THE QUALITY OF THE SIRET RIVER IN SIRET SECTION SIMILARITIES AND DIFFERENCES OF THE RESULTS OBTAINED FOR THE SAMPLES COLLECTED IN COMON BY THE ROMANIAN AND UKRAINIAN

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ABSTRACT: *This article describes the evolution of water quality of Siret River at the entrance in Romania for a 5 years period. The correlation of the determined physical, chemical and biological indicators offer an overall image of their season, annual and multi-annual variation but also their ranging into quality classes.*

The comparative study of the results obtained by the Romanian and the Ukrainian side for the samples collected in common, highlights the similarities and differences between the methods and methodologies used in analyzing water quality of the two countries.

Keywords: *analysis, indicators, concentration.*

Introduction

Assessment of water quality into the Siret River in Romania is achieved by monitoring surface water quality.

The purpose of monitoring is to know the effect of the pollution sources and cleaning, in order to take the immediate and future measures for the protection of water resources and for the checking of the measures which have been taken.

Water quality analysis is monitored by physical, chemical and biological analysis on certain points and with a certain frequency.

Types of the monitoring programs and number of sections monitored by the SGA Suceava in the water quality laboratory (Directiva 2000/60/CE) are presented in Table. 1

Determination of water quality in terms of physical and chemical indicators is correlated with the biological analyses, the environmental conditions having a major influence on benthic fauna, thus obtaining a complete picture of it (ord. 161/2006).

Table 1

Monitoring programs and monitoring section number

Monitoring programs	Number of sections monitored			
	River	Lake	Groun-dwater	Waste water
Surveillance	13	13	155	-
Operational	15	4	23	46
Drinking	7	2	8	-
Reference	4	1	-	-
Ichthyofauna	23	13	-	-
Vulnerable areas	3	-	38	-
Protection of habitats and species	2	5	-	-
International Conventions	1	-	-	-

The monitoring of Siret River at the border is carried out jointly with the Ukrainian side based on a cooperation protocol, which provides water sampling from the Siret river at the border, in order to establish quantities of existing pollutants in the river, at the transit of the two countries. [1]

We used the data base of physical,

chemical and biological indicators for the period 2004-2008 obtained from the archives of Suceava Water Management System, in order to make a classification on quality classes. [2]

The framing in quality classes was done under the Order 161/2006 concerning the chemical elements and the chemical and physical-chemical quality standards in surface water. The results and conclusions we reached are set out below

Experimental

Basic methods for studying the evolution of river water quality during a 5 year period were: the processing of experimental data, analysis, graphical methods of data analysis, analytical comparison. [3-8]

It was considered a mediation of multiannual values to see the progress in a period exceeding one year, to eliminate the inherent variations due to a complex overlapping of hydrological, physical, chemical, biological and technical factors.

1. Physical-chemical analyses

1.1 pH

Measure the activity of hydrogen ions (SR ISO 10523/1997), the normal range of variation of pH is between 6,5-8,5 pH units.

Values in the last 5 years fall within the range noted, however, the 2008 average of 8.12 pH Units is slightly higher than during previous years.

The values recorded (Fig. 1) have no dramatic developments, the range of values generally ranging between 7 and 8.3 pH Units. It is noted that most values are higher than 8, at the upper part of the range, which means a trend of slight alkaline water. The minimum value of pH was 6.8 and it was registered in May 2004 and the maximum value was registered also in2004 but in November the same year, having the largest amplitude.

Comparatively, in the graphical representation it can be observed that the values determined by Ukrainian side are consistently higher, but they do not exceed

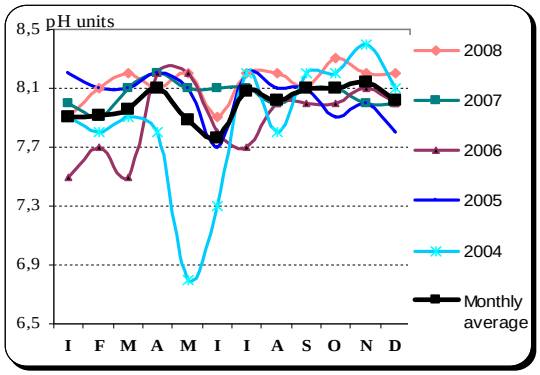

Fig. 1 Annual evolution of pH values on section Siret - Siret (2004-2008)

the maximum permitted by the applicable law (Fig. 2).

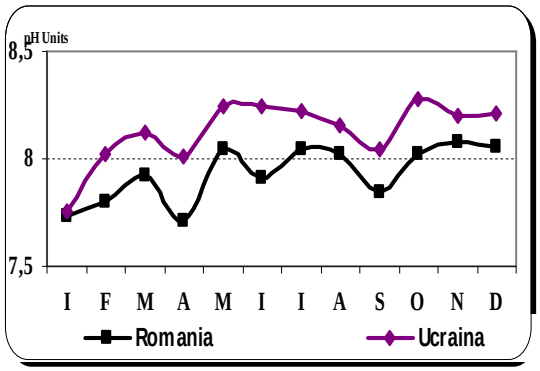

Fig. 2 Comparative evolution of pH values on section Siret - Siret (2008)

1.2 Dissolved oxygen

As a dissolved gas, oxygen behaves as such: with increasing temperature in the summer, the concentration decreases, then increase during the cold period of the year.

The amount of dissolved oxygen in water varies according to atmospheric pressure, water temperature, the content of mineral salts and organic substances (SR EN 25814 ISO 5814/ -1999). This concave variation is unchanged; the minimum values determined are invariably recorded each year in the hot season as seen in Fig.3. Even in summer, the minimum concentrations recorded (7.93 mg/l O September 2007) included the river in class II, which means water with a good

ecological status.

The variations in time of the values for dissolved oxygen are dependent on:
- the amount of oxygen resulting from photosynthesis
- oxygen consumption of organisms in the ecosystem
- temperature, depth and stratification of water
- load of organic substances of Water
- loads strong reducing agents of water

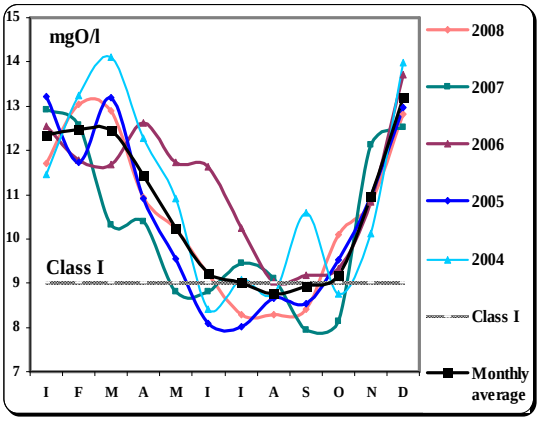

Fig. 3 Annual dissolved oxygen regime on Section Siret - Siret (2004-2008)

Fig. 4 shows the dependence of dissolved oxygen on the content of organic matter and temperature: with the arrival of the warm season the amount of organic matter present in water increases due to weaker amount of dissolved oxygen.

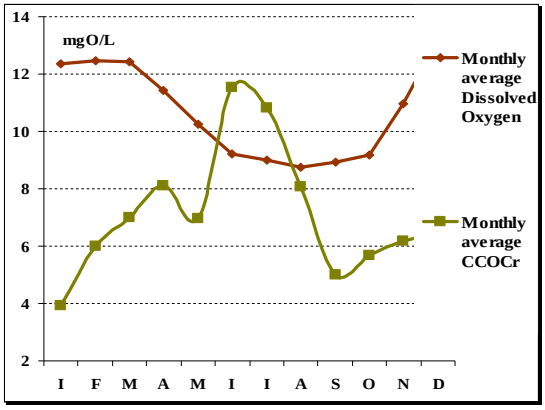

Fig. 4 Comparative evolution of the monthly averages for dissolved oxygen and COD the Siret - Siret section - 2008

For the samples collected in common we have:
- Average values for 2008:Romania - 10,53 mg/l, Ucraina - 9,82mg/l,
- Maximum for 2008 Romania - 13,19mg/l, Ucraina - 13,09mg/l,
- Minimum 2008 Romania - 8,33mg/, Ucraina - 6,08mg/l (Trufaş 2003)

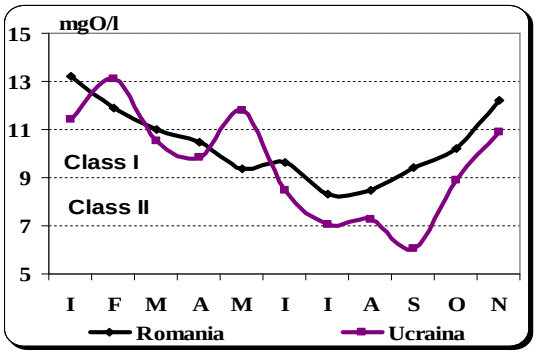

Fig. 5 Comparative evolution of the concentration of dissolved oxygen - section Siret Siret (2008)

The differences in evolution of the dissolved oxygen appear at the minimum values recorded of the two countries, is generally due to samplings techniques and transportations.

1.3 Chemical oxygen demand (COD)

COD puts into evidence the amount of organic matter present in water oxidable with $K_2Cr_2O_7$ (ISO 15705:2002).

The COD (quantity of organic matter) does not exceed the limits of Class II. High concentrations are generally reported in June, July, August.

During the cold of the year when the activity of micro organisms is reduced, flow rates are relatively constant, the amount of organic matter is low, and CODr variations are insignificant. In the studied period, the maxims values do not exceed class II , which means a good ecological status (Mănescu 1994).

Graphical representation of mean monthly values of the studied period (fig. 6) shows that in warm months registers a slight increase, and the maximum values do not exceed class II, therefore showing a good ecological state.

Monthly peaks have a similar running of the minima, the background thermal and flow variations.

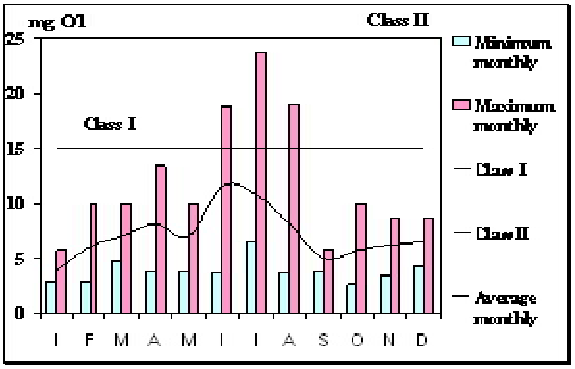

Fig. 6 The average change, monthly minima and maxims on COD values Section Siret - Siret (2004-2008)

1.4 Biochemical oxygen demand (BOD5)

BOD5 basic element in the correlation between the amount of organic matter existing in the water and biological activity of micro organisms (SR EN 1899-1/2003), the maximum values was recorded in June, July, August. The mean in the period under review shows an increase in June, July, August and a decrease in winter.

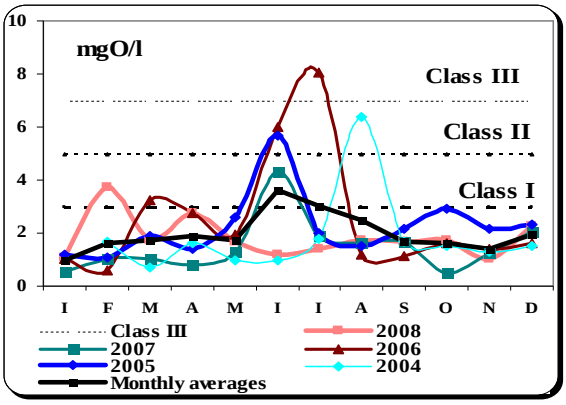

Fig. 7 Evolution BOD5 concentration on Section Siret - Siret (2004-2008)

It is observed (Fig. 7) so that during the summer months high temperatures and intense biological activity had put their mark on the BOD5 values meaning an increase value and significantly lower values in winter. During the studied period, there is a similarity between the evolution of average COD (Fig. 6) and BOD5 (Fig. 7), in both cases the maximum values were recorded during the summer months, once with an increased amount of organic substances in water.

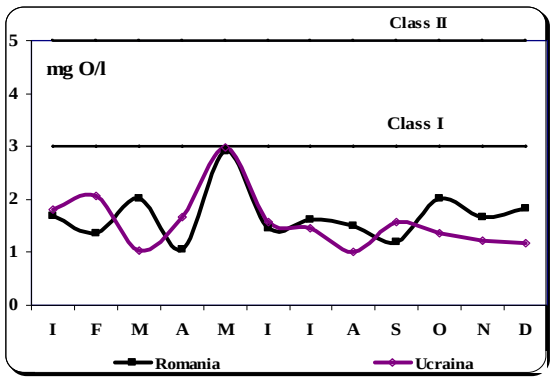

Fig. 8 Comparative evolution of the concentration of BOD5 in Section Siret - Siret (2008)

It can be observed the increase of maximums in the warm period in June, July, August generally. The highest value was determined in 2006, reaching a maximum value of 8.04 mg/l, which has put the river (ord.161/2006) in IVth quality class (Fig. 7).

In 2008 the results obtained by the two countries have a similar trend, the difference from the results recorded in February and March does not change the class of the river (Fig 8).

1.5 Ammonium nitrogen (N-NH_4)

Variations concentration of ammonium ion in the studied period, are not dependent by temperature regime as

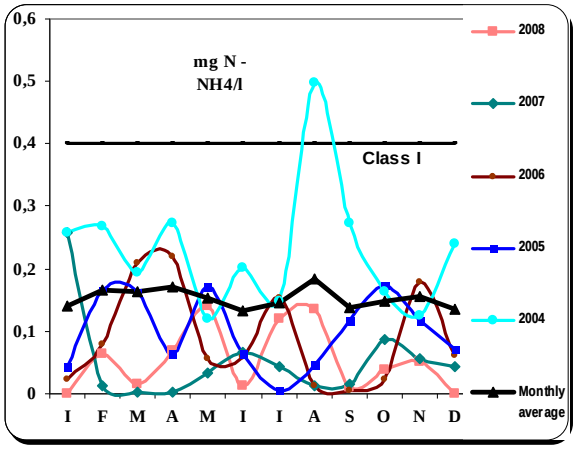

Fig. 9 Evolution of the concentration of N-NH4 by Section Siret - Siret (2004-2008)

shown and do not exceed the limit value of 0.4 mg N/L for class I. The maximum recorded value was 0.498 mg N / l, which means one II class - good ecological status.

It is interesting the comparison

between the values determined by the two laboratories since they use two different methods (fig.10).

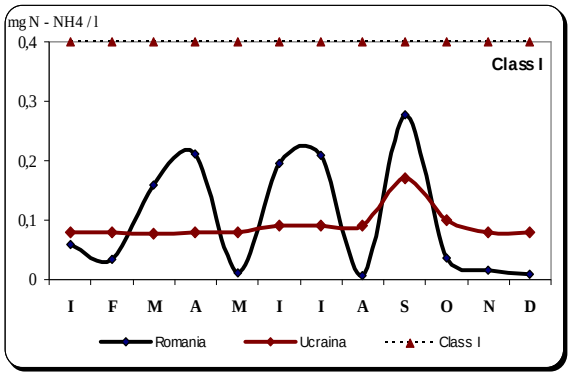

Fig. 10 Comparative evolution of the concentration of N-NH4 in Section Siret - Siret (2008)

Ukrainian part determined the ion ammonium content by treating the sample with Nessler reagent (STAS 6328/85) and this method is not so sensitive for low concentrations, and the Romanian side had determined the ion ammonium content by the reaction of ammonium ions content salicylate and hypo-chlorite in the presence of sodium nitroprusiat (SR ISO 7150-1/2001) (the method using Nessler reagent is repealed due to its toxicity and because the method with the nitroprusiat obtain better performance at low levels).

1.6 Nitrogen from nitrates and nitrites (N - NO_2, şi N – NO_3)

The presence of nitrites in water is generally due to the existence of insufficiently treated sewage (Mănescu, 1994). Regarding the N-NO2 concentration variation, in October 2005 it was recorded a maximum value of 0.072 mg / l N which includes the river in class IV, the maximum frequency values during the studied period being up to the concentration of 0.03 mg N/l. When referring to N-NO3 concentration, it can be observed a slight increase during cold, season plateau of variation is generally up to 2 mg / l.

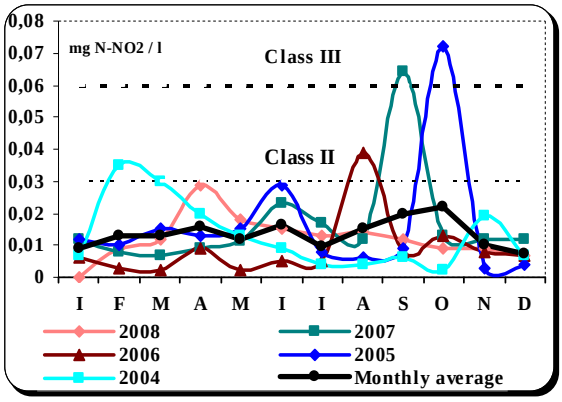

Fig. 11 Evolution of the concentration of N-NO2 by section Siret - Siret (2004-2008)

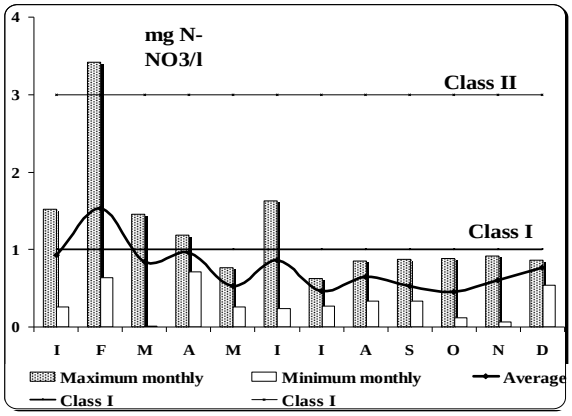

Fig. 12 The average change, monthly minima and maxims on N-NO3 by section Siret - Siret (2004-2008)

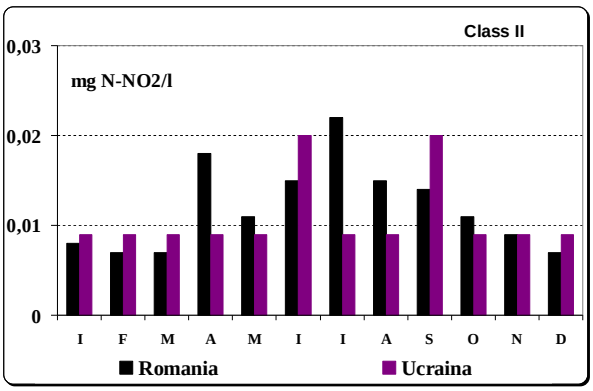

Fig. 13 Comparative evolution of concentration N-NO2 by Siret - Siret section – 2008

A single maximum of 3.42 mg / l was recorded in February 2007, and then the river is included in class III (ord.161/2006). When referring to concentration N-NO2 there are sensitivity differences between the used methods.

For nitrates (fig.14) it is showed a similar trend (no significant differences) of

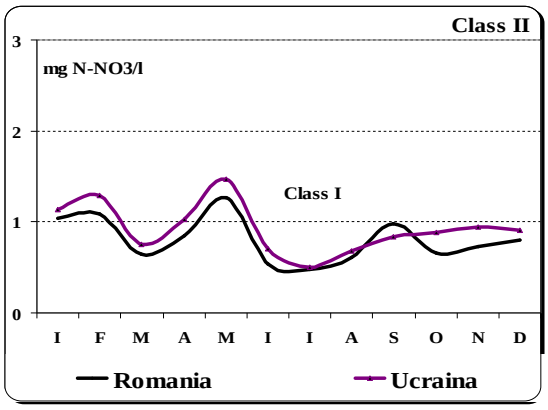

Fig. 14 Comparative evolution of N-NO3 in Section Siret - Siret (2008)

nitrates concentration recorded by the two laboratories, since the principle of determining the methods used is identical.

1.7 Total mineral nitrogen, total phosphorus

For total mineral nitrogen, the quality class determined according to values is of maximum II, the maximum concentration recorded being 1.28 mg N/l.

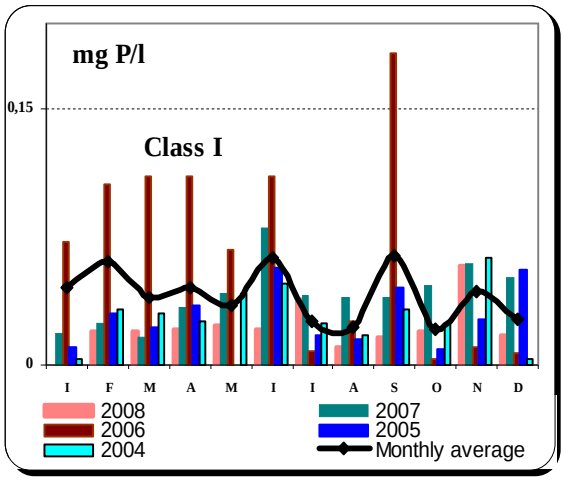

Fig. 15 Evolution of the concentration of P in Section Siret - Siret (2004-2008)

For the samples collected in common, the variability of determined values falls within ± 0.29 mg N/l, the large differences are recorded in November and October.

Determined values for total P did not exceed class II (0.4 mg P/l) generally the variation values ranging up to 0.15 mgP/l (class I).

It is noted that during the monitored period only during September 2006 it was recorded a value of 0,183 mg P/L, which included the river in class II (fig.15).

Table 2

Comparative values of total mineral N concentration in 2008

Monthly	Romania mg N/l	Ucraina mg N/l
January.	1.112	1.219
February	1.13	1.379
March	0.82	0.084
April	1.076	1.119
May.	1.284	1.559
June	0.748	0.81
July	0.71	0.599
August	0.634	0.779
September	1.275	1.03
October	0.708	0.989
November	0.753	1.039
December	0.811	0.999

Analyzing the values for phosphorus from orthophosphate, from both laboratories (Fig. 16), it can be observed that concentrations do not exceed class II (ord161/2006).

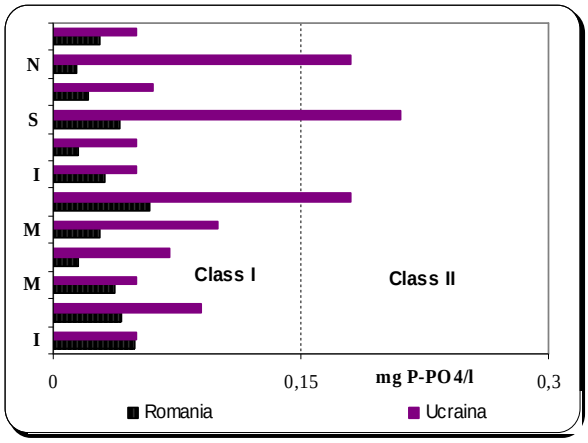

Fig. 16 Comparative evolution of the concentration of P-PO4 in Section Siret - Siret (2008)

We can differentiate the fact that the values obtained by the Romanian side are constant in class I and those obtained by the Ukrainian side had higher values but also with different trend. In this case, the class of quality obtained by the two laboratories is different, but the ecological status of the river is good.

1.8 Iron

The General area of variation of the concentration of iron is frequently included

between 0 and 0.3 mgFe / l, which corresponds to quality class I.

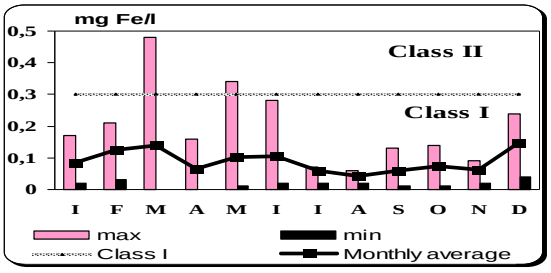

Fig. 17 Evolution maxims, minima and average monthly concentration of Fe on Siret - Section Siret (2004-2008)

Fig. 17 shows that values exceeding class I are very rarely recorded: thus we have a maximum of 0.48 mg / l in March 2005 and another value of 0.34 mg Fe / l in May 2008, which implies a class II of the river on the analysis of daily samples.

Monthly average values indicate a decrease of the iron concentrations in general during the months of July, August, September, higher values being recorded during the cold months of the year: January, February, March, December (archive SGA Suceava).

The trend of the values obtained by the two countries in iron determination is similar, with no major differences.

1.10 Other metals

Among the metals determined by the Romanian part we mention: beryllium, boron, aluminum, titanium, vanadium, chromium, manganese, cobalt, nickel, copper, zinc, arsenic, selenium, molybdenum, silver, cadmium, tin, antimony, tellurium, barium, mercury , cadmium, titanium, lead, uranium.

The only element which was overrun is tin found, the value determined is 4.9 mg / l and the limit is 2.2 mg/l (ord.161/2006).

1.11 Priority and priority hazardous substances

The indicators analyzed include the determination of chlorobenzenes group (Pentachlorobenzene, Trichlorobenzenes, Hexachlorobenzene, Endosulfan,) pesticides (Alachlor, Aldrin, Lindan, Isodrin, Dieldrin, Endrin) herbicides, insecticides and fungicides with N and P (Chlorpyrifos, Chlorfenvinphos, Trifluralin, Atrazine, Simazine, Benzo(k)fluoranthene, Benzo(a)pyrene, Benzo(b)fluoranthene, Benzene, Anthracene, Naphthalene, Polyaromatic hydrocarbons, Lead, Mercury, Nickel, Benzo(g,h,i)perylene, Indeno(1,2,3-cd)pyrene.

The values obtained for these determinations by atomic emission spectrometry technique with inductively coupled plasma, there are not exceed ances of the allowed concentration limits

2. Biological determination

In order to determine the factors who modify the water quality, the biological methods are based on the relationships between organisms and abiotic conditions. The living creatures who lived in those waters form two distinct types of biocoenosis - the plankton, less represented by organisms and the benthic organisms, abundant, varied. The benthic biocoenosis is represented by benthic algae and benthic macroinvertebrates (Antonescu 1963).

Table 3

Classes of surface water quality by saprobic index (ord.161/2006)

Saprobic index	Contamination	Quality class	Ecological status
<1,8	Contamination absent, weak	I	Very good
<2.3	Moderate pollution	II	Good
<2.7	Moderate to critical pollution	III	Moderate
<3.2	Strong contamination	IV	Poor
>3.2	Strong contamination	V	Bad

Among the analysed bioindicators, the benthic macroinvertebrates of rivers have specific characteristics depending on the characteristic of the substrata, water velocity, water chemistry and the river

benthos are poorer than in streams benthos.

Phytobenthos is represented by benthic autotroph algae. Their major role is the synthesis of organic substances from water and are the basis of most food chains in the water. After the identification of these organisms we are making an assessment of water quality, due to rapid response of organisms to changes in environmental conditions, calculating the saprobic index. In according with Order 161/2006 and saprobic index we establish following water quality class (table 4):

Table 4

Quality classes depending on Siret -Siret section biomarkers (2004-2008)

Indicator	**2004**	**2005**	**2006**	**2007**	**2008**
River Siret – Siret Quality class					
Plankton	II	II	II	II	II
Zoobentos	II	II	II	II	II
Benthic algae	II	II	II	-	-

Depending of biological analysis in the section examined we distinguish a high diversity of organisms, the number and diversity is close related with the characteristic of the substrate and the water chemistry.

1 The planktonic biocoenosis is reprezented by taxonomic groups: Bacillariophyceae, Euglenophyta şi Clorophyceae

2 The benthic algae are represented by taxonomic groups: Bacillariophyceae, Cyanophyceae

3 The zoobenthos is represented by taxonomic group: Ephemeroptera, Trichoptera, Diptera (SGA Suceava archive)

Results and discussion

The data presented in this material can be concluded:

- The general physical-chemical indicators make the ranking of the river in class II - according to the annual average (2004-2008), (Order 161/2006 art. 6. 1 letter a),
- Concentrations determined from metal and priority hazardous substances do not show value that exceeds the allowed limits,
- Biomarkers values are in close correlation with the physical, chemical, including the river in grade II.
- Environmental status of the river is good
- For the samples collected in common with the Ukrainian side, the differences arising between the analytical results are due to different sensitivity of different used methods and equipment.

Conclusions

The conclusion is that for those 5 monitored years, there were not changes in the quality class of the river, because industrial activity upstream did not increase in intensity amid economic stagnation Chernivtsi region of Ukraine, and due to increased capacity Self-purification generated large flows of this river.

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