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Water pollution

IDENTIFICATION OF THE AQUATIC ECOSYSTEMS INTEGRATING VARIABLES IN THE SUCEAVA HYDROGRAPHIC BASIN AND THEIR CORRELATIONS

G. BATRINESCU[a], E. BIRSAN[a], G. VASILE[a], B. STANESCU[a], E. STANESCU[a], I. PAUN[a], M. PETRESCU[a], C. FILOTE[b]*

[a]*National Research and Development Institute for Industrial Ecology – ECOIND, 90–92 Sos. Panduri Street, District 5, 050 663 Bucharest, Romania*
E-mail: *ecoind@incdecoind.ro*
[b]*University 'Stefan cel Mare' Suceava, 13 Universitatii Street, 720 229 Suceava, Romania*
E-mail: *filote@eed.usv.ro*

Abstract. The purpose of this paper is to show the results of the investigation of the environmental components quality (surface water, groundwater and sediments) in the winter – spring 2008 campaigns. The systemic characterisation of the physicochemical and biological environment is realised by development of investigation program of the water body represented by the Suceava river and main affluents: Pozen, Solonet and Salcea streams. Based on the investigations performed, the time and space evolution of the main stock-up (surface water and sediment) and cycling (phytoplankton, zooplankton and macrozoobenthos components) reservoirs characteristics of the aquatic ecosystems in the analysed area are shown. Also, investigations of the underground water aim to underline connections between its quality and surface water quality. Therefore, accumulation of sediments of the chemical quality indicators was follow-up. The investigations results were integrated in the mathematical model using Spline functions to mark out evolution and transportation: oxygen regime (as COD and BOD) and nutrients (ammonium, nitrates, nitrites, total nitrogen, total phosphorus) for the Suceava river; salt (TDS, chlorides, sulphates, sodium) for the Solonet stream. The solutions of the equations can be used in modelling and estimations predictions of water river parameters for established period of time.

Keywords: aquatic ecosystem, water body, investigation program, abiotic and biotic components, modelling.

AIMS AND BACKGROUND

The relationship between quality and quantity of surface water on the one hand, and health of the peoples, on the other, is an acute problem of nowdays, as water is one of the most important environmental factors that contributes to quality of life.

The European Commission has adopted Directive 2000/60/EC amended by Directive 2008/32/CE, which establishes the framework for Community action in

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* For correspondence.

the field of water policy. The general aim of this directive is to establish a framework for the protection and management of surface waters in the European Union by reaching 'good' condition of all bodies of water in the natural scheme of Europe until 2015, preserving 'good' and 'very good' condition for bodies of water where there already was achieved a 'good' ecological potential for heavily modified and artificial water bodies; compliance with the environmental objectives set by the other Directives in water protected areas[1].

The main objectives of the Directive are: damage prevention, protection and improvement of aquatic ecosystems condition, taking into account their water requirements, permanent interactions between aquatic ecosystems and terrestrial adjacent ecosystems and wetlands; promote sustainable water use based on the long-term protection of water resources; enhance protection and improve the condition of aquatic environment by specific measures for the progressive reduction of emissions and loss of priority substances and the total or staged closure of emissions and loss of hazardous priority substances in water; groundwater pollution prevention and progressive reduction of their pollution; reduce the adverse effects of dangerous hydrometeorological phenomena – floods and droughts.

These objectives will be achieved through proper management of the aquatic environment of the basins of the rivers and the proper combination of limit values and environmental quality standards to control discharges into water bodies[2].

The objective of this study is to assess the quality of the Suceava river water, in order to emphasise the effects induced by discharges of wastewater under various degrees of purification, by defining and tracking in time and space the changes of the characteristics of storage tanks (water surface and sediment) and cycling (phytoplankton, zooplankton and macrozoobentos) based on the interaction between surface waters and groundwater.

EXPERIMENTAL

The Suceava river is part of the Siret river basin, it springs in the north of the country from Bukovina Obcinele (Mestecanis Obcina) of the Lucina massive and after 170 km, it flows into the Siret river, near Liteni.

In order to determine the control sections for surface water and sediment, it was aimed to cover the entire emissary route and a number of its representative tributaries (i.e. Pozen, Solonet and Salcea brooks), taking into account information on businesses in the Suceava county which are allowed to exhaust and/or get supplied from the Suceava river and its tributaries, provided by the Suceava Water Management System, part of the National Company 'Romanian Waters'.

Field investigations have highlighted the following aspects about water as natural resource and economic activities carried out over the river course Suceava:

– throughout the Suceava river human settlements are using groundwater as a source of drinking water, from Brodina until Liteni wells were identified in individual households;

– economic activities are concentrated in urban settlements, the largest city is the city of Suceava, followed by Radauti, Dornesti, Milisauti, Partestii de Jos;

– prevalence of agricultural activities in rural settlements, followed by operating activities and wood processing (in Brodina, Faget, Radauti, Partestii de Jos, Todiresti, etc.), food industry (Radauti, Milisauti, etc.);

– field observations have highlighted the pervasive exploitation of mineral aggregates along the Suceava river (in Dornesti, Upper Vicovu, Milisauti, Darmanesti, Mihoveni, Liteni, etc.).

In the area of interest, 3 surface water and sediment sampling campaigns were organised in February, March, May 2008, and groundwater campaigns in March and May, aiming to establish the quality of these components of environment in order to distinguish any pollution as a result of activities in the area and the changes in time.

In the winter campaign for the month of February there were taken samples from 20 control sections, and in the spring campaign (March/May) samples were collected from 27 control sections, aiming to evaluate the physicochemical and hydrobiological parameters. Geographical location of control sections was done using the technique of Satellite Positioning via GPS (Global Positioning System) (Fig. 1).

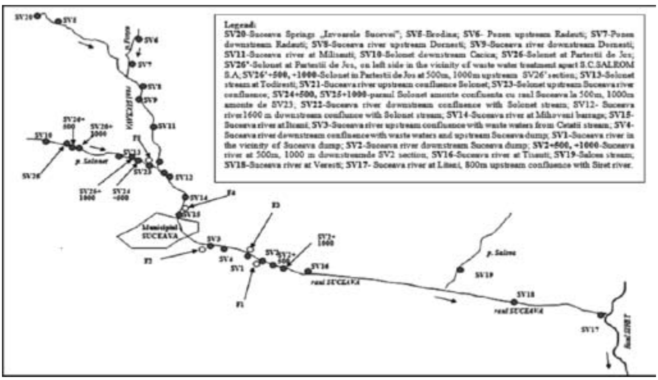

Fig. 1. Location of sections

To assess the quality of groundwater aquifers in the area of mutual interaction with surface water (the Suceava river) 5 drilling control objectives were performed taking into account the spots located in the area of interest and that can generate pollution: F1 and F2 upstream/ downstream location of the deposit waste (sections near the sampling SV2 and SV4); F3 near the discharge point of effluent purification station of the city of Suceava, corresponding section of SV1; F4 ‘Itcani’ in the area of namesake neighbourhood, near the section SV15; F5 ‘Solonet’ in the confluence of the Suceava river with Solonet brook, near SV23.

Sampling in order to realise analytical and hydrobiological investigations was conducted in accordance to the standards and methodologies in effect[3–7].

RESULTS AND DISCUSSION

Values of determined parameters were compared with the limits established by current regulations, according to MMGA Order No 161/2006 for the approval of the Norm regarding reference objectives for grading the quality of surface water (Tables 1 and 2) (Ref. 8).

Table 1. Quality standards for surface water according to MMGA Order No 161/2006

Indicators	M.U.	Class quality / ecological status under Order No 161/2006				
		I (very good)	II (good)	III (moderate)	IV (weak)	V (bad)
TDS	mg/l	500	750	1000	1300	>1300
COD	mg O_2/l	10	25	50	125	>125
BOD	mg O_2/l	3	5	7	20	>20
Ammonium ($N–NH_4^+$)	mg N/l	0.4	0.8	1.2	3.2	>3.20
Nitrates ($N–NO_3^-$)	mg N/l	1	3	5.6	11.2	>11.2
Nitrites ($N–NO_2^-$)	mg N/l	0.01	0.03	0.06	0.3	>0.3
Total nitrogen	mg/l	1.5	7	12	16	>16
Total phosphorus	mg P/l	0.15	0.4	0.75	1.2	>1.2
Chlorides	mg/l	25	50	250	300	>300
Sulphates	mg/l	60	120	250	300	>300
Sodium	mg/l	25	50	100	200	>200
Saprobic index Phytoplankton	–	1.8	2.3	2.7	3.2	>3.2

Table 2. Standards for quality sediment (fraction <63 μm) according to MMGA Order No 161

Indicators	M.U.	Quality standard under Order No 161/2006
Copper	mg/kg d.s.	40
Zinc	mg/kg d.s.	150
Cadmium	mg/kg d.s.	0.8
Lead	mg/kg d.s.	85

Table 3 presents the results of physicochemical analysis performed on samples of surface water from the 3 campaigns. Based on the analyses of these investigations, the quality indicators ammonium, sulphates and TDS, are shown the existence of an ecological 'very good' and 'good' state in all sections of the studied aquatic emissary (the Suceava river and its main tributaries), except an 'ecological moderate state' in February 2008 on the Solonet brook (SV13) for the quality indicator TDS.

Table 3. Analytical results of surface water samples from the Suceava river and its tributaries – the campaigns of the 2008 winter–spring sampling

Indicators/ sample cod	TDS (mg/l)			COD (mg O_2/l)			BOD (mg O_2/l)			Ammonium ($N–NH_4^+$) (mg N/l)			Nitrates ($N–NO_3^-$) (mg N/l)		
Period	Feb.	March	May	Feb.	March	May	Feb.	March	May	Feb.	March	May	Feb.	March	May
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
SV 20	180	124	132	6.6	5.4	5.12	2.07	1.53	2.12	<DL	0.17	0.14	0.54	1.87	0.64
SV 5	200	234	186	8.4	8	10.2	2.51	2.61	4.48	<DL	0.25	0.09	0.66	0.34	0.55
SV 5′	–	120	–	–	7.2	–	–	2.43	–	–	0.37	–	–	0.65	–
SV 6	346	300	322	7.2	6.6	5.44	2.78	1.94	2.33	<DL	0.08	<DL	2.00	1.62	0.94
SV 7	410	364	416	12.4	8.2	6.08	4.01	2.84	2.82	0.06	0.26	0.11	3.21	3.06	2.00
SV 8	260	70	92	8.8	5.6	7.36	2.56	1.42	3.12	<DL	0.13	<DL	1.41	1.44	0.73
SV 9	262	216	274	7.2	6	5.12	2.37	1.58	1.98	<DL	0.18	0.09	1.54	1.65	0.85
SV 11	274	218	190	7.4	6.8	6.72	2.60	1.78	2.94	0.1	0.09	0.16	1.78	1.34	1.21
SV 13	812	–	–	18.4	–	–	5.10	–	–	<DL	–	–	1.83	–	–
SV12	362	–	–	96	–	–	40.50	–	–	<DL	–	–	1.71	–	–
SV 21	–	206	308	–	16.8	6.4	–	3.47	2.48	–	0.17	0.06	–	2.14	0.58
SV 22	–	260	540	–	6	9.28	–	1.56	2.92	–	0.12	0.11	–	1.71	0.47
SV 23	–	460	512	–	9.2	7.36	–	2.80	2.86	–	0.33	<DL	–	1.25	0.49
SV24+500	–	492	–	–	10	–	–	2.64	–	–	0.039	–	–	3.21	–
SV25+1000	–	464	–	–	12	–	–	3.07	–	–	0.09	–	–	1.445	–
SV 10	466	414	316	10.8	10	7.68	3.44	3.26	3.33	<DL	0.118	<DL	1.06	1.224	1.16
SV26	–	694	–	–	15.2	–	–	3.91	–	–	0.134	–	–	2.54	–
SV 26*	–	–	714	–	–	9.28	–	–	3.297	–	–	0.020	–	–	0.29
SV 26*+500	–	–	540	–	–	16	–	–	5.67	–	–	0.042	–	–	0.305
SV 26*+1000	–	–	460	–	–	8	–	–	3.77	–	–	0.034	–	–	0.33
SV 14	350	262	340	7	5.4	5.44	2.76	1.63	2.14	<DL	0.16	0.074	1.61	1.35	0.99

to be continued

Continuation of Table 3

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
SV 15	366	276	256	24.8	7.6	8.64	9.20	2.47	3.07	<DL	0.262	0.100	1.62	2.72	1.19
SV 3	382	274	304	7.6	6.0	7.36	2.78	1.51	2.76	<DL	0.26	0.029	1.89	1.98	1.26
SV 4	382	276	354	9.2	5.2	5.76	3.42	1.50	2.07	0.093	0.48	<DL	1.57	1.81	1.65
SV 1	390	264	346	10.4	12.8	13.12	3.67	3.50	4.25	0.202	0.34	0.21	1.82	1.3	1.47
SV 2	230	262	336	8.8	6.0	5.44	2.51	1.89	2.24	0.381	0.45	<DL	1.78	1.14	1.37
SV 2+500	–	258	294	–	11.6	8.00	–	3.03	2.94	–	0.51	0.042	–	1.16	0.815
SV 2+1000	–	152	158	–	13.6	10.56	–	3.90	3.69	–	0.62	0.127	–	0.6	1.775
SV 16	356	316	334	18.0	16.8	8.96	4.16	3.87	3.61	0.046	0.325	0.102	1.82	1.505	1.57
SV 19	524	430	354	67.2	11.2	9.92	27.30	2.77	3.73	0.42	0.264	0.074	6.27	6.54	1.63
SV 18	412	270	326	6.8	10.8	9.60	1.74	2.79	3.94	0.22	0.196	0.089	1.73	2.29	1.57
SV 17	420	280	350	9.6	14.0	7.36	3.52	3.54	3.24	0.234	0.199	0.120	1.80	1.505	1.84

Indicators/ Sample cod	Nitrites ($N–NO_2^-$) (mg N/l)			Total nitrogen (mg N/l)			Total phosphorus (mg P/l)			Chlorides (mg/l)			Sulphates (mg/l)			Sodium (mg/l)		
Period	Feb.	March	May	Feb.	March	May	Feb.	March	May	Feb.	March	May	Feb.	March	May	Feb.	March	May
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
SV 20	0.02	0.005	0.002	1.52	3.26	3.96	0.02	0.07	0.02	27.5	7.01	10.5	15.8	13.0	26.3	4.9	2.58	3.44
SV 5	<DL	0.004	<DL	5.86	6.26	4.98	0.03	0.29	0.02	19	8.76	7.01	20.7	15.5	40.0	6.8	3.83	2.83
SV 5′	–	0.005	–	–	5.24	–	–	0.14	–	–	8.76	–	–	17.0	–	–	5.00	–
SV 6	0.02	0.020	0.006	9.90	8.26	5.14	0.07	0.23	0.03	17.2	17.5	14.0	31.7	28.0	26.1	11.6	10.10	5.95
SV 7	0.13	0.020	0.390	5.32	4.12	8.46	0.19	0.08	0.12	46.5	26.3	21.0	36.4	27.3	37.9	28.5	15.60	11.60
SV 8	<DL	0.004	0.010	3.64	5.90	5.84	0.03	0.08	0.11	17.2	17.5	14.0	25.2	14.7	19.9	10.8	8.13	4.22
SV 9	<DL	0.004	0.007	4.66	2.90	2.26	0.032	0.12	0.03	21	14.0	14.0	25.4	14.9	18.5	11.2	7.72	3.99
SV 11	0.02	0.010	0.010	3.66	8.94	7.40	0.09	0.06	0.05	121	15.7	15.7	29.3	18. 6	27.6	12.8	16.80	4.89

to be continued

Continuation of Table 3

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
SV 13	<DL	–	–	2.46	–	–	0.01	–	–	243	–	–	69.2	–	–	168.0	–	–
SV12	0.030	–	–	4.60	–	–	0.02	–	–	41.3	–	–	34.7	–	–	33.8	–	–
SV 21	–	0.040	0.004	–	2.44	1.11	–	0.4	0.04	–	17.50	17.5	–	28.6	22.3	–	9.33	7.97
SV 22	–	0.010	0.004	–	2.56	2.38	–	0.87	0.03	–	26.30	61.3	–	28.4	45.0	–	23.1	63.1
SV 23	–	0.007	0.002	–	6.62	0.94	–	0.44	0.03	–	87.60	77.1	–	55.7	46.7	–	67.5	30.1
SV24+500	–	0.007	–	–	3.76	–	–	<DL	–	–	91.08	–	–	39.97	–	–	60.9	–
SV25+1000	–	0.007	–	–	8.26	–	–	0.35	–	–	87.57	–	–	37.94	–	–	76.75	–
SV 10	<DL	0.004	0.004	3.52	3.26	7.86	0.046	0.09	0.06	34.43	70.06	52.55	79.2	10.34	42.43	51.9	59.85	27.5
SV26	–	0.005	–	–	3.76	–	–	0.18	–	–	197.90	–	–	71.59	–	–	210.4	–
SV 26*	–	–	<DL	–	–	2.46	–	–	0.032	–	–	112.50	–	–	77.69	–	–	58.65
SV 26*+500	–	–	0.011	–	–	1.64	–	–	0.19	–	–	115.90	–	–	77.24	–	–	77.1
SV 26*+1000	–	–	0.004	–	–	1.22	–	–	0.31	–	–	133.10	–	–	77.1	–	–	75.25
SV 14	0.024	0.012	0.016	2.34	3.94	2.24	0.037	0.06	0.105	39.60	24.52	17.51	34.32	19.94	21.64	30.3	12.63	7.94
SV 15	<DL	0.015	0.037	2.64	3.46	2.90	0.020	0.46	0.057	51.65	22.77	17.51	36	31.76	26.96	35.3	13.77	7.96
SV 3	0.009	0.012	0.021	4.84	4.84	6.02	0.053	0.3	0.178	40	26.27	17.51	37.3	37.12	59.61	29.7	15.21	8.55
SV 4	0.036	0.021	0.290	5.00	3.58	6.60	0.182	0.89	0.178	38	22.77	17.51	37.9	29.24	30.5	30.5	14.39	9.95
SV 1	0.060	0.006	0.270	11.60	3.58	5.24	0.161	0.47	0.074	43.04	21.02	21.02	37.3	36.13	44.61	31.2	14.45	9.665
SV 2	0.082	0.015	0.240	3.70	3.54	4.28	0.101	0.44	0.094	37.87	21.02	21.02	38.8	29.34	32.16	30.3	14.77	10.04
SV 2+500	–	0.048	<DL	–	3.74	1.84	–	0.84	0.110	–	24.52	24.52	–	25.56	29.42	–	14.72	9.74
SV 2+1000	–	0.045	<DL	–	4.32	1.34	–	0.24	0.122	–	24.52	19.27	–	22.47	25.25	–	14.53	9.05
SV 16	0.057	0.019	0.008	3.40	7.16	2.38	0.202	0.12	0.067	69	26.27	21.02	37.99	25.38	33.79	37.4	15.28	11.96
SV 19	0.413	0.071	<DL	8.06	7.58	6.16	0.026	0.07	0.072	34.43	24.52	45.54	79	24.7	26.06	26.9	16.07	5.945
SV 18	0.091	0.019	0.002	3.18	3.60	1.70	0.124	0.14	0.094	68.87	28.02	21.02	40.3	31.9	24.68	42.4	17.12	12.91
SV 17	0.060	0.024	<DL	3.52	3.74	2.38	0.194	0.14	0.07	86.08	29.77	21.02	40.8	30.92	30.73	40.4	16.35	13.21

Legend: <DL – below the detection.

Spatio-temporal evolution of physicochemical characteristics for storage (surface water and sediment) and cycling (phytoplankton, zooplankton and macro-zoobentos) tanks quality indicators which have induced environmental conditions modification for the Suceava river and its major tributaries are presented in the graphical form in Figs 2–10, as follows:

ENVIRONMENTAL COMPONENT – SURFACE WATER

Figure 2: For the indicator of quality organic loading (measured as COD) the existence of an ecological 'very good' and 'good state' in most sections of the aquatic emissary studied, except the values recorded punctual in SV12 section (the Suceava river downstream to the confluence with the Solonet brook) and SV19 (the Salcea brook) in February 2008 with the 'ecological state weak' can be observed. An organic loading expressed by COD is higher in the pouring area (SV17) compared with the origin area (SV20) in all investigation campaigns.

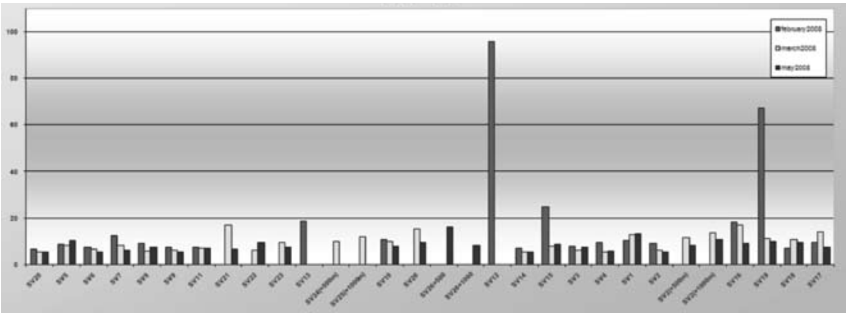

Fig. 2. Evolution of COD – surface water of the Suceava river and tributaries winter–spring campaign 2008

Figure 3: For the quality of organic loading (measured as BOD) it is found that there are insignificant differences between the investigation campaigns, with the existence of an 'ecological very good and 'good state' for most sections of the aquatic emissary studied, except in February 2008 in: SV12 (the Suceava river downstream to the confluence brook Solonet) with an ecological bad state, SV15 (the Suceava river at Itcani) with 'ecological status weak' and SV19 (the Salcea brook) with an 'environmental bad state' in May 2008, and 'ecological state moderate' for the Solonet brook (SV26′ + 500).

Figure 4: A relatively uniform trend for quality indicator nitrates on the entire Suceava river route, the existence of 'very good' and 'good' ecological state, except 'moderate' ecological state for the Pozen brook downstream Radauti (SV7) in February and the Solonet brook upstream the Suceava river (SV24+500) in March, environmental state 'weak' for the Salcea brook in February and March.

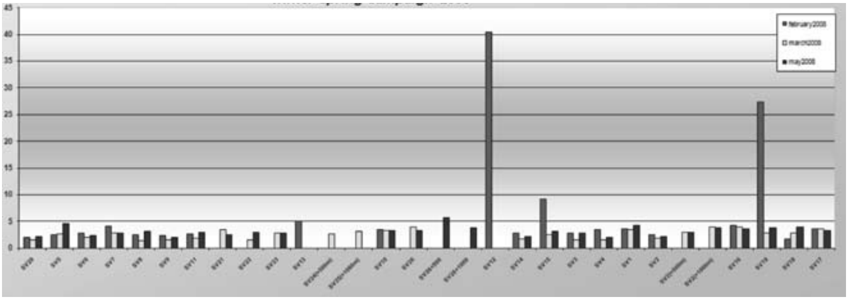

Fig. 3. Evolution of BOD – surface water of the Suceava river and tributaries winter–spring campaign 2008

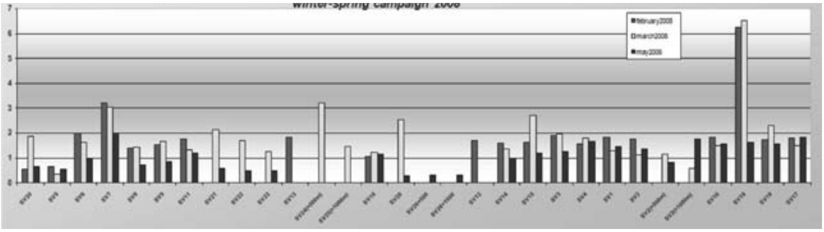

Fig. 4. Evolution of nitrates – surface water of the Suceava river and tributaries winter–spring campaign 2008

Spatio-temporal evolution of the zooplankton component shows:

– the entire section studied in all investigation campaigns presents a small number of organisms from zooplankton, both in terms of numerical abundance and abundance in the biomass;

– in February, on the upper – middle water course of the Suceava river there are species of rotiferas, cladoceras and/or copepodas and on the lower course of emissary species of rotiferas or cladoceras dominate; in March and May for the entire studied section there are present organisms from zooplankton species of cilias, rotiferas, cladoceras, copepodas or rhizopodas;

– in terms of the numerical density the lowest values were recorded in February for control sections: SV4, SV1, SV2 in the area of the waste deposit of the municipality of Suceava and the SV19 on Salcea brook; in March for SV2+500, +1000 and in May SV17, SV4÷SV2+1000. We mention that in March organisms from zooplankton were absent in sections SV1, SV2.

ENVIRONMENTAL COMPONENT – SEDIMENT

Simultaneously with investigations carried out for the environment component – the surface water, physicochemical and biological samples of sediment from the Suceava river and its tributaries (Pozen, Solonet and Salcea) were taken and characterised. For sediment quality indicators standardised by MMGA Order No 161/2006 (iron, copper, zinc, cadmium, lead) were considered and also physico-chemical parameters measured for the surface water (chloride and sodium).

Following the spatio-temporal evolution of physical, chemical and biological parameters of sediment in the sampling for the winter–spring 2008, it was found that:

– values by the tens and hundreds of mg/kg d.s. for quality indicators sodium and chloride; there were recorded values g/kg d.s. for sodium in the control section SV1 (the Suceava river right in the landfill of the Municipality of Suceava);

– exceedance of the limit allowed for the quality indicator cadmium in most control sections and for quality indicator zinc only in the control section SV7 (the Pozen brook downstream Radauti) in spring campaign 2008;

– the quality indicator copper is within the limits allowed for the majority of sections, except sections: SV9 in winter campaign and SV20, SV7, SV26+500 in the spring;

– values by the tens and hundreds of g/kg d.s. for the total iron on the entire section of aquatic emissary studied;

– on the upper course of the Suceava river (in sections of SV20, SV5, SV5′ and SV6), benthonic macroinvertebrates present a rich heterogeneous, being present bodies from the following groups: mites, amphipodas, ephemeropteras, plecopteras, trichopteras (benthos elements indicators of low impurification), followed by oligochete and/or chironomide; for all other control sections, complexity and diversity of benthonic biocenosys are drastically reduced, dominating in different proportions oligochetas and/or chironomidas;

– the absence of benthonic macroinvertebrates in sections SV11 and SV2 in winter 2008, and sections SV23, SV3 and SV1 in spring campaign 2008.

ENVIRONMENTAL COMPONENT – GROUNDWATER

Results of tests carried out on samples taken from the 5 drillings, in the two harvest campaigns are presented in Table 4.

Analysis of results from analytical determination compared with the limit imposed by Drinking Water Law 458/2002 completed by Law No 311/2004 reveals the following:

– the quality indicators: pH, nitrates, nitrites (except drilling F4 in March), chlorides, sulphates (except F3 drilling in March–May), sodium in the May campaign, are included in the limits imposed.

Table 4. Characteristics of water samples from control drillings – March/May 2008

Indicators	UM	F1		F2		F3		F4		F5		Permissible limit values under Drinking Water Law
		March	May	March	May	March	May	March	May	March	May	
pH	–	6.97	6.80	6.92	6.79	6.39	6.50	6.78	6.66	7.29	6.96	6.5–9.5
TDS	mg/l	1123	919	791	734	1012	888	922	1004	546	474	–
COD	mg O_2/l	15.75	20.61	5.10	8.99	5.50	5.89	14.80	2.17	5.00	13.64	5
Ammonium	mg/l	0.91	3.51	0.67	0.35	0.29	0.25	0.44	0.04	0.26	0.13	0.5
Nitrates	mg/l	2.23	3.65	1.01	0.558	1.18	1.577	7.68	6.71	4.56	5.67	50
Nitrites	mg/l	0.11	0.051	0.037	0.044	0.015	0.058	2.69	0.476	0.06	0.17	0.5
Total phosphorous	mg/l	0.03	0.08	0.023	0.026	0.021	0.248	0.071	0.040	0.019	0.12	–
Chlorides	mg/l	203.16	95.11	72.31	74.73	65.42	50.95	89.53	88.32	103.30	56.05	250
Sulphates	mg/l	201.42	133.53	92.76	80.44	350.80	255.74	173.44	170.36	70.57	64.60	250
Sodium	mg/l	510	165.70	446	78.95	277	35.36	308.60	36.02	424.10	60.75	200

In Table 4 evolution from upstream to downstream of quality parameters investigated in surface water and in groundwater is represented graphically; there is found a greater load for quality indicators sodium, sulphates in groundwater aquifers than in surface water (natural background). The indicator 'sodium' has very high values in March, which decrease significantly in the next sampling campaign. The exception is the 'organic load' (expressed as COD) which has significant values for both types of water investigated.

APPROXIMATION BY SPLINE FUNCTIONS INTERPOLATION ANALYSIS OF PHYSICAL AND CHEMICAL INDICATORS VARIATION

The realisation of a quality estimation model of the physical and chemical indicators required the analyses of the physical and chemical indicators variation, on different river sections using Spline functions. Consequently, we will have a polynomial segment approximation of indicators evolution on certain river sections, others than the monitored sections during the 2008 winter–spring campaigns.

THEORETICAL CONSIDERATIONS

Spline functions are piecewise polynomial functions that tie together with a certain number of their derivates forming nodes[9]. In order to approximate f: $[a, b] \rightarrow$ R by a function S, we use the following method: the interval $[a, b]$ is divided in n subintervals which correspond to the following points:

$$a = x_0 < x_1 < \ldots < x_k < x_{k+1} < \ldots < x_n = b \tag{1}$$

It is necessary for this function to be determined using the 2 polynomials $(S_k)_{k=\overline{0,n-1}}$, S_k: $[x_k, x_{k+1}] \rightarrow$ R, one of them on each interval in such a way that at the endpoints in relation (1) the S function be several times differentiable. We consider any 2 sections in S function where $y = S_k(x)$, $x \in (x_k, x_{k+1})$ and $y = S_{k+1}(x)$, $x \in (x_{k+1}, x_{k+2})$ are equal at the coordination point (x_{k+1}, y_{k+1}). The result is that the set of functions $(S_k)_{k=\overline{0,n-1}}$ forms a piecewise polynomial curve, which is denoted by $S = (S_k)_{k=\overline{0,n-1}}$. We can notice that instead of approximating the f function by a single polynomial on the whole interval $[a, b]$, we approximate this function by n polynomials. Thus, we can obtain an approximated function S which can be used in solving different approximation and interpolation problems. The S function that we thus obtained is named Spline function. The name Spline comes from the thin rods called 'spline', used by specialists to transform the rectilinear movement in rotation movement. This instrument helps to fit curves through given points. From a practical point of view, the cubic Spline functions are the most important ones. They are functions with smooth, continuous curves. When they are used for interpolation, these functions do not have oscillatory behaviour which is characteristic to high degree polynomials. The cubic Spline functions are easy to calculate and use.

A function $S \in C^2[a, b]$ is called cubic Spline function for a set of points $a = x_0 < x_1 < \dots x_k < x_{k+1} < \dots x_n = b$ corresponding to f, if there exist n cubic polynomials, $S_k(x)$, $k = \overline{0,n-1}$, with the properties:

$$S(x) = S(x_k) = s_{k0} + s_{k1}(x - x_k) + s_{k2}(x - x_k)^2 + s_{k3}(x - x_k)^3,\ x \in [x_k, x_{k+1}],\ k = \overline{0,n-1} \quad (2)$$

$S(x_k) = y_k = f(x_k)$, $k = \overline{0,n}$ (the cubic Spline function passes through all data points);

$S_k(x_{k+1}) = S_{k+1}(x_{k+1})$, $k=\overline{0,n-2}$ (the cubic Spline function is a continuous function);

$S_k'(x_{k+1}) = S_{k+1}'(x_{k+1})$, $k=\overline{0,n-2}$ (the cubic Spline function is a smooth function);

$S_k''(x_{k+1}) = S_{k+1}''(x_{k+1})$, $k=\overline{0,n-2}$ (the second derivative is continuous).

If the cubic Spline function satisfies the condition $S''(x_0) = S''(x_n) = 0$ then it is called the natural Spline function. This condition is based upon the solution of the following problem: from all the functions $g \in C^2[a, b]$ which satisfy the condition $g(x_k) = y_k$, $k = \overline{0,n}$, we choose the function g that minimises the integral $\int_a^b (g''(x))^2 \mathrm{d}x$.

The solution to this problem resides in the natural cubic Spline function and has to display a minimum oscillatory behaviour since $g''(x)$ is small. The condition $S''(x_0) = S''(x_n) = 0$ has the interpretation that $S(f)$ is linear on $(-\infty, x_0)$ and $[x_n, \infty)$.

CALCULUS METHOD OF THE COEFFICIENTS

The calculus method of the coefficients s_{kj}, $k = \overline{0, n-1}$, $j = 1,3$, for the construction of natural cubic Spline function is:

$$s_{k0} = y_k,\ k = \overline{0, n-1} \quad (3)$$

$$s_{n2} = s_{n0} = 0 \quad (4)$$

$$s_{k2} = \frac{1}{\lambda_k}\left(b_{k0} - (x_{k+1} - x_k)s_{k+1,2}\right),\ k = \overline{n-1,1} \quad (5)$$

$$d_{k0} = \frac{3}{h_k h_{k-1}}\left(h_k s_{k-1,0} - (h_{k-1} + h_k)s_{k0} + h_{k-1}s_{k+1,0}\right), k = \overline{0, n-1} \quad (6)$$

$$h_k = x_{k+1} - x_k \quad (7)$$

where

$$\lambda_1 = 2(x_2 - x_0) \quad (8)$$

$$\lambda_{k+1} = 2(x_{k+2} - x_k) - \frac{(x_{k+1} - x_k)^2}{\lambda_k} \quad (9)$$

$$b_{10} = d_{10} \quad (10)$$

$$b_{k+1,0} = d_{k+1,0} - \frac{(x_{k+1} - x_k)}{\lambda_k} b_{k0}, k = \overline{1, n-2} \quad (11)$$

$$s_{k1} = \frac{y_{k+1} - y_k}{x_{k+1} - x_k} - \frac{x_{k+1} - x_k}{3}(2s_{k2} + s_{k+1,2}), k = \overline{0, n-1} \quad (12)$$

$$s_{k3} = \frac{s_{k+1,2} - s_{k2}}{3(x_{k+1} - x_k)} \overline{0, n-1} \quad (13)$$

CALCULUS MODELS OF THE COEFFICIENTS

Calculus models of the coefficients s_{kj} for the following set of points are shown in the table below.

Using Mathematica, we calculate the s_{kj} coefficients according to relations (3)–(13), we replace them in relation (2) and thus obtain function (14) which approximates the concentration evolution on the monitored sections. The graphical representation of function (14) is as shown in Fig. 5.

	s_{k0}	s_{k1}	s_{k2}	s_{k3}
$s_{0j}S_{n-1}$	59.85	102.013	0	–6.69016
	210.35	–23.427	–50.1762	14.2448
	76.75	–53.1937	35.2928	15.3893
	60.90	–6.35893	58.3768	–38.9179

$$S(x) = S(x_k) = s_{k0} + s_{k1}(x - x_k) + s_{k2}(x - x_k)^2 + s_{k3}(x - x_k)^3, x \in [x_k, x_{k+1}], k = \overline{0, n-1} \quad (14)$$

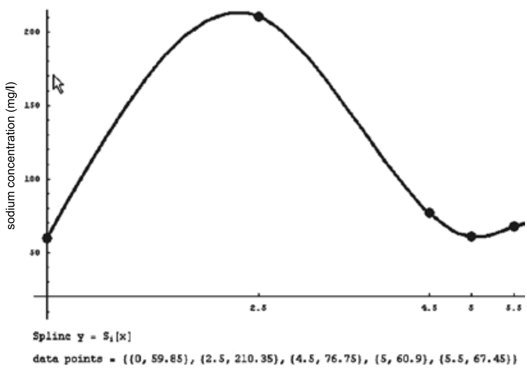

Fig. 5. The Spline function which describes the evolution of sodium concentration in the monitored sections (Table 1)

The results were obtained by using Spline functions for the evolution modelling of physical and chemical indicators taken from the Suceava and Solonet rivers (Table 5).

– Evolution of physical and chemical indicators on the Suceava river (Fig. 6).

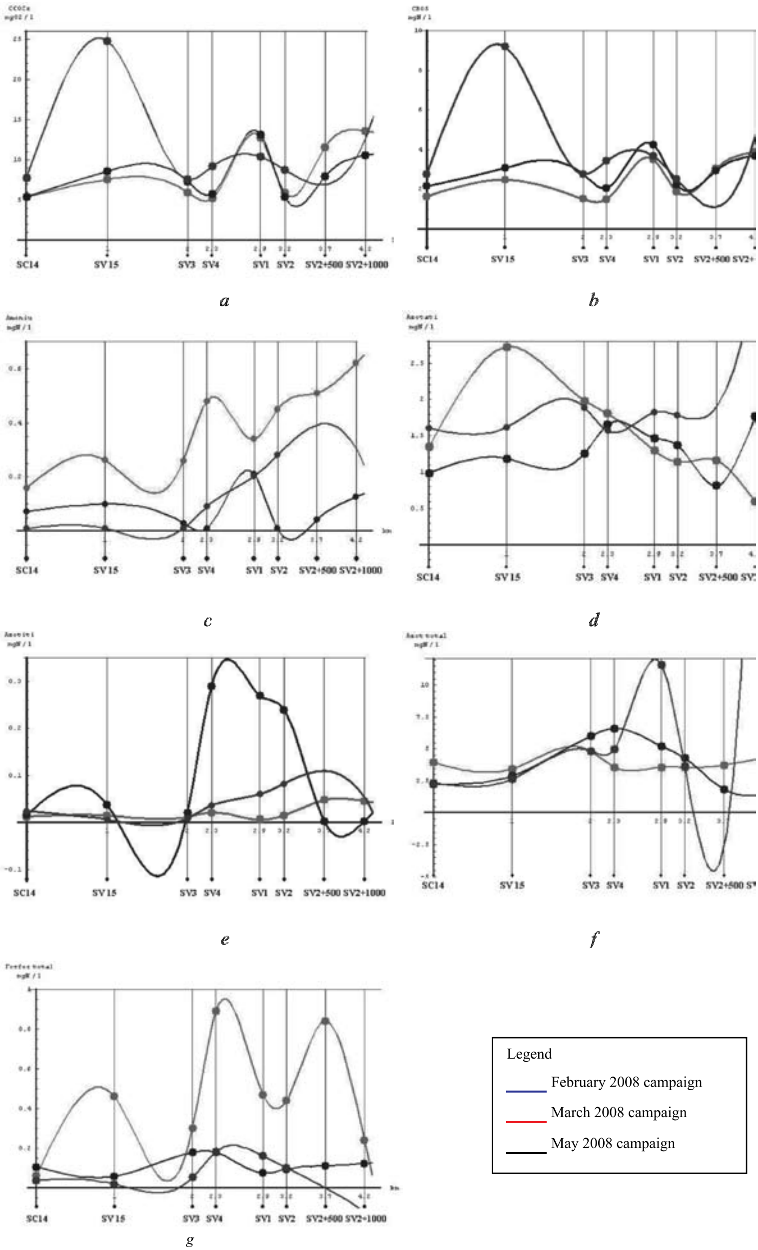

Fig. 6. Spline functions analysis of physical and chemical indicators on the Suceava river: *a* – COD; *b* – BOD; *c* – ammonium ion N–NH_4^+; *d* – nitrates N–NO_3^-; *e* – nitrite N–NO_2; *f* – total nitrogen; *g* – total phosphorus

Table 5. Spline function calculus example of sodium concentration variation on the Solonet river (spring campaign)

x_k (km), $k = \overline{0, 3}$	0	2.5	4.5	5	5.5
$f(x)$ (Na concentration, March campaign the Solonet river)	59.85	210.35	76.75	60.9	67.45
SVi (the Solonet river sections)	SV10	SV26	SV25	SV24	SV23

CONCLUSIONS

Investigations conducted in the winter–spring campaign 2008 in the considered area demonstrates:

➢ For environmental component – surface water**:**

– lengthways the entire emissary existence of 'very good' and 'good' environmental conditions, except damage points in the area of the landfill of the Municipality of Suceava and Solonet and Pozen brooks;

– value of saprobe index induces 'very good' and 'good' ecological state over the entire emissary; biocenosys zooplankton showed a reduced number of zooplankter.

➢ For environmental component – sediment:

– overcoming of the values accepted for the quality indicator cadmium in most control sections;

– benthonic macroinvertebrates present a rich heterogeneity on the upper emissary studied, the complexity and diversity oh this biocenosis being drastically reduced in other sections.

➢ For environmental component – groundwater:

– high values of quality indicator organic loading for all drillings and for quality indicator ammonium in the landfill area.

Investigations results have been integrated into a mathematical model using Spline functions that will be used later for estimating the prediction of the evolution of quality parameters in determined time intervals.

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