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The physical and chemical characteristics of Danube water quality in Serbia

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Nearly 100% of Serbian territory is in the Danube River Basin
Danube tributaries in Serbia: Drava, Sava, Tisa, Velika Morava, Tamish and Timok

The river flows (from upstream to downstream) through 11 countries: **Germany, Austria, Slovakia, Hungary, Croatia, Serbia, Montenegro, Romania, Bulgaria, Moldavia and the Ukraine.** Additional basin countries are **Poland, Czech Republic, Switzerland, Italy, Slovenia, Albania, Bosnia-Herzegovina and FYR of Macedonia.**

Multivariate statistical techniques

- It is well known that **environmental data** are usually characterized by **high variability**, **because of a variety of natural and anthropogenic influences**
- The best approach to avoid misinterpretation of environmental monitoring data is the **application of multivariate statistical** (chemometric) **methods for environmental data classification and modeling**

Statistical analysis – Factor analysis & Cluster analysis

- Multivariate statistical approaches allow deriving hidden information from the data set about the possible influences of the environment on water quality
- Factor analysis **(FA)**/Principal component analysis **(PCA)**
- Cluster analysis **(CA)**

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FA/PCA attempts to explain the correlations between the observations in terms of the underlying factors, which are not directly observable
FA/PCA yields the general relationship between measured chemical variables by showing multivariate patterns that may be help to classify the original data

- **CA** grouped observation stations into clusters under the similarity of surface water quality parameters
- The basic objective of **CA** is to discover natural grouping of objects

Water quality monitoring

- **The Republic Hydrometeorological Service of Serbia (RHSS)** undertakes systematic monitoring of quantitative and qualitative characteristics of the surface and ground water in order to determine, analyze and supervise the water regime on the territory of Serbia under the Water Act and in compliance with the Regulation of the Systematic Waters Quality Testing passed by the Government of the Republic of Serbia

- **Factor analysis(FA)/principal component analysis (PCA), cluster analysis (CA)**, were applied for **the evaluation of variation**s and for the interpretation of a **water quality data set of the Danube and Tisza obtained during 2011. year of monitoring of 14 parameters at 14 different sites**

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Data sets - provided by the RHSS consists of **annually average values of 14 water quality variables** measured during 2011. year in a quality monitoring network of Danube and Tisa obtained from 14 monitoring stations

- The selected parameters for the estimation of surface water quality characteristics:

✓ Temperature **(T)**
✓ suspended solids **(SS)**
✓ dissolved oxygen **(DO)**
✓ total hardness **(TH)**
✓ **pH**
✓ electrical conductivity **(EC)**
✓ ammonium nitrogen **(NH_4-N)**
✓ nitrate nitrogen **(NO_3-N)**
✓ Orthophophates **(PO_4-P)**
✓ total phosphorous **(TP)**
✓ calcium **(Ca^{2+})**
✓ magnesium **(Mg^{2+})**
✓ biochemical oxygen demand **(BOD_5)**
✓ surface-active substances **(SAS)**

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1. Bezdan
2. Apatin
3. Bogojevo
4. Bačka Palanka
5. Novi Sad
6. Slankamen
7. Čenta
8. Pančevo
9. Banatska Palanka
10. Martonoš
11. Padej
12. Novi Bečej
13. Žabalj
14. Titel

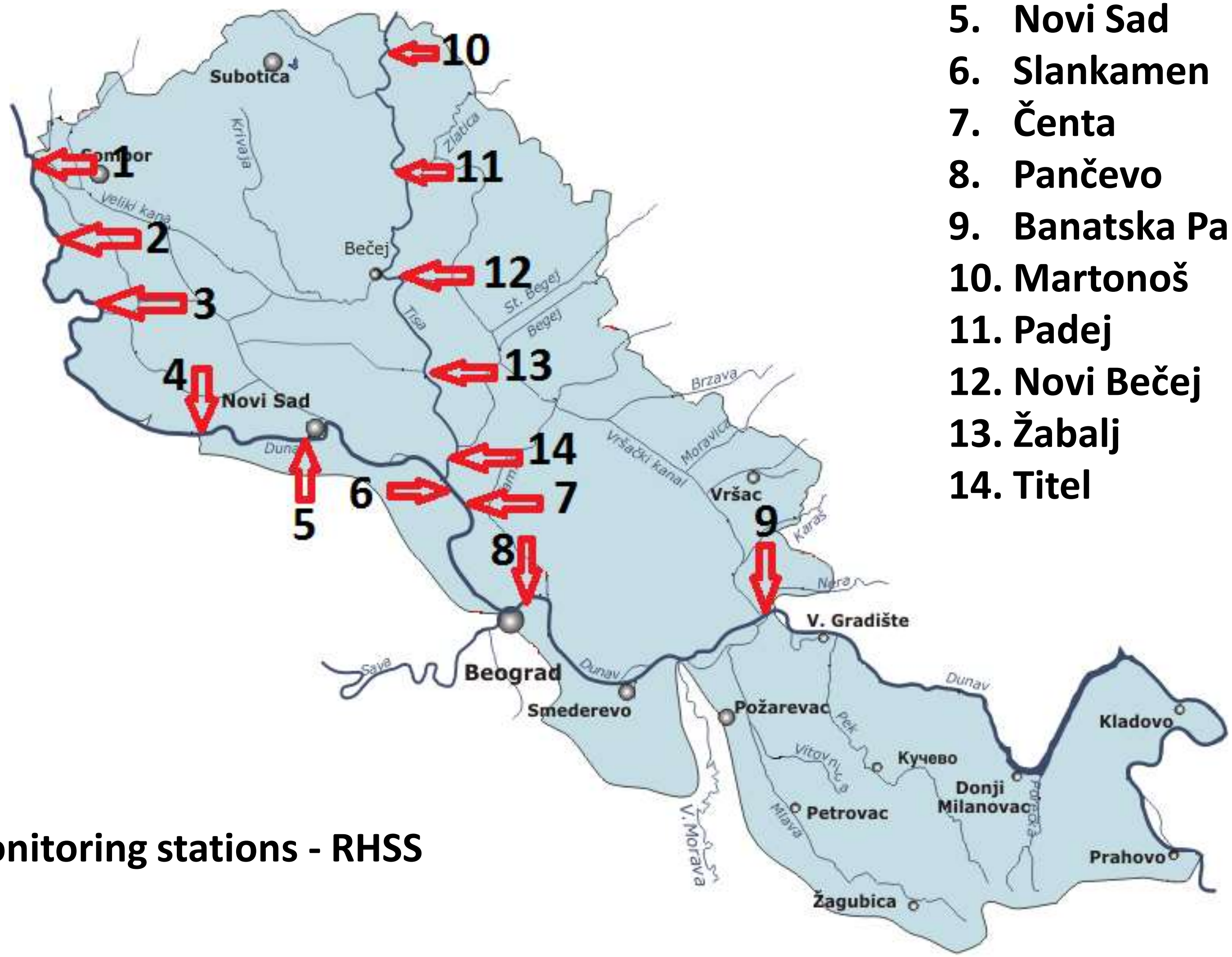

Figure 1. Monitoring stations - RHSS

Factor analysis(FA)/principal component analysis (PCA)

All mathematical and statistical computations were carried out using Microsoft Office Excel 2007 and software package Statistica (version 10) for Windows. The correlation matrix of variables was generated; factors extracted; rotated by Varimax rotation

TABLE 1. CORRELATION MATRIX OF WATER QUALITY PARAMETERS

	T	SS	DO	UT	pH	EC	NH4-N	PO4-P	NO3-N	TP	Ca2+	Mg2+	BOD5	SAS
T	1.00	-0.04	-0.42	-0.23	-0.36	-0.08	0.34	-0.29	-0.14	-0.19	-0.30	-0.20	-0.16	-0.11
SS	-0.04	1.00	-0.52	-0.80	-0.50	0.71	0.24	-0.29	-0.81	0.84	-0.67	-0.80	-0.55	-0.37
DO	-0.42	-0.52	1.00	0.87	0.90	-0.63	-0.75	0.45	0.82	-0.55	0.76	0.87	0.77	0.18
UT	-0.23	-0.80	0.87	1.00	0.72	-0.75	-0.54	0.47	0.92	-0.72	0.90	0.98	0.75	0.23
pH	-0.36	-0.50	0.90	0.72	1.00	-0.55	-0.89	0.41	0.74	-0.53	0.58	0.74	0.58	0.33
EC	-0.08	0.71	-0.63	-0.75	-0.55	1.00	0.32	-0.06	-0.88	0.86	-0.46	-0.82	-0.60	-0.48
NH4-N	0.34	0.24	-0.75	-0.54	-0.89	0.32	1.00	-0.37	-0.56	0.29	-0.45	-0.55	-0.48	-0.20
PO4-P	-0.29	-0.29	0.45	0.47	0.41	-0.06	-0.37	1.00	0.20	-0.09	0.59	0.40	0.39	-0.20
NO3-N	-0.14	-0.81	0.82	0.92	0.74	-0.88	-0.56	0.20	1.00	-0.85	0.73	0.95	0.76	0.38
TP	-0.19	0.84	-0.55	-0.72	-0.53	0.86	0.29	-0.09	-0.85	1.00	-0.54	-0.75	-0.64	-0.33
Ca2+	-0.30	-0.67	0.76	0.90	0.58	-0.46	-0.45	0.59	0.73	-0.54	1.00	0.81	0.66	-0.09
Mg2+	-0.20	-0.80	0.87	0.98	0.74	-0.82	-0.55	0.40	0.95	-0.75	0.81	1.00	0.75	0.35
BOD5	-0.16	-0.55	0.77	0.75	0.58	-0.60	-0.48	0.39	0.76	-0.64	0.66	0.75	1.00	-0.15
SAS	-0.11	-0.37	0.18	0.23	0.33	-0.48	-0.20	-0.20	0.38	-0.33	-0.09	0.35	-0.15	1.00

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TABLE 2. FACTOR LOADING MATRIX AND TOTAL VARIANCE EXPLAINED

Variable	Factor Loadings (Varimax raw) (Extraction: Principal components (Marked loadings are >.700000)		
	Factor (1)	Factor (2)	Factor (3)
T	0.178444	**-0.783452**	-0.033570
SS	**-0.893240**	-0.055120	0.017465
DO	0.633462	**0.716273**	0.113039
TH	**0.853742**	0.442813	0.160692
pH	0.524868	**0.771396**	-0.097859
EC	**-0.894248**	-0.087347	0.272784
NH_4-N	-0.289276	**-0.809000**	0.052125
PO_4-P	0.190532	0.475637	0.611846
NO_3-N	**0.912950**	0.351281	-0.099223
TP	**-0.941284**	0.031246	0.116898
Ca^{2+}	0.673728	0.424296	0.472286
Mg^{2+}	**0.875157**	0.430031	0.026470
BOD5	**0.711038**	0.315939	0.393084
SAS	0.286753	0.201967	**-0.858465**
Eigenvalue	6.682123	3.439296	1.639835
Variance (%)	**47.7294**	**24.5664**	**11.7131**

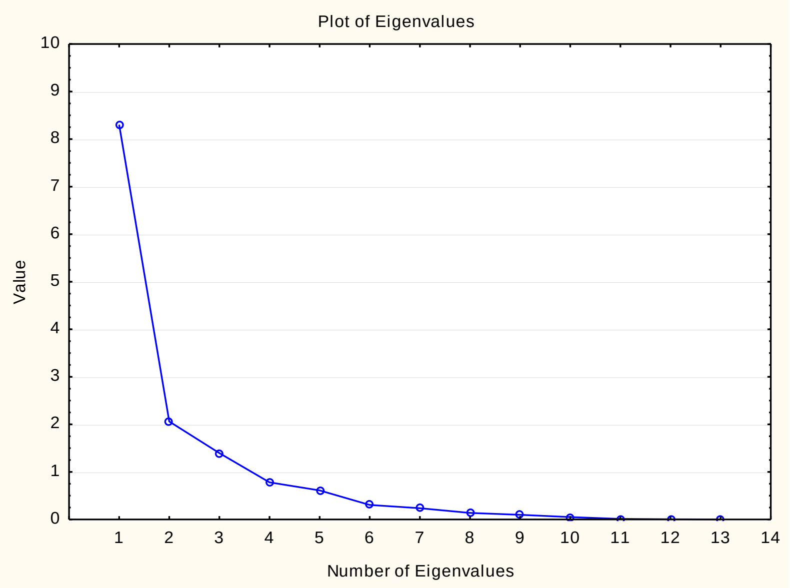

Figure 2. Scree plot

Only those factors having high eigenvalues,
forming the **“cliff”** should be retained

The application of FA/PCA analysis has led to identification of **three latent factors** responsible for the data structure.

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Cluster analysis

- The joining or tree clustering method uses the dissimilarities (similarities) or distances between objects when forming the clusters. Similarities are a set of rules that serve as criteria for grouping or separating items.

- The similarities-dissimilarities are quantified through Euclidean distance measurements, the distance between two objects, i and j, is given as:

$$d_{ij}^2 = \sum_{k=1}^{m} \left(z_{ik} - z_{jk}\right)^2$$

- **Single linkage (nearest neighbor) -** distance between two clusters is determined by the distance of the two closest objects **(nearest neighbors)** in the different clusters.
- This rule will, in a sense, *string* objects together to form clusters, and the resulting clusters tend to represent long "chains."

This data analysis gives an idea of how the single water quality parameters should be compared and related to one another, if the sample is treated with all parameter values simultaneously, not separately

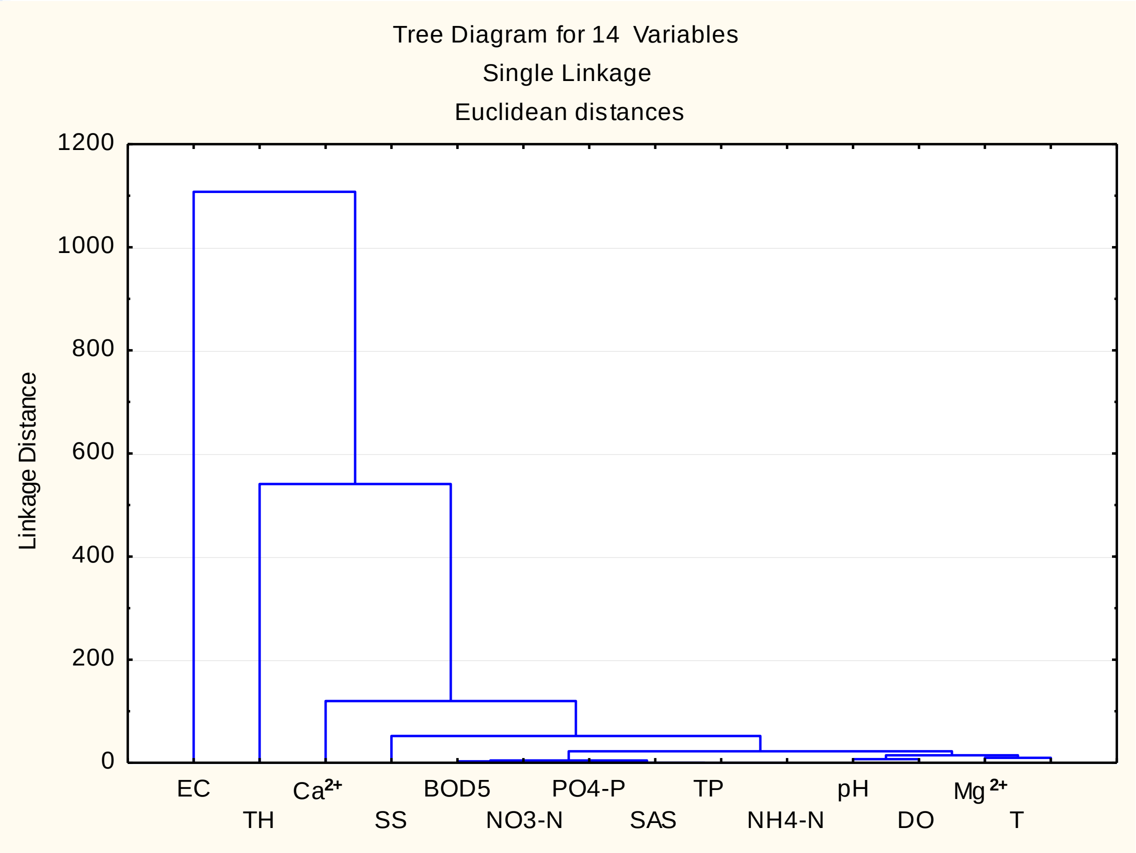

Figure 3. Dendrogram for the 14 studied parameters

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Cluster analysis grouped 14 monitoring stations into two clusters of similar surface water quality characteristics.

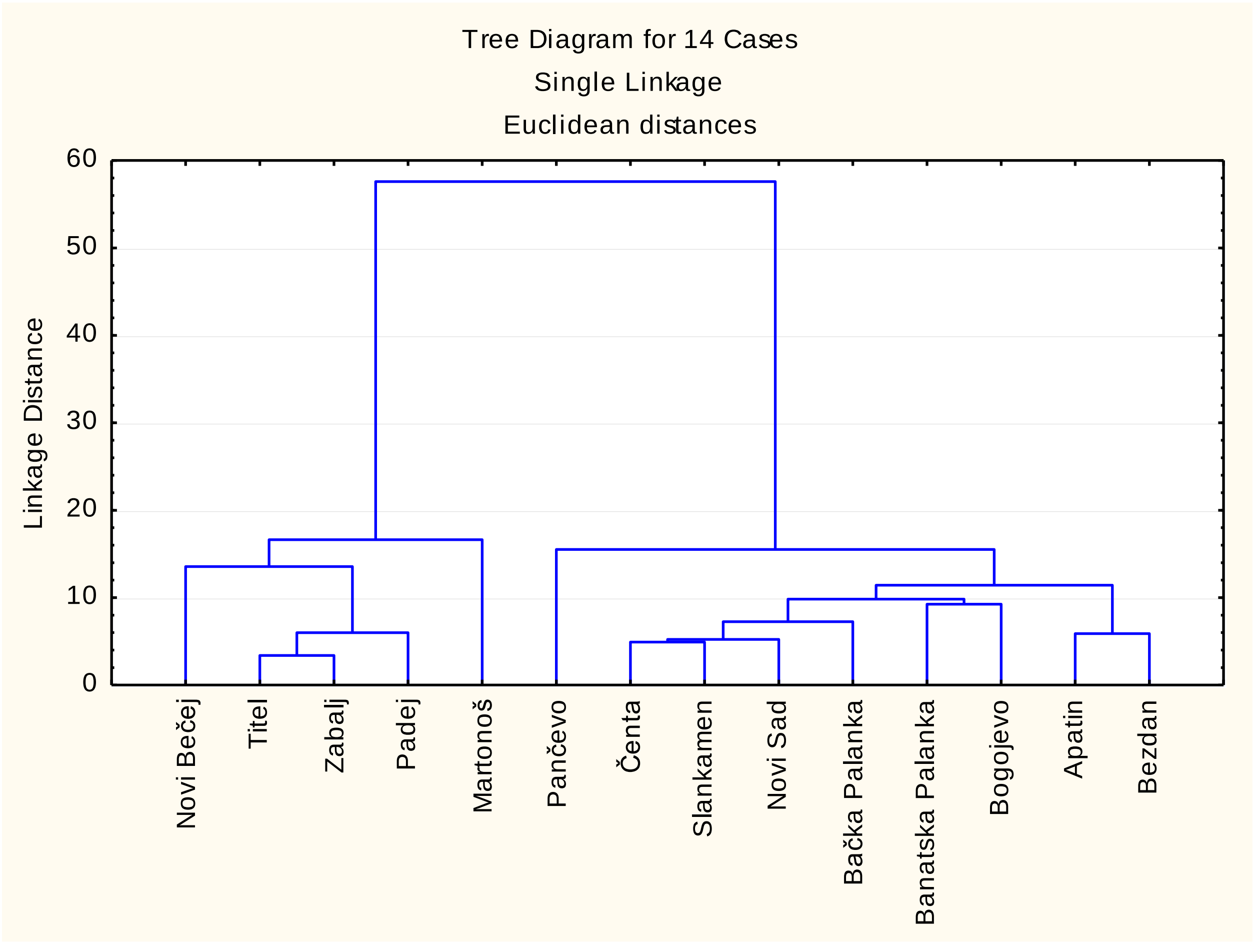

Figure 4. Denogram for the 14 observations stations F1 (SS, TH, EC, NO_3-N, TP, Mg, BPK_5)

Cluster analysis grouped 14 monitoring stations into two clusters of similar surface water quality characteristics.

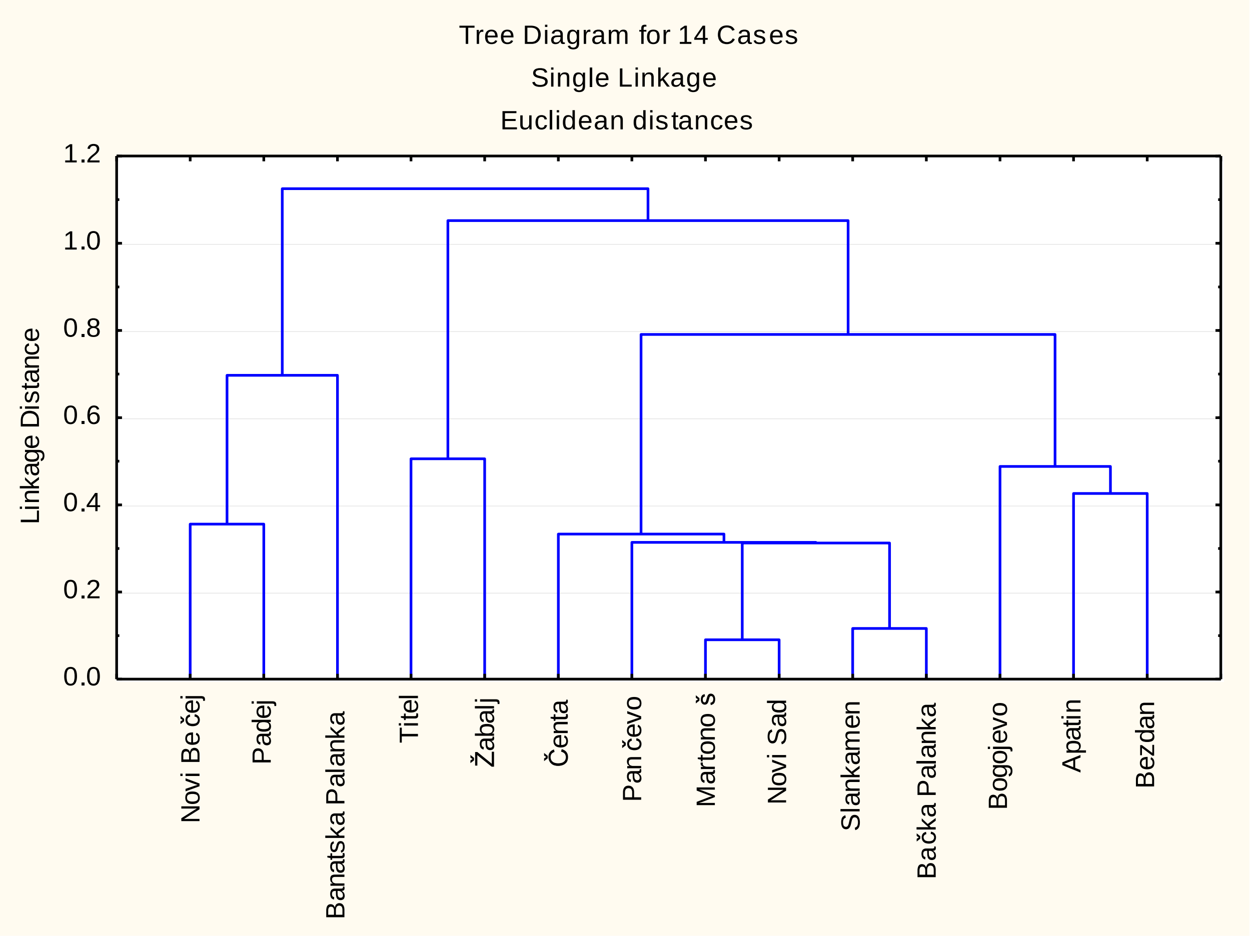

Figure 5. Denogram for the 14 observations stations F2 (T, O_2, pH, NH_4-N)

ICPDR-TNMN

- Within the frame of Internationational Commision for the Protection of the Danube River **(ICPDR)** activity Trans-National Monitoring Network **(TNMN)** had been established
- ICPDR and TNMN experts defined five clases system for the evaluation of water quality Which are mainly in accordiance with Water Framework Directive **(WFD)**

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Water classification used for TNMN

Determinand	Unit	Class				
		I	II TV	III	IV	V
		Class limit values				
Oxygen/Nutrient regime						
Dissolved oxygen*	$mg.l^{-1}$	7	6	5	4	< 4
BOD_5	$mg.l^{-1}$	3	5	10	25	> 25
COD_{Mn}	$mg.l^{-1}$	5	10	20	50	> 50
COD_{Cr}	$mg.l^{-1}$	10	25	50	125	> 125
pH	-		> 6.5* and < 8.5			
Ammonium-N	$mg.l^{-1}$	0.2	0.3	0.6	1.5	> 1.5
Nitrite-N	$mg.l^{-1}$	0.01	0.06	0.12	0.3	> 0.3
Nitrate-N	$mg.l^{-1}$	1	3	6	15	> 15
Total-N	$mg.l^{-1}$	1.5	4	8	20	> 20
Ortho-phosphate-P	$mg.l^{-1}$	0.05	0.1	0.2	0.5	> 0.5
Total-P	$mg.l^{-1}$	0.1	0.2	0.4	1	> 1
Chlorophyll-a	$\mu g.l^{-1}$	25	50	100	250	> 250

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Based on the data obtained and classification of surface water, according to the TNMN standards, The Danube and Tisa river belongs to the classes I and II.

TABLE 3. WATER QUALITY PARAMETERS – Danube and Tisza- monitoring stations

Parameters	Min.	Max.
SS	15 mg/l	44.33 mg/l
	Bezdan	Martonoš
TP	0,08 mg/l	**0,14 mg/l**
	Novi Sad	Žabalj
PO4-P	0,033 mg/l	0,069 mg/l
	Martonoš	Žabalj
NH4-N	0,05 mg/l	0,13 mg/l
	Bezdan, Apatin, Bogojevo, Bačka Palanka	Banatska Palanka
NO3-N	0,90 mg/l	1,71 mg/l
	Novi Bečej	Bezdan
BOD5	1,68 mg/l	2,51 mg/l
	Padej	Bezdan
pH	7,96	8,25
	Žabalj	Bezdan, Apatin
EC	456,67 µS/cm	543,70 µS/cm
	Bačka Palanka	Titel
SAS	0,02 mg/l	0,05 mg/l
	Bezdan, Apatin, Novi Sad, Banatska Palanka, Martonoš, Žabalj, Titel	Slankamen

- **TP content indicates the deterioation of the water quality by nutrient impact**
- **Increasing of orthophosphate content is most probably because of the irrigation from the agricultural lands, and also because of the untreated communal wastewater**

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Conclusion

- The factor analysis generated 3 significant factors which explain 84 % of the variation in the data set
- **CA** could be useful tool in designing optimal sampling strategy, which could reduce the number of monitoring stations
- **CA** gives an idea of how the single water quality parameters should be compared and related to one another
- According to the above data, ***there is no significant variation in water quality parameters between observation stations***
- Concentrations of parameters were in the range of Class I and II, according the water classification used for TNMN **and also to the current Serbian regulations (**Regulation on emission limit values in surface and ground waters and the deadlines for the achievement thereof)
- This could be explained by the fact that Rivers Danube and Tisa have high *self*-purification *capacity*

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Thank you for your attention!