.g., suspended solids, total phosphorus; ammonium) at extreme values exacerbating both watercourses to classes IV and V. The value of the synthetic pollution index (i.e., a combined effect of all considered parameters) showed a higher degree of water pollution in watercourse Subic (on average 2.00) than Tatarnica (on average 0.72). Also, cluster analysis for watercourse Tatarnica detected two groups of parameters (mostly related to nutrients and organic matter), indicating more complex impacts on water quality during the observed period, in which elucidation thus established water quality monitoring program would be of great importance.

Keywords Drainage · Channelized watercourse · Water quality monitoring · Water pollution · Land use

Introduction

Surface water bodies are the most vulnerable and irreplaceable environmental resources, particularly in the zones of external (anthropogenic) influences (Mulliss et al. 1996; Ouyang et al. 2006; Ren et al. 2014; Robson et al. 2006; Su et al. 2011; Yu et al. 2012). Their ecological condition can be easily compromised but hard and slow to return to a satisfactory (sustainable) state. Concerns for the quality of (surface) water resources, their protection, conservation, improvement, and controlled abstraction are some of the basic and widely-accepted postulates of the sustainable water management practice nowadays (Allan 2012; Boeuf and Fritsch 2016; FAO 2011; Ondrasek et al. 2014). The issue of surface water quality might be especially pronounced in the case of urban and industrial areas, given the relatively concentrated (vs. rural areas) facilities and anthropogenic activities (e.g., municipal/industrial waste waters, industrial plants) that may potentially induce adverse impacts on the surrounding areas and jeopardize their ecological value (Ahiablame et al. 2011; Angyal et al. 2016; Nabelkova et al. 2004;

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Poudel et al. 2013; Savic et al. 2013, 2017; Yu et al. 2012). One such representative example was for the first time systematically detected and elaborated in the main channelized drainage watercourses of Tatarnica and Subic (Savic et al. 2013), close to Novi Sad, as the second most populated town of the Republic of Serbia (Fig. 1).

Canalized watercourses of Tatarnica and Subic primarily have hydrotechnical and ameliorative functions as a crucial part of a complex channel network of the ameliorative (drainage) systems in Vojvodina. The main tasks and purpose of this ameliorative channel network is regulation of underground water table in the surrounding, mostly arable (rural) area, by collection and canalization of the excessive surface/groundwater to other hydraulic components of the Vojvodina basin, i.e., Danube River catchment area (Savic et al. 2013, 2015a, b, 2017). Such water bodies and their coastal elements also represent an oasis for varied accompanying biota, thus making ecological corridors, contributing to biodiversity, and generally adding environmental values to these mostly lowland rural areas (de Souza et al. 2013; Savic et al. 2013, 2015b). Furthermore, some watercourse sections of Tatarnica and Subic are directly connected to the peripheral urban/industrial zones and facilities, and thus exposed to their influences as well (Fig. 1).

Systematic and continuous monitoring of the water quality might be highly important for the complex aquatic ecosystems, contributing to their sustainable management in view of the influence of different point/non-point sources of pollution (Savic et al. 2017) from rural (e.g., agriculture) or urban (e.g., industrial/municipal) areas. Monitoring of water quality can enable detection and identification of different causes and processes that trigger quality changes in a particular water ecosystem (Evans et al. 2007; Glinska-Lewczuk et al. 2016; Ma et al. 2009; Peng et al. 2015; Su et al. 2011). However, systematic monitoring of quality of watercourses Tatarnica and Subic is not included in the national surface water quality monitoring program. Water quality of these watercourses is controlled within the scope of individual, relatively small-scale research projects (e.g., Halasz et al. 2007; Ivanovsky et al. 2016; Savic et al. 2013, 2015b), although there might be a strong need for systematic and long-term monitoring of their quality. Therefore, the aim of this study was to characterize the importance of the multi-year quality monitoring of these relatively small but crucial (for the whole Vojvodina Province, i.e., Danube catchment area) watercourses.

Materials and methods

Locations

Analyzed watercourses Tatarnica and Subic are located along the peripheral parts of Novi Sad (45°16′N, 19°50′E), the administrative and industrial center of Vojvodina Province, and the second most populated city in Republic of Serbia (Fig. 1). In the past, both watercourses were relatively small natural streams; over time, they have been reconstructed and integrated into the regional ameliorative drainage system of Vojvodina (Savic et al. 2015b). Watercourse Tatarnica, about 20 km west of Novi Sad, is the principal drainage channel for 4750 ha. Hydraulic properties of Tatarnica comprise the total length of about 10 km and water table level across the channel profile maximally to 2 m. Tatarnica watercourse drains water from dominantly intensively managed agricultural (rural) area, either gravitationally and/or by pump station support (4.0 m^3/s) (Savic et al. 2015b), and finally flows into Danube River at chainage km 1277. In contrast to Tatarnica, the watercourse Subic and its catchment basin are located on the periphery of the suburban areas (Fig. 1). The Subic catchment area is about 4100 ha, and its main watercourse (about 10 km long) has similar hydraulic properties to Tatarnica, with water levels fluctuating between 1 and 2 m and draining into Danube River at the chainage km 1249 by means of gravitation and pump stations (4.0 m^3/s). Its catchment area encompasses predominantly agricultural but also urban/industrial areas.

Land and climate characteristics in both catchment areas are similar. Close to Danube, there are predominantly alluvial soils, whereas black soil and chernozem are common in the other parts of the basin (Pavlovic et al. 2017). Such soils have high fertility and are suitable for intensive vegetable production in this area. The climate is continental with average annual precipitation of about 600 mm and the average yearly temperature of about 11 °C (Milosevic et al. 2015).

Sampling, analyses, and data processing

During the 8-year period (2006–2013), surface water samples from each sampling point at each watercourse (Tatarnica and Subic) were collected once a month, generating in total 96 samples per location. Water samples were taken at the channel chainages km 1 + 200 (45°14′10.49″N; 19°35′52.66″E, Tatarnica) and km 0 +

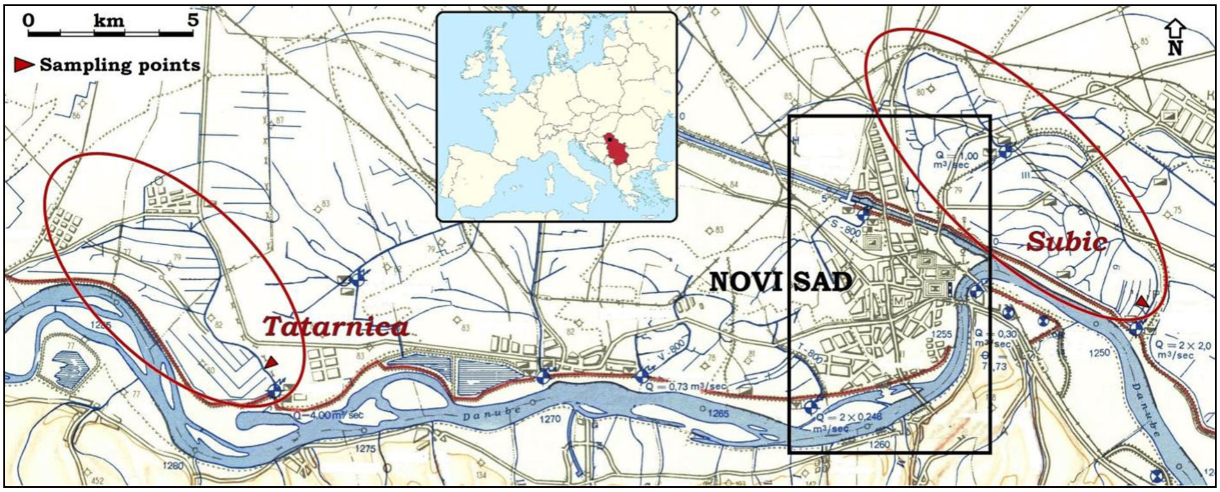


Fig. 1 Two drainage watercourses Tatarnica and Subic (red ovals) in areas of Novi Sad and water sampling points (red triangles)

150 (45°14′58.00″N; 19°55′26.48″E, Subic) (Fig. 1). Sampling of surface water and sample conservation and transport were done according to the current standard procedures and methods, EN ISO 5667–1:2008, EN ISO 5667–3:2007, and ISO 5667–6:2014, as used in the surface water quality monitoring scheme in Republic of Serbia (http://www.iss.rs/en; Ilijevic et al. 2012; Pesic et al. 2015).

Chemical analyses of water samples were carried out according to standard methods in accredited laboratories (http://www.iss.rs/en; SRPS ISO/IEC 17025:2006) National Hydrometeorological Service of Serbia as well as the Institute of Public Health in Novi Sad. In this study, we presented the following parameters: biological oxygen demand BOD_5, chemical oxygen demand of $KMnO_4$, dissolved oxygen, nitrate (NO_3-N), nitrite (NO_2-N), ammonium (NH_4-N), total phosphorus (P), and suspended solids (e.g., Brankov et al. 2012; Ilijevic et al. 2012; Pesic et al. 2015).

Based on the chemical analyses, the evaluation of water quality in observed watercourses Tatarnica and Subic into five classes was done according to the applicable national water quality classification for surface water bodies (Table 1) (Elezovic et al. 2015; Official Gazette RS 74/ 2011; 50/ 2012; Pamer et al. 2011). For instance, an acceptable water quality condition is considered as “good and better” ecological potential, i.e., surface water from I and II class, whereas outside of this class, ecological water potential is valued as moderate (III class), weak (IV class), and bad (V class) (Table 1).

In addition, a comparison of water quality in the two observed watercourses was provided by the pollution indices (Pi—single pollution index for individual parameters and Ps—synthetic pollution index for all analyzed parameters together). The Pi and Ps indices were calculated using the following equations:

$$Pi = \frac{Ci}{Si} \quad and \quad Ps = \frac{1}{n}\sum_{i=1}^{n} Pi$$

where *Ci* is the measured concentration and *Si* is the standard value of the *i*th parameter of water quality, and *n* is the number of parameters evaluated. Standard value (*Si*) represents limiting value for the I and II water quality class in surface water bodies (good and better ecological potential) determined by national legislative (Official Gazette RS 74/ 2011; 50/ 2012; Table 1) (Milanovic et al. 2011; Takic et al. 2017). The values

Table 1 National water quality classification of surface waters bodies

Parameters	Limit values for classes (mg/L)			
	I and II	III	IV	V
Dissolved oxygen	> 5	5–3	3–2	< 2
BOD_5	< 6	6–9	9–20	> 20
COD	< 10	10–20	20–50	> 50
NH_4-N	< 0.2	0.2–0.8	0.8–1.0	> 1.0
NO_2-N	< 0.03	0.03–0.12	0.12–0.30	> 0.30
NO_3-N	< 3	3–6	6–15	> 15
Total P	< 0.3	0.3–0.4	0.4–1.0	> 1.0
Suspended solids	< 25	–	–	> 25

Official Gazette RS 74/2011; 50/2012

$Pi \leq 1$ and $Ps \leq 1$ indicate that the water quality met the standards. If $Pi > 1$ and $Ps > 1$, water is regarded as polluted. The reciprocal of the formula for Pi is used for the dissolved oxygen (DO) parameter (Li et al. 2009; Ma et al. 2009; Peng et al. 2015; Wang et al. 2008). In this analysis, weight coefficients (Wi) were not assigned to quality parameters (Li et al. 2009; Ouyang et al. 2006; Xia et al. 2012). The descriptive and procedural data analyses (e.g., Student *t* test, Pearson correlation analysis, cluster analyses) were performed using Statistica 13.2. The most widely used type of correlation coefficient is Pearson (r) or linear or product-moment correlation, calculated in this software package as was presented in the next equation:

$$r_{xy} = \frac{\sum_{i=1}^{n}\left(x_i - \overline{x}\right)\left(y_i - \overline{y}\right)}{\sqrt{\sum_{i=1}^{n}\left(x_i - \overline{x}\right)^2 \sum_{i=1}^{n}\left(y_i - \overline{y}\right)^2}}$$

where x_i and y_i represents detected monthly values of certain parameter and $\overline{x}$ and $\overline{y}$ their average values over the period of observation. The same approach using the Pearson coefficient for interpretation of water quality parameters was used in many other similar studies (e.g., Barakat et al. 2016; Pantelic et al. 2013; Xia et al. 2012).

Results and discussion

Monthly and average annual values for watercourses Tatarnica and Subic were given (Fig. 2, left side) in relation to the prescribed limits for the I and II class of surface water bodies (Official Gazette RS 74/ 2011; 50/ 2012). For almost all the considered parameters, there were values that exceeded the limit criteria for the I and II classes, as well as the extreme values that indicated the episodic occurrences of some forms of pollution (i.e., classes IV and V).

Summary display of water quality classification suggested that the most common problem regarding water quality in both watercourses was an increased concentration of organic matter, expressed through increased biological (BOD_5) and chemical (COD) oxygen demand (Fig. 3). For instance, more than 30% of Tatarnica samples and more than 70% of Subic samples had BOD_5 above the limit value of I and II class; similarly, more than 30% (Tatarnica) and more than 90% (Subic) of samples had COD above these limits. Concentrations of ammonium (33% of samples in Subic and 65% in Tatarnica) and total phosphorus (20 and 82%, respectively) most frequently differ from the referent limit values (Fig. 3). The water quality was higher in the watercourse Tatarnica, where the percentage of samples in the I and II water quality class (67–100%) was significantly higher in comparison to Subic (6.3–100%) in all the measured parameters, except N-nitrate (all samples from both locations belonged to the I and II class) (Fig. 3). The difference between the two watercourses for the stated COD value was above 10-fold (68.3/6.3%) and in the case of total P about 4.5-fold (79.9/17.7%), (Fig. 3).

The significant differences in the majority of corresponding values of quality parameters between observed watercourses was confirmed by the *t* test ($P \leq 0.05$) for most observed variables, except NO_3-N and NO_2-N (Table 2). Although observed sites of the two watercourses are relatively close to each other and have catchment area of similar sizes with similar agroecological characteristics (pedology, climate, agronomy), there is no strong correlation in monthly values of water quality parameters. Only for NO_3-N the Pearson correlation coefficient was low to moderate ($r = 0.44$), whereas for all other observed parameters, r corresponded to very weak or negligible correlation (Table 2). The most likely explanation for a difference in the *t* test values and weak correlation was unequal input of non-point and point pollution from the catchment areas of these watercourses, regarding the quantities, seasonal dynamics, and anthropogenic factors (Ouyang et al. 2006; Yang et al. 2013). The asymmetric distribution of some statistical parameters (e.g., skewness ≥ 1; kurtosis > 0; Table 2) indicated an impact of possible anthropogenic factors on water quality, such as direct release of untreated (or insufficiently treated) effluents from agricultural, urban, and/or industrial zones (Savic et al. 2017). Also, constant heterogeneity of data series (CV > 30%, greater in Subic than Tatarnica for most measured parameters) may be due to different seasonal or anthropogenic impacts. Highly likely potential sources of contaminants are municipal impacts of suburban settlements, city garbage landfill, power plants and heating plants, industry of pharmaceutical and food products, and paint industry which are located in the vicinity of both observed watercourses.

Figure 2 (right part) shows the values and distribution of single pollution index (Pi) for the studied parameters of water quality for watercourses Tatarnica and Subic.

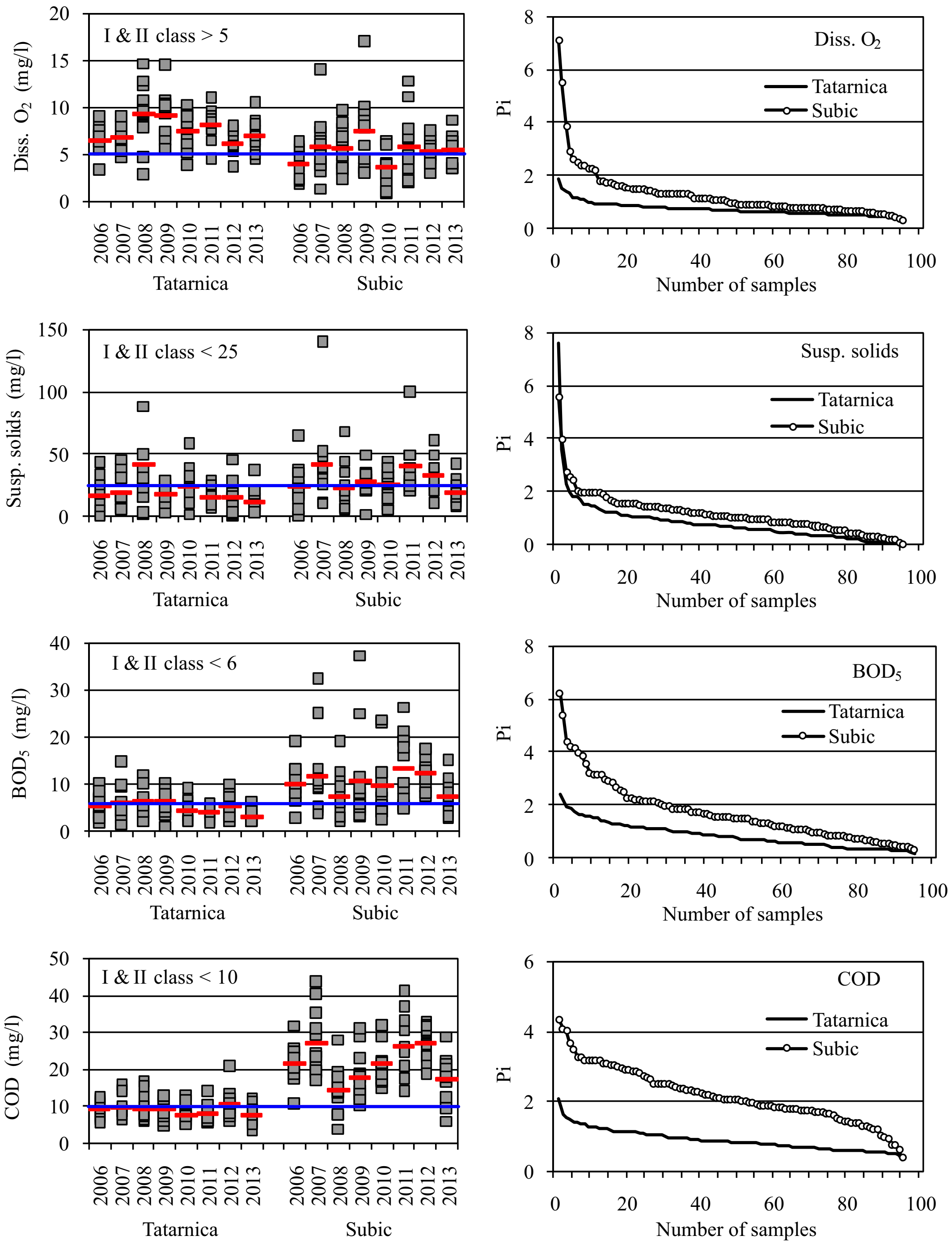


Fig. 2 Left part: Monthly and average annual (red line) values of measured parameters in relation to limit values for the I and II water quality class (blue line). Right part: The single pollution index (*Pi*) value for particular water quality parameter (2006–2013)

For most of the displayed parameters observed, values of Pi were significantly higher in samples from watercourse Subic than watercourse Tatarnica (Fig. 2 and Table 3). Maximum values of index (Pi) indicated a high level of contamination in watercourse Subic, for example, 31 (for NH_4-N) or 18 (for total P), with values up to

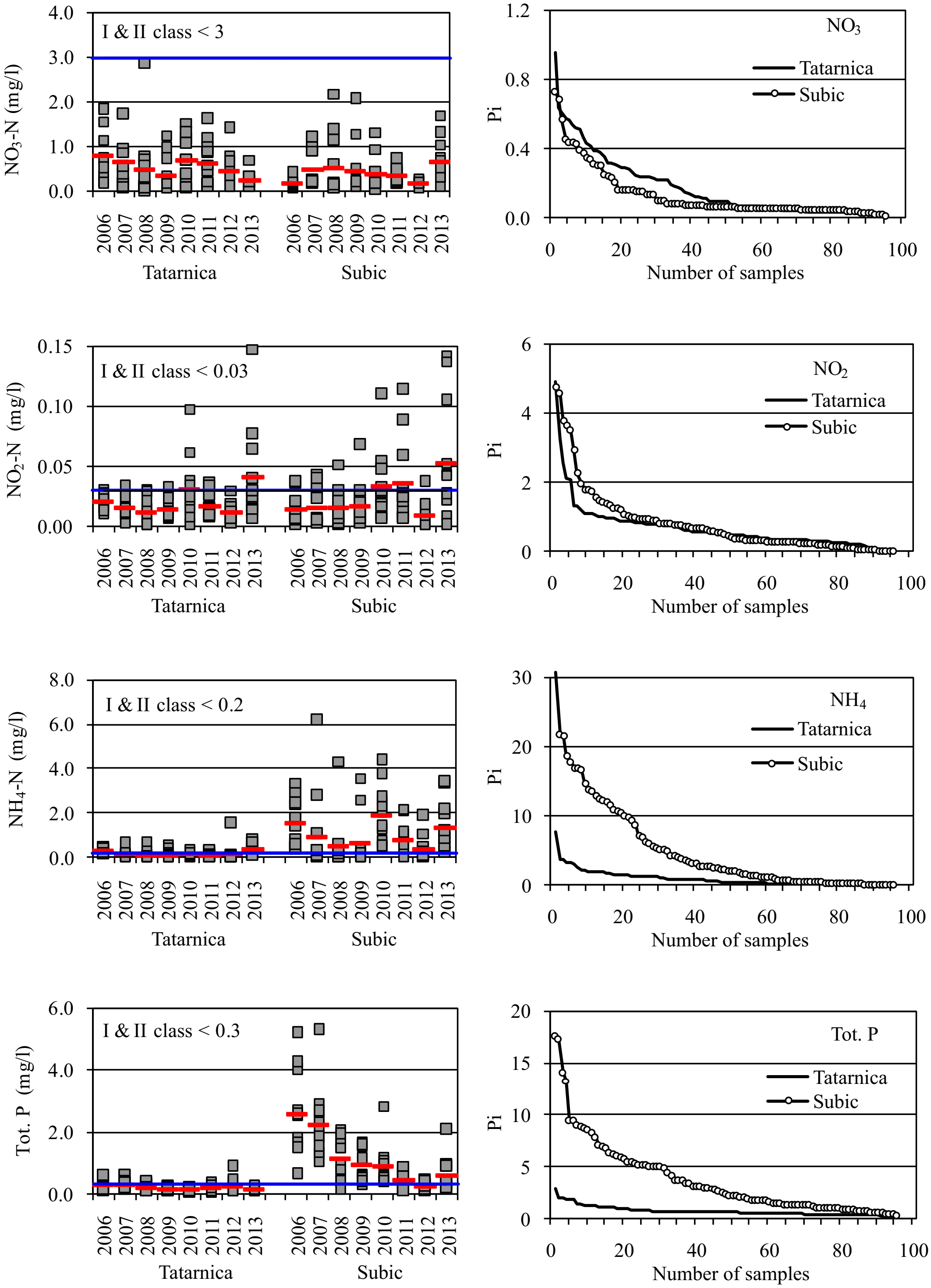
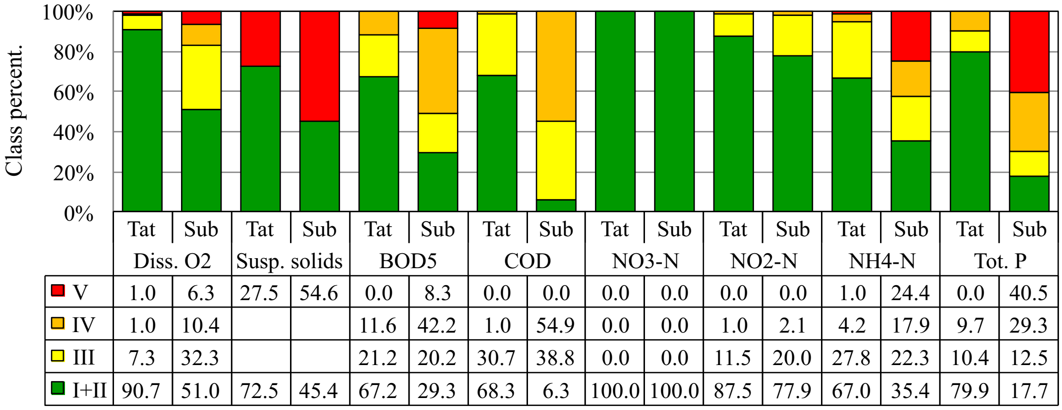


Fig. 2 (continued)

6-fold higher than in Tatarnica. Also, in watercourse Subic together with the larger Pi index values, the total number of samples with values Pi > 1 was significantly higher than in Tatarnica (Table 3). This indicates not



	Diss. O2		Susp. solids		BOD5		COD		NO3-N		NO2-N		NH4-N		Tot. P	
	Tat	Sub	Tat	Sub	Tat	Sub	Tat	Sub	Tat	Sub	Tat	Sub	Tat	Sub	Tat	Sub
🟥 V	1.0	6.3	27.5	54.6	0.0	8.3	0.0	0.0	0.0	0.0	0.0	0.0	1.0	24.4	0.0	40.5
🟧 IV	1.0	10.4			11.6	42.2	1.0	54.9	0.0	0.0	1.0	2.1	4.2	17.9	9.7	29.3
🟨 III	7.3	32.3			21.2	20.2	30.7	38.8	0.0	0.0	11.5	20.0	27.8	22.3	10.4	12.5
🟩 I+II	90.7	51.0	72.5	45.4	67.2	29.3	68.3	6.3	100.0	100.0	87.5	77.9	67.0	35.4	79.9	17.7

Fig. 3 Percentage of analyzed samples in various water quality classes in watercourses Tatarnica and Subic (2006–2013)

only a degree of deterioration in quality compared to the standard values but also the duration and consistency of such deterioration. For example, Pi > 1 values were recorded in more than 90% of the samples (i.e., 89 out of 96) for COD, more than 80% of samples for total P, about 70% for BOD, etc. These values were 2- to 6-fold higher in watercourse Subic than Tatarnica. The largest difference was found for dissolved oxygen (Tatarnica 8.3% and Subic 48%) (Fig. 2 and Table 3).

The value of synthetic pollution index (Ps), which includes the combined effect of all the considered parameters, clearly showed a higher degree of water pollution in watercourse Subic (Ps values 0.4–2.1, avg. 0.72, median 0.66) than Tatarnica (Ps values 0.7–7.4, avg. 2.00, median 1.74). Accordingly, Tatarnica could be categorized as clean watercourse or with light pollution whereas Subic as watercourse with light to significant and serious pollution (Ma et al. 2009) (Fig. 4). The characteristic average and maximum values of Ps index were 2.8-fold and even 3.7-fold respectively higher for watercourse Subic vs Tatarnica (Table 3). The distribution of samples with values Synthetic Ps > 1 was also

Table 2 Some of descriptive and procedural statistical parameters of water quality characteristics in watercourses Tatarnica and Subic

Parameter	Watercourse	Min. (mg/L)	Max. (mg/L)	Mean (mg/L)	St.dev. (mg/L)	CV (%)	Skewness	Kurtosis	t	r
Diss. O_2	Tatarnica	2.70	14.70	7.59	2.23	29.32	0.60	0.98	6.10*	0.18
	Subic	0.70	17.00	5.38	2.73	50.76	1.34	3.39		
Susp. solids	Tatarnica	1.00	190.00	20.52	22.32	108.77	5.05	35.06	− 2.92*	0.01
	Subic	1.00	140.00	29.49	19.65	66.63	2.41	10.68		
BOD_5	Tatarnica	1.20	14.60	5.15	2.86	55.50	0.92	0.59	6.92*	0.32
	Subic	2.10	37.50	10.37	6.74	64.95	1.52	2.82		
COD	Tatarnica	3.30	20.70	8.92	2.99	33.51	1.01	1.61	14.88*	0.27
	Subic	3.90	43.50	21.73	7.79	35.88	0.34	0.08		
NO_3-N	Tatarnica	0.010	2.860	0.524	0.539	102.81	1.67	3.12	1.85	0.44
	Subic	0.030	2.180	0.392	0.435	110.95	2.20	4.82		
NO_2-N	Tatarnica	0.001	0.148	0.020	0.020	100.10	3.70	18.54	− 1.12	0.02
	Subic	0.001	0.143	0.024	0.029	117.91	2.42	6.31		
NH_4-N	Tatarnica	0.010	1.560	0.185	0.223	120.41	3.10	14.61	− 6.17*	0.20
	Subic	0.010	6.160	0.989	1.242	125.64	1.69	2.79		
Total P	Tatarnica	0.062	0.880	0.217	0.138	63.61	2.12	5.84	− 8.23*	0.22
	Subic	0.096	5.320	1.127	1.064	94.41	1.86	4.05		

n = 96; *t* critical ($p \leq 0.05$) = 1.98

t *t* test value, *r* Pearson correlation coefficient

*Statistically significant at the $P \leq 0.05$ level

Table 3 Statistics for single (Pi) and synthetic (Ps) water pollution indices in watercourses Tatarnica and Subic

Parameter	Watercourse	Poll. index (Pi)				Pi > 1 (% of samples)
		Min	Max	Average	St.dev.	
Diss.O_2	Tatarnica	0.34	1.85	0.72	0.25	8.3
	Subic	0.29	7.14	1.26	0.97	47.9
Susp. solids	Tatarnica	0.04	7.60	0.82	0.89	27.1
	Subic	0.04	5.60	1.18	0.79	54.2
BOD_5	Tatarnica	0.20	2.43	0.86	0.48	32.3
	Subic	0.35	6.25	1.73	1.12	69.8
COD	Tatarnica	0.33	2.07	0.89	0.30	31.3
	Subic	0.39	4.35	2.17	0.78	92.7
NO_3-N	Tatarnica	0.01	0.95	0.17	0.18	0.0
	Subic	0.01	0.73	0.13	0.15	0.0
NO_2-N	Tatarnica	0.03	4.93	0.67	0.67	12.5
	Subic	0.03	4.77	0.81	0.95	21.9
NH_4-N	Tatarnica	0.05	7.80	0.93	1.12	32.3
	Subic	0.05	30.80	4.94	6.21	63.5
Total P	Tatarnica	0.21	2.93	0.72	0.46	19.8
	Subic	0.32	17.73	3.76	3.55	81.3
Synthetic poll. Index (Ps)	Tatarnica	0.40	2.09	0.72	0.25	8.3
	Subic	0.66	7.39	2.00	1.11	86.5

significantly higher in watercourse Subic (83 months; 86.5%) than Tatarnica (8 monthly samples; 8.3%).

We applied the cluster analysis to group the data and parameters with similar characteristics and thus identify the factors that were associated with the variation in quality (Abbas et al. 2008; Pamer et al. 2011; Shrestha and Kazama 2007; Voza et al. 2015). Accordingly, in this study, cluster analysis was employed with the aim to identify similar parameters which impact the water quality and the origin of contamination across the observed area (e.g., Matijevic et al. 2015). On the dendrogram for watercourse Tatarnica, there were two sub-clusters (Fig. 5a): one consisting of nutrients (potential causes of eutrophication, i.e., the nitrogen compounds and total P) and other comprising parameters that indicate the presence of organic matter (BOD_5, COD, and dissolved O_2). Respectively, there are grouped factors indicating impact of point and diffuse pollution sources. In watercourse Subic, these sub-clusters are not so distinct (except for observed nutrients), indicating the presence of numerous and varied influences in the monitoring period (Fig. 5b).

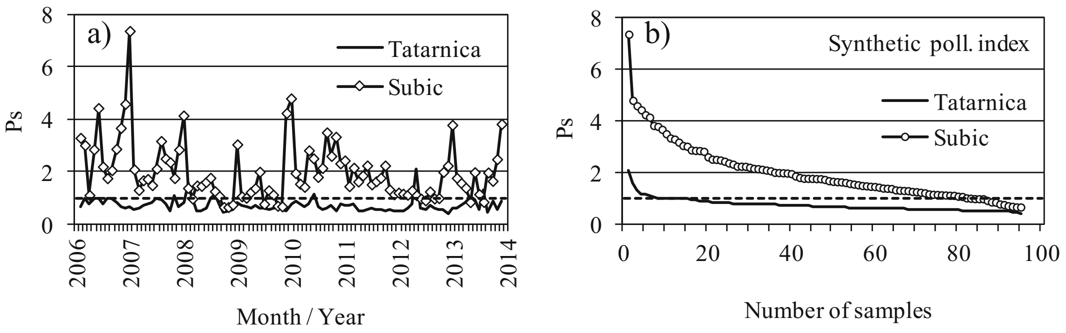


Fig. 4 Values of synthetic pollution index (Ps); Tatarnica and Subic, 2006–2013. **a** Chronological order. **b** Number of samples Ps > 1

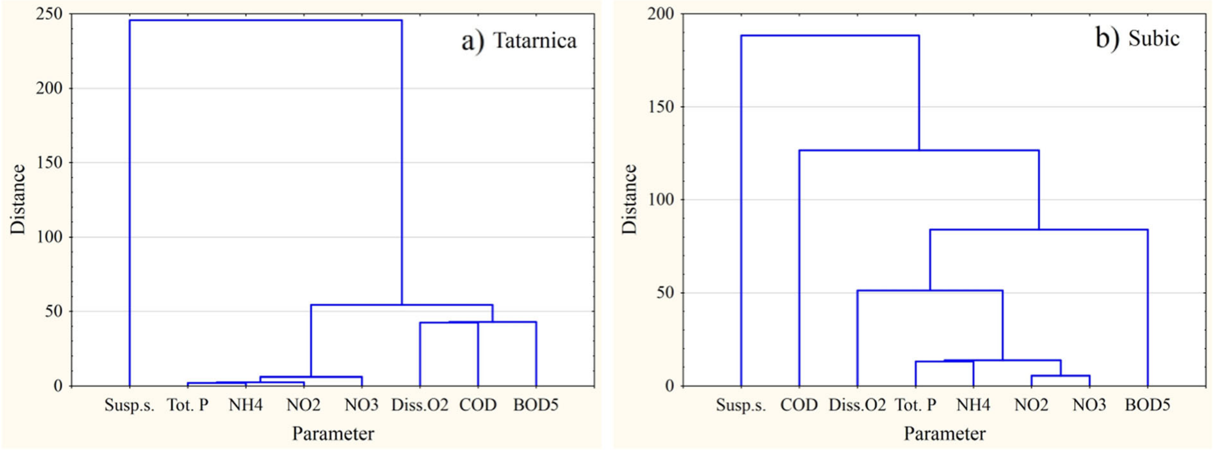


Fig. 5 Cluster analyses dendrograms in observed locations. **a** Tatarnica. **b** Subic

Conclusions

The results show that in the analyzed watercourses, it is necessary to apply the principles of integrated management practices with the purpose of pollution control/reduction and the preservation of satisfactory quality conditions of observed surface water bodies. Results also suggest that the proximity of the urban area and the present pollution locations in the basin of watercourse Subic have highly likely significantly affected the lower conditions of water quality in watercourse Subic in relation to watercourse Tatarnica. A relatively higher proportion of water samples from watercourse Subic (vs Tatarnica) was outside classes I and II, which was also confirmed by significantly higher values of pollution index (Pi, Ps) for Subic. Establishment of regular water quality monitoring on watercourses Tatarnica and Subic (currently absent) is of great importance for the analysis of the sources, types, and degrees of pollution on deterioration of water quality and the possible consequences to the environment. These relatively small, channelized water streams are important water bodies, especially in the vicinity of settlements, agricultural farmland, or protected natural areas, whereby they serve hydrotechnical, ameliorative, and environmental functions.

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