ASSESSMENT OF THE DANUBE CHEMICALS DISCHARGE IN MODERN PERIOD

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Abstract: The Danube annual chemical discharge was calculated on the basis of data processing of systematic observations of Ukraine National Hydrometeorological service in the Reni section line (168 km) for the period 1989-2001. The dynamics of outflow of the Danube water chemical composition separate elements is shown for the specified period and the comparative analysis of chemical discharge at 50-60 years is carried out. The information on influence of both water run-off and separate ions concentration on dynamics of a chemical discharge is submitted. The conclusion concerning determining influence of annual flow on dynamics of ion discharge is made.
Keywords: water runoff, chemicals discharge, ions concentration.

Introduction

The Danube River is one of the largest rivers of the world. It crosses the areas of eight countries, which use the river's water for drinking water supply and different branches of economy. The Danube water metamorphization is observed best of all in the central and low parts of the river, where the great industrial objects are situated (Cherniavska, 1993). In the lower Ukrainian part of the Danube the influence of differently directed natural processes and man-maid river pollution are integrated, and the magnitudes of chemical discharge into the Black Sea are determined. The Danube waters are one of the most important constituents of its coastal area balance. 310 km^3 of water go to the Black Sea with water flow annually, and the part of the Danube makes 203 km^3. River fresh water spreads up to 10 km from the mouth and reaches 6 – 14% isohalines (Natural conditions …, 1999). The regression formulas have been found out to calculate quantitatively the seawater salinity fields depending on river run-off and the wind (Mikhailov, 1988). Under the favorable meteorological conditions the water defreshing reaches the center of the Black Sea Northwestern part (Sovga, 2002).

The Danube chemicals discharge was calculated for the first time by O.M. Almazov, who had the data of the 1948-1950 and 1958-1959 periods (Almazov, 1962). He showed that the Danube ion discharge fluctuated according to the river water content and it made 40.9 – 42.9 million t/year within arid years and 59.8 – 63.5 million t/year within years with the water content being higher than the average of many years. The work of Cherniavska A.P. and some others is devoted to the Danube ions discharge within 1980 – 1990 (Cherniavska, 1993).

Since 1990 the social-political conditions have changed in Ukraine and in many other countries situated near the Danube. Theses events have been accompanied by serious economic crisis and decrease of economy loading on water ecosystems. According to the data (Mykhailova, Mykhailov, 2002) the period of 1989 – 2001 refers to the period of considerably changed river water run-off. As a result of it the necessity appeared to determine the Danube River chemical run-off in modern period.

Materials and methods.

The results of systematic observations of National Hydrometeorological service of Ukraine were used as the initial data.

The calculations of the Danube ions discharge were made according to the method of direct calculation by widely known formula:

$$R = W * C,$$

where R – ion discharge; W – water run-off volume; C – substance concentration.

The calculations were made for each year and with detailed elaboration due to definite hydrologic phases. On the basis of hydrograph partition the periods of high water,

low water and floods were singled out and it allowed to find out genetically identical water masses.

The reliability of chemical run-off results is known to be determined by hydro-chemical data representativeness, completeness of the range of observations, inaccuracy of substances concentration defining and averaging (Smirnov at all, 1989). It is determined by the fact that the conditions of water chemical content formation vary greatly in the annual cycle and they are accompanied by considerable chemical components concentration variations. The results of water run-off observations are more complete and long-term in comparison with available data about chemical water content. The researches of the influence of sampling frequency on ion run-off calculation accuracy have defined the standards of necessary sampling frequency, which is 1 sampling each 10 days within summer low water, and considerably larger number of sampling within high water and flood periods (Peleshemko at all, 1983). Taking into account the above-mentioned information one can declare that the available data on chemical water content did not meet the requirements. Taking into account the fact that the term sample data characterize the solute magnitudes of a definite period only, the graphic data interpolation with an approximating polynomial has been made. Three nearest points from the time cell under study have been chosen for the analysis and the interpolation was consecutively performed between two of them. If the time cell was too long and there was a relatively large number of nodal points, the partial interpolation of the lower order was used. The received data were combined to form a general interpolation function. It is caused by the fact that if the distance between nodal points is long, the accuracy is not high, as a matter of fact, the interpolation polynomials of the higher order fluctuate greatly at the ends of the cell and it distorts function behavior.

The season average chemicals concentration was defined by approximating function integration, and the annual chemicals run-off made the sum of hydrologic phases calculation results (Hydrochemistry handbook, 1989).

Na+K content was determined by calculation method. The initial data amount included about 7.5 thousand items. The run-off of elements soluted in water was considered.

The Reni section line (168 km), which is situated lower than the last tributary and higher than the river delta begins, was used as the design one. The calculation was made within the period of 1989 – 2001, which was characterized by considerable decrease of economy activity and included almost the same amount of years when the water content was 25% and the provision was 75%.

Results and their discussion.

The results of the calculations are given in Table 1.

Table 1. The Danube River ions discharge, near Reni city, million t/year

Year	Cations			Anions			$\sum$ of ions
	Ca^{2+}	Mg^{2+}	$Na^+ + K^+$	HCO_3^-	SO_4^{2-}	Cl^-	
1989	7.47	2.62	12.32	35.19	12.40	8.76	78.82
1990	6.92	2.09	7.26	27.37	7.25	7.40	57.85
1991	10.17	3.03	9.04	40.71	10.18	8.48	81.22
1992	7.23	2.26	10.14	33.97	10.66	6.15	70.29
1993	6.48	2.25	8.37	28.31	9.36	5.44	59.01
1994	8.71	2.67	8.87	35.34	12.00	6.20	75.49
1995	6.56	3.41	8.73	40.60	9.05	6.56	75.68
1996	9.81	4.29	12.89	49.16	14.31	9.01	99.46
1997	9.77	2.73	13.14	48.27	11.41	7.48	92.98
1998	9.58	3.29	9.79	43.41	11.46	6.90	84.99
1999	11.48	4.32	12.11	55.27	13.78	7.79	105.07
2000	8.24	2.69	10.81	41.95	9.92	6.10	79.71
2001	8.44	2.62	5.57	32.58	8.99	5.57	62.86

First of all let us dwell on fluctuation of total salts content discharge (R_i). According to the received data the intensity of salts inflow within the term under study has almost doubled – from 58 million ton in 1990 up to 105 million ton in 1999. Against a background of slight deviations, which were observed in some years, one can notice a tendency to the Danube ion run-off increase, what was the most characteristic feature of the 1996 – 1999 period (Figure 1).
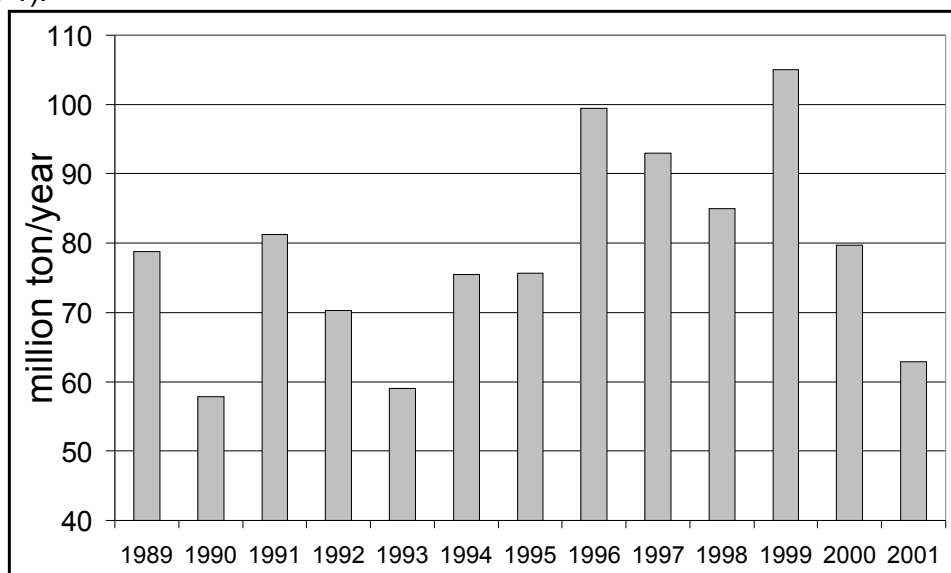

Figure 1 The Danube ions discharge dynamics, Reni city within 1989 – 2001

The increase of river soluble substances discharge can be predetermined by a number of factors, among which the water run-off volume is one of the most important (Materials of the first international complex expedition …, 1988). The notion of geochemical discharge coefficient (K), which characterizes the amount of substances coming into the river system from 1 km^3 of water and is calculated by formula: $K = R_i$ (thousand tons)/W (km^3). According to its geochemical nature, this magnitude must be constant. I.e., K magnitude decrease will indicate decrease of element under study chemical discharge, and K coefficient increase will indicate increase of element under study chemical run-off (Table 2).

Table 2. K coefficient amount in the Danube River basin, thousand tons/km^3

Year	Ca^{2+}	Mg^{2+}	$Na^+ + K^+$	HCO_3^-	SO_4^{2-}	Cl^-	$\sum$ ions
1989	42	15	70	199	70	50	447
1990	52	16	55	207	55	56	437
1991	51	15	46	206	51	43	410
1992	42	13	59	197	62	36	408
1993	42	15	54	184	61	35	384
1994	48	15	49	196	67	34	418
1995	31	16	42	194	43	31	361
1996	42	18	55	209	61	38	422
1997	44	12	59	215	51	33	414
1998	43	15	44	196	52	31	384
1999	44	16	46	210	52	30	400
2000	38	12	50	195	46	28	370
2001	41	13	27	159	44	27	307

Among cations, as a matter of fact, freely soluble sodium cations (42 – 70 thousand tons/km^3) are coming into the Danube River system, and among anions hydrocarbonates (184 – 209 thousand tons/km^3) prevail.

Within the period under study the amount of dissolved salts, which came from $1 km^3$ of water, decreased from 450 to 300 thousand tons/km^3. The basic changes occurred due to freely soluble chlorine salts sodium and potassium.
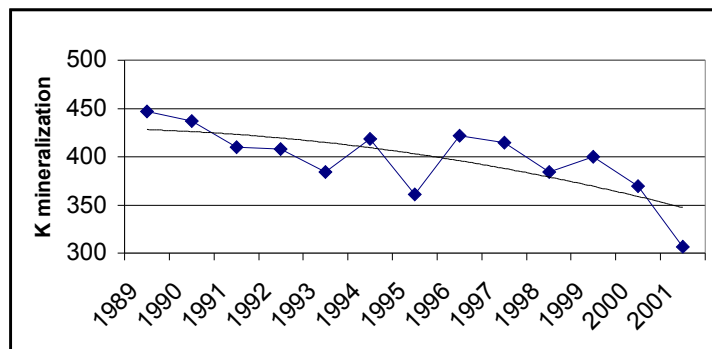

Figure 2. Variations of the discharge geochemical coefficient magnitude in the Danube River basin during 1989 – 2001

The received results were compared with the magnitudes of the Danube ion run-off within 50-60s of XX c. (Almazov, 1962). To compare the results with the modern data the average flow year of the end of the 50s, with the water content of 203 km^3, and similar 2001, with the water content of 205 km^3 were taken. The ion run-off of the mentioned years was 59.4 million t/year and 62.9 million t/year correspondingly. Having balanced them by the water content, we received the magnitudes of 59.4 million t/year and 62.3 million t/year. Thus, modern R_i exceeded the same indicator of the 60s at 5%. Comparing the years when the water content was higher than the average of many years, 1948 and 1995 correspondingly, one can notice that their ion run-off varied greatly. According to the O.M. Almazov's data, R_i in 1948 was 59,8 million t/year (W=211km^3), and according to our data the ion run-off in 1995 was 75.7 million /year (W=209.6 km^3). Having estimated its water content we have got 76.2 million t/year. Thus, modern ion run-off exceeds the indicators of the 60s at 20%. Relying on this data one can make a conclusion that modern ion run-off somehow exceeds the indicators of the 60s and this difference increases together with the water run-off magnitude.

Other authors have noticed the same regularity for the waters of the Dnister and South Buh Rivers. It is indicated in the work (Zakrevsky at all, 1988) that in comparison with the 50s the ion run-off of the mentioned rivers was 2.2 and 1.6 times more in 1971-1989 correspondingly.

The Danube average run-off of many years is almost 4 times as large as the Dniper one but the Danube R_i is only twice as large as the Dnieper ions discharge within the same period.

The hydrocarbonate ions prevail among the elements brought by the Danube chemicals discharge and their relational part was about 52% during the period under study. The role of calcium and sulphate ions is less important and their average content was 13.4% and 14.3% correspondingly (Figure 2). The contribution of chloride and sodium ions into chemicals run-off is less noticeable. Magnesium ions have the smallest part (4.2%) and it is a characteristic feature of other rivers in flat part of Ukraine (Zakrevsky at all, 1988). Such distribution of chemical run-off among basic ions can be explained by the chemical content of the Danube water, the prevailing anions of which are HCO_3^- (46 – 70 %-equ) and Ca^{2+} (35 – 60 %-equ). According to the O.A. Alekin's classification the Danube water refers to hydrocarbonate class of the second type calcium group (Figure 3).
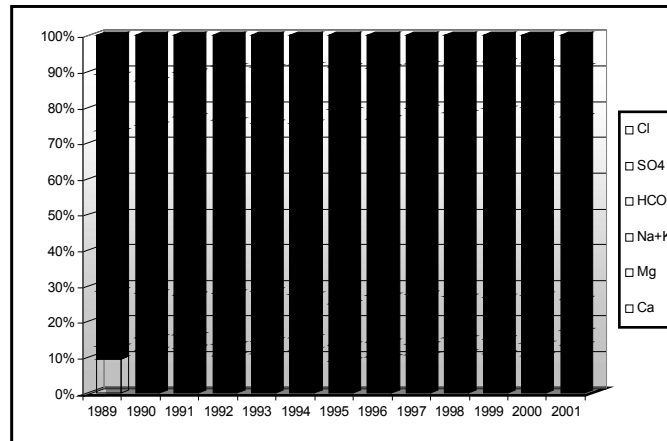
Figure 3. Relational part of some ions in the Danube water run-off formation

The analysis of the run-off subdivision among different ions showed some differences depending on water content of the year. So the relational part of the prevailing HCO_3^- ion during dry and moderately dry years has increased at 5 – 7%. The relational part of Cl^-; SO_4^{2-} and Na^+ ions was increasing at 2 – 3% during dry years. It proves that hydrocarbonate ions come into riverbed network due to basin chemical erosion, while underground constituent of water nutrition influences the formation of chloride, sulphate and sodium ions content.

The subdivision of the Danube ion run-off among different ions in modern period and during 1948 – 1959 has noticeable differences too (Table 3). The years with middle water content and similar magnitudes of water run-off volume were chosen for the comparison. The Table 3 shows that the part of hydrocarbonate ions has noticeably decreased and the part of sulphate ions has increased correspondingly among anions in modern period. The relative role of calcium has decreased and the role of magnesium has increased among cations.

Table 3. The Danube run-off subdivision due to chemical content

Years of researches	W, km³	Cations, % ionic discharge			Anions, % ionic discharge		
		Ca²⁺	Mg²⁺	Na⁺+K⁺	HCO₃⁻	SO₄²⁻	Cl⁻
Averange steam-flow period 1948 – 1959	203	17.2	3.6	4.3	59.9	9.4	5.5
2001	205	13.4	4.2	8.9	51.8	14.3	8.9

The received data indicate the transformation of the Danube River water chemical content due to elimination of calcium carbonate from solution phase. This process is likely to be connected with Dzherdap hydrosystem creation and settling of great amount of suspended matter in the water basin. It caused decrease of the Danube lower part turbidity and in sequence to intensification of phytoplankton development, which regulates the river gas regime and promotes carbonate-calcium balance shift to $CaCO_3$ settling. The character of the hydrocarbonate ions subdivision due to river length can prove this opinion. The increase of $Cl^-+SO_4^{2-}/HCO_3^-$ correlation in the lower part of the Danube in comparison with its central and higher parts was shown in the work (Cherniavska, 1993).

Variations of several ions run-off in different years depend directly upon changes of river general ion run-off. At that the closeness of interconnection is estimated by correlation coefficients, which vary for different ions within the limits of 0.61 – 0.97. The minimum values characterize chloride ions and the maximum – hydrocarbonate ones, and we consider it to be connected with different dissolubility of mentioned ions. The dependence of ion run-off from prevailing hydrocarbonate ion discharge is approximated by the equation:

$R_i = 1.7004R_{HCO_3^-} + 11737$.

Subdivision of the Danube ion run-off according to seasons is irregular (Table 4). The major part of substances dissolved in water was coming during high water period and for some ions and general R_i it made about 46.6% – 48.5% from annual run-off of the corresponding ingredient. And their limit values varied greatly (Table 4).

	Spring flood	Flood	Low water
Ca^{2+}	$\dfrac{21.4 - 73.1}{46.6}$	$\dfrac{13.6 - 58.9}{34.2}$	$\dfrac{5.2 - 45.8}{19.2}$
Mg^{2+}	$\dfrac{17.3 - 80.8}{48.5}$	$\dfrac{14.2 - 58.4}{31.4}$	$\dfrac{4.4 - 51.2}{20.1}$
$Na^{+}+K^{+}$	$\dfrac{14.8 - 71.6}{46.5}$	$\dfrac{13.9 - 56.3}{33.2}$	$\dfrac{4.9 - 44.1}{20.3}$
HCO_3^{-}	$\dfrac{17.0 - 72.2}{47.3}$	$\dfrac{14.9 - 58.1}{33.0}$	$\dfrac{4.6 - 46.2}{19.8}$
SO_4^{2-}	$\dfrac{19.5 - 76.0}{49.5}$	$\dfrac{13.4 - 57.3}{30.7}$	$\dfrac{5.4 - 47.5}{19.8}$
Cl^{-}	$\dfrac{19.1 - 73.1}{46.8}$	$\dfrac{14.8 - 57.9}{32.6}$	$\dfrac{5.3 - 47.8}{20.9}$
$\sum$ ions	$\dfrac{17.7 - 72.3}{47.6}$	$\dfrac{14.7 - 57.9}{32.6}$	$\dfrac{4.9 - 46.7}{19.8}$
W	$\dfrac{18.6 - 74.3}{47.5}$	$\dfrac{14.0 - 56.2}{32.6}$	$\dfrac{4.14 - 46.5}{19.9}$

From 30.7% to 34.2% elements dissolved in water come into river system during the period of floods, during the low water period the chemical run-off of some ions and their sums are minimal and vary within the limits of 19.2% – 20.9%. Data given in Table 4 and many works of other authors (Materials of the first international complex expedition…, 1988) prove that such seasonal subdivision is characteristic for the Danube water run-off too. So one can make a conclusion that the amount of ion run-off is determined by the water content of the river. According to (Alekin, Brazhnikova, 1964) the process of water chemical content formation when the large amount of water from melted snow and rainwater comes cannot be considered as a simple dilution of riverbed waters by low mineralized water from melted snow. Large magnitudes of chemical run-off indicate that an intensive chemical erosion of water basin occurs. The percentage subdivision of the Danube chemical run-off almost coincides with the percentage subdivision of its water run-off.

At the same time the researches performed in the Dnieper basin have shown that the subdivision of ion run-off in this basin is more smoothed in comparison with the water one. Such differences indicate different nutrition types of mentioned rivers and differences in lithologic surface of the basins.

The dependence of chemical run-off from the water one allows to suppose that the annual water content influences the chemical elements discharge. All the results were grouped according to the water run-off volume for that and W=203 км³ was considered to be an average magnitude of many years (Figure 4). During dry and moderately dry years weighted-mean water content ion run-off was slightly different and was 71.5 and 69.3 million t/year, during wet years R_i increased up to 93.0 million t/year.
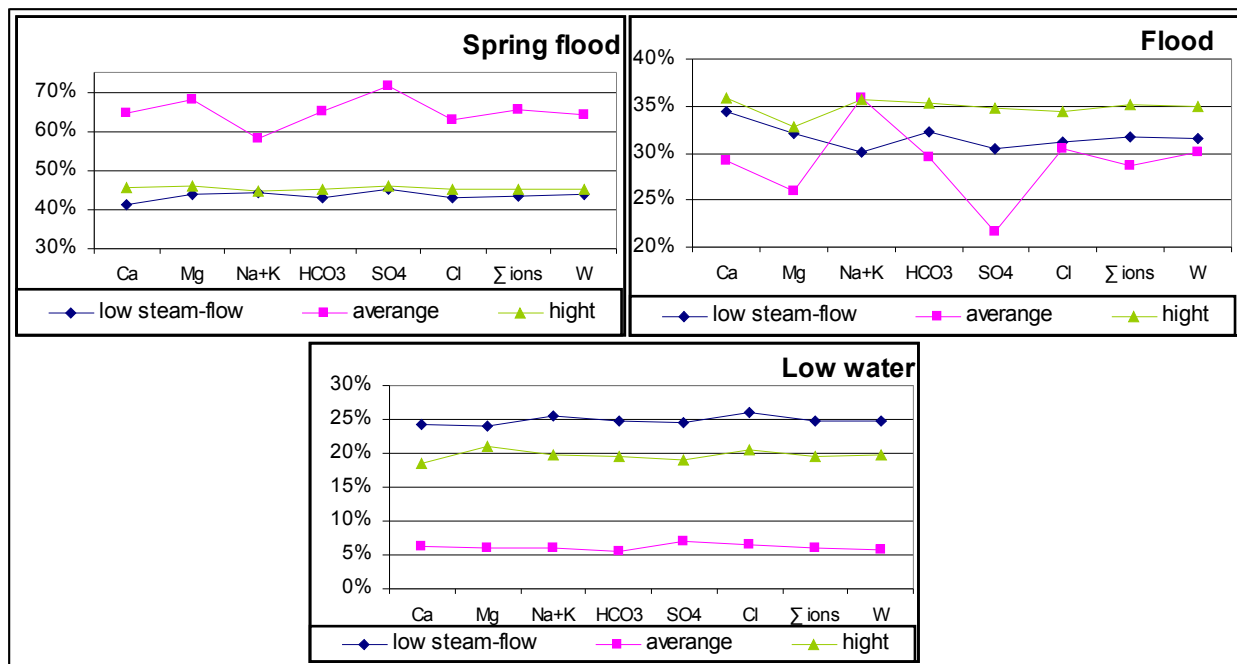
Figure 4. Seasonal subdivision of the Danube chemical and water run-off during years with different probability of average magnitude exceeding

Figure 4 shows that conditions of the Danube water chemical content formation differ greatly within periods with different water content. The role of high water is prevailing within periods of moderate water content, when hydrograph of the run-off with high spring rise of water level, which is characteristic for East-European rivers. Low water plays the leading role in chemical elements discharge within dry years. At the same time more mineralized groundwater dominates in river nutrition. This fact influences R_i absolute values too. The general ion run-off, as was mentioned above, within dry years overcomes R_i magnitude for average years. The floods play the leading role during wet periods when river nutrition is predetermined by coming of water from melted snow or rainwater.

According to the formula of the river ion run-off calculation it depends directly on substance concentration and river water run-off volume.

Substances concentration influence.

The content of dissolved ions in the Danube water is characterized by great changeability. Chloride ions and magnesium concentrations double within the year, and Na+K ones – increase in 2.6 times. For calcium, HCO_3^- and SO_4^{2-} correlation of maximal and minimal magnitudes is about one and a half times. The interdependence of dissolved substances concentrations and the Danube water expenditures is observed. An increase of water expenditures is followed by decrease of chemical components concentration, which is characteristic for rivers of humid zone with well-washed grounds (Figure 5).
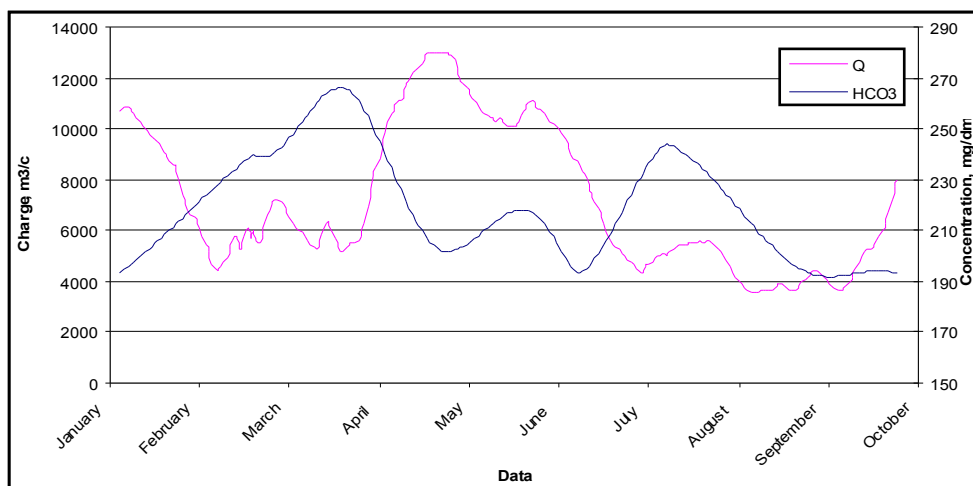
Figure 5. Annual inner dynamics of hydrocarbonate content and the Danube River water expenditures

But the connection of basic ions run-off with water mineralization is insignificant, r=0,23. The closeness of connection of some ions content with corresponding elements discharge differs greatly depending on ingredient under study. This connection is insignificant for the majority of indicators except Mg^{2+} and $Na^{+}+K^{+}$ r >0,5 (0.6 i 0.63 correspondingly).

The influence of chemical components concentration upon their run-off formation depends greatly on water content of the year. According to performed calculations (Table 5), within wet years correlation coefficients of the indicators under study are high, and it proves the leading role of substance coming from the basin surface. Within dry years the dependence of element discharge upon its concentration in water is much less.

Table 5. Closeness of dependence (correlation coefficient) of chemical component run-off upon its concentration in the Danube River water

	Ca^{2+}	Mg^{2+}	$Na^{+}+K^{+}$	HCO_3^-	SO_4^{2-}	Cl^-	$\sum$ ions
low stream-flow	0,62	-0,06	0,72	0,29	0,73	0,73	0,15
hight stream-flow	0,71	0,89	0,84	0,71	0,87	0,85	0,72

River water content influence.

The Danube ion run-off is directly proportionally connected with its water content and it is indicated by simultaneous variation of mentioned parameters (Figure 6).
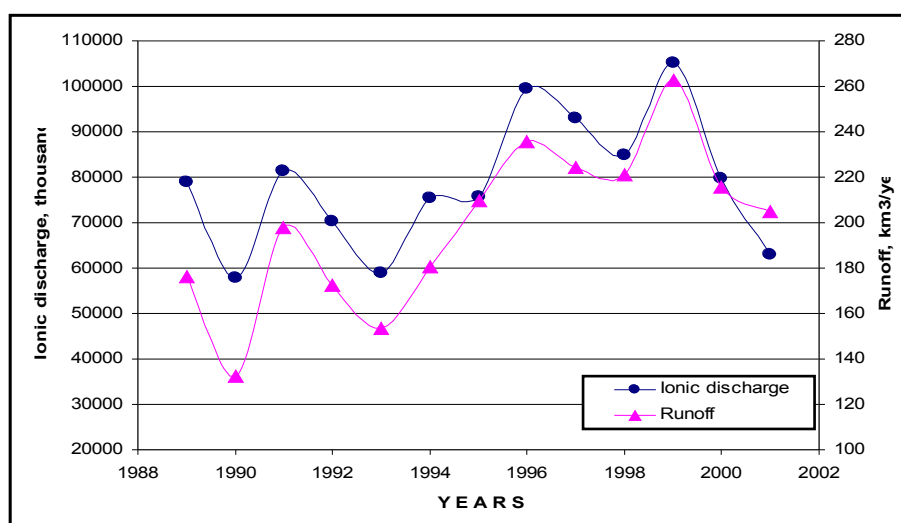

Figure 6. Dynamics of the Danube ion and water run-off within 1989 – 2001

In order to define closeness of R_i and W connection within the period under study correlation coefficient r was calculated, its magnitude was 0.87, and it indicates that the connection is rather close. An average squared error of correlation coefficient δ_r was 0.066. Ratio of correlation coefficient and its squared error was 13.2. According to (Aivazyan, 1985) if correlation magnitude is r/δ_r >3, correlation coefficient is considered to be reliable and completely reflects the connection under study.

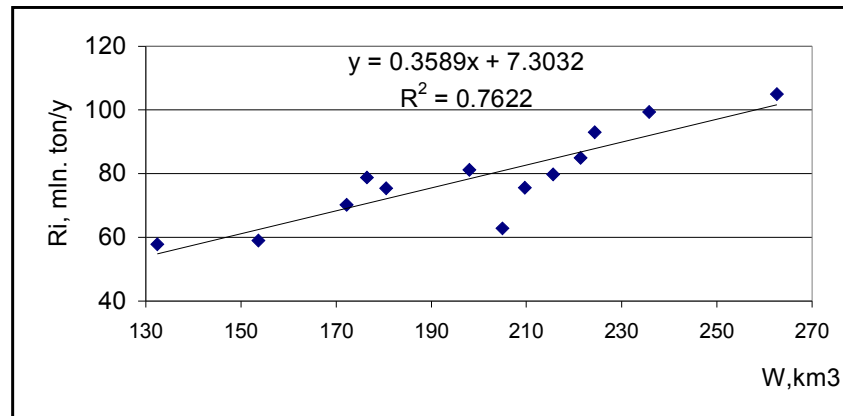The diagram and analytical expression of mentioned dependence can be seen at Figure 7.

Figure 7. Dependence of water run-off on the Danube water content, Reni city. r=0,87

Figure 7 shows that the data for years with water content close to average one of many years (W=203 км^3) differ most of all from theoretical dependence line R_i = f (W). It indicates different genetic conditions of complicated process of the Danube ion run-off formation. While within dry years ground nutrition with its more mineralized water is the most important, during moderately dry period high water plays the leading role in water run-off formation (Figure 4). At that time the chemical composition of water is characterized by insignificant mineralization and dilution plays the leading role in the process of its formation. It explains considerable decrease of chemicals discharge during water run-off increase within the period approaching average magnitude of many years.

The research of connection closeness of water run-off and some ions discharge was also performed. For cations Ca^{2+}, Mg^{2+}, Na^++K^+ correlation coefficient of their run-off with the water one was considerable and reached 0.78; 0.85 and 0.53 correspondingly. Lower degree of sodium and potassium run-off connection with water content is likely to be connected with the fact that this parameter was defined by calculation method. Connection of anions discharge with water content is more heterogeneous. The run-off of prevailing hydrocarbonate ion is almost completely determined by the water volume, and the correlation coefficient of mentioned parameters is 0.94. Correlation coefficient between SO_4^{2-} and W was lower and reached 0.65, and it can indicate an important role of groundwater in sulphate ions run-off formation. Discharge of chloride ions does not depend on water content (r=0.29). It may be connected with discrete coming of run-off water, the most characteristic ion of which is Cl^-.

This material allows to make a conclusion that water run-off plays an important role in formation of chemical discharge from the Danube basin territory. So while taking hydrotechnic measures connected with water run-off decrease, coming of dissolved chemical substances to coastal shelf of Northwestern part of the Black Sea will also decrease.

Studying coming of dissolved substances with river water into the sea we should also pay attention to their behavior in coastal area. While coming of the majority of ions may be explained by processes of simple mixing, the behavior of calcium ion, which is characterized by the highest degree of nonconservativeness among studied components, in the "river – mouth – sea" system will be more complicated. Calcium carbonate compounds refer to low dissoluble substances and can change the phase state, if physical-chemical conditions were

violated suddenly and while coming from fresh to sea ecosystems. Within the period under study the Danube water was satiated by calcium carbonate and it was shown in saturation

index $SI_{CaCO_3} = \lg(\dfrac{a_{Ca^{2+}} \cdot a_{CO_3^{2-}}}{K_{CaCO_3}})$, while HCO3$^-$ content varied from 158 to 219 mg/dm^3 and pH

– from 7.74 to 8.19. The degree of saturation with calcium carbonate varied from 1.09 to 3.17 times within the period under study (Table 6).

Table 6. The Danube water degree of saturation with calcium carbonate

Year	Ca^{2+}, mg/dm3	SI	Saturation degree, time
1989	43,6	0,283	1,92
1990	52,5	0,32	2,09
1991	53,1	0,089	1,23
1992	41,8	0,35	2,24
1993	43,0	0,501	3,17
1994	48,8	0,29	1,95
1995	41,9	0,405	2,54
1996	35,1	0,386	2,43
1997	38,2	0,15	1,41
1998	42,7	0,039	1,09
1999	43,8	0,424	2,65
2000	38,1	0,39	2,45

In spite of solution saturation there was no fall-out of hemogeneous calcium carbonate in the Danube water, i.e. metastable state was observed, when kinetics of chemical reactions is very slowed down. Insignificant concentration of CO$_3^{2-}$ and dissolved humus substances are stability factors of carbonate system.

Some suppositions can be made concerning behavior of calcium carbonate while mixing of river- and seawater. Some oppositely directed processes will take place while mixing of river- and seawater. On one hand, increase of water pH as a result of phytoplankton vital functions and Ca^{2+} and CO$_3^{2-}$ concentrations will contribute to shifting of balance to the right and increase of solution saturation with calcium carbonate. On the other hand, ion power increase will cause decrease of Ca^{2+} and CO$_3^{2-}$ activity coefficients and increase of calcium carbonate dissolubility. Correlation of these processes will determine the direction of calcium carbonate system transformation. Most likely, saturation index will increase in summer and it may cause partial conversion of CaCO$_3$ to hard phase. In winter saturation index of coastal water will decrease.

Conclusions

1. The Danube ions discharge into the Black Sea in modern period (1989 – 2001) was calculated and its dynamics was shown. An average amount of ions discharge within mentioned period was 78.73 million ton/year, and limits of its variation were 57.9 million ton/year and 105.1 million ton/year.

2. Performed researches showed that chemicals discharge from the Danube basin is determined by natural factors predominantly.

3. The Danube chemical discharge changeability is determined by concentrations of elements dissolved in water and river water content. Volume of water run-off plays the leading role among these factors.

4. An equilibrium status of carbonate-calcium system of Danube water was calculated by the method of computer thermodynamic modeling. The specified system is shown to be in a supersaturation status regarding to calcium carbonate. However, shift of an equilibrium status to the formation of sediment is restrained by insignificant concentration of carbonate ions and humic organic substances.

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