ACADEMIA ROMÂNĂ
Revue Roumaine de Chimie
http://web.icf.ro/rrch/

Rev. Roum. Chim.,
2015, *60*(10), 935-941

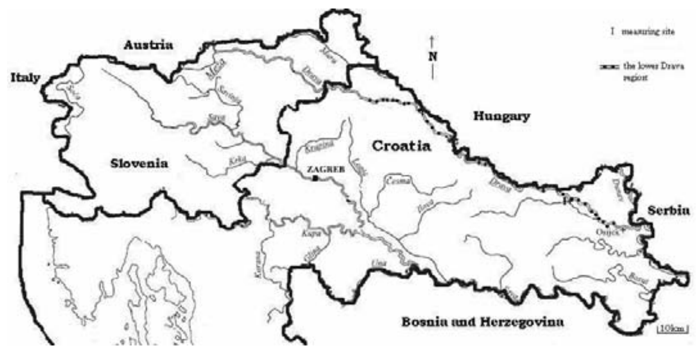
ANALYSIS AND ASSESSMENT OF AVAILABLE WATER SOURCES IN EASTERN CROATIA

Vlatka GVOZDIĆ,[a] Josip BRANA,[b] Kornelija OREŠKOVIĆ,[c] Dinko PUNTARIĆ,[d] Domagoj VIDOSAVLJEVIĆ,[d,e*] Matijana JERGOVIĆ,[f] Ida PUNTARIĆ,[g] Eda PUNTARIĆ,[h] Marina VIDOSAVLJEVIĆ[i] and Andrijana MÜLLER[d]

[a] J. J. Strossmayer University, Department of Chemistry, Osijek, Cara Hadrijana 8a, HR 31000 Osijek, Croatia
[b] J. J. Strossmayer University, Department of Physics, Osijek, Trg Ljudevita Gaja 6, HR 31000 Osijek, Croatia
[c] Department of Water treatment, wastewater treatment and water control "Kombel", Kralja Tomislava 198/a, HR 31551 Belišće, Croatia
[d] J. J. Strossmayer University, Faculty of Medicine, Osijek, Josipa Huttlera 4, HR 31000 Osijek, Croatia
[e] General Hospital, Vukovar, Bolnička 5, HR 32000 Vukovar, Croatia
[f] Public Health Institute, Department of Health Ecology, Zagreb, Mirogojska cesta 16, HR 10000 Zagreb, Croatia
[g] Zagreb County Community Health Center, Ljudevita Gaja 37, HR 10430 Samobor, Croatia
[h] Croatian Environment Agency, Trg maršala Tita 8, HR 10000 Zagreb, Croatia
[i] County General Hospital, Vinkovci, Zvonarska 57, HR 32100 Vinkovci, Croatia

Received November 3, 2014

The aim of this study was to determine certain metals, metalloids and phosphorus in samples of water from wells located in eastern Croatian zones in order to assess water quality and to monitor possible war consequences such as metal contamination. Inductively coupled plasma mass spectrometry (ICP-MS) was used to collect the results of the following elements: Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Hg, Li, Mn, Mg, Ni, P, Pb, Sb, Si, Sn, Sr, Tl, U, V and Zn. Although the results of this study confirmed that there is a significant environmental issue related to elevated values of arsenic (max. 250.40 μg L^{-1}), overall results did not show abnormalities in concentrations of monitored weapon related elements. Also, we have collected and analysed data for the Drava River, part of the Danube basin, which is partially the source of drinking water production. Eleven physicochemical parameters were analysed in order to assess the water quality characteristics of the Drava River water in the north-eastern part of Croatia during an eight-year period (January 2000-January 2008). Over the whole period most parameters kept within the desirable water quality limits while ammonia and nitrite nitrogen concentrations were higher during the last four measurement years. The principal component analysis technique (PCA) was performed to order the parameters that are most important in assessing variations of the river water quality data. Generally, the analysis of water quality revealed that the Drava River water chemistry is in the second part of the analysed period (2005-2008) slightly affected by anthropogenic activities that caused the observed variations in its quality.



INTRODUCTION

Water pollution has become a growing threat to human society and natural ecosystems in the last two decades. The water is the medium, which allows the occurrence of many chemical reactions essential for life as well as circulation of minerals, vitamins, hormones and other chemical substances in the body. An exposure to toxic contaminants that are often globally present in the surface water,

* Corresponding author: domagoj.vidosavljevic@gmail.com

groundwater and drinking water, can result in significant risk for human health. Arsenic in water is a well known contaminant of natural origin and its presence depends on the geological characteristics of the soil that contains groundwater. Elevated concentrations of arsenic in drinking water are associated with an increased risk of bladder, skin and lung cancer, as well as changes in skin pigmentation and peripheral vascular diseases.[1] The maximum allowed concentration of arsenic in drinking water is 10 μg L^{-1}, although until recently it was 50 μg L^{-1}.

The results of previous studies showed that the occurrence of elevated values of As (from 10 to 610 μg L^{-1}) in groundwater, presents a significant environmental problem in the southern part of the Pannonian Basin.[2] Groundwater samples from the well-field supplying the city of Osijek in eastern Croatia were found to have high As concentrations, ranging from 16 to 358 μg L^{-1}, with a mean value of 240 μg L^{-1}, vastly higher than the World Health Organization's provisional guide value of 10 μg L^{-1} in drinking water.[3] Combat activities during the 1991-1995 war in Croatia were most intensive in this part of the country, causing heavy casualties and destruction. The environmental consequences of these military operations have also been studied.[1] Differences in metal and metalloid As concentrations in serum, hair and urine between populations from eastern Croatian areas exposed to moderate (Našice) and heavy fighting (Dalj, Čepin, Vladislavci and Osijek) suggest the need for extensive monitoring of metal and metalloid As concentrations in water for drinking.[1] Part of our work consisted of determination of 24 elements (metals, metalloids and phosphorus) in water wells located in eastern Croatian zones with the aim of assessing water quality and monitoring of possible war consequences in metal contamination.

Considering that Croatia needs to adopt the new EU Drinking Water Standard for arsenic (10 μg L^{-1}) by the year 2015, the country is facing challenges in finding alternative water resources. In eastern Croatia because of the excessive exploitation of groundwater with high arsenic concentrations, a surface water resource like the Drava River could be a good alternative. Although regular metal monitoring of the Drava River showed that concentrations of Pb, Cd, and Hg increased in the river water during the war period, the results of a recent study suggest that ten years after the end of the war in Croatia, there is no evidence of the contamination of the surface waters by trace metals as a consequence of military activities.[4,5]

Since the Drava river, which ends in the Danube, is the major supplier of drinking water, a waste water recipient as well an essential water supplier for agriculture, industry, recreation and environment, its monitoring and protection is of great importance. The quality of the Drava River water in the section of the river from Belišće to Nemetin is analysed by the Croatian National and County Institutes approximately 12 times per year. However, day-by-day multiannual studies on the measured physicochemical factors in the Drava River water are not frequent.[6,7] The results of surface water quality monitoring is an enormous data matrix composed of large sets of parameters, which are very difficult to interpret and draw meaningful conclusions. Therefore, in this study we used the power of chemometrics to identify important factors influencing river water quality in the period from January 2000-January 2008. This study was carried out to assess the pollution level of the Drava River water in order to appreciate the impact of various factors on the quality of the river water as well as to assess its suitability for the treated water used for drinking, industrial purposes, swimming, recreation and aquatic life.

MATERIALS AND METHODS

Study area and sampling sites

The surface water is collected in the Slavonian region, specifically Osijek-Baranja county which is located in the north-eastern, Pannonian part of Croatia (330,506 population and comprises 4,152 km^2). The measurement site is located downstream from the town of Belišće at 45.41ºN, 18.25 ºE. The average temperature is 11 ºC (spring: 11ºC, summer: 21ºC, autumn: 11.8 ºC, winter: 0.2ºC).

A total of 51 well water samples were collected. Study sites were from areas exposed to heavy combat (Čepin: 45.3º N, 18.34º E, Vladislavci: 45.28º N, 18.34º E) to the Dalj area: 45.29º N, 18.59º E) which was not as heavily bombed. Dalj remained under enemy occupation for a long time and it held many arms storage sites. We chose to monitor mainly the elements that best describe combat–relevant pollution: Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Hg, Li, Mn, Mg, Ni, P, Pb, Sb, Si, Sn, Sr, Tl, U, V and Zn.

Hydrological data and analytical procedures

The eleven monitored parameters and their abbreviations are: water level (WL, expressed in cm), water temperature (WT, expressed in ºC), turbidity (Turb, expressed in NTU), pH (expressed in pH unit), total suspended solids (TSS, expressed in mg L^{-1}), conductivity (EC, expressed in µS cm^{-1}), chemical oxygen demand (COD, expressed in mg $L^{-1}O_2$) ammonia nitrogen (expressed in NH_4-N, mg L^{-1}), nitrite nitrogen (expressed in NO_2-N, mg L^{-1}), sulphates (SO_4^{2-}, expressed in mg L^{-1}) and chlorides (Cl^-, expressed in mg L^{-1}). Ammonia nitrogen, nitrite nitrogen and sulphates were determined spectrometrically, chlorides and permanganate consumption were determined by the usual titrimetric methods and total suspended solids were determined gravimetrically. The turbidimeter, pH-meter and conductometer were used to measure water turbidity, pH and conductivity. The Drava River water samples were collected on workdays during the eight year sampling period (January 2000-January 2008).

Concentrations of Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Hg, Li ,Mn, Mg, Ni, P, Pb, Sb, Si, Sn, Sr, U, V, Zn and Tl in samples of well water were determined using inductively coupled plasma mass spectrometry (ICP-MS, ELAN DRC-e, Perkin Elmer, Waltham, MA, USA). The data are expressed in µg L^{-1}.

Computational methods

We applied the most widely used multivariate statistical technique in environmental sciences: Principal Component Analysis (PCA). PCA can be used for classification of data, finding similarities and outliers and allows us to observe the sources of variation in complex data set. The purpose of this analysis is to find simple underlying principal components (PCs) and to attribute physical meaning to them. More details on this method can be found elsewhere.[9] Statistical calculations were performed by the software package Statistica 7.

RESULTS

Descriptive statistics

In terms of investigated elements it has been found (Table 1) that well water with exceptions of the concentrations of Fe (Vladislavci: mean 842,68 µg L^{-1}, Čepin: mean 226,39 µg L^{-1}), MAC (Maximum Allowed Concentration) 200 µg L^{-1}, concentrations of As (Vladislavci: mean 16,32 µg L^{-1}, Čepin: mean 184,34 µg L^{-1}), MAC 10 µg L^{-1} and concentrations of Mn (Vladislavci: mean 66,71 µg L^{-1}, Dalj mean 70,167 µg L^{-1}), MAC 50 µg L^{-1} is in accordance with national Croatian limits for drinking water.[10] The results of Kruskal-Wallis tests showed that mean concentrations of all 24 analyzed elements in three villages did not differ significantly ($p = 0.864$).

We have analysed Drava River water samples that were taken as a part of the regular screening of river water quality and were characterized by eleven physicochemical parameters. Table 2 summarizes the 90th percentile of different physicochemical water quality parameters during the eight-year study.

Principal component analysis

In order to evaluate the most significant parameters in river water quality assessment, the PCA method was performed. Due to the obvious difference in water quality data (see Table 2), the PCA was divided into two separate periods (2000-2004 and 2005-2008). In both periods the PCA method extracted four significant factors with the eigenvalues greater than 1 and as a consequence, 74 and 76% of the variance of the original data my be explained, which is large enough to give adequate representation of the data.

Table 1

Descriptive statistics of the data

Element/ µg L^{-1}	MAC	Vladislavci		Čepin		Dalj	
		Mean	Maximum	Mean	Maximum	Mean	Maximum
Al	200	2.46	8.52	4.70	26.43	9.44	118.90
As	10	16.32	160.16	184.34	250.40	1.43	8.85
B	1000	90.12	333.80	270.68	338.30	65.88	172.20
Ba	700	42.23	86.53	71.22	84.51	75.94	311.30
Cd	5	0.042	0.19	0.003	0.018	0.016	0.07

Table 1 (continued)

Co	NR	0.22	1.03	0.15	0.173	0.42	3.84
Cr	50	1.11	5.97	4.25	17.05	1.56	5.09
Cu	2000	12.18	51.23	8.21	23.11	4.21	15.56
Fe	200	842.68	5536.75	226.39	592.50	99.11	871.90
Hg	1	0.027	0.11	0.047	0.150	0.095	0.29
Li	NR	3.04	12.20	33.27	43.53	4.61	12.29
Mg	NR	24.76	51.34	48.67	60.36	34.92	83.62
Mn	50	67.15	564.00	49.00	56.64	70.00	1285.00
Ni	20	5.07	12.10	1.43	3.25	5.58	16.96
P	NR	0.106	0.50	0.66	0.84	2.72	35.47
Pb	10	1.14	3.91	0.26	1.15	0.48	2.61
Sb	5	0.038	0.088	0.002	0.010	0.055	0.14
Si	NR	174.07	463.50	3.24	38.91	109.33	335.22
Sn	NR	0.08	0.51	0.005	0.026	0.019	0.07
Sr	NR	214.26	444.60	209.57	278.60	401.14	839.20
Tl	2*	0.002	0.006	0.0002	0.001	0.007	0.04
U	30*	3.14	9.01	0.001	0.012	4.25	13.32
V	5	0.98	3.46	0.016	0.186	1.06	4.14
Zn	3000	394.78	1582.59	41.67	132.20	75.59	397.38

MAC - maximum allowed concentration according to Croatian legislation[10]
* – maximum contaminant level according to USEPA [11]
NR – not regulated

Table 2

The 90th percentile of physicochemical water quality parameters

Parameter/Year	90% th Percentile							
	2000	2001	2002	2003	2004	2005	2006	2007
Electrical conductivity	445	345	350	360	330	343	406	363
Water temperature	23	23	22.4	25	19	22	23	24
pH	8.2	8.2	8.1	8.2	8.2	7,9	8,1	8.1
Turbidity	16	11	12.5	10.9	26	27	20	19.5
Water level	310	260	255	170	372	340	223	201
Total suspended solids	37.2	31.1	47.1	42.2	99	83	82	70.2
Chemical oxygen demand	3.1	2.9	3.5	3.7	3.95	3.8	3.7	3.78
Ammonia nitrogen	0.22	0.21	0.20	0.23	0.42*	0.49*	0.49*	0.41*
Nitrite nitrogen	0.008	0.009	0.009	0.007	0.010	0.09*	0.05*	0.09*
Chlorides	11.0	9.5	11.7	10.9	12.7	10	14.1	11
Sulphates	26.2	27.3	29.8	33.2	29.3	24	29.3	25

* Results that were not within the prescribed limits of class I or II according to the Croatian Water Classification Act (CWCA).12

Table 3

Principal component loadings of the data set (2000-2004)

Variable	PC1	PC2	PC3	PC4
WL	0.670	0.490	0.415	0.003
WT	0.640	-0.560	-0.310	0.011
Tu	0.413	0.807	0.022	0.050
TSS	0.386	0.313	-0.300	0.457
pH	0.268	-0.258	-0.142	-0.807
EC	-0.806	0.108	0.142	-0.106
COD	0.105	0.227	-0.866	0.060
NH_4-N	-0.080	0.603	-0.270	-0.466
NO_2-N	-0.127	0.556	0.060	-0.216
SO_4^{2-}	-0.809	0.132	-0.107	0.139
Cl^-	-0.913	0.063	-0.192	0.038
Eigenvalues	3.41	2.28	1.26	1.01
Variance (%)	31.07	51.84	63.32	74.34

Table 4

Principal component loadings of the data set (2005-2008)

Variable	PC1	PC2	PC3	PC4
WL	0.590	0.540	-0.130	-0.07
WT	0.820	0.015	0.125	0.290
Tu	0.150	0.850	0.040	0.003
TSS	0.110	0.240	0.770	0.037
pH	-0.099	0.012	-0.160	0.770
EC	-0.920	-0.150	0.097	0.136
COD	0.032	0.770	0.170	0.127
NH_4-N	0.001	0.860	0.011	-0.013
NO_2-N	0.076	0.072	0.110	0.650
SO_4^{2-}	-0.140	-0.074	0.800	-0.120
Cl^-	-0.920	0.015	-0.013	0.055
Eigenvalues	3.32	2.0	1.3	1.1
Variance (%)	30.26	50.36	63.9	76.88

DISCUSSION

The results presented in this study show the occurrence of elevated values of As, Mn and Fe in the analyzed samples of well water. Except for arsenic, iron and manganese, the concentration levels of the remaining elements that were analysed in the water samples, were below the maximum allowed concentrations. Many studies conducted in eastern Croatia have reported the significant correlation between As, Fe and Mn in groundwater.[2,3] However, these elements mainly originated from natural sources as a result of geological composition of the soil,[8] thus, the input of these elements from combat activities is negligible. The most probable arsenic sources are the minerals deposited in deeper aquifers during the Middle and Upper Pleistocene.[8] The elements thallium and uranium are not included in standard monitoring and control of the quality of drinking water in Croatia. Since thallium and uranium have biological effects on the human body in terms of their toxicity, it was desirable to determine their presence in drinking water. According to the Environmental Protection Agency (EPA), the maximum contaminant level (MCL) for thallium and uranium in water is 2 and 30 $\mu g\ L^{-1}$ respectively.[11] The measured values of thallium and uranium in water samples were not elevated in any observed place and thus, should not pose a risk to human health.

The legislation valid for this measurement period in the Republic of Croatia regulates standards for water use and protection and ranges the five classes for the quality of surface water evaluation.[12] The 90th percentile level of pH, electrical conductivity, chemical oxygen demand and nitrite nitrogen concentrations according to the Croatian Water Classification Act indicated that river water quality falls into category I, which includes surface water used for drinking or in the food industry (in its natural state or after disinfection), as well as water used for rearing high-quality species of fish. Nitrogen in water may provide information about pollution. Since NH_4-N is one of the first steps in organic matter decomposition, higher NH_4-N points to recent pollution, while elevated concentrations of NO_2-N point to more remote contamination.[7] According to the results obtained from investigations of ammonia nitrogen concentrations during the first four years, the Drava River falls into the prescribed Class II category which implies that water is used in its natural state for swimming and recreation and the treated water is used for drinking and other industrial purposes (Table 2). A more pronounced problem for the Drava's water quality is elevated ammonia and nitrite nitrogen concentrations especially during the last three observed years.

Characterization of changes in surface water quality is an important aspect for evaluating the potential impact of natural and anthropogenic sources of pollution.

In order to evaluate the most significant parameters in river water quality assessment, the PCA method was performed. Again, due to the obvious difference in water quality data (Table 2), the PCA was divided into two separate periods (2000-2004 and 2005-2008). In both periods the PCA method extracted four significant factors with the eigenvalues greater than 1 and as a consequence, 74 and 76% of the variance of the original data my be explained, which is large enough to give adequate representation of the data (Tables 3 and 4).

The factor loadings may be classified as strong > 0.75, moderate (0.75-0.50) and weak (0.50-0.30). Table 3 shows that the first factor accounted for 31.07% of the total variation in the data and that the main sources of variations are electrical conductivity, sulphates and chlorides (mineral-related factor) with strong loadings, and temperature and water level with moderate loadings. The second factor (physical) which accounted for 20.76% of the total variations was strongly weighted with turbidity (Tu) but moderately weighted with nutrient factors (NH_4-N and NO_2-N). The Drava River bed and floodplain sediments consist of sands, mud and gravelly sands so, along the Drava River in many places sand and gravel are being exploited, which can result in the occurrences of sudden temporal variations of total suspended solids and turbidity values at any time during the year.[6,7] The third (COD, organic-related) and fourth factors loaded heavily with pH accounted for a much lower percentage of variance as compared to the first two PCs. The results of the PCA technique demonstrate that water level, temperature, ammonia nitrogen and nitrite nitrogen concentrations play a minor role in the water quality description. Although the second PCs included the variables NH_4-N and NO_2-N, none of them were highly loaded.

The PCA indicates that the most relevant variables defining water quality in the second period of measurements (Table 4) are related to temperature, conductivity , and chloride, but not less relevant ones are Tu, COD and NH_4-N (turbidity, oxidizable components of water and nutrients, see PC2). The influence of various waste inputs as well as agricultural activities (anthropogenic influences) on the loadings in second observed period proved to be considerable. Also, the noticeable difference is visible in component PC4 (12.9%) which is quite highly correlated with NO_2-N concentrations, pointing to a less deterioration of the Drava's water quality. However, the median concentration of NH_4-N between the two observed periods increased from 0.18 mg L^{-1} to 0.27 mg L^{-1} which is still lower value compared to other European rivers (0.3 mg L^{-1} to 0.8 mg L^{-1}) and rivers of Danube River basin (0.25 mg L^{-1} to 1.0 mg L^{-1}).

Advantages of the principal components interpretation are reflected in the ability to explain the physical nature and strength of variables in each component. Both, a very high number of data and proper frequency of observations, helped to obtain meaningful components which enabled us to provide reliable information about the variables responsible for the variation in water quality of the Drava River. The proposed methodology makes it possible to identify the major processes controlling variations in the studied aquifer and can be useful in aquifers where hydro chemical data are available. Unlike studies that deal with data recorded in weekly or monthly intervals, the present study is specific as it deals with the water quality parameters collected during daily intervals covering the most complete range of data for the Drava River. Although PCA demonstrated deteriorating conditions of water quality, situation is relatively better in comparison with other European Rivers. Furthermore, the results obtained in this research have shown that concentration of organic matter is reduced in comparison to values obtained through examination of water quality of Drava in the period between 1966 and 1990 (pre-war period).[4] Considering the positive trend of decreasing of heavy metal burden[4,5] total coli form bacteria,[7] and organic matter it should be easier to achieve the prescribed drinking water standards as long as the general pollution at this location is prevented.

CONCLUSIONS

Overall results presented in this study show that the quality of the analyzed well water samples is not adequate for human consumption. Although the results confirm the occurrence of the elevated values As, Mn and Fe (situation similar to that observed elsewhere in the Pannonian Basin) the mean concentrations of selected weapons-related elements were not elevated and did not differ significantly regardless of the level and type of combat activity.

The results of this study indicate a relatively low level of pollution of the Drava in this area considering the 11 physicochemical parameters that were monitored over the first four year period (2000-2004). The anthropogenic influences become more noticeable in the second measurement period (2005-2008) therefore, continuous and more frequent monitoring is necessary.

Acknowledgements: This study is part of the project "Investigation of long term effects of war on population" by the Ministry of Science, Education and Sports of the Republic of Croatia. Analyses were performed at the Department of Health Ecology, Zagreb Institute for Public Health.

REFERENCES

1. M. Jergović, M. Miškulin, D. Puntarić, R. Gmajnić, J. Milas and L. Šipoš, *Croat. Med. J.*, **2010**, *51*, 451.
2. M. Habuda-Stanić, M. Kuleš, B. Kalajdžić and Ž. Romić, *Desalination*, **2007**, *210*,157.
3. Ž. Romić, M. Habuda-Stanić,B. Kalajdžić and M. Kuleš, *Appl Geochem*, **2011,** *26*, 37.
4. K. Vitale,M. Marijanović-Rajčić and A. Senta, *Croat Med J*, **2002**, *43*, 485.
5. V. Roje, J. Dautović, N. Mikac and G. Kniewald, "Distribution of trace metals in surface waters and artesian well waters from war-affected regions of Croatia", in: "Book of Abstracts" (Workshop on Mitigation of environmental consequences of war in Croatia: risk assessment of hazardous chemical contamination), Zagreb, 2005.
6. V. Gvozdić, J. Brana, N. Malatesti and D. Roland, *J Hydroinform*, **2012**, *14*, 1051.
7. V. Gvozdić, J. Brana, D. Puntarić, D. Vidosavljević and D. Roland, *Arh Hig Rada Toksikol*, **2011**, *62*, 325.
8. M. Ujević, Ž. Duić, C. Casiot, L. Sipos, V. Santo, Ž. Dadić and J. Halamić, *Appl Geochem*, **2010**, *25*,1017.
9. V. Gvozdić, J. Brana, N. Malatesti, D. Puntarić, D. Vidosavljević and D. Roland, *Coll Antrop*, **2011**, *35*, 1135.
10. Book of regulations on health safety of drinking water. Official Bulletin of the Republic of Croatia, Narodne novine, No.47, Zagreb, 2008 (in Croatian).
11. Drinking Water Contaminants. U.S. Environmental Protection Agency, 2009. See also: http://water.epa.gov/drink/contaminants/upload/mcl-2.pdf
12. Croatian Water Classification Act, Official Bulletin of the Republic of Croatia, Narodne novine. No.77, Zagreb,1998, Croatia (in Croatian).