Report nº 2 (2019)

of the postdoctoral project

“Streamwater quality real-time data analysis”

Acronym: SQRTDA

Project leader:

Andrei-Emil Briciu (Ștefan cel Mare University of Suceava)

Mentor:

Adrian Graur (Ștefan cel Mare University of Suceava Ștefan cel Mare University of Suceava)

SUCEAVA, 2019

CONTENT

1. Introduction 3

2. Study area 5

3. Data and methods 8

4. Analyses 10

5. Conclusions 24

1. Introduction

"Streamwater quality real-time data analysis" is a scientific project of postdoctoral research funded by UEFISCDI, which aims to implement a Suceava River monitoring network upstream and downstream of the homonymous city for the collection of data on the physical and chemical properties of river water. The data obtained serves scientific analyzes and the results of the measurements can be viewed by the public in real time.

In order to achieve the project objectives, the following water quality parameters were chosen (minimum parameters required): electrical conductivity, dissolved oxygen, pH and ORP (Oxidation Reduction Potential). Additional parameters are added to these parameters: water level, water temperature.

The monitoring is performed upstream and downstream of the city of Suceava to capture the characteristics of the water immediately before entering the city and, respectively, the impact of the city on the flowing water downstream, where it can be optimally measured after the waters from the city's sewage treatment plant are well mixed with the waters of the river.

In accordance with the provisions of the work plan of the project from the Funding Application and those of the Implementation Plan of the project from the Financing Contract, the following progress has been made in 2019 in the implementation of the project:

- real-time monitoring of water quality and recording of measurement data (continuation of activity started in 2018);

- verification in the field of the operation and security of the equipment and the representativeness of the monitoring sites;

- conducting statistical and wavelet analyzes on own time series with a length of 1 year, freely accessible on the project website (in the activity report for 2019 - http://water.usv.ro/REPORT2019.pdf);

- realization of script files detailing all the steps used in the processing of water quality data (accessible on the project website in the Publications section - http://water.usv.ro/water-11-02524-s001.zip);

- writing at least 2 open access scientific articles with ISI indexing; 2 scientific articles were published that use the data obtained in the project, thank the project and can be found in the scientific journal Water (ISSN 2073-4441; CODEN: WATEGH), with impact factor 2,524 (Clarivate Analytics), being in Q2 (yellow area)) according to the Impact Factor criterion:

Briciu, A.-E .; Graur, A.; Oprea, D.I .; Filote, C. A Methodology for the Fast Comparison of Streamwater Diurnal Cycles at Two Monitoring Points. Water 2019, 11, 2524, https://doi.org/10.3390/w11122524

Briciu, A.-E. Changes in Physical Properties of Inland Streamwaters Induced by Earth and Atmospheric Tides. Water 2019, 11, 2533, https://doi.org/10.3390/w11122533

In writing is a scientific article that analyzes the water temperature of Suceava River.

- presentation of the scientific results of the project at at least 2 international scientific conferences; the data obtained through the research project were presented at 4 international scientific conferences: Environmental Quality and Land Use (XIIth edition, Suceava, Romania), Present Environment and Sustainable Development (XIVth edition, Iasi, Romania), GEO'19 Geography and Geology (IXth edition, Corfu, Greece), International Multidisciplinary Scientific GeoConference SGEM 2019 Extended Sessions SGEM Vienna Green (XIXth edition, Vienna, Austria).

Following participation in the Vienna conference, an article in extenso is accepted for publication in the conference volume (with Scopus indexing and which is proposed for ISI indexing):

Briciu, A.-E .; Graur, A.; Oprea, D.I .; Filote, C. Monitoring of Suceava River Upstream and Downstream of the Homonymous City in 2018 and 2019. SGEM Vienna Green Conference Proceedings, 2019 (in press).

2. Study area

The Suceava River runs through the middle of the city of Suceava (fig. 1) and is affected by the city through the wastewater it receives from the city's wastewater treatment plant, through uncontrolled wastewater discharged in some parts of the city and through the urban heat island. Suceava city has a population of approximately 100,000 inhabitants (including commuters), while the metropolitan area of the city reaches 150,000 inhabitants. The population affects through the uncontrolled discharges the water quality of some local, small, tributary rivers of the Suceava River, such as: Dragomirna, Șcheia, Pârâul Cetăţii, Podu Vatafului.

Suceava River in the studied area crosses a low plateau area, Suceva Plateau. The climate is temperate continental, with rainy summers. The 600 mm rainfall/year isohyet crosses the Suceava metropolitan area. The annual flow regime of the Suceava river presents high spring waters, when the snow melts, and large summer waters, when the torrential rains occur.

The monitoring point upstream of the city of Suceava is located in the small lake behind the mobile dam of Mihoveni (47.681°N, 26.2°E - fig. 2). The monitoring point downstream from the city of Suceava is located near the locality of Tișăuți (47.618°N, 26.323°E - fig. 3), downstream of the former garbage dump of the city and of the discharges of the urban water treatment plant.

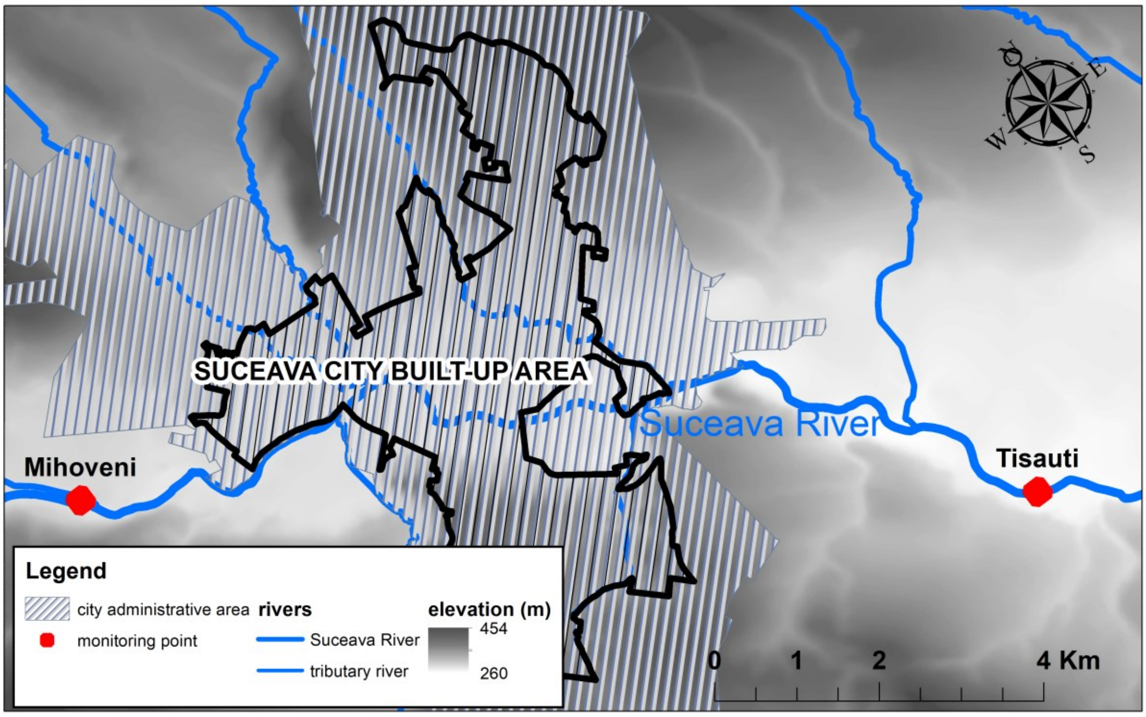


Fig. 1. Location of permanent monitoring sites in relation to Suceava city.

Fig. 2. Permanent monitoring site upstream of Suceava city (Mihoveni).

Fig. 3. Site of permanent monitoring of Suceava River downstream of Suceava city.

More details about the study area (such as data on flows and urban tributaries) can be found in the scientific articles that analyze the data obtained from the Suceava River water monitoring system, implemented through this project:

Briciu, A.-E.; Graur, A.; Oprea, D.I.; Filote, C. A Methodology for the Fast Comparison of Streamwater Diurnal Cycles at Two Monitoring Points. Water 2019, 11, 2524, https://doi.org/10.3390/w11122524

Briciu, A.-E.; Graur, A.; Oprea, D.I.; Filote, C. Monitoring of Suceava River Upstream and Downstream of the Homonymous City in 2018 and 2019. SGEM Vienna Green Conference Proceedings, 2019 (http://water.usv.ro/preprint.pdf).

In the last article listed, land use in the study area can be analyzed according to CORINE Land Cover data from 2018. Land use is directly important in the floodplain of Suceava river, where there are industrial activities, with potential pollutants.

3. Data and methods

The location of the equipment at the upstream monitoring point / Mihoveni corresponds to the left bank of the Suceava river, while the apparatus from the downstream monitoring point / Tișăuți is located approximately in the middle of the river.

The data collected by the sensors are transmitted by the Tube 300R to the server, from where they can be viewed through the HydroVu application, incorporated in the research project's website on the DATA page, accessible through the menu (http://water.usv.ro/data.php).

Each site of permanent monitoring of the water of the Suceava River has a set of instruments consisting of In-Situ equipment, as follows:

- AquaTROLL 500 multiparameter sonde, having sensors for measuring the following streamwater parameters: pressure/level (accuracy: ± 0.1% full scale (9 m), resolution: 0.01% full scale), temperature (accuracy: ± 0.1°C, resolution: 0.01°C), electric conductivity (accuracy: ± 0.5% of reading +1 µS/cm, rezoluție: 0.1 µS/cm), dissolved oxygen (accuracy: ± 0.1 mg/L, resolution: 0.01 mg/L), pH (accuracy: ± 0.1 unități pH , resolution: 0.01 pH) and ORP (accuracy: ± 5 mV, resolution: 0.1 mV) – the sensors meet the precision criteria mentioned in the Funding Application;
- Tube 300R telemetry unit - instrument with the ability to temporarily store and transmit data from measurements, being also equipped with a barometer (to compensate the air pressure measured by the AquaTROLL 500, so to obtain the water level).

Further measurements on the temperature and electrical conductivity of the water in the study area, as well as the air temperature, were carried out with the instruments TruBlue 585 CTD, TruBlue 275 Baro and iButton DS1922L-F5 #.

The data analyzed in this scientific report and in the mentioned scientific articles correspond to the continuous monitoring period October 10, 2018 - October 9, 2019 (except for the dissolved oxygen parameter, for which there is no continuous viable data between November 7 - December 5, 2018). During the one-year period (365 days) mentioned, the data were collected with an hourly frequency.

The methods by which the data obtained in the field were processed to obtain graphs and to perform wavelet analyzes are described in detail in the article "A Methodology for the Fast Comparison of Streamwater Diurnal Cycles at Two Monitoring Points" (Briciu et al., Water 2019, 11, 2524, https://doi.org/10.3390/w11122524). This article describes the use of the MATLAB program for smoothing and filtering raw data, wavelet decomposition, continuous rectified wavelet analysis (WTREC), wavelet coherence analysis (WTC) and realization of daily average profiles for the selected parameters. The types of wavelet waves used for data analysis are Haar and Morlet.

The codes used in the MATLAB console for data processing are grouped into 3 script files with the extension .m: transform.m, analyze.m and compare.m. These files can be found in the archive that represents additional material of the mentioned scientific article (where they are explained in detail) and on the project website, at http://water.usv.ro/water-11-02524-s001.zip.

The analyzes in this report use WTREC, CWT and, in addition to the mentioned article, XWT, which is the crosswavelet analysis. It runs from the console with a command

xwt(a,b), [1]

where a and b are the time series for comparison in the workspace. These time series must have the same data string length and sampling frequency. The result of the analysis is a scalogram that shows the power of resembling two strings of data through a color palette and the phasing or phase shifting of their signals by arrows with different orientations. The mother-wavelet used in the analyzes in this report is Morlet.

4. Analyses

NOTE: Some analyses and observations have been removed from this report under the embargo policy in order to ensure the research team's priority in publishing results in peer-reviewed journals. The full report is deposited at UEFISCDI.

The hourly measurements made were summarized in tables 1-3, where the monthly and annual averages, the annual standard deviations are calculated and the monthly and annual minimum and maximum values are highlighted.

The water level had maximum monthly values in May in both monitoring points. Very large differences are observed at the annual maximum values and at the annual standard deviations. These have higher values downstream of the city and indicate an increase in the degree of rainwater collection in the metropolitan area of Suceava city. This increase is due to the increased impermeability downstream of the Suceva river basin (between monitoring points) as a result of the numerous surfaces covered with concrete, asphalt, stone and roofs. The rainwater collected in the city of Suceava is, to a large extent, rapidly evacuated to the Suceava river, contributing to the increase of the maximum values recorded. The highest monthly maximum values are recorded in June at both points.

Dissolved oxygen (DO) has an approximately inverse evolution to that of water temperature due to the dependence of the amount of gas dissolved on the temperature of the liquid. The highest monthly average values were measured in December at both permanent monitoring points, while the lowest monthly minimum values for the year were measured in August-September. The annual average dissolved oxygen is almost 2 mg / L lower downstream from the upstream part of it. The difference is caused by water pollutants, which consume oxygen for chemical reactions.

The specific conductivity (SC, at 25 ° C) has a naturally dependent evolution on the precipitations that fall in the Suceava river basin. In periods between rains, SC tends to values of approx. 600 µS / cm, while in rainy times, the SC is approaching 300 µS / cm. The lowest values are recorded in May and the highest values at the end of autumn and winter. The annual values show an increase of the mean, minimum, maximum and standard deviation from Mihoveni to Tișăuți, caused by the contamination of the water, especially with the water from the treatment plant.

Table 1. Mean, minimum and maximum monthly values of the water parameters of the Suceava river studied at the monitoring point upstream of the city of Suceava (in Mihoveni).

	DO (mg/L)	SC (µS/cm)	ORP (mV)	pH (unit)	level (m)
Monthly averages					
J	13.1	587.1	427.5	8.4	0.7
F	12.7	498.5	432.6	8.5	0.8
M	11.6	424.9	422.2	8.5	0.8
A	10.7	410.9	405.9	8.5	0.8
M	9.7	369.0	394.7	8.4	1.0
J	8.6	414.1	372.7	8.4	0.9
J	8.6	493.2	424.3	8.5	0.8
A	7.8	471.1	423.4	8.5	0.8
S	8.4	514.5	455.7	8.5	0.7
O	10.8	512.5	383.2	8.4	0.7
N	12.2	543.3	413.2	8.4	0.7
D	13.3	557.7	392.6	8.5	0.7
Monthly minima					
J	11.9	554.9	378.2	8.3	0.7
F	11.6	386.8	399.1	8.3	0.7
M	10.4	331.0	374.5	8.3	0.8
A	8.8	275.9	376.4	8.2	0.7
M	7.3	224.6	318.8	7.9	0.5
J	7.3	251.4	293.1	7.9	0.7
J	5.9	309.8	373.0	8.2	0.7
A	5.2	400.2	374.9	8.3	0.7
S	5.3	482.0	430.0	8.3	0.6
O	8.0	474.0	301.3	8.0	0.6
N	8.8	497.6	392.8	8.1	0.7
D	11.4	494.9	359.8	8.3	0.6
Monthly maxima					
J	14.7	659.2	447.6	8.6	0.8
F	13.9	573.1	449.2	8.5	1.0
M	13.8	517.8	443.1	8.6	1.0
A	12.2	489.3	435.8	8.6	1.4
M	11.6	444.7	431.2	8.6	1.4
J	10.0	537.8	444.0	8.6	1.5
J	10.9	543.2	459.0	8.6	1.1
A	9.9	550.9	457.8	8.7	0.9
S	10.7	548.0	469.5	8.6	0.7
O	13.9	561.4	470.3	8.7	0.7
N	14.6	594.4	434.2	8.5	0.8
D	15.2	635.6	427.5	8.6	0.8

Table 2. Mean, minimum and maximum monthly values of the water parameters of the Suceava river studied at the monitoring point downstream of the city of Suceava (in Tișăuți).

	DO (mg/L)	SC (µS/cm)	ORP (mV)	pH (unit)	level (m)
Monthly averages					
J	12.4	699.2	409.7	8.3	0.8
F	12.2	568.9	371.4	8.4	1.0
M	10.4	477.2	370.7	8.1	1.0
A	8.5	459.8	333.4	8.5	1.0
M	8.4	403.3	328.0	8.3	1.4
J	7.5	444.3	288.5	8.3	1.3
J	6.1	536.7	297.9	8.1	0.8
A	6.1	529.1	256.9	8.1	0.7
S	6.0	590.2	305.7	7.8	0.5
O	7.9	576.0	372.4	8.0	0.7
N	8.4	643.3	381.9	8.0	0.7
D	12.4	660.1	341.5	8.6	0.8
Monthly minima					
J	9.3	626.8	337.2	7.6	0.7
F	10.3	440.4	323.9	7.8	0.8
M	8.3	371.7	287.4	7.9	0.9
A	5.4	301.1	286.4	8.0	0.9
M	4.8	250.5	289.9	7.6	1.1
J	3.7	283.3	220.8	7.9	0.9
J	2.5	361.3	219.7	7.7	0.7
A	2.9	445.7	197.0	7.6	0.5
S	2.1	549.0	202.3	7.5	0.4
O	4.2	516.0	266.9	7.6	0.4
N	5.8	585.7	297.3	7.7	0.7
D	8.6	570.7	281.1	8.0	0.6
Monthly maxima					
J	15.8	778.2	460.4	8.6	0.9
F	13.9	708.3	442.8	8.6	1.2
M	13.7	576.8	412.2	8.6	1.4
A	11.0	526.9	391.6	9.1	2.1
M	11.1	471.3	378.2	8.8	2.2
J	9.8	606.3	364.0	8.8	2.6
J	9.1	589.0	345.8	8.9	1.4
A	10.6	593.4	312.7	8.6	1.0
S	10.0	625.6	425.1	8.3	0.6
O	12.7	622.6	437.2	8.6	0.8
N	11.9	794.4	424.1	8.5	0.9
D	14.7	779.9	413.2	9.3	0.9

Table 3. Annual statistical indicators of the water parameters of the Suceava River studied in the two monitoring points.

	DO (mg/L)	SC (µS/cm)	ORP (mV)	pH (unit)	level (m)
Mihoveni					
Average	10.60	483.07	412.16	8.45	0.79
Minimum	5.21	224.61	293.09	7.89	0.51
Maximum	15.16	659.16	470.27	8.71	1.47
Standard dev.	2.06	72.35	32.11	0.09	0.12
Tişăuţi					
Average	8.82	549.00	338.01	8.22	0.90
Minimum	2.12	250.51	196.97	7.47	0.40
Maximum	15.81	794.36	460.42	9.29	2.56
Standard dev.	2.69	97.90	52.97	0.31	0.31

The pH and ORP values are less contrasting from one month to the next and from one monitoring point to the other. Lower values can be observed in the late summer and early autumn, when the low level of the Suceava river, correlated with the high air temperature, predisposes to low values. There are decreases in pH and ORP downstream as a result of urban wastewater discharges.

The evolution of the hourly values of some parameters shows diurnal and annual cyclicities (fig. 4-7). These cyclicalities are manifested separately for each parameter. There are some atypical variations in the water level in Mihoveni, caused by mobile dam operations (during floods).

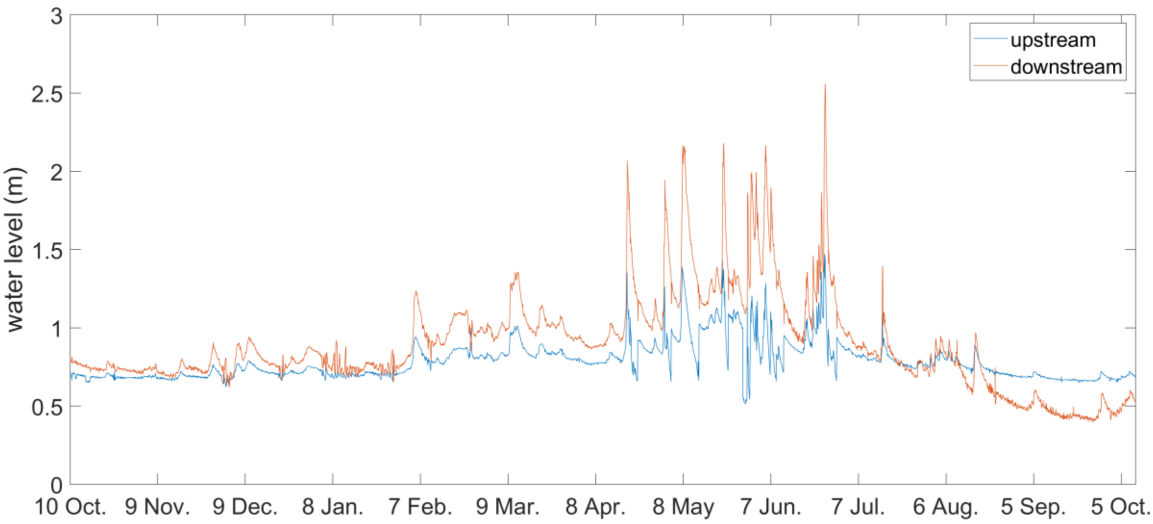
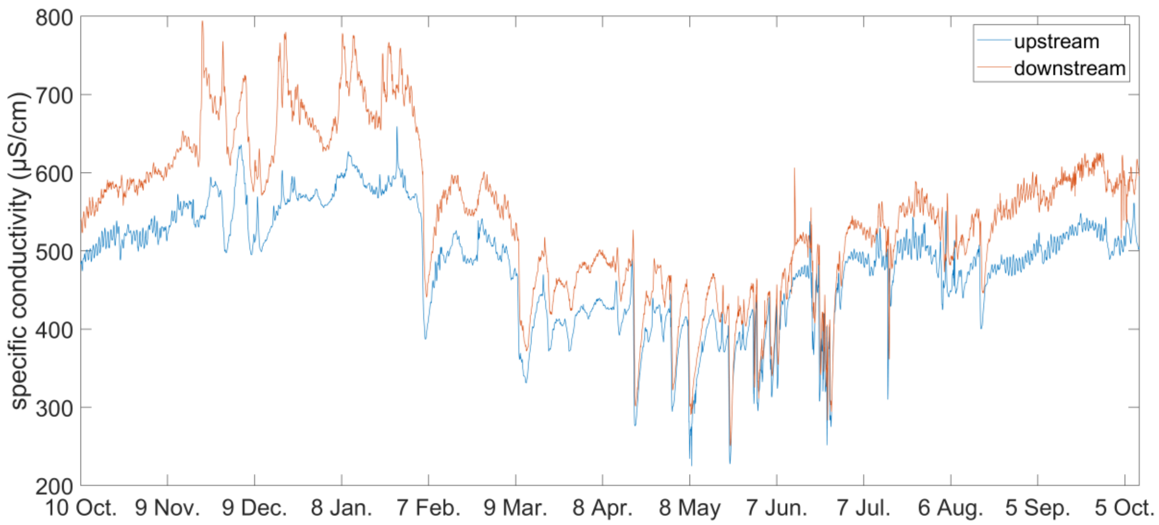
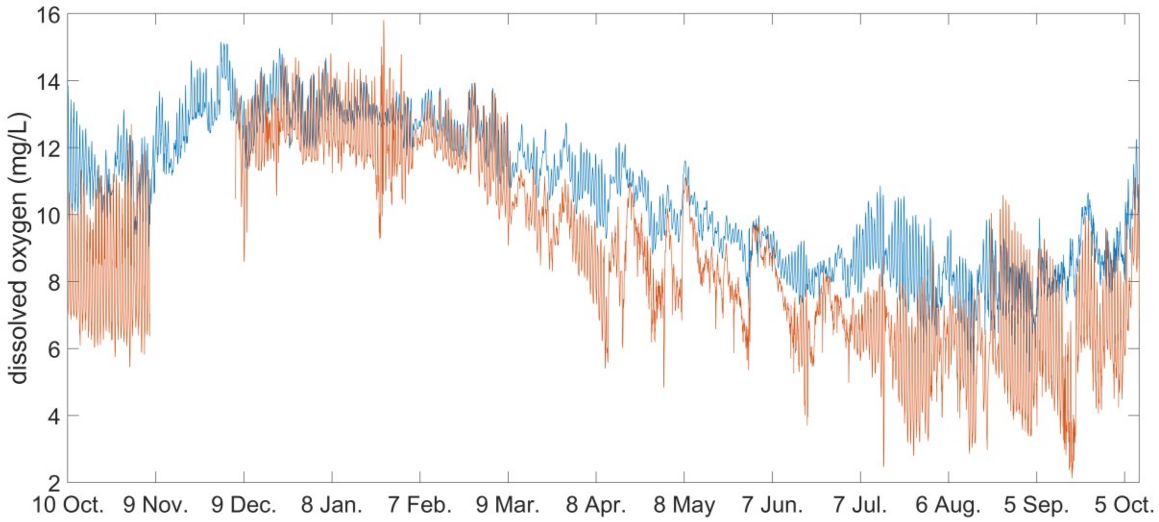


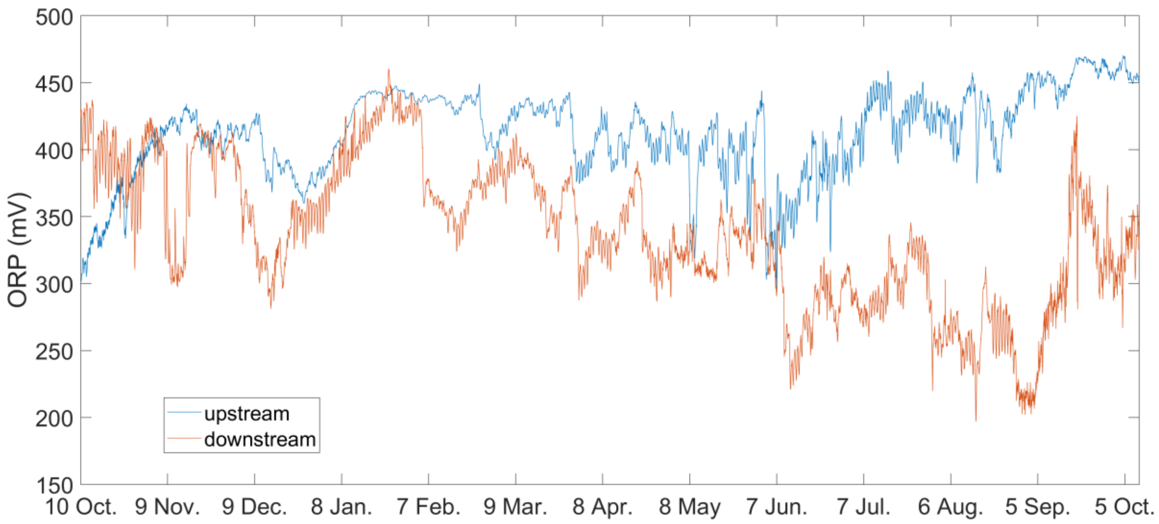
Fig. 4. Evolution of the hourly values of the water level of the Suceava River for 365 days, between October 10, 2018 - October 9, 2019 in Mihoveni (upstream of Suceava city) and in Tișăuți (downstream).



a



b



c

Fig. 5. Evolution of the hourly values of SC (a), DO (b) and ORP (c) in Suceava river water for 365 days, between October 10, 2018 - October 9, 2019 in Mihoveni (upstream of Suceava city) and in Tişăuți (downstream).

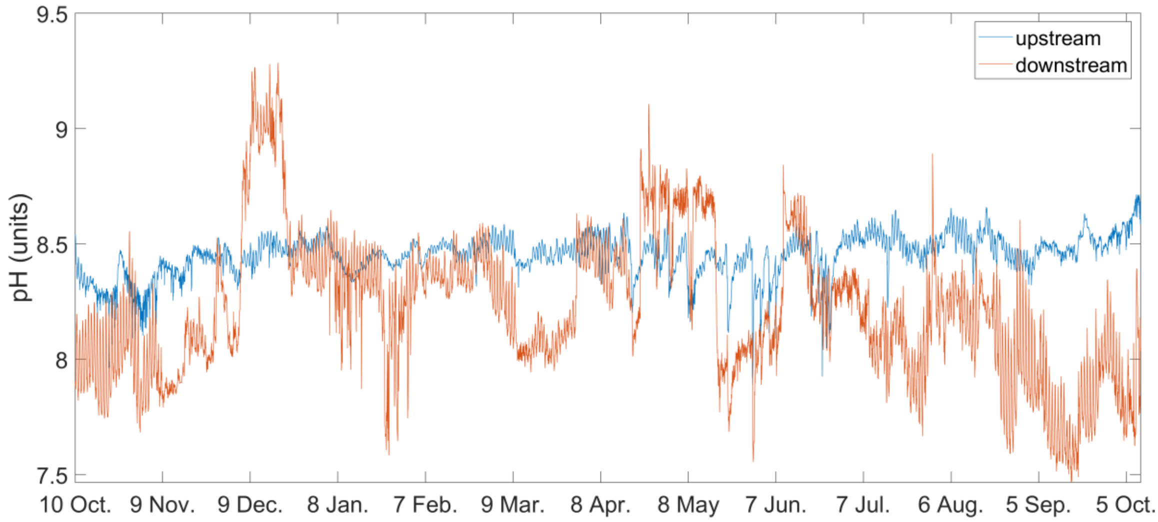


Fig. 6. Evoluția valorilor orare ale pH-ului apei râului Suceava timp de 365 zile, în perioada 10 octombrie 2018 - 9 octombrie 2019 la Mihoveni (amonte de orașul Suceava) și la Tișăuți (aval).

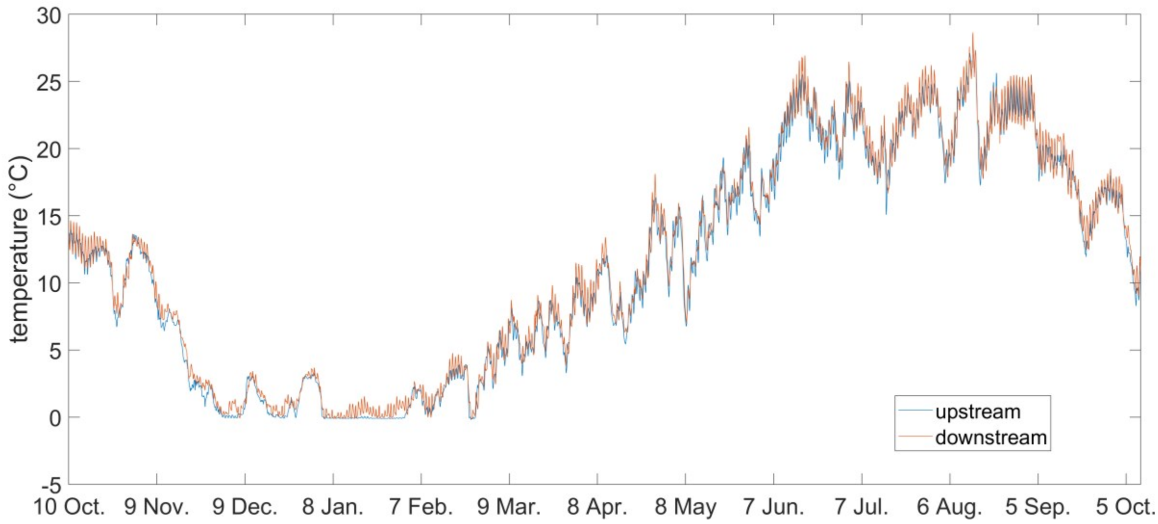


Fig. 7. Evolution of the hourly values of the water temperature of Suceava river for 365 days, between October 10, 2018 - October 9, 2019 in Mihoveni (upstream of Suceava city) and in Tișăuți (downstream).

The WTREC scalograms are useful for identifying major events and periodicities in data strings (Fig. 8-10). The areas with statistical significance are represented by areas having a red color and surrounded by a black line. We notice the period of the great summer waters, which also affect SC. In the case of SC, ORP, pH and DO, a diurnal cyclicity is observed in the form of a horizontal strip (near the periodicity of 24 h on the vertical axis). This band is discontinuous due to the non-linearity of the hydrological processes. Specifically, there is a very large variation of the diurnal cycles for the same parameter at the same monitoring point. Many factors affect the diurnal cycles, caused by the evapotranspiration in the river basin, e.g. big waters.

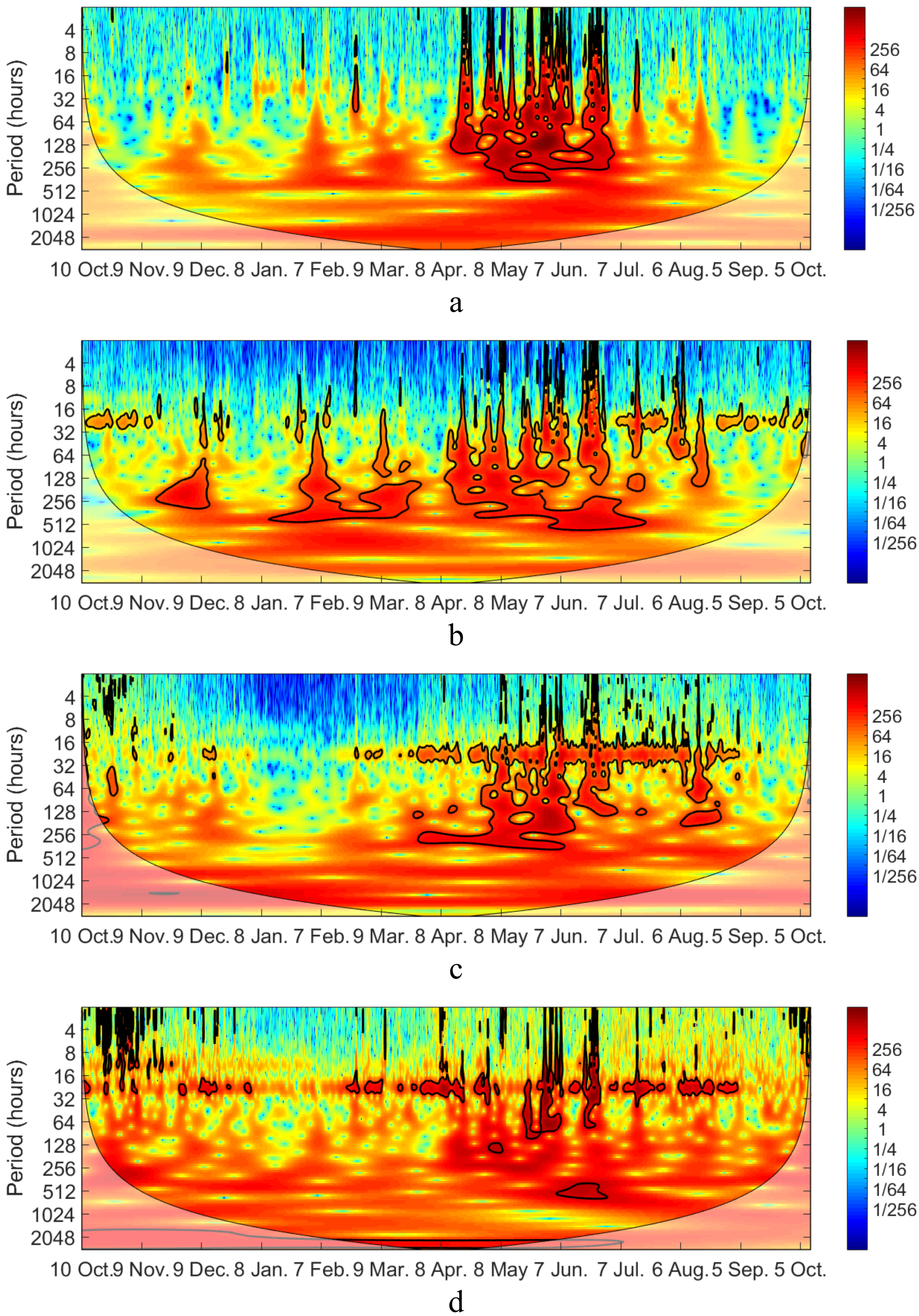
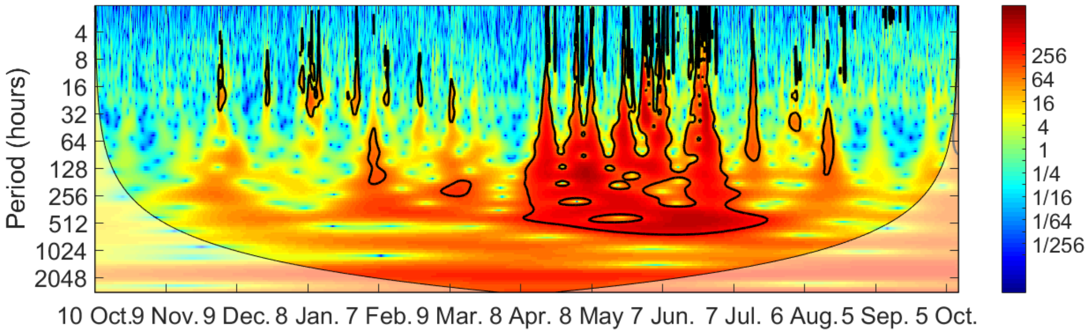
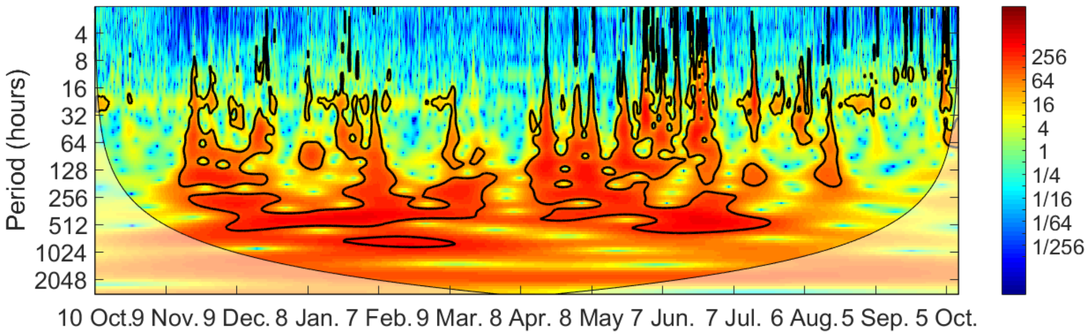


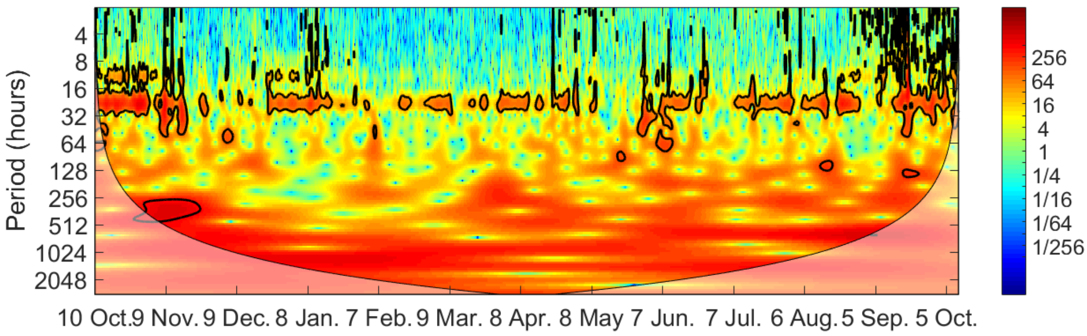
Fig. 8. Continuous wavelet analysis (WTREC) of hourly values of level (a), specific conductivity (b), ORP (c) and pH (d) of Suceava river water measured in Mihoveni (upstream of Suceava city) for the period October 10, 2018 - October 9, 2019.



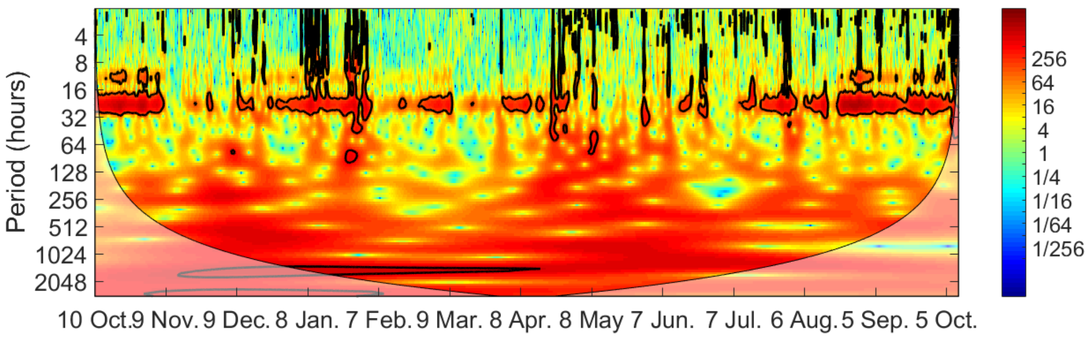
a



b



c



d

Fig. 9. Continuous wavelet analysis (WTREC) of hourly values of level (a), specific conductivity (b), ORP (c) and pH (d) of Suceava river water measured in Tişăuţi (downstream of Suceava city) for the period October 10, 2018 - October 9, 2019.

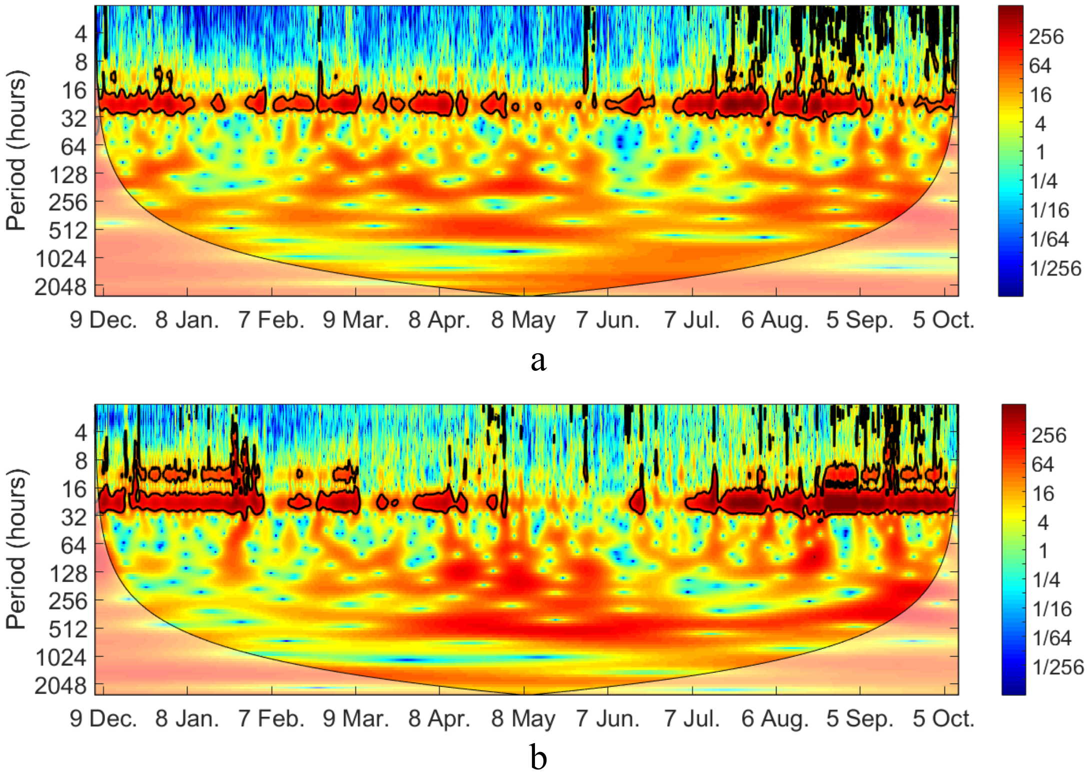
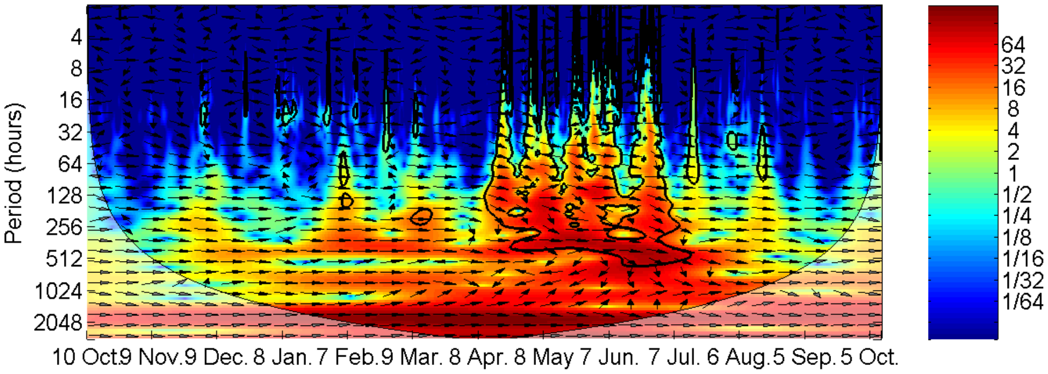


Fig. 10. Continuous wavelet analysis (WTREC) of the hourly values of oxygen dissolved in Suceava river water measured at Mihoveni (a) and Tișăuți (b) between December 6, 2018 - October 9, 2019.

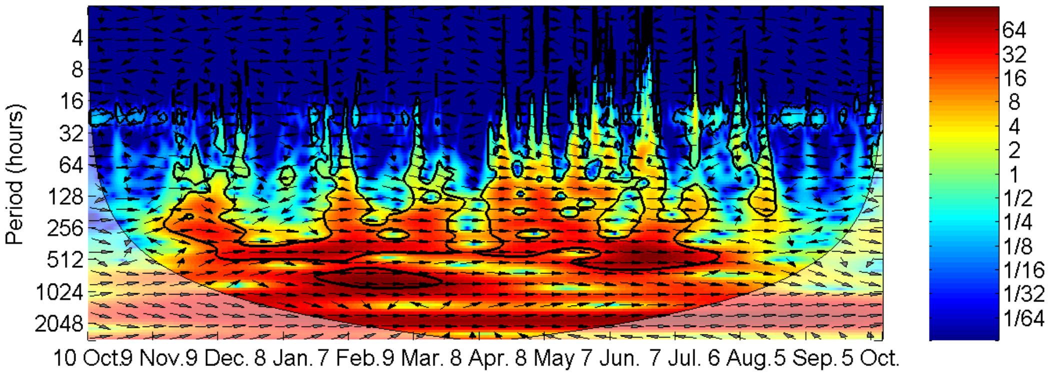
Technical details regarding the wavelet analyzes performed are provided in the methodology sections of the 2 open access articles published in the Water journal, mentioned in the Introduction chapter of this report. These articles also detail the diurnal cyclicalities specific for the level, SC, OD, ORP and pH, both on an annual scale and at the level of several representative days for the basic level leakage, between rains.

Cross-wavelet analysis produces a scalogram that is similar to a two-dimensional correlation between 2 data strings. On the horizontal axis is the linear time, while on the vertical axis are the time scales at which periodicities may or may not occur. The intensity of the correlation is measured with a palette of colors from blue to red, the latter color becoming dominant at low / wide frequencies (with large number of hours) if the time series involved in the analysis have similar long-term evolutions. The arrows on the scalograms indicate the phase (when the phase arrows point to the right) or the anti-phase (to the left) of the evolution of the 2 time series.

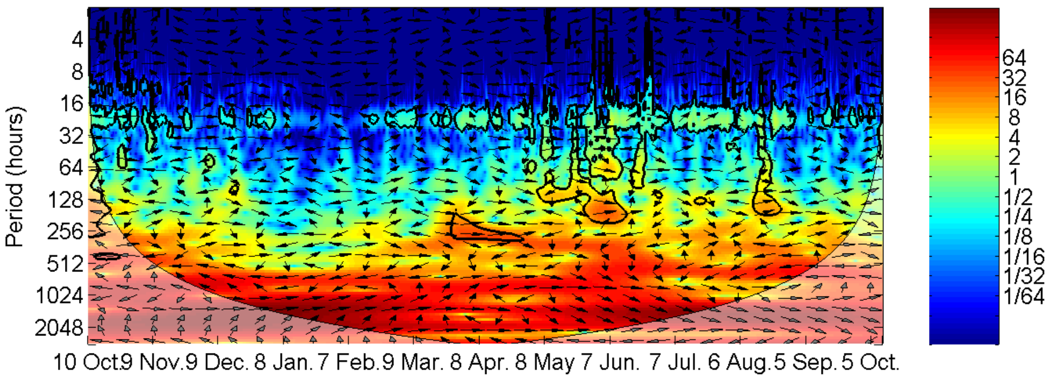
The time series of Do, ORP and pH have good correlation of the shapes of the diurnal cycles upstream and downstream of Suceava city, especially for DO.



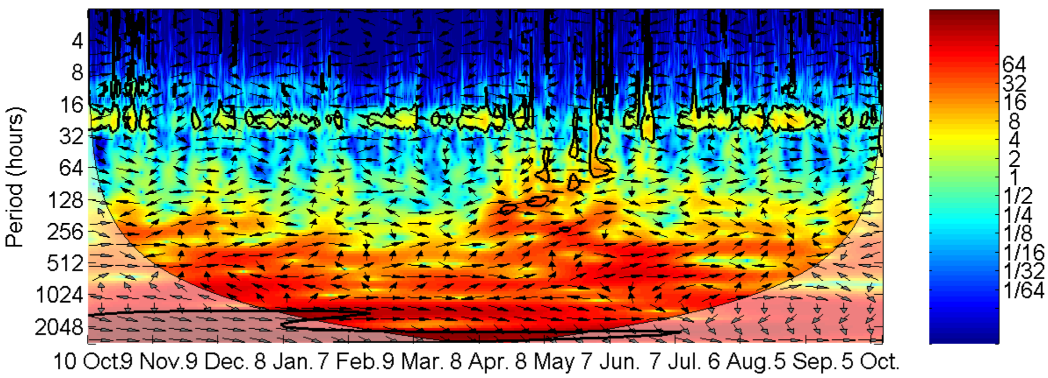
a



b



c



d

Fig. 11. Cross- wavelet analysis (XWT) of hourly values of level (a), SC (b), ORP (c) and pH (d) of Suceava river water measured in Mihoveni and Tișăuți between October 10, 2018 - October 9, 2019

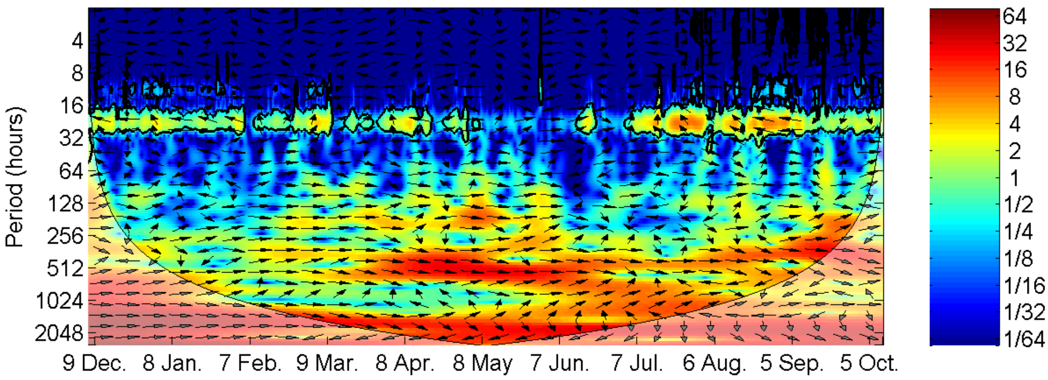


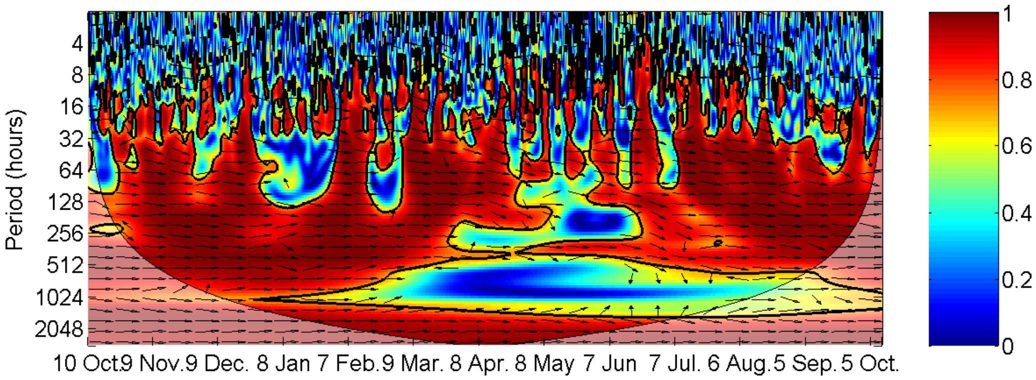
Fig. 12. Cross-wavelet analysis (XWT) of hourly values of oxygen dissolved in Suceava river water measured at Mihoveni and Tișăuți between December 6, 2018 - October 9, 2019.

The analysis of the wavelet coherence (CWT) of two time series shows the intensity of the co-variance of the detected periodicities. Thus, the water level in the 2 monitoring points has similar evolutions (in the phase) throughout the year, except at the sub-diurnal scale throughout the year and at the over-scale during the summer and of the high waters (Fig. 13.a). The high waters have different behaviors in Mihoveni and Tișăuți, on one hand due to the mobile dam, which raises the weirs during the floods, leading to the temporary decrease of the water level, and, on the other hand, due to the rainwater collected in excess from the metropolitan impervious surfaces.

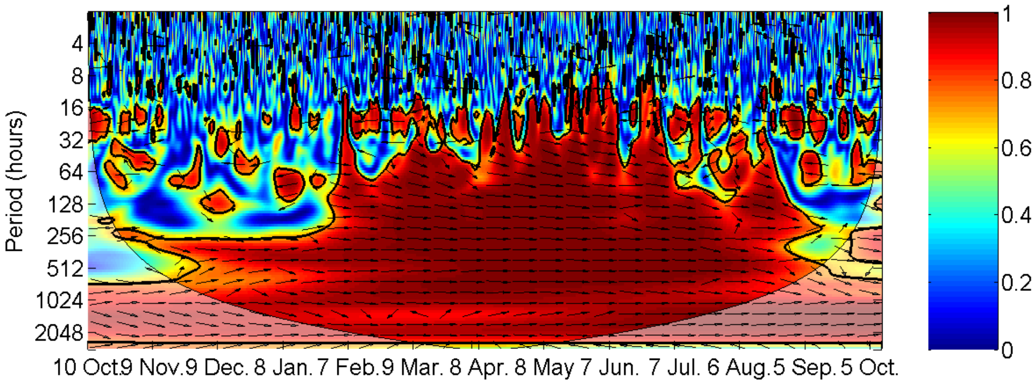
The SC has diurnal cycles that are almost in the antiphase, while the super-diurnal evolution, especially the super-weekly, is in phase, especially during the high summer waters (Fig. 13.b). The latter observation implies that rains reduce the conductivity values at a common denominator, regardless of the location of the monitoring site and the sources of pollution.

Daytime cycles that are approximately antiphase also record ORP, pH and DO (Figs. 13-14). A similar long-term evolution is missing for these parameters, except for the DO, which has a super-weekly evolution that is in phase for the 2 permanent monitoring points (but has a low statistical representativeness).

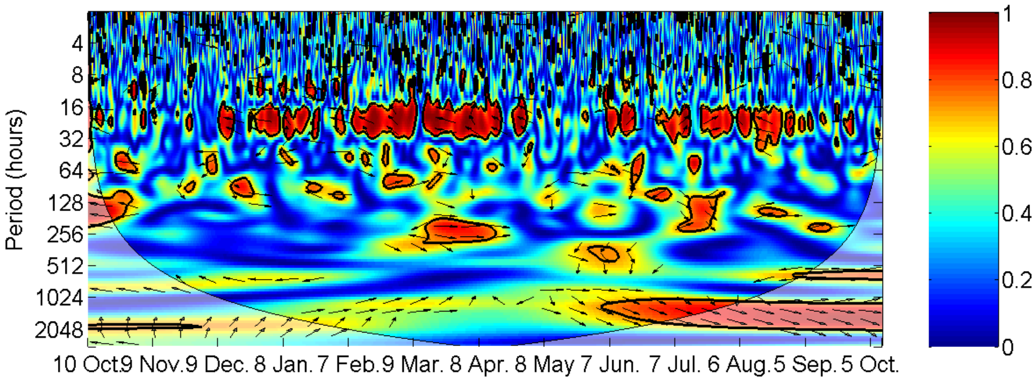
The limited length of time series has consequences on the detection of periodicities through wavelet analysis. Thus, the annual cyclicality does not appear on the scalograms because a longer string of data is needed which will increase the size of the influence cone. Inside it, the colors are rendered at maximum intensity and indicates that the detected periodicities are not affected by edge effects, which are increasingly important at lower frequencies / higher wavelengths. The vertical scale relevant to the 365-day string is limited to approximately 100 days.



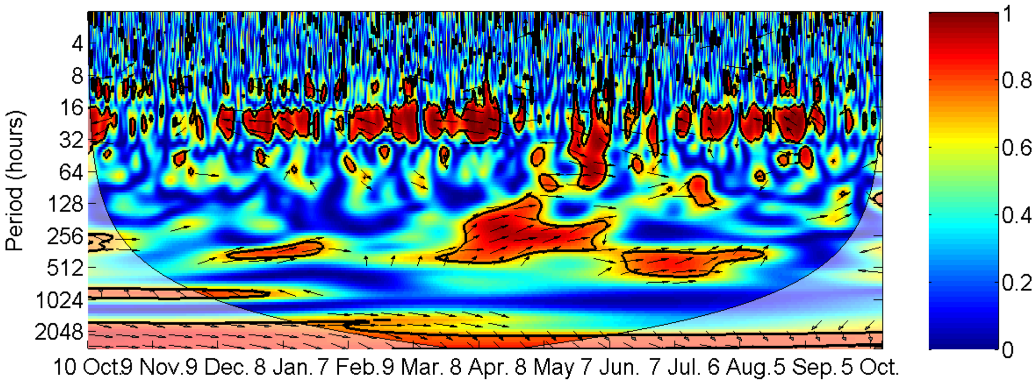
a



b



c



d

Fig. 13. Wavelet coherence analysis (WTC) of hourly values of level (a), SC (b), ORP (c) and pH (d) of Suceava river water measured in Mihoveni and Tişăuți between October 10, 2018 - October 9, 2019

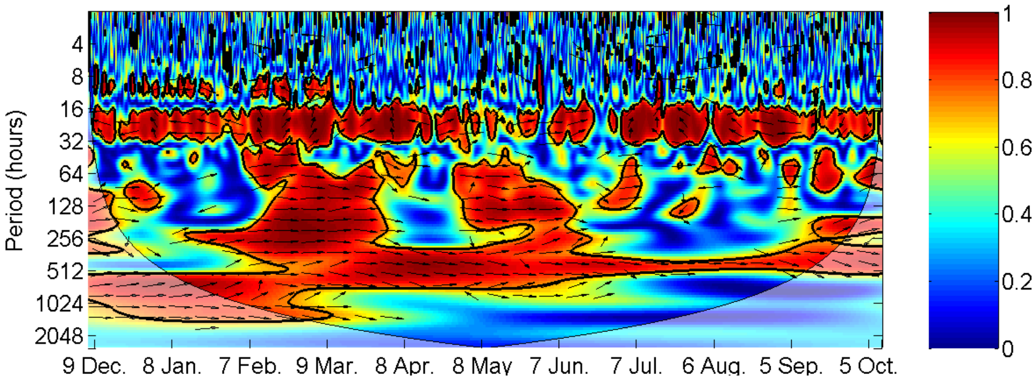
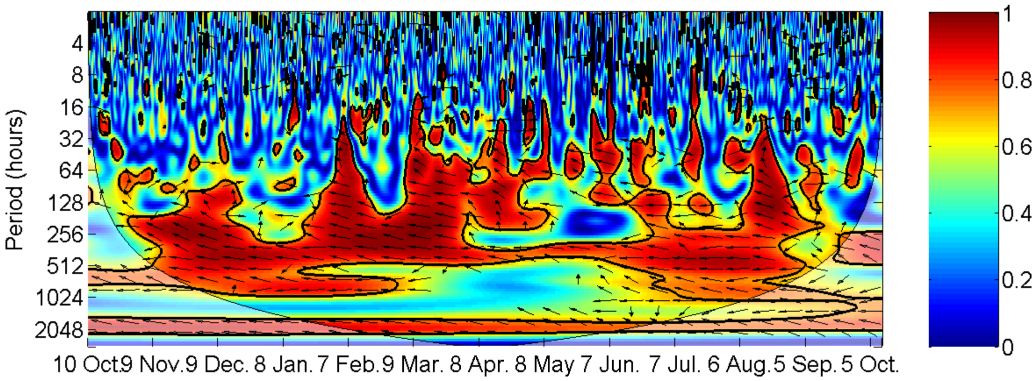
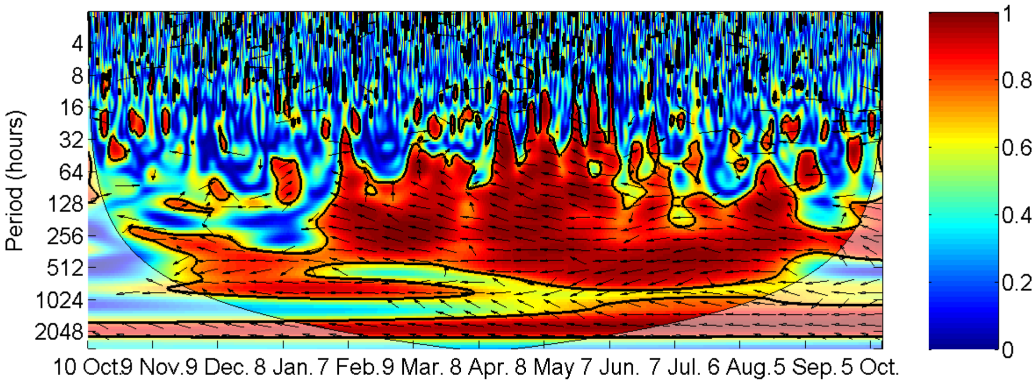


Fig. 14. Analysis of the wavelet coherence (WTC) of the hourly values of the dissolved oxygen in the Suceava river water measured at Mihoveni and Tișăuți between December 6, 2018 - October 9, 2019.

The analysis of the wavelet coherence (WTC) performed between different parameters for the same monitoring point shows possible causal relationships between the analyzed parameters (fig. 15-16). The constant antiphase and with high statistical significance between the diurnal cycles of SC and pH are observed at both monitoring points.



a



b

Fig. 15. Analysis of the wavelet coherence (WTC) of the hourly values of the specific level and conductivity measured at Mihoveni (a) and Tișăuți (b) between October 10, 2018 - October 9, 2019.

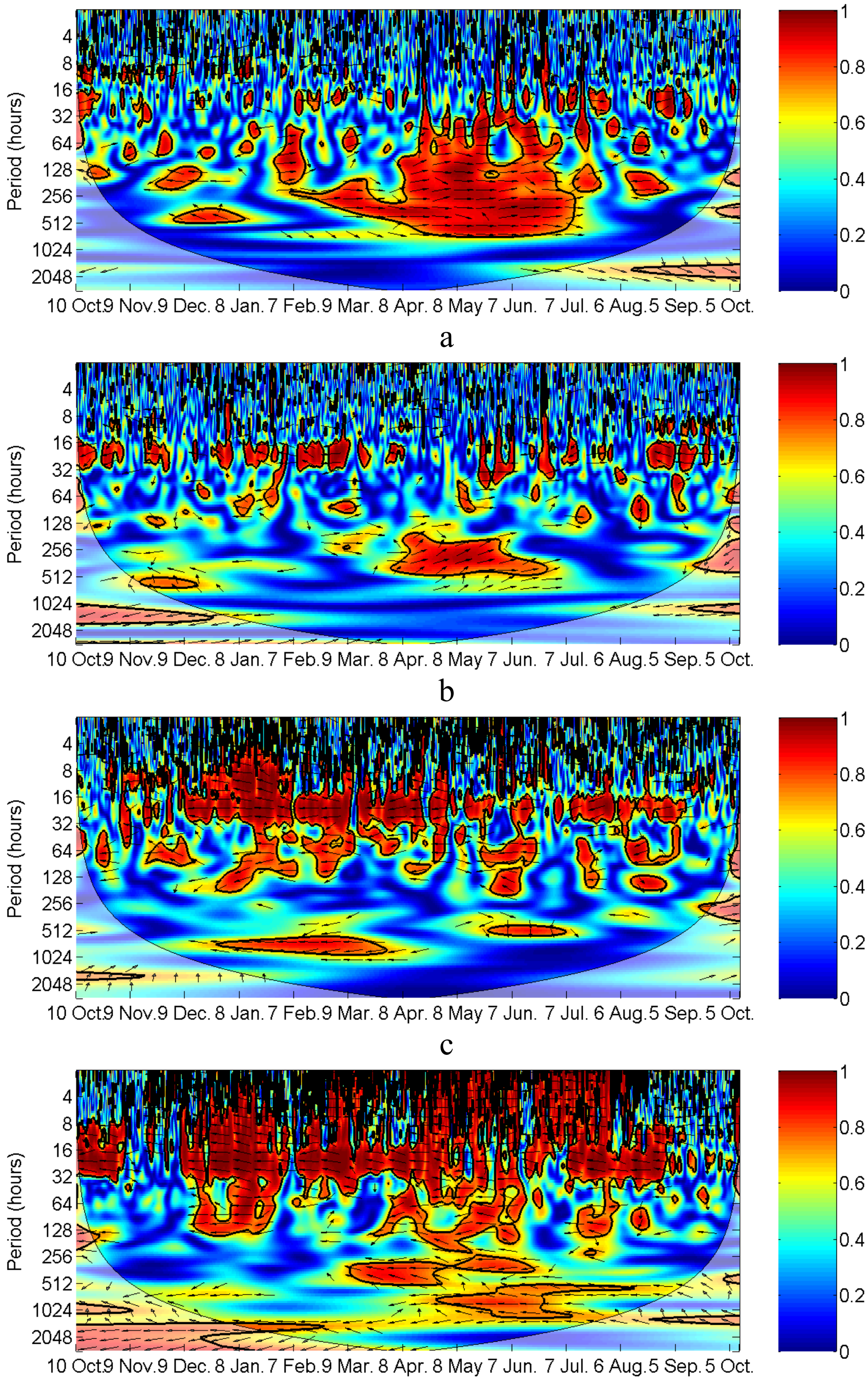


Fig. 16. Analysis of the wavelet coherence (WTC) of the hourly values of the specific conductivity and pH measured in Mihoveni (a) and Tișăuți (b) between October 10, 2018 - October 9, 2019; idem for pH versus ORP upstream (c) and downstream (d).

1. Conclusions

The measurements made allowed for the analysis of 365 days long time series. The analyzed parameters are: water level, temperature, specific conductivity, dissolved oxygen, ORP and pH.

In order to understand the data, statistical indicators were calculated, graphs were made and wavelet analyzes were applied. The applied wavelet analyzes are of the type of continuous wavelet transformations, of the type of cross wavelet analyzes and of the type of wavelet coherence analyzes.

The present report and the scientific studies published so far from the project data have focused on the analysis of the diurnal cycles, which are a good indicator of the transformations to which Suceava River is subjected after the transit of the homonymous city.

Through the discharge of urban wastewaters and through the urban heat island, the city of Suceava changes the characteristics of the Suceava River. Thus, between October 10, 2018 - October 9, 2019, the average annual values of the parameters measured upstream (Mihoveni) and respectively downstream (Tișăuți) of Suceava city were: 10.6 mg/L vs 8.82 mg/L - dissolved oxygen, 483.07 µS/cm vs 549 µS/cm - specific conductivity, 412.16 mV vs 338.01 mV – ORP and 8.45 vs 8.22 - pH.

Acknowledgement: *This work was supported by a grant of Ministery of Research and Innovation, CNCS - UEFISCDI, project number PN-III-P1-1.1-PD-2016-2106, within PNCDI III.*