

Assessment of water quality in the upper course of Siret River (N-E Romania)

GABRIELA SASU, CRISTINA BLANARU, OANA ONOFREI¹, ROXANA NECHIFOR², VIOLETA VASILACHE³

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1 Introduction

The adoption of the Water Framework Directive (60/EC/2000) represented a significant step forward in the management of water resources; according to its provisions, by 2015 the water bodies should reach the "good ecological status", meaning that besides the assessment of water chemical quality and biological communities, the hydromorphological integrity of the aquatic habitat is taken into consideration.

In Romania, the responsible authority for water quality management is the National Administration Romanian Waters, by its 11 Regional Water Branches, comprising the major watersheds of Danube tributaries (www.rowater.ro). Siret Water Branch (SWB) comprises four divisions: Suceava, Neamt, Bacau, Vrancea.

Among the Romanian tributaries, Siret River has the highest discharge (average 250 m³/s, www.rowater.ro/dasiret) at the confluence with the Danube River (rkm 155, upstream of the city of Galati).

The paper presents the assessment of water quality based on physico-chemical and biological quality elements over the period 2005-2009, in the upper course of Siret River.

2 Material and methods

With a length of 599 km (90% belonging to Romania and 10% to Ukraine), Siret River is the third longest tributary of the Danube and has the largest catchment in the country (46289 km², with 42890 km² in Romania) with a mean elevation of 485 m. For the ecological assessment, three sections of Upper Siret River were investigated: Upstream Siret - near the border with Ukraine, Hutani - downstream of two reservoirs and Lespezi - located after the confluence with two tributaries (Fig.1)

The monitoring included physico-chemical parameters (temperature, pH, suspended solids, major anions and cations, oxygen balance, nutrients), inorganic and organic pollutants (heavy metals, phenols, detergents) and phytoplankton, benthic algae, macrozoobenthos (abundance and saprobic index). The chemical analyses were carried out monthly, the biological investigations seasonally (three times/year for algae and macrozoobenthos) or once in three years (for fish) (SWBR, 2009). The data of fish fauna were processed by Siret Water Branch Bacau.

The following physico - chemical parameters were considered for this study: pH, total solids (TS), dissolved oxygen (DO), chemical oxygen demand (COD), biochemical oxygen demand (BOD), chloride, sulphate, calcium, magnesium, sodium, bicarbonates, conductivity. For nutrients, phosphates, ammonium, nitrite, nitrate and total nitrogen were determined, while for inorganic pollutants, the content of iron, manganese, copper and zinc was assessed.

The water quality is classified in 5 classes, according to EU- WFD and Romanian standards (class I- high, II- good, III- moderate, IV- poor, V- bad). The sensitivity of the aquatic communities to environmental stress was assessed by the saprobic index SI (Pantle & Buck, 1955; Sladeczek, 1973): according to the benthic species,

1 National Administration Romanian Waters, Siret Water Branch, Suceava Water System Management, 48 Universitatii Street, RO-720228, Suceava, Romania, e-mail sasu_gabriela@yahoo.com, bla_cristina@yahoo.com, oana69reg@yahoo.com

2 National Administration Romanian Waters, Siret Water Branch, 1 Cuza Vodă street, RO- 600274, Bacau, Romania e-mail roxana.nechifor@das.rowater.ro

3 Stefan cel Mare University Suceava, Food Engineering, 9 Universitatii street, RO-720225, violetaren@yahoo.com

water is classified in five classes: class I-oligosaprobic, class II-beta-mesosaprobic, class III- beta- alpha-mesosaprobic, class IV- alpha-mesosaprobic and class V-polysaprobic.

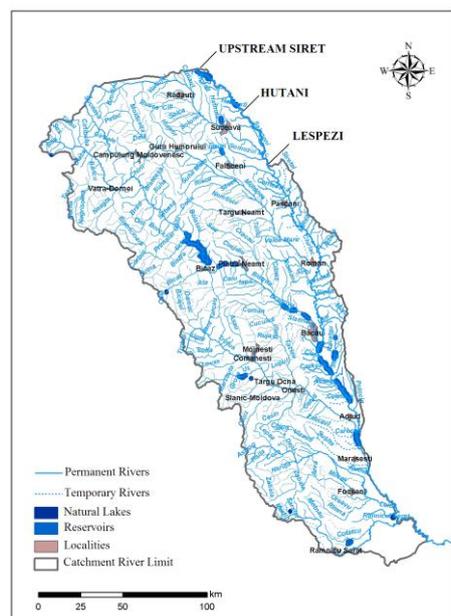


Figure 1. Location of sampling sites along the Siret River Catchment: Upstream Siret, Hutani and Lespezi.

3 Results and discussion

3.1 Physico-chemical quality elements

According to most of the physical and chemical parameters, the water quality of the investigated stretch between 2005-2009 could be generally classified in class II (Table 1). Sodium, chloride and sulphate concentrations were low in Upstream Siret and Hutani sections, but the content of calcium and magnesium could classify this stretch as class II according to Order 161/2006; in Lespezi, the content of chlorides, sulphates and calcium, magnesium indicates also class II. However, the chemical oxygen demand (COD) indicates class I in the upper part, increasing to class II in Lespezi.

The nutrients content is generally low in the upper sections (class I), but the high amount of nitrites could classify these stretches as class II (Tables 1, 2). The content of heavy metals is generally below the standard limits for class I, but manganese reached high concentrations in Upstream Siret in 2009, classifying this stretch as class III, while Hutani was considered class II in 2005 according to Order 161/2006.

Table 1. Average values (\pm S.D., $n = 12$) for selected chemical quality elements in the Upper Course of Siret River in 2005-2009 (in grey italics, values exceeding the standard limits for class I, Romanian Order 161/2006).

Siret River	Year	COD-Cr (mg O ₂ /l)	NH ₄ -N (mg/l)	NO ₂ -N (mg/l)	NO ₃ -N (mg/l)	Total P (mg/l)
Upstream Siret	2005	6.12 \pm 2.007	0.101 \pm 0.0584	<i>0.016\pm0.0189</i>	0.775 \pm 0.4084	0.030 \pm 0.01798
	2006	7.90 \pm 6.540	0.090 \pm 0.0786	0.009 \pm 0.01	0.902 \pm 0.2967	0.060 \pm 0.05842
	2007	6.28 \pm 3.46	0.054 \pm 0.0695	<i>0.017\pm0.0155</i>	0.857 \pm 0.8975	0.040 \pm 0.01768
	2008	7.49 \pm 2.502	0.058 \pm 0.0496	<i>0.013\pm0.0059</i>	0.671 \pm 0.252	0.0229 \pm 0.01308
	2009	7.61 \pm 1.784	0.057 \pm 0.0495	<i>0.012\pm0.0058</i>	0.794 \pm 0.2887	0.032 \pm 0.01814

Hutani	2005	8.11±2.224	0.186±0.1554	0.017±0.0068	0.456±0.2662	0.041±0.03508
	2006	9.03±3.956	0.173±0.0984	0.043±0.1055	0.774±0.4182	0.053±0.06453
	2007	8.63±3.41	0.107±0.0717	0.019±0.0146	0.570±0.3628	0.053±0.03675
	2008	8.74±1.877	0.102±0.0823	0.027±0.0329	0.722±0.2412	0.042±0.02190
	2009	8.22±2.032	0.064±0.0435	0.014±0.0072	0.752±0.3568	0.033±0.01604
Lespezi	2005	12.85±5.539	0.236±0.2418	0.081±0.0581	0.477±0.3583	0.012±0.00877
	2006	14.50±12.123	0.366±0.2968	0.097±0.0486	0.562±0.6472	0.016±0.01724
	2007	13.46±6.586	0.181±0.2425	0.060±0.0347	0.837±0.1367	0.093±0.03863
	2008	11.91±3.641	0.221±0.14	0.041±0.0276	0.190±0.1278	0.022±0.03861
	2009	12.05±3.987	0.298±0.1603	0.034±0.0278	0.088±0.0569	0.006±0.00769

The main point sources of organic pollution in the Upper Course of Siret River are urban wastewaters from Acet- Suceava- Siret Agency, Psychiatric Hospital Varful Campului - Botosani, ApaGrup Botosani and other municipal units; the emissions of these units exceeded the COD, ammonium, phosphorus, nitrites even in 2009 (SWBR, 2009).

The bad management of households contributes to diffuse pollution. At the end of 2006 only 51% of urban agglomeration (>2000 pers.) from Siret River Catchment were connected to the centralized sewer system (SWBR, 2009). In addition, agriculture contributes to diffuse pollution. Nitrogen emissions are 58% from agriculture and 15% from urban agglomerations for the year 2005; phosphorus emissions are 33 % from agriculture and 45 % from urban agglomerations in Siret River Catchment (SWBR, 2009).

Table 2. Average values (\pm S.D., $n = 12$; for Mn $n = 3$) for selected chemical quality elements in the Upper Course of Siret River in 2005-2009 (in grey italics, values exceeding the standard limits for class I, Romanian Order 161/2006)

Siret River	Year	Cl (mg/l)	SO ₄ (mg/l)	Ca (mg/l)	Mg (mg/l)	Fe (mg/l)	Mn (mg/l)	Cu (µg/l)	Zn (µg/l)
Upstream Siret	2005	12.8±2.70	37.4±7.66	72.7±20.0 1	17.0±13.2 6	0.10±0.13 4	0.004	2.85	40.8
	2006	10.8±3.39	42.0±6.81	66.6±17.8 1	11.0±4.65	0.10±0.16 1	-	-	-
	2007	13.5±3.60	30.2±5.67	58.0±15.9 2	11.5±4.46	0.07±0.06 5	-	-	-
	2008	11.4±2.35	30.5±6.25	54.0±18.8 3	10.7±5.93	0.15±0.10 1	-	-	-
	2009	13.3±2.39	42.0±34.56	58.2±13.5 7	10.1	0.06±0.05 5	0.135	4.02	30
Hutani	2005	11.9±3.49	40.3±10.03	53.6±12.5 7	20.5±13.3 0	0.06±0.08 3	0.070±0.1126	19.10	73.4
	2006	11.8±3.93	45.2±7.45	68.5±12.4 0	13.4±6.28	0.09±0.08 9	-	-	-
	2007	14.6±6.31	34.9±7.43	59.9±17.1 9	18.2±10.7 8	0.06±0.06 4	-	-	-
	2008	12.8±2.47	36.3±6.28	48.4±14.1 2	20.0±17.5 3	0.09±0.05 8	0.004	-	-
	2009	14.2±3.41	29.5±8.67	53.2±6.69	12.7	0.06±0.02	-	-	-

	9					6			
Lespezi	2005	26.4±7.17	73.3±36.86	79.7±11.5 <i>1</i>	26.5±7.58	0.13±0.08 4	0.025	6.20	0.00
	2006	26.6±10.8 <i>1</i>	106.2±59.3 <i>3</i>	94.5±30.5 <i>1</i>	15.7±9.12	0.13±0.09 7	-	-	-
	2007	20.8±7.63	36.9±8.09	42.9±9.36	22.6±6.19	0.02±0.00 9	-	-	-
	2008	21.1±7.60	49.3±19.05	65.2±35.0 <i>6</i>	11.4±5.94	0.09±0.16 3	-	-	-
	2009	31.4±6.43	40.2±22.67	61.6±42.8 <i>3</i>	-	0.02±0.00 5	0.041±0.0558	-	-

3.2 Biological quality elements

Monitoring of phytoplankton diversity helps to assess changes in nutrients input and contributes to pollution control. The phytoplankton diversity revealed low pollution in the Upper Course of Siret River: Bacillariophyceae were dominant in abundance (74%), followed by Chlorophyceae (12%), Euglenophyceae (3%) and Chrysophyceae (2%). The chlorophyll-a content ranged between 4.68 – 8.35 µg/l in all the investigated stretches (Table 3).

Over 20 species of benthic diatoms were identified in Hutani site. The saprobic index (1.93- 2.16) classified the stretch as beta-mesosaprobic between 2005 and 2009. In this section, the phytobenthos is dominated by Bacillariophyta (98 %) and Cyanophyta (2 %), with high densities from June to September.

Benthic macroinvertebrates are commonly used for the quality assessment of rivers (Birk & Hering, 2002). Along the investigated stretch, the highest diversity was recorded by Diptera (10 taxa), followed by Ephemeroptera (9 taxa), Oligochaeta (8 taxa) and Trichoptera (5 taxa); molluscs (Gastropoda 3 taxa, Bivalvia 2 taxa), Heteroptera (2 taxa) and Hirudinea (2 taxa) were also identified.

EPT-taxa (Ephemeroptera, Plecoptera and Trichoptera) dominated in the Upstream Siret, where they represented up to 52% in abundance, while Diptera recorded 34%. Downstream, the EPT-taxa decreased in abundance to 34%. The abundance of Oligochaeta increased in Lespezi section (23%), probably as a consequence of the increased organic pollution (COD-Cr content above the limits for class I). In the Upper Course of Siret River, a general decrease of EPT-taxa and an increase of Diptera abundance was noticed over the years (Table 4).

Regarding saprobic index classes (SI), most stretches along the Upper Course of Siret River can be considered as beta-mesosaprobic, except for the sections Upstream Siret in 2009 and Lespezi in 2006 and 2007 that were classified as beta-alpha-mesosaprobic.

Two out of four main tributaries, Suceava and Somuzu Mare, affect the water quality of the Upper Course of Siret River. Only few stretches, usually in the headwater region, can be classified as oligosaprobic; most of the investigated sites are beta-mesosaprobic, except for stretches affected by organic pollution, which belong to the beta-alpha-mesosaprobic category (the lower course of Suceava and Somuzu Mare Rivers – class III, affected by organic pollution from wastewater discharges and fisheries - data from the SWB reports 2006-2009).

Table 3. Phytoplankton abundance (%), content of chlorophyll-a (µg/l) and saprobic index (in italics- class II, in bold- class III, Romanian Order 161/2006) in the investigated stretch between 2005 – 2009

Siret River	Year	Bacillario- phyceae	Chloro- phyceae	Eugleno- phyceae	Chryso- phyceae	Cyanobacteria	Chl-a	Saprobic index
Upstream	2005	91.6	4.96	1.8	-	1.46	-	<i>2.07</i>
Siret	2006	96.73	3.2	-	-	-	-	<i>2.08</i>
	2007	67.14	18.89	-	4.3	-	6.3	<i>2.11</i>

	2008	71.5	15.67	2.92	2.43	1.19	-	2.06
	2009	84.58	2.48	3.16	1.5	3.23	-	2.18
Hutani	2005	81.6	1.36	1.26	2.1	4.97	-	2.09
	2006	92.3	0.6	-	1.36	1.8	-	2.10
	2007						4.68	
	2008							
	2009							
Lespezi	2005	81.6	9.06	8.16	-	1.14	-	2.18
	2006	92.3	2.3	1.33	-	2	-	2.43
	2007	77.9	11.53	1.6	-	2.4	8.35	2.22
	2008	73.86	7.07	3	7.9	6.26	-	2.06
	2009	70.8	15.50	3.16	4.5	6.03	-	1.80

Table 4. Macroinvertebrates abundance (%) and saprobic index (in italics – class II, in bold- class III, Romanian Order 161/2006) in the investigated stretch between 2005 – 2009

Siret River	Year	EPT taxa	Diptera	Oligochaeta	Molluscs	Heteroptera	Hirudinea	Saprobic index
Upstream Siret	2005	87.6	12.2	-	-	-	-	2.08
	2006	57.8	21.8	14.9	-	-	-	1.92
	2007	57.7	26.5	9.6	0.73	2.8	-	1.84
	2008	56.0	40.1	3.2	1.1	-	-	1.86
	2009	-	67.0	24.1	3.1	3.1	2.5	2.69
Hutani	2005	48.2	29	-	-	22.7	-	2.24
	2006	34.0	37.8	8.3	16.6	-	-	2.15
	2007	48.3	17.5	8.2	0.73	0.73	-	2.04
	2008	23.3	49.4	20.6	-	1.76	-	2.04
	2009	27.2	64.1	0.86	-	5.2	-	1.97
Lespezi	2005	68.7	-	-	6.2	-	12.5	2.27
	2006	59.4	17.7	-	11.4	-	5.2	2.10
	2007	17.5	43.1	8.6	4.36	-	20.4	2.39
	2008	12.9	40.9	37.3	3.33	1.9	3.33	2.12
	2009	10.5	50.0	21.6	-	15.5	0.9	2.05

The fish community is considered a good indicator of the overall anthropogenic impact (Schiemer, 2000, Lasne et al., 2007). There are many EU methods for assessing the ecological quality of the small and medium sized rivers based on ichthyofauna diversity. The scores from the European Fish Index (EFI) were evaluated; however, EFI is sensitive to water quality pressures, but not very good to emphasize hydromorphological pressures. The EFI produces a score between 0 and 1, which is directly translated into an EQ- class (1- high; 2- good; 3- moderate; 4- poor; 5- bad).

In 2006, 77 fish specimens of 8 species were collected from the three sites, which belong to the cyprinid river zone. In the first section, Upstream Siret, the EFI index was 0.624 (class 3), in Hutani section 0.895 (class 2) and in Lespezi section 0.748 (class 2). In the upper part, the dominant fish species were *Rhodeus sericeus amarus*, *Carassius auratus*, *Cyprinus carpio*, *Esox lucios*, *Alburnus alburnus* while for the downstream stretches, the dominant species were *Chondrostoma nasus* and *Leuciscus cephalus*. The EFI index class 3 for the Upper Siret indicates organic pollution originating mainly from wastewater discharged into the river.

4 Conclusions

Formerly in 2005 at its mouth, Siret was among the most polluted Danube tributaries with respect to organic pollution (UNECE, 2007); according to the report of National Administration Romanian Waters (NARW, 2007) the water quality in Siret River catchment was moderate to poor, class II - IV.

Our study shows that, after 2005, the water quality in the Upper Course of Siret River slightly improved and encompasses mostly class I or II in terms of physical-chemical conditions and specific pollutants, and class II in terms of biological quality elements. Some quality elements have exceeded the limits of class I, such as suspended solids, due to substrata characteristics (the geology of Upper Course of Siret River is siliceous, calcareous rocks mixed with organic soils).

Households affect water quality: nitrite concentrations were constantly high in the three sections studied in the Upper Course of Siret River. The content of heavy metals is generally below the standard limits for class I; only manganese reached high concentrations in Upstream Siret in 2009 (class IV) and Hutani in 2005 (class III). To reduce input from point sources of organic pollution further management measures are needed, such as a permanent monitoring of wastewater discharged into rivers and financing investments to modernize or build wastewater treatments plants in the Upper Course of Siret River.

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