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PHYSICO–CHEMICAL CHARACTERISTICS AND WASTEWATER QUALITY INDEX FOR EVALUATING THE EFFICIENCY OF TREATMENT PROCESS EFFLUENT

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Abstract
As is known all forms of life depend on water. Water is a vital part of many metabolic processes inside the body. By increasing the world population, increasing global pollution and global warming, fewer people benefit from water. This problem can be solved by increasing water production, better distribution and disruption existing resources. For this reason, water is a strategic resource for many countries. Regarding to this, is important to protect the water resources from the action of pollutants and to monitor the quality of the water already existing. Wastewater is composed of different proportions of residual water from domestic or industrial origin and rainwater. To evaluate the quality of wastewater various parameters are available but for common people it is difficult to understand the meaning of this values. The concept of Water Quality Index (WQI) has been developed by representing it as numeric value for easy and quick understanding of quality of the water. This study aimed to assess the wastewater quality of 8 sampling stations in Valcea County. The data were collected over a five years' period (2013-2017) from each sampling point and the physical-chemical parameters were analysed to evaluate the variations registered in the study period.

Keywords*: basic statistical, quality index, wastewater*

Introduction
The influent composition at the entrance of the wastewater treatment plant is due to the different types of contaminants present in the initial waters. For example, the wastewater can contain mainly organic compounds and various microorganisms (bacteria, viruses, parasites) while the rainwater can contain especially inorganic and mineral compounds (Petrescu et al 2017, Bucur et al 2010).
In 1970s the concept of Water Quality Index (WQI) has been developed for easy understanding of water quality by representing it as numeric value between 0 (Poor) to 100 (Excellent) (Mudiya 2012, Vijayan et al 2016). Similarly, the wastewater quality index (WWQI) may be considered as a useful tool to provide information about the degree to which the wastewater is polluted by human activities. Wastewater quality index is a dimensionless number that depends on the combination of chemical, physical, and microbiological parameters. It consists of sub-index scores attributed to each parameter by comparing the measurement values

with the specified parameter estimation curve and calculated in the final index (Dede et al 2017).

In this paper the wastewater quality index of the effluents from different wastewater treatment plants was evaluated. The samples were taken with a monthly frequency between 2013 and 2017, from eight sampling points situated in Valcea County. The parameters considered for this study were. The wastewater quality assessment was based on the comparison of the experimentally determined values with the limits imposed by the legislation, NTPA-001 Quality Norm (NTPA 001 2005). The analytical results were used for the evaluation of the wastewater quality index (WWQI) and, based on basic statistical technique, were correlated with sampling points.

Materials and Methods

Sampling

This study evaluates the quality of effluents from eight wastewater treatment plants situated in Valcea County, Romania: Ramnicu Valcea, Govora, Babeni, Olanesti, Calimanesti, Dragasani, Horezu and Voineasa (Figure 1). The effluents are discharged in local emissaries or directly in Olt River. The samples were taken with a monthly frequency between 2013 and 2017. Samples were collected in polythene bottles and preserved, function of the type of indicators, by acidulation at pH <2 or by keeping them at 4^0C, in the dark.

Figure 1. VALCEA County, location of sampling points

Reagents and chemicals

For calibration of the equipment, for calculation of the uncertainty of measurement, and also for plotting points in control charts Reference Materials (MR) and Certified Reference Materials (MRC) were used. All the reagents (Merck and Sigma) used in the determinations were of analytical purity.

Methods

The physical-chemical parameters: pH, Suspended solids (SS), Total dissolved solids (TDS), Chemical Oxygen Demand (COD), Bio-chemical Oxygen Demand (BOD_5), chlorides (Cl^-), ammonia (NH_4^+), Total Phosphorus (P), Sulphides (S^{2-}), Total oil and grace (TOG), Anionic surfactants (AS), sulphate (SO_4^{2-}), Total Nitrogen (TN) were analysed using electrochemical, volumetric, UV-VIS spectrometry and combustion methods. All analyses were performed under accreditation system, according to SR EN ISO 17025:2015 reference standard (SR EN ISO 17025:2015, 2005).

Water Quality Index

The Water Quality Index has become an important decision-making tool for the authorities. In the same sense, the development of Water Quality Indicators has become an important tool for authorities and is easy to understand for population various methodologies are available for determining the quality of wastewater.

The Canadian Water Quality Index (CCMEWQI) (CCME 2001, 2005) provides a comprehensive method of calculating quality index that allow the transmission of water quality information to the management involved in water quality testing.

The wastewater quality index (WQI) measures the scope, frequency and amplitude of water quality over runs and then combines the three measures into a score. The higher the score, the better the water quality is. The wastewater quality (WQI) index is a useful tool for assessing the degree of wastewater pollution.

The mathematical expression for the Quality Council of the Canadian Council of

$$WWQI = 100 - \frac{\sqrt{F_1^2 + F_2^2 + F_3^2}}{1.732} \quad (1) \qquad F_1 = \frac{Failed\ tests}{Total\ tests} \times 100 \quad (2)$$

$$excursion = \frac{\text{Failed tests value}}{\text{guidelaine value}} - 1 \quad (3) \qquad nse = \frac{\sum excursion}{\text{Total of tests}} \quad (4) \qquad F_3 = \frac{nse}{1.01nse + 0.01} \quad (5)$$

Ministers for the Environment (CCMEWQI) is:

where: Scope (F1) = number of quality indicators determined, whose values exceed the maximum allowed by law, Frequency (F2) = Number of tests of determined quality indicators, the values of which exceed the maximum allowed by the legislation, and Amplitude (F3) = individual value for each test of the determined quality indicators, the values of which exceed the maximum allowed by the legislation. The index values function of the main characteristics of wastewater are described in Table 1.

Table 1. Criteria according to Canadian Council of Ministers of the Environment, Water Quality Index (CCMEWQI)

Designation	Index Value	Description
Excellent	95-100	All measurements are within objectives virtually all of the time
Good	80-94	Conditions rarely depart from natural or desirable levels
Fair	65-79	Conditions sometimes depart from natural or desirable levels
Marginal	45-64	Conditions often depart from natural or desirable levels
Poor	0-44	Conditions usually depart from natural or desirable level

Results and Discussion

Using the Water Quality Indicator of the Canadian Environment Ministers Council (CCMEWQI), the quality of effluents from 8 wastewater treatment plants from Valcea county was assessed.

The results obtained for the analysed parameters were compared with the maximum limits allowed by the NTPA-001 (Table 2).

Table 2. Maximum admissible value (MAV) according to NTPA-001 Quality Norm

Determined parameter	MU	MAV
pH	pH units	6.5-8.5
SS	mg/L	35(60)
TDS	mg/L	2000
COD	mg O_2/L	125
BOD_5	mg O_2/L	25
Cl^-	mg/L	500
NH_4^+	mg/L	2(3)
P	mg/L	1(2)
S^{2-}	mg/L	0.5
TOG	mg/L	20
AS	mg/L	0.5
SO_4^{2-}	mg/L	600
TN	mg/L	10(15)

In this study, for the assessment of wastewater quality, 4184 samples were taken monthly, in a period of 5 years. 13 Parameters have been tested for WQI determination. On the basis of monthly average values, the descriptive statistics as average, minimum, maximum, standard deviation were evaluated. Function of the results obtained for all the analysed parameters only that one exceeding the imposed limits were selected (Table 3÷ Table 10).

Table 3. Basic statistics of physical and chemical variables for Ramnicu Valcea effluent (2013–2017)

Analytes	MU	Spring		Summer		Autumn		Winter	
		Mean ± SD	Min Max	Mean± SD	Min Max	Mean ± SD	Min Max	Mean ± SD	Min Max
SS	mg/L	33.80 ±8.3	26.60 46.40	30.27 ±6.33	24.00 36.4	29.07 ±5.54	24.00 34.40	36.92 ±12.5	26.00 50.25
NH_4^+	mg/L	5.92 ±1.95	3.99 8.69	3.68 ±0.58	3.18 4.28	3.24 ±0.79	2.61 4.11	5.83 ±4.65	1.82 10.40
P	mg/L	1.00 ±0.47	0.54 1.52	0.72 ±0.59	0.56 1.70	0.87 ±0.20	0.68 1.06	0.66 ±0.28	0.43 0.95

The parameters which exceeded the maximum admissible limits from Ramnicu Valcea wastewater Treatment Plant, were: suspended solids, ammonia and total phosphorus (Table 3).

Suspended solids presented average values between 36.40 mg/L to 50.25 mg/L. These values provided information on effluent turbidity during four seasons. Ammonia resulting from the degradation of N-containing organic substances in their molecule indicates a very high concern (Paun et al 2017). The values obtained for ammonium indicator varied from 4.11 to 10.40 mg/L. The highest value obtained for phosphorus indicator was up to 1.70 mg/L was recorded in summer time.

Table 4. Basic statistics of physical and chemical variables for Govora effluent (2013–2017)

Analytes	MU	Spring		Summer		Autumn		Winter	
		Mean ± SD	Min Max	Mean± SD	Min Max	Mean ± SD	Min Max	Mean ± SD	Min Max
SS	mg/L	51.53 ±13.6	39.20 64.20	41.17 ±9.34	32.80 50.80	47.20 ±8.05	40.80 56.00	71.33 ±30.0	42.00 99.00
TDS	mg/L	1663 ±902	846.4 2761	1202 ±469	965.2 1850	1625 ±454	1230 2103	2112 ±1112	1096 3199
COD	mg O_2/L	143.0 ±75.76	67.20 229.4	124.0 ±78.8	80.66 228.4	171.4 ±83.0	92.16 249.6	258.3 ±114	131.9 345.6
BOD_5	mg O_2/L	49.28 ±25.0	25.80 78.62	43.40 ±27.4	28.49 79.76	60.65 ±25.7	37.32 85.14	89.15 ±40.7	46.05 125.4
NH_4^+	mg/L	16.47 ±9.96	8.13 27.38	27.40 ±8.62	22.54 38.98	38.90 ±3.56	35.24 42.20	25.17 ±9.90	16.38 35.84
AS	mg/L	0.78 ±0.50	0.41 1.20	0.69 ±0.23	0.43 0.87	1.07 ±0.57	0.60 1.69	1.05 ±0.62	0.54 1.41

Table 5. Basic statistics of physical and chemical variables for Babeni effluent (2013–2017)

Analytes	MU	Spring		Summer		Autumn		Winter	
		Mean ± SD	Min Max	Mean ± SD	Min Max	Mean ± SD	Min Max	Mean ± SD	Min Max
SS	mg/L	36.27 ±9.14	29.80 52.40	33.60 ±10.2	24.60 44.40	29.20 ±7.72	19.60 34.40	35.33 ±6.97	29.00 44.50
NH_4^+	mg/L	7.52 ±2.70	4.62 10.50	5.03 ±1.59	3.48 6.59	5.12 ±0.48	4.26 7.44	7.27 ±2.78	4.06 9.97
AS	mg/L	0.26 0.15	0.19 0.53	0.28 ±0.10	0.19 0.38	0.27 ±0.08	0.18 0.35	0.36 ±0.13	0.24 0.53

Table 6. Basic statistics of physical and chemical variables for Olanesti effluent (2013–2017)

Analytes	MU	Spring		Summer		Autumn		Winter	
		Mean ± SD	Min Max	Mean ± SD	Min Max	Mean ± SD	Min Max	Mean± SD	Min Max
SS	mg/L	34.60 ±11.2	31.00 50.20	38.93 ±13.9	26.00 53.20	33.87 ±8.75	24.80 41.60	32.33 ±5.75	27.00 38.00
COD	mg O_2/L	46.40 ±13.2	41.44 67.20	89.60 ±25.7	61.44 107.5	101.8 ±24.4	78.72 126.9	62.40 ±23.3	45.60 81.60
BOD_5	mg O_2/L	15.63 ±9.79	14.26 28.06	29.62 ±11.1	17.28 37.97	37.14 ±11.3	26.73 48.64	20.28 ±11.5	9.53 31.69
NH_4^+	mg/L	9.21 ±5.95	8.98 18.26	22.12 ±5.19	17.89 27.23	14.95 ±2.28	12.48 16.95	9.29 ±5.11	4.32 14.39
S^{2-}	mg/L	0.05 ±0.18	0.02 0.55	0.76 ±0.34	0.41 1.07	0.62 ±0.45	0.32 1.08	-	-
AS	mg/L	0.34 ±0.26	0.29 0.71	0.54 ±0.33	0.39 0.90	0.30 ±0.26	0.20 0.59	0.28 ±0.08	0.22 0.37

Table 7. Basic statistics of physical and chemical variables for Calimanesti effluent (2013–2017)

Analytes	MU	Spring		Summer		Autumn		Winter	
		Mean ± SD	Min Max	Mean ± SD	Min Max	Mean ± SD	Min Max	Mean ± SD	Min Max
SS	mg/L	36.27 ±15.8	26.00 64.80	32.93 ±4.27	29.20 36.60	34.13 ±6.55	31.2 42.40	38.58 ±9.93	30.50 49.00
COD	mg O_2/L	157.4 ±63.9	72.26 223.3	220.5 ±57.6	142.0 250.6	208.0 ±84.9	122.8 272.6	216.8 ±86.2	132.0 297.6
BOD_5	mg O_2/L	53.79 ±21.8	25.63 74.76	73.84 ±17.5	48.52 80.82	74.24 ±24.5	43.24 88.68	74.23 ±32.0	44.39 106.4
Cl^-	mg/L	1876 ±321	1376 2285	2179 ±251	2041 2502	1938 ±251	1747 2222	1947 ±223	1723 2165
TN	mg/L	10.31 ±4.94	8.02 21.78	12.22 ±2.73	10.23 15.32	11.35 ±2.13	6.29 25.93	10.98 ±2.30	8.82 13.33
P	mg/L	0.79 ±0.33	0.47 1.15	1.19 ±0.43	0.73 1.51	1.04 ±0.39	0.56 1.33	1.14 ±0.79	0.52 2.03
AS	mg/L	0.27 ±0.16	0.20 0.61	0.41 ±0.14	0.25 0.61	0.46 ±0.15	0.34 0.60	0.29 ±0.10	0.21 0.40

Table 8. Basic statistics of physical and chemical variables for Dragasani effluent (2013–2017)

Analytes	MU	Spring		Summer		Autumn		Winter	
		Mean ± SD	Min Max	Mean ± SD	Min Max	Mean ± SD	Min Ma	Mean ± SD	Min Max
SS	mg/L	42.87 ±11.4	36.60 60.20	37.00 ±10.1	28.00 47.00	35.60 ±10.5	26.00 46.00	42.17 ±9.71	33.50 51.50
BOD_5	mg O_2/L	31.83 ±12.9	19.89 42.28	23.81 ±10.9	12.75 34.36	34.75 ±14.5	21.36 49.92	24.76 ±7.86	18.04 33.33
NH_4^+	mg/L	16.01 ±3.69	11.95 19.05	17.66 ±9.26	10.96 25.63	10.23 ±0.57	9.63 10.67	11.05 ±2.97	7.84 13.40
P	mg/L	1.86 ±0.47	1.55 2.39	1.81 ±0.99	0.79 2.70	2.16 ±0.53	1.71 2.72	1.66 ±0.40	1.24 1.99
AS	mg/L	0.82 ±0.47	0.43 1.36	1.01 ±0.59	0.51 1.51	1.32 ±0.63	0.92 2.05	0.78 ±0.29	0.45 0.98

Table 9. Basic statistics of physical and chemical variables for Voineasa effluent (2013–2017)

Analytes	MU	Spring		Summer		Autumn		Winter	
		Mean ± SD	Min Max	Mean ± SD	Min Max	Mean ± SD	Min Max	Mean± SD	Min Max
SS	mg/L	37.53 ±13.9	26.20 63.40	41.60 ±11.5	30.40 52.00	38.00 ±14.4	24.80 52.40	44.50 ±10.5	34.00 54.50
COD	mg O_2/L	42.56 ±32.6	38.40 111.3	164.1 ±12.2	155.5 172.8	30.72 ±2.72	28.80 32.64	45.60 ±5.85	42.00 51.60
BOD_5	mg O_2/L	10.21 ±14.8	4.95 42.86	26.59 ±32.7	2.67 61.92	9.88 ±5.51	4.63 15.17	10.91 ±8.61	3.95 20.28
NH_4^+	mg/L	8.64 ±5.59	4.67 18.51	4.12 ±3.10	1.98 6.84	6.30 ±2.78	4.46 8.82	9.95 ±6.28	4.91 16.53
AS	mg/L	0.32 ±0.13	0.23 0.54	0.35 ±0.12	0.26 0.46	0.26 ±0.09	0.19 0.36	0.26 ±0.12	0.15 0.37

Table 10. Basic statistics of physical and chemical variables for Horezu effluent (2013–2017)

Analytes	MU	Spring		Summer		Autumn		Winter	
		Mean ± SD	**Min Max**	**Mean ± SD**	**Min Max**	**Mean ± SD**	**Min Max**	**Mean ± SD**	**Min Max**
SS	mg/L	49.27 ±20.2	28.80 80.60	52.20 ±20.8	38.00 75.40	44.93 ±15.4	31.60 61.60	41.00 ±13.7	31.00 57.50
COD	mg O_2/L	70.72 ±31.6	49.92 97.92	103.3 ±39.7	74.88 144.0	80.64 ±13.2	69.12 92.16	53.75 ±22.9	53.75 86.15
NH_4^+	mg/L	10.17 ±7.25	5.66 16.99	19.63 ±10.3	10.49 28.49	15.78 ±3.67	12.67 19.82	17.33 ±9.57	7.13 24.63
AS	mg/L	0.54 ±0.10	0.45 0.70	0.88 ±0.47	0.57 1.41	1.18 ±0.72	0.68 1.98	0.46 ±0.12	0.26 0.57

Regarding to Wastewater Treatment Plant from Govora, parameters that have overtaken the maximum admissible limits were: suspended solids, total dissolved solids, chemical oxygen demand, biochemical oxygen demand, ammonia, anionic surfactants (Table 4). For the suspended solids average values were situated between 50.80 mg/L to 99.00 mg/L, COD varied from 228.4 to 345.6 mgO_2/L, and CBO_5 from 78-62 to 125.4 mgO_2/L. The ammonia levels were found from 27.38 to 42.20 mg/L.

In WWTP from Babeni, higher values than maximum admissible limits were recorded for: suspended solids, ammonia, anionic surfactants (Table 5). Suspended solids values were situated between 44.40-52.40 mg/L, ammonia concentration ranged from 6.59 mg/L to 10.50 mg/L, some of which are about 5 times higher than the maximum admissible NTPA 001.

Regarding the wastewater Treatment Plant from Olanesti, the parameters with higher values than the maximum admissible limits were: suspended solids, chemical oxygen demand, biochemical oxygen demand, ammonia, sulphides, and anionic surfactants (Table 6). The suspended solids values ranged from 41.60-53.20 mg/L in summer, for COD the highest value was 126 mg O_2/L, the maximum level obtained for CBO_5 was 48.64 mg O_2/L, while for ammonia the highest average value of the concentration was about 13 times higher than the value admitted by NTPA 001 and recorded in summer time. For sulphides parameter values were found between 1.07 mg/L and 1.08 mg/L.

In WWTP from Calimanesti the exceeding parameters were: suspended solids, chemical oxygen demand, biochemical oxygen demand, chlorides, total nitrogen, and anionic surfactants (Table 7). Suspended solids varied from 36.60 to 64.80 mg/L, the COD concentrations were found in the range of 223.3 and 297.6 mg O_2/L, CBO_5 varied from 74.76 to 106.4 mgO_2/L. Chlorides ranged from 2165 mg/L to 2502 mg/L, total nitrogen from 13.33 to 21.78 mg/L and total phosphorus from 1.15 to 2.03 mg/L.

Parameters with concentration higher than the maximum admissible limits for WWTP from Dragasani were: suspended solids, biochemical oxygen, Ammonia, total phosphorus, anionic surfactants (Table 8). Suspended solids varied from 46.00 to 60.20 mg/L, BOD_5 ranged from 33.33 to 42.28 mgO_2/L and the highest value for ammonia was 13 times higher than the maximum admissible limit. Total phosphorus levels ranged between 1.99 and 2.72 mg/L, while anionic surfactants were situated between 0.98 to 2.05 mg/L.

In WWTP from VOINEASA parameters exceeding the maximum admissible limits were: suspended solids, biochemical oxygen demand, chemical oxygen demand, ammonia, anionic surfactants (Table 9). Suspended solids were determined to be from 52.00 to 63.40 mg/ L, COD levels ranged from 51.60 to 111.3 mg O_2/L, while the highest average concentration found for CBO_5 was 61.92 mg O_2/L. The ammonia results varyed from 6.84 to 18.51 mg/L and for anionic surfactants the highest value was 0.54 mg /L.
The parameters which exceeded from maximum admissible limit for WWTP from Horezu were: suspended solids, chemical oxygen demand, ammonia, anionic surfactants (Table 10). Suspended solids values were situated between 57.50 to 80.60 mg/L, the highest value for COD was 144 mg/L, while the ammonia concentration was about 14 times higher than the admitted value by NTPA 001 and was recorded in summer time.
Based on determined results, sub-index used to obtain the water quality index of the Canadian Council of Ministers for the Environment (CCMEWQ) were calculated (Table 11).
In Table 11, the value of the Canadian Environment Ministers' Water Quality Indicators corresponds to fair designation which means acceptable quality class for the effluent of the Ramnicu Valcea Wastewater Treatment Plant. For the other effluents the calculated index corresponds to marginal designation, which means that the values of the determined parameters often break the limits imposed (NTPA001)

Table 11. Values of water quality sub-index and index (CCMEWQ) calculated for each sampling point

Sampling point	F1	F2	nse	F3	Index Value	Designation
Govora	14.29	7.62	2.067	67.39	59.98	Marginal
Ramnicu Valcea	36.36	10.45	0.861	14.67	76.57	Fair
Olanesti	77.78	13.64	0.305	462.6	47.16	Marginal
Babeni	55.56	16.99	0.324	24.49	63.60	Marginal
Horezu	62.50	30.50	0.904	47.48	51.38	Marginal
Voineasa	62.50	16.49	0.375	27.28	59.49	Marginal
Dragusani	66.67	38.05	1.145	53.38	46.02	Marginal
Calimanesti	72.73	44.67	0.628	38.58	45.92	Marginal

Conclusion

In this study, a new index has been proposed for evaluating the wastewater quality index regarding to the efficiency of the effluent treatment process, to represent the quality of the final effluent and to quickly evaluate whether it would be adequate for its final destination. The developed wastewater quality index can be very useful in managing treated wastewater for reuse or disposal purposes. The application of this types of indexes is that it can help in decisions for reuse purposes and assessing the improvement in treatment procedure.

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