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ХИМИЯ НА МОРЕТО

On the recent dynamics of some chemical parameters along the Bulgarian sector of the Danube River

Alexander Stoyanov, Galina Shtereva, Anton Krastev, Ognyana Hristova, Lidia Mihova, Ilia Shterev
Institute of Oceanology, Bulgarian Academy of Sciences, Varna, Bulgaria

Along the main factors influencing negatively the Black Sea ecosystem the Danube river could be considered the key contributor with its annual flow of about 200 - 202 km^3 draining an area of about 817 000 km^2, e.g. exceeding almost twice the surface area of Black Sea itself. The indirect "Bulgarian share" in the pollution of Black Sea originated from a catchment area of 49 600 km^2, e.g. 6 % of the total Black Sea watershed with an annual flow of 1.8 km^3 per year.

More important among the Bulgarian Danube tributaries are the following river valleys: Lom, Ogosta, Iskar, Vit, Ossam, Yantra and Russenski Lom. Smaller, shorter and of low water flow are the rivers: Topolovetz, Voinishka, Vitbol, Archar, Skomlia, Tzibritza, Suhodolia, Topchijska, Senkovetz, Karagiol and Suha.

The Bulgarian part of the Danube river watershed covers 42 912.6 km^2, e.g. accounting for about 38.69 % of the country area. The population inhabiting the Danube river catchment area has increased in number from 3 003 506 in 1934 to 3 766 298 people in 1992. The density of the population was highest in 1985 - 3 969 604 inhabitants, e.g. 44.35 % from the total population of the country (Y e a r B o o k.., 1991).

This region is characteristic with a variety of industrial and economic activities.

The main contributors of pollution are: industry (72.0 %), agriculture (10.2 %) and transport (3.7 %) - Fig. 1. The industry is one of the main consumer of water, over 93.0 % of the total amount is used for the manufacture. Typically high water consuming branches are: the energetic (86.5 %) and the chemical, petroleum and rubber industry (4.5 %). Among the other branches of the national economy agriculture utilizes about 5.8 % of the total amount of the water used (including 4.4 % for irrigation). The building industry, forestry, transport and communication have an insignificant share in water consuming.

From the total amount of the discharged waste waters into the main Danube river tributaries the industrial waste effluent accounts for more than 78.2 %, the transport - 4.8 %, the municipality industry - 11.8 %, the agriculture - 4.8 % and the building industry - 1.0 % respectively (K r a s t e v, K r a s t e v a, S t o y a n o v, 1995).

From all the drained waste waters 98.7 % are not treated. The different industry branches account for about 93.7 % of the total untreated waste waters discharged into the Danubian tributaries, ranked in the following order: energetic, electricity and heat production - 87.5 %, chemical and petroleum industry - 4.2 % and food industry - 0.6 % (Fig. 2).

Both the agriculture and forestry are

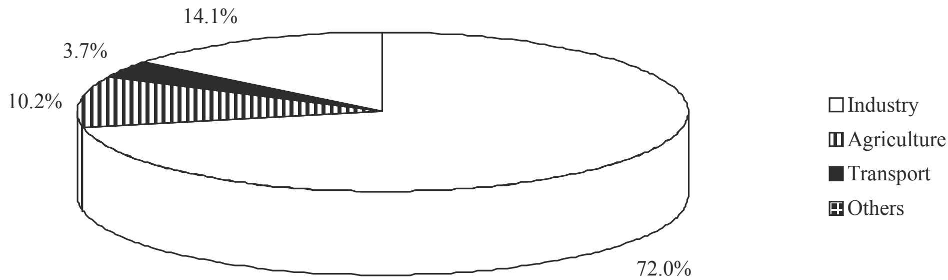

Fig. 1. Main contributors of pollution

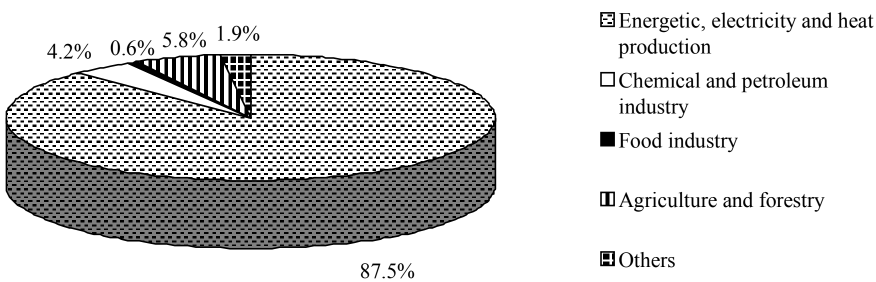

Fig. 2. Untreated waste waters discharged into the Danubian tributaries along the Bulgarian sector

responsible for about 5.8 %. Of the total pollutants discharged into the Danube river drainage basin (1 564 000 kg per day) 78.2 % are industrial contribution of the chemical and petroleum industry in particular (13.4 %). The discharge from the latter is highest into the rivers: Ogosta -28.5 %, Russenski Lom - 27.0 %, Ossam - 15.9 % and Iskar - 12.1 %.

The industrial plants responsible for the highest pollution are: the oil industrial plants in Pleven and Russe towns, the poliamide fabric plant in Vidin, the chemical firm “Himko” in Vratza, the chemical plants in Sofia (Ravno pole), “Sviloza” in Svishtov, the pharmaceutics plant (antibiotics) in Razgrad, the chemical firm “Latex” in Bialla and the chemical industry plants in Silistra.

Of all wastes, especially the solid ones, the greatest share is discharged into the river waters by the food industrial plants (27.5 % of the total). The negative effects of this industry is best expressed over the river Vit waters in its middle and lower course in particular - accounting for over 86.3 % of the pollution. The cellulose - paper making industry accounts for about 4.5 % of the total pollution of the river waters. The influence is strongest upon the Iskar river (24.0 % of its total pollution) and upon the Ossam river - 17.6 %. The leather furrier industry together with the bootware manufacture are another serious pollution source of the Danube river drainage basin, accounting for about 4.2 % of all total pollutants. The impact of this industry is strongest on the Yantra river and its tributary Rossitza. The textile industry accounts for 1.1 % of the total waste water discharge to the Iskar river and for about 7.1

% to the Ogosta river. The wood - processing industry in Troyan, Belli and Cherni Ossam discharges its waste waters into the Ossam river accounting for about 6.3 % of the overall pollution of the river (K r a s t e v, K r a s t e v a, S t o y a n o v, 1995).

The comparison between the data periods 1975-1980 and 1981-90 shows that the nutrien content in all the rivers increases during the second period. This increasing is considerable in the river Iskar, Ossam, Yantra and Russenski Lom under the influence of the agriculture, industrial and municipal waters (Table 1).

The total input of nutrients from the Bulgarian watershed into Danube river for the period 1992 - 1993 is following: 7 720.10 tons per year of $N_{NH_4^+}$, 25 505.38 tons per year of $N_{NO_3^-}$ and 2 476.96 tons per year of $P_{PO_4^{3-}}$. The results reveal that $N_{NH_4^+}$ totally decreases in all rivers. Decreasing of $N_{NO_3^-}$ and $P_{PO_4^{3-}}$ is established in the most of the rivers and that could be related both to the reduction in the capacity of the industrial production and to some new waste waters treatment plants putting into operation.

The scientific study of the Danube river water chemistry and its influence on the Black Sea chemistry was conducted by Institute of Oceanology since 1950 at st. Russe (R o z h d e s t v e n s k y, 1962, 1979, 1985, 1986, 1991, 1998).

The aim of our investigations is to assess the current status were conducted during the period July 1995 - June 1996 on the base of determination of the main chemical parameters: dissolved oxygen, alkalinity, POC, nutrients ($P_{PO_4^{3-}}$, $N_{NO_2^-}$, $N_{NO_3^-}$, $N_{NH_4^+}$ and Si), metals (Fe and Mn), total suspended matter in the Danube river at station Silistra on monthly to weekly sampling frequency. All parameters are analyzed by standard methods (L u r e, 1973, P o t a p o v a, 1980)

The variability of **dissolved oxygen** is closely related to the temperature changes (Fig. 3), only the cases of oversaturation respond to Chl. *a* maxima (S t o y a n o v et al., 1997). Its values are in the range from 5.51 to 14.38 ml/l. The maximum in March is considerably higher than absolute maximum (10.36 ml/l) for long-term monitoring 1950-1985 (R o z h d e s t v e n s k y, 1991).

The nutrients dynamic follows the hydro-meteorological features of the period with significantly higher concentrations in winter. The minimum values are during the summer period closely related to the increase in temperature, the decrease of water level and increase of biological uptake.

During our studies the maximum of **phosphate phosphorus** (0.09 mg/l) was established in December and the absolute minimum (0.02 mg/l) - in August. Relatively high concentrations of phosphates were established in February and March (Fig. 4). This is due to the extensive rainfall during the long winter period. Therefore, the minimum is shifted to August instead of May-June by R o z h d e s t v e n s k y (1991).

The maximum **nitrite nitrogen** concentration during the 1975-80 period at Silistra is 20 μg/l at high level of the river in May-June, and the minimum is 11 μg/l - at low level in August (T s a n k o v, P e c h i n o v, 1990).The absolute maximum of $N_{NO_2^-}$ during our study is 83 μg/l in April. The absolute minimum 1 μg/l is registered in

Table 1. Average data of nutrient content in the rivers from Bulgarian watershed

River	NH_4,mg/l	NH_4,mg/l	NO_3 mg/l	NO_3 mg/l	PO_4,mg/l	PO_4,mg/l
	1975-90	1992-93	1975-90	1992-93	1975-90	1992-93
Ogosta	6.00	2.80	11.70	6.77	0.23	0.15
Iskar	1.38	0.89	13.00	4.89	0.38	0.28
Vit	4.23	2.60	3.29	4.01	0.65	0.68
Ossam	0.98	0.87	7.63	5.32	0.42	0.19
Yantra	1.70	1.05	4.06	4.56	0.41	0.72
Rus.Lom	9.30	1.96	22.06	3.09	1.69	1.71

October. As an average result from the whole investigated period, the average content of $N_{NO_2^-}$ amounts to 21 µg/l, i.e. it almost equals the above mentioned average maximum for the period of 1975-1985.

The maximum of **nitrate nitrogen** ($N_{NO_3^-}$) during our study is in March (9.76 mg/l). It is considerably higher than the maximum for the period of 1975-1985, because of the heavy snowfall. The minimum is in September (0.25 mg/l) and close to the values in July and October. The average content of $N_{NO_3^-}$ during the investigated period is 3.20 mg/l. The increasing of $N_{NO_3^-}$ in 1995-96 period compared to previous periods is as follows: 1.6 times compared to 1992-1993 (Y e a r B o o k s… 1992, 1993); 2.9 times compared to 1978-1986 (T s a n k o v, P e c h i n o v, 1990) and 4.4 times compared to 1967-1974 (I v a n o v, 1978). Other words, for about 20 years the nitrate nitrogen has increased by 4 times. This is quite alarming result, especially considering that according to C o c h i a s h u, P o p a (1981), G o m o i u, C o c h i a s h u (1985) and C o c h i a s h u (1990) $N_{NO_3^-}$ in Romanian seawaters has increased by 2 to 8 times for the period of 1971-1990. Increase in $N_{NO_3^-}$ by 3-4 times is also observed at Bulgarian shelf zone (S t o y a n o v, 1995; R o z h d e s t v e n s k y, 1991).

The minimum of **ammonium nitrogen** during our study is in July, 1995, and it is within the interval of 0.11 ÷ 0.14 mg/l (Fig. 4), i.e. almost 3 times lower than the above pointed average minimum for the period of 1975-1985 at Silistra. The average content 0.49 mg/l is closed to average value for 1978-86period, but is 4 times higher than that for 1967-74period.

For the 1995-96 period **dissolved silicon** changes from 0.12 to 3.54 mg/l with an average annual value of 2.06 mg/l, which is lower than the value received by R o z h d e s t v e n s k y (1991) - 3.23 mg/l. The absolute maximum is in February and the minimum – in August. Observations show that low level of dissolved *Si* (< 0.62 mg/l) is maintained during the whole August and the

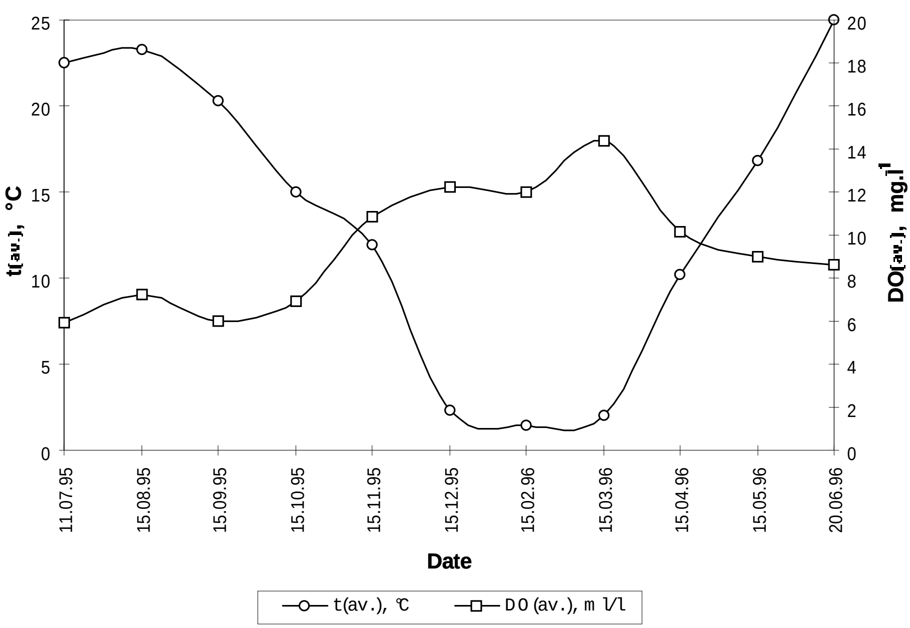

Fig. 3. Dynamic of average dissolved oxygen and t* by months at st. Silistra.

first part of September. In this period of water shortage river supply is restricted and the consumption of dissolved *Si* as a nutrient is more intensive. Relatively higher concentrations during second half of September, when the water columns are high, are probably due to the lower consumption. A second maximum is apparent in April, coincident with the maximum water level (Fig. 5).

In comparison to the other nutrients, Si shows a constantly high concentrations (above 3 mg/l) during the whole winter and the maximum is not so sharply expressed as for example, for the nitrate nitrogen.

In seasonal aspect the concentration of Si changes as follows: winter > spring > autumn > summer. Similar is the distribution of suspended matter. The relationship between the two parameters is logical, considering their sources of entering into the river. Therefore, in the seasons of full water, abundant river flow, the content of suspended matter and dissolved Si is always high.

The metals dynamic data reveal the dominance of terigenous input, with maximum in winter - spring (*Fe* = 917.9 and 769.2 μg/l; *Mn* = 407.3 and 151.8 μg/l, respectively) and minimum (*Fe* = 118.4 μg/l; *Mn* = 55.5 μg/l) in summer (Fig. 6) Two maximums in February and in April demonstrate the prevailing terigenic import of *Fe* in the Danube waters (the first is on the account of its suspended form and the second one – on the dissolved form). Suspended *Fe* preveails during the autumn-winter period, but dissolved *Fe* – during the spring. The recorder decrease in the *Fe* content as compared to the data of the previous periods could be related mainly to the barrier role of the hydrotechnical complex “Zhelezny vrata” (Rozhdestvensky, 1985). The average concentrations of metals at Silistra station during 1967- 74 period are: 1.2 mg/l *Fe* and 0.023 mg/l *Mn* (Tsachev, Ivanov, 1978).

In contrast to the iron, the prevailing form of the manganese is its dissolved form. Total manganese has a maximum (407.38 μg/l) in February and a second one (151.80 μg/l) - in May. In these months are also established the maximums of its both forms. These are better expressed during the first period, and for the dissolved form - also during the second period with the increase in the water level. The interannual dynamic of the *Mn* content

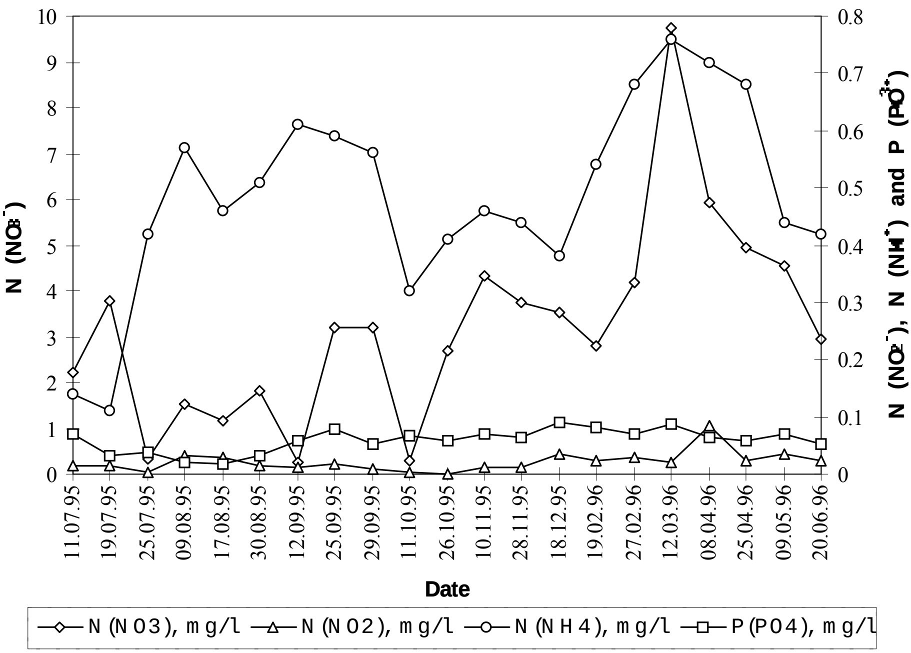

Fig. 4. Dynamic of nutrients (nitrogen and phosphorous)

depends on the river level. It usually increases for high water level (Rozhdestvensky, Shtereva, 1985). In seasonal aspect, the maximum values of the total, dissolved and suspended manganese are in winter, and the minimum values are in summer.

For the period of our investigations, total **suspended matter** changes in the range of 2.1 ÷ 140.0 mg/l with minimum in July-August. Low concentrations in October and November correspond to the minimum in October, established by Rozhdestvensky (1991).The average content of SM is as follows: SiO_2 – 37.6 %, Al_2O_3 – 25.4 %, CaO – 10.8 %, MgO – 1.4 %, P_2O_5 – 0.25 % (Rozhdestvensky, 1998). Prevailing size of SM is 0.10-0.01mm (50.6 %).

In seasonal aspect winter and spring are more dynamic. In summer, when the water temperature rises, suspended matter content depends also on the autohtonic suspended matter production, related to the eutrophication processes.

The considerable amount of suspended matter in February and April (Fig. 7) is due to the intensive flow of snow-rain waters, the heavy rainfall in the end of the winter and spring on the territory of the country, which caused floods in many areas. The maximums (86.0 and 140.0 $mg.l^{-1}$) coincide with the suspended metals maximum and with the second large values of the river flow, when the abrasion processes have an impact on the water collection. At increased water flow it is natural to have intensification of the abrasion processes on the shore along Danube as well as along its tributaries. Therefore, the values of SM during this period of the year, are considerably above the average annual value of 24.8 $mg.l^{-1}$.

In seasonal aspect winter and spring are more dynamic. In summer, when the water temperature rises, suspended matter content depends also on the autohtonic suspended matter production, related to the eutrophication processes. Average seasonal results for that period show a maximum of suspended matter (82.2 $mg.l^{-1}$) in the winter hydrological season and a minimum (10.4 $mg.l^{-1}$) - in the summer hydrological season.

The higher share of non-organic

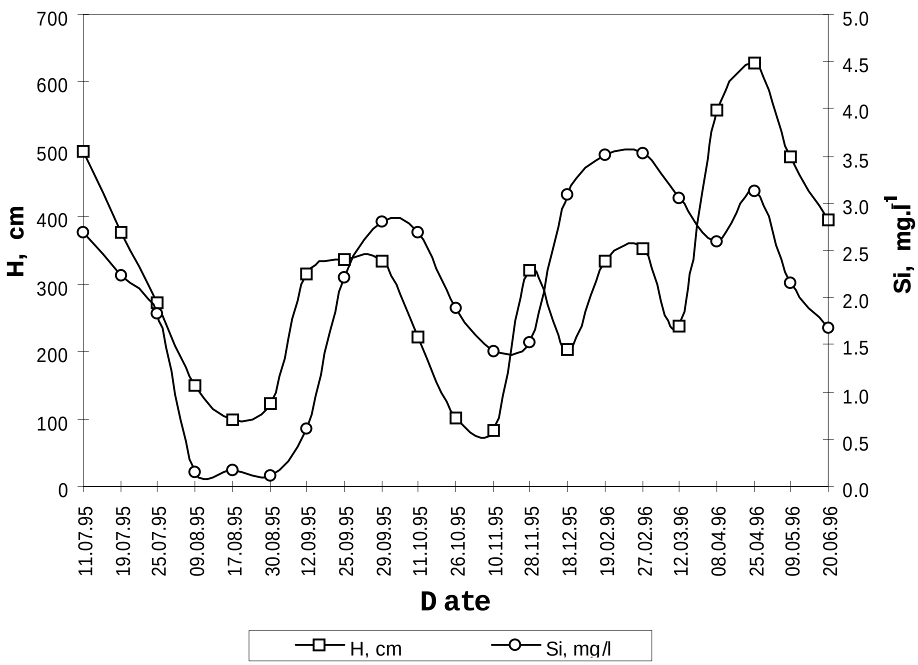

Fig. 5. Distribution of Si and water level (H) at st. Silistra

ingredients in the suspended matter relates to the spring full waters. The suspended matter of non-organic nature increases with the increase of the waters and the terrygenic flow. Production of organic matter during this time of the year is still low, therefore it has low impact on the composition of river suspensions.

Organic compounds are less well studied in quantitative and qualitative aspects, compared to the mineral content of the river waters. Since in the published literature there is no comment of the distribution of **particulate organic carbon** (POC) in the river waters, we can not make a comparison with some previous periods and derive some trends. Organic matter in Danube is estimated by some indirect indices as permanganate oxidizability and biochemical oxygen demand (BOD_5). The finding of increased organic pollution in the last decade is based on this observations. For instance, at the town of Rousse this increase is 15 ÷ 25 % (T s a n k o v, P e c h i n o v, 1990) as a result of the discharge of faecal-domestic and industrial waste waters. For our area of study - the town of Silistra - an increase in BOD_5 values after Arzhesh influx is reported (I v a n o v, 1978).

In relation to BOD_5 and oxidazibility organic content of Danube has minimum in April. Maximum is respectively in December - for the oxidizability, and in January - for BOD_5.

Our study (1995-1996) show a minimum of POC during spring (May) in relation to the increase of the water level. Excluding the maximum (16.3 mg/l), all other values of this parameter fall within the ranges of 0.42 ÷ 7.32 mg/l. During autumn – winter season the curve of POC corresponds in general to the curve of the total content of suspended matter (Fig. 8).

In spring, when the river level increases and the production of organic matter is still low, the high values of suspended matter correspond to the minimum of organic suspensions. In this relation, the ratio

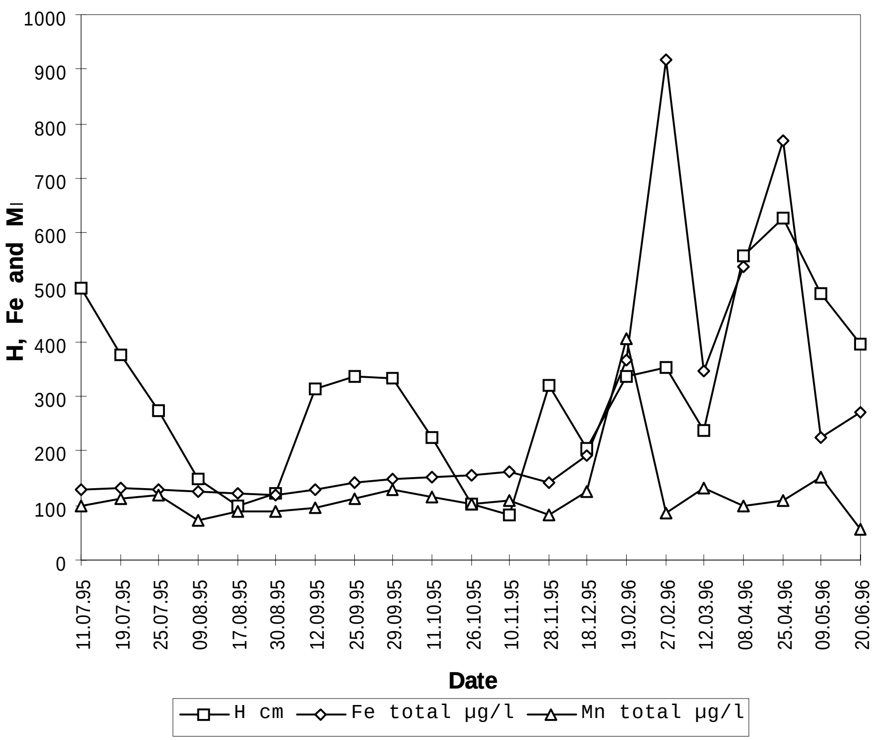

Fig. 6. Water level (H) and total Fe and Mn at st. Silistra.

POC/SM will give us more information.

In spring this ratio, expressed in percentages, is lower than 10%, which shows low share of organic matter in the total suspension. In support of this are the values of Chl. *a*, which are not high. The maximum share of POC in the total SM registered in August corresponds to the extremum of Chl. A, established by Moncheva. The relationship of Chl. *a* with the ratio POC/SM is more apparent than the relationship with the dynamic of each of these parameters POC and SM (S t o y a n o v, 1997).

All these results give ground to draw the following conclusions:

The vaiability of DO is closely related to the temperature changes, only the cases of oversaturation respond to the Chl a maxima. In comparison to historical data (the period 1967 - 1993) an increasing in both the average annual value and the maximum of the DO is evident.

The Nutrients ($P_{PO_4^{3-}}$, $N_{NO_2^-}$, $N_{NO_3^-}$, $N_{NH_4^+}$ and Si) dynamics follows the hydro-meteorological features of the period - significantly higher concentrations. The minimum values are during the summer period closely related to increase in temperature, the decrease of water level and the increase of biological uptake. In comparison to the long-term historical data there is a trend in decreasing of $P_{PO_4^{3-}}$, Si and an increase in the concentration of $N_{NO_3^-}$.

The dynamic of the ratio POC/SM suggests the importance of alohtonic suspended organic matter.

The metal (*Fe* and *Mn*) dynamic data reveal the dominance of terigenous input, with maximum in winter-spring and minimum in summer. The recorded decrease in the *F*e content as compared to the data in the period after 1992 could be related mainly to the

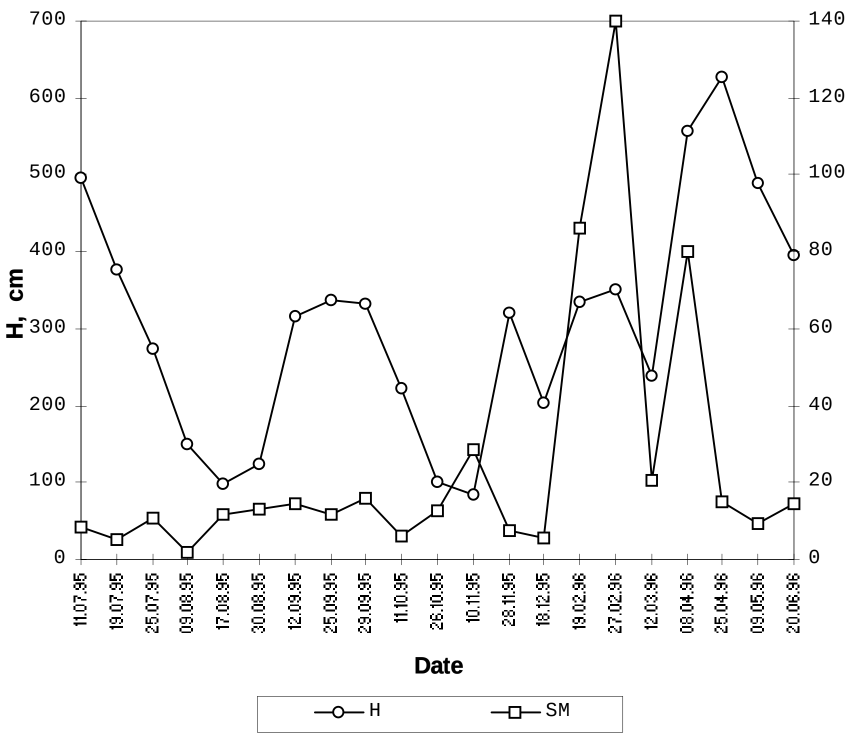

Fig. 7. Water level (H) and suspended matter (SM) at st. Silistra

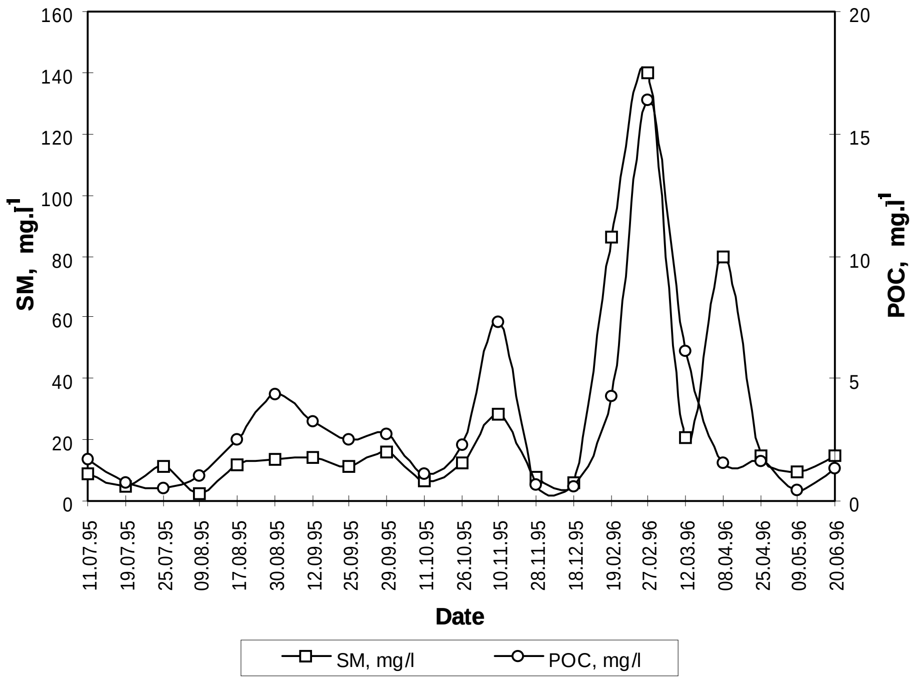

Fig. 8. Distribution of POC and SM at st. Silistra

barrier impact of the hydrotechnical complex “Zhelezny vrata”.

The results from the present study suggest that the level of the eutrophication of the Danube river remains high despite the trend of decrease of the Bulgarian river input after 1990. During the last several years the pollution of Danube river is reduced mainly due to reduction in the industrial activities, e.g. the results do not represent the real contribution in case of normal industrial and agricultural operation.

All this point to the necessity of future monitoring on the dynamic of the main pollutants, which will help decision-makers to implement relevant measures for reducing the anthropogenic input into Danube river.

References

C o c i a s h u, A., L. P o p a. 1981. Dinamique de la matiere dans les eaux marines devant le littoral Roumain da la mer Noire. Cecretari Marine, 14, 13 - 29.

C o c i a s h u, A. 1990. Donnes sur l’azote et le phosphore inorganique dans la zone centrale du littoral Roum. Da la mer Noire. Rapp. Comm. Int. Mer. Medit., 32, 61 pp.

G o m o i u, M., A. C o c i a s h u. 1985. Donees preliminaires sur la substance organique des sediments superf. Du plateau cont. Romain de la mer Noire. Rapp. Comm. Int. Medit., 29, 197 - 199.

I v a n o v, K. 1978. Hydrochemical Regime of Bulgarian Part of Danube River. Sofia, BAS, 79 - 98 (in Bulgarian).

L u r e, J. 1973. Unified Methods for Water Analyses. M. Chemistry, pp. 376 (in Russian).

P o t a p o v a, L. I., P. N. C u p r i n, L. F r o l o v a. 1980. Determina-tion of Organic Carbon in the Bottom Sediments. In: Methods of Organic Matter Investigations in the Ocean. M., Nauka, 50 - 56.

R o z h d e s t v e n s k y, A. 1962. Chemistry of the Danube Waters and Their Influence on the Black Sea Waters. In: Bull. Central Inst. Fish., Varna, 3, 199 - 243 (in Bulgarian).

R o z h d e s t v e n s k y, A. 1979. Specifics of Lower Danube in 1975 and Influence on the Black Sea. BAW-SIL, XIX, Jbilaumstagung Donauforschung, Sofia, 91 - 86 (in Russian).

R o z h d e s t v e n s k y, A. 1985. Dissolved and Suspended Iron in Lower Danube Waters. Oceanology, BAS, Sofia, 14, 23 - 28 (in Russian).

R o z h d e s t v e n s k y, A. 1986. Chemisher und Schwebstoffabflus der Donau im Schwarzen Meer. BAW-SIL. Limnologische Berichte der X Jubilaumstagund Donauforschung, Sofia, 93 - 102.

R o z h d e s t v e n s k y, A. 1991. Hydrochemistry of Lower Danube. Oceanology, BAS, Sofia, 20, 3 - 15 (in Russian).

R o z h d e s t v e n s k y, A. 1998. Geochemistry and hydrochemistry of the Danube inflow and atmospheric presipitation with connection of the Black Sea sediments. Proceeding s of Inst. of Ocean., v.2, 20 - 26.

R o z h d e s t v e n s k y, A., G. Shtereva .1985. Manganese and Cupper in Danube river waters. Oceanology, Sofia, 13, 30 - 36.

S t o y a n o v, A. 1995. Hydrochemical Processes in the Western Part of the Black Sea Under the Influence of Natural and Antropogenic Factors. Dr. Sci. Thesys, 342 pp. (in Bulgarian).

T s a c h e v, Ts., K. I v a n o v. 1978. Determining of the Pollution in the Bulgarian Part of the Danube River, Sofia, BAS, 272 - 284 (in Bulgarian).

T s a n k o v, K., D. P e c h i n o v. 1990. Danube River Pollution. In: Bulg. J. Meteor. Hydrol., BAS, 2, 1, 79 - 92 (in Russian)

Y e a r B o o k of the State of Environment Of Republic of Bulgaria. 1989. Sofia, 1991, 365.

Y e a r B o o k of the Ministry of the Environment .1992 - 1993. Sofia

K r a s t e v, T., T. K r a s t e v a, A. S t o y a n o v. 1995. Report Danube EROS 2000 Project, Part I, Varna, 34p.

S t o y a n o v, A., I. S h t e r e v, G. S h t e r e v a, S. M o n c h e v a, L. M i h o v a, A. K r a s t e v. 1997. Report Danube EROS 2000 Project, Part III, Varna, 43p.

Динамика на някои химични параметри в българската част на р. Дунав

Александър С. Стоянов, Галина П. Щерева, Антон И. Кръстев, Огняна Д. Христова, Лидия Д. Михова, Илия А. Щерев

(Резюме)

През периода юли 1995 – юни 1996 година в района на гр. Силистра са проведени наблюдения (средно 2 пъти месечно) върху качеството на дунавските води по следните показатели: разтворен кислород (DO), алкалност, биогенни елементи (N, P), суспендирано вещество и метали. Получените ртезултати са сравнени с данни на други автори от предишни периоди по отношение на сезонната динамика, положението на минимумите и максимумите.

DO се влияе от температурните промени и максимума на хлорофила, когато се наблюдава пресищане на водата с DO. Биогените бележат ниски стойности през лятото и високи през есенно-зимния или зимно-пролетния сезон. Динамиката на Fe и Mn показва доминиране на теригенния внос. Суспедираните форми на металите, POC и Si са в пряка зависимост от речното ниво. Въпреки намаленото постъпване на N и P с българските притоци степента на еутрофизация на речните води остава висока.

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