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# MULTIVARIATE ANALYSIS APPLIED TO PHYSICOCHEMICAL PARAMETERS OF TREATED WASTEWATER EFFLUENTS DISCHARGED IN TELEAJEN RIVER

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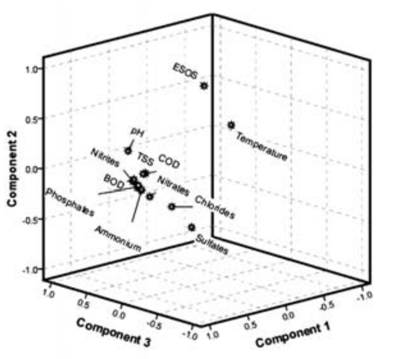
The paper presents a multivariate analysis of the physicochemical parameters of the effluents discharged into the upstream part of Teleajen River from Maneciu-Ungureni wastewater treatment plant. Time series of 13 effluent parameters were analyzed using data recorded in 2011. The objective was to determine possible relationships of interdependence between the effluent variables for the identification of a minimum set that explains the reduction of the water quality in the area. The principal factor formed by the contaminants is responsible for the effluent pollutant load. Temperature is the extrinsic seasonal factor, while pH can be regarded as an efficiency factor of the water treatment process. The presented technique provides an assessment framework of the monitored sites synthesizing the interactions between effluent parameters.




## INTRODUCTION*

Water is one of the major resources that support life and, consequently, the existence of biosphere. Water composition varies widely in relation to the hydrographical basin characteristics depending on the nature of watershed's land cover and geology, the seasonal variation, the water utilizations and the chemical properties of receiving waters. Rainfall and snowmelt produce significant changes, both quantitative and qualitative, because of the surface transport of all kinds of impurities (germs, suspensions, pesticides, fertilizers etc.). Besides these inevitable modifications, the composition of surface waters changes in some areas because of their utilization for various purposes (domestic use, industry, agriculture, etc.). One of the major issues of water management is the pollution originating from many sources of anthropogenic activities, mostly due to uncontrolled or ineffective removal of various liquids, solid wastes or residues. The most common effect of water chemical pollution is determined by the cumulated influence of pollutants on various biological processes that occur in natural waters. Consequently, the ecological balance of the different water biocenoses is so sensitive that any persistent changes in water composition can lead to harmful disturbances and unexpected long-term consequences. The natural processes of purification might be slowed down or even stopped by affecting the existent microorganisms, which will contribute to serious economic and environmental issues due to the extinction of vulnerable aquatic flora and fauna species.

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Water treatment controls are designed to reduce the amount of discharged pollutants by controlling the volume and the rate of runoff discharge. Pollutants are primarily removed by solid settling, filtration, percolation, chemical precipitation and/or biological uptake.[1] Chemical pollution causes difficulties in the water treatment because treatment plants are ineffective in totally removing chemical pollutants, especially if they are present in low quantities.[2] Wastewater discharges may suddenly distort physicochemical and biological properties of water when discharge regulations and norms do not comply. Water quality standards provide the obligatory framework through physical, chemical, biochemical, radiological and microbiological methods, as well as sampling methods and terminology, for obtaining standardized information with an important communication role in supplying answers concerning the trends of the environmental conditions.[3]

Multivariate statistical techniques are useful for the evaluation and interpretation of large complex data sets for getting better information about the water quality and design of monitoring network for effective management of water resources.[4] Factor analysis might be a valuable screening tool for unexpected fluctuations in water pollution assessments.[5-8] The identified factors are attributed to various sources of pollutants by noting the dependence of the factors on the significant elements.

The paper presents a multivariate analysis of the physicochemical parameters of the wastewater effluents discharged in Teleajen River (Roumania). Estimation of the impact on the water quality in this sub-basin of the Buzău-Ialomiţa watershed was obtained by monitoring the effluents of Măneciu-Ungureni wastewater treatment plant (WWTP), which discharges into the upstream part of the river. The main outcomes of this approach are the prioritization of the pollutants and the identification of existent bilateral interactions, which have contributed to the developing of a multi-source screening technique of pollution load useful in establishing the required level of control for the prioritized pollutants. Such approach might provide potential improvements of the existent Teleajen River Watershed management plan.

Studies on the pollution of these surface waters are scattered and discontinued, ascertaining the need for more complete information on the seasonal variation and the effect of effluents on the quality of downstream river waters and receptors. Future work will address these issues.

## EXPERIMENTAL

Teleajen River has a length of 122 km, a sinuosity coefficient of 1.54 and an average slope of 0.013 (altitude of 1760 m at source and 81 m at river mouth). Its watershed has an area of 1656 $km^2$. In the northern mountainous area of Teleajen Valley there are plenty of tourism resources, which are directly related to the water resources, both in terms of ensuring the quality and quantity requirements. The water quality belongs to the first category based on the measurements performed in Cheia and Măneciu control sections,[9] 18 and 22 km from the source of Teleajen River, for water organic load indicators, chemical indicators of water pollution (ammonium, phosphates and sulfates) and heavy metals (chromium, cadmium, iron and zinc). In the Gura Vitioarei's control section (55 km from the source) the water quality corresponds to the second category due to the downstream sources including several water treatment stations, which are constantly increasing the pollutant load. The experiments have been carried out with effluents originating from Măneciu-Ungureni WWTP, which discharge effluents in Teleajen River at 30 km from the stream source (Fig. 1).

Consequently, time series of 13 effluent parameters such as: water temperature, pH, total suspended solids (TSS), extracted substances with organic solvents (ESOS), biochemical oxygen demand (BOD), chemical oxygen demand (COD), nitrites, nitrates, ammonium, phosphates, sulfates, chlorides and detergents were analyzed to test the interactions between the monitored variables in situations of frequent exceedances of the limit values. Data presented in this paper were selected from January 2011 to December 2011.

The monitoring of the effluents was accomplished by discrete sampling followed by chemical analysis in the laboratory. Table 1 summarizes the monitored parameters, the corresponding method of analysis and the standard applied to determine a specific parameter of the effluent.[10]

SPSS (SPSS Inc., Chicago, IL, 2011) was used to perform descriptive, associative and factor analysis using the recorded time-series.

Descriptive statistics was applied to identify the characteristics of each monitored parameter in terms of central tendency, dispersion and distribution. Central tendency showed the location of the distribution for each parameter including the mean, median and mode. Dispersion measured the spread in the data set including the standard deviation, coefficient of variation, range, minimum and maximum. Distribution was estimated using skewness and kurtosis to describe time series distribution's symmetry and shape.

Pearson product moment correlations were used between each pair of variables to identify potential bivariate associations. These correlation coefficients measured the strength of the linear relationship between the variables.

Factor analysis (FA) is achieved using several techniques of factor extraction: principal components method, varimax criterion, quartimax criterion and rotation axes. An extensive literature review of the FA utilization in environmental studies was performed,[11] having a paragraph dedicated to water supply, waste and sewage water. FA analysis involves defining factors capable to condense a lot from initial information (variables). The objective is to find the relationship of interdependence between several variables, in order to determine the minimum set that explains a particular phenomenon. The classification structures of variables and the latent factors controlling wastewater quality were retrieved using exploratory factor analysis (EFA) with principal components factoring, which is a successfully used analysis technique in various fields of environmental monitoring.[12] FA reduces the number of measured variables identifying specific latent factors and the corresponding underlying factor structure.[13]

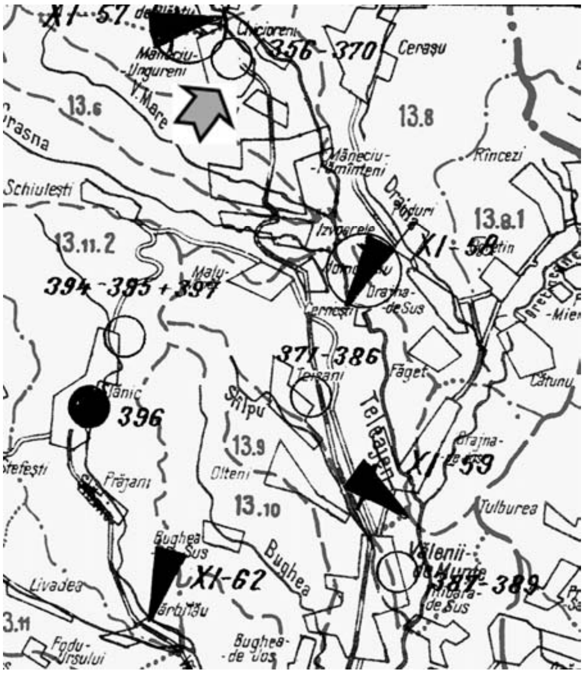


Fig. 1 – Location of the Măneciu-Ungureni Wastewater Treatment Plant.

*Table 1*

Dataset of monitored wastewater effluent parameters, maximum limit value (L.V. from the G.D. Governmental decision no. 188/2002 – ANNEX 3 NTPA-001/2002) and the corresponding method of analysis

| Parameter | Measurement unit | Maximum limit value (L.V.) | Standard method of analysis |
|---|---|---|---|
| pH | pH units | 6.5-8.5 | SR ISO 10523-97 |
| Temperature | °C | 35.00 | - |
| Total Suspended solids | mg/l | 60.00 | SR ISO 6060-96; STAS 6953-81 |
| Extracted substances with organic solvents | mg/l | 20.00 | SR 7587-96 |
| Biochemical Oxygen Demand | mg $O_2$/l | 25.00 | SR EN 1899-2/2002 |
| Chemical Oxygen Demand - $K_2Cr_2O_7$ | mg $O_2$/l | 125 | SR ISO 6060-96 |
| Nitrates ($NO_3^-$) | mg/l | 25 | SR ISO 7890-2:2000; SR ISO 7890-3:2000; SR ISO 7890/1-98 |
| Nitrites ($NO_2^-$) | mg/l | 1.00 | SR EN 26777:2002 |
| Ammonium ($NH_4^+$) | mg/l | 2.00 | SR ISO 5664:2001; SR ISO 7150-1/2001 |
| Phosphates ($PO_4^{3-}$) | mg/l | 4.00 | SR EN 1189-2000 |
| Sulfates ($SO_4^{2-}$) | mg/l | 600.00 | STAS 7601-70 |
| Chlorides ($Cl^-$) | mg/l | 500.00 | STAS 8663-70 |
| Detergents | mg/l | 0.50 | SR EN 903:2003; SR ISO 7875/2-1996 |

## RESULTS AND DISCUSSION

### Prioritization of pollutants

The composition of wastewater effluent varies from plant to plant according to the treatment efficiency and contributory sources having direct influence on the pH. Wastewaters treated to leave the wastewater treatment plant were monitored through several parameters according to the water management authorization. Significant associated frequencies of the limit values exceeding were observed for ammonium (60.62%), phosphates (28.57%), TSS (21.24%), detergents (20.85%) and BOD (20.52%).

Numerical descriptors included mean, median, mode, standard deviation, minimum, maximum, range, interquartile range and C.V.% as a normalized measure of dispersion of a probability distribution – table 2. Mode indicator showed the most frequent value occurring in the time series of each parameter. The most dispersed time series were observed for Nitrites, Detergents and BOD after computing the corresponding coefficients of variations (C.V.%). All parameters, excepting the temperature, presented high C.V.s (>45%), which gave valuable information regarding the spread in the data set together with standard deviation, range, minimum and maximum values. Distribution was estimated using skewness and kurtosis in describing the time series distribution's symmetry and shape. All parameters, excepting pH (normal distribution) and temperature (slight left skew asymmetry), presented right-skewed (positive) asymmetric distributions. Temperature and pH showed distributions with longer tails (platykurtic distribution) and observations clustered more. The other parameters had shorter tails (leptokurtic distribution).

Table 2 contains comprehensive information usable for the prioritization of the analyzed pollutants.

**Effluent parameters associations**

Interpretation of the correlation matrix showed the degree of association between physicochemical parameters (Table 3). Since numerous significant Pearson correlation coefficients have been observed ($p<0.01$), ranking of the coefficients was established in four groups: a) c > 0.7 (10 correlations), b) 0.7> c >0.5 (18 correlations), c) 0.5> c >0.3 (15 correlations) and d) 0.3> c >0.15 (20 correlations). From 78 possible bilateral associations only 15 were not correlated ($p<0.05$), most of them belonging to ESOS variable, which was correlated only with the water temperature.

*Table 2*

Descriptive statistics of the effluents' parameters recorded between January 2011 and December 2011

| Indicator | pH | Temperature | TSS | ESOS | BOD | COD | Nitrites ($NO^{2-}$) | Nitrates ($NO^{3-}$) | Ammonium ($NH^{4+}$) | Phosphates ($PO_4^{3-}$) | Sulfates ($SO_4^{2-}$) | Chlorides ($Cl^-$) | Detergents |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Number of samples | 259 | 259 | 259 | 259 | 229 | 259 | 259 | 259 | 259 | 259 | 259 | 259 | 259 |
| Number of exceedings | 0 | 1 | 55 | 26 | 47 | 36 | 24 | 15 | 157 | 74 | 0 | 0 | 54 |
| Associated frequency | *0.00* | *0.39* | *21.24* | *10.04* | *20.52* | *13.90* | *9.27* | *5.79* | *60.62* | *28.57* | *0.00* | *0.00* | *20.85* |
| Mode | 5 | 8.01 | 18.47 | 12.01 | 20 | 72.01 | 0.201 | 10.7 | 2.01 | 2.011 | 109.6 | 194 | 0.34 |
| Median | 11.0 | 7.90 | 32.60 | 11.14 | 16.00 | 82.21 | 0.18 | 12.45 | 3.04 | 2.20 | 102.3 | 114.0 | 0.22 |
| Average | 11.3 | 7.73 | 43.23 | 17.00 | 30.32 | 96.23 | 0.54 | 14.12 | 6.61 | 3.72 | 115.1 | 125.2 | 0.83 |
| Minimum | 3.00 | 6.50 | 8.20 | 6.93 | 3.00 | 16.26 | 0.01 | 2.60 | 0.06 | 0.07 | 20.10 | 10.13 | 0.00 |
| Maximum | 22.0 | 8.56 | 282.1 | 136.3 | 300.0 | 456.0 | 9.72 | 51.12 | 54.34 | 25.90 | 400.5 | 387.9 | 13.02 |
| Range | 19.0 | 2.06 | 273.9 | 129.4 | 297.0 | 439.7 | 9.71 | 48.52 | 54.28 | 25.84 | 380.4 | 377.8 | 13.02 |
| Interquartile range | 10.0 | 0.79 | 31.21 | 3.42 | 12.00 | 43.38 | 0.24 | 5.83 | 8.43 | 2.71 | 56.18 | 66.56 | 0.30 |
| Standard deviation | 5.63 | 0.46 | 36.49 | 20.64 | 46.70 | 63.09 | 1.32 | 6.86 | 8.67 | 4.23 | 59.24 | 56.96 | 1.99 |
| C.V.% | 49.5 | 5.90 | 84.41 | 121.4 | 154.0 | 65.57 | 242.8 | 48.60 | 131.3 | 113.7 | 51.47 | 45.49 | 238.7 |
| Skewness | 0.14 | -0.52 | 2.72 | 3.96 | 3.58 | 2.92 | 4.79 | 2.23 | 2.93 | 2.84 | 1.71 | 1.57 | 3.78 |
| Kurtosis | -1.21 | -0.71 | 10.71 | 16.10 | 13.24 | 11.17 | 25.26 | 6.98 | 10.86 | 8.67 | 4.09 | 4.00 | 14.90 |

*Table 3*

Correlation matrix of physicochemical parameters of the final effluents discharged in Teleajen River between January 2011 and December 2011 using the Pearson correlation coefficient:* Correlation is significant at the $p < 0.05$ level (two-tailed);** Correlation is significant at the $p < 0.01$ level (two-tailed). Total suspended solids (TSS), Extracted Substances with Organic Solvents (ESOS), Biochemical Oxygen Demand (BOD), and Chemical Oxygen Demand (COD - $K_2Cr_2O_7$)

| Variables | Temperature | pH | TSS | ESOS | BOD | COD | Nitrites | Nitrates | Ammonium | Phosphates | Sulfates | Chlorides | Detergents |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Temperature | 1 | | | | | | | | | | | | |
| pH | -0.171** | 1 | | | | | | | | | | | |
| TSS | 0.206** | 0.216** | 1 | | | | | | | | | | |

*Table 3 (continued)*

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ESOS | 0.327** | 0.091 | 0.032 | 1 | | | | | | | | | |
| BOD | 0.201** | 0.305** | 0.744** | 0.015 | 1 | | | | | | | | |
| COD | 0.217** | 0.263** | 0.588** | 0.056 | 0.786** | 1 | | | | | | | |
| Nitrites | 0.150* | 0.280** | 0.674** | -0.037 | 0.811** | 0.663** | 1 | | | | | | |
| Nitrates | -0.001 | 0.209** | 0.432** | -0.003 | 0.604** | 0.568** | 0.513** | 1 | | | | | |
| Ammonium | 0.182** | 0.298** | 0.678** | -0.072 | 0.744** | 0.603** | 0.727** | 0.458** | 1 | | | | |
| Phosphates | 0.053 | 0.234** | 0.584** | -0.054 | 0.711** | 0.536** | 0.697** | 0.465** | 0.587** | 1 | | | |
| Sulfates | 0.021 | 0.098 | 0.277** | -0.120 | 0.364** | 0.299** | 0.259** | 0.352** | 0.378** | 0.236** | 1 | | |
| Chlorides | 0.152* | 0.160* | 0.400** | -0.056 | 0.506** | 0.472** | 0.483** | 0.450** | 0.514** | 0.451** | 0.414** | 1 | |
| Detergents | 0.177** | 0.248** | 0.589** | -0.006 | 0.759** | 0.645** | 0.733** | 0.582** | 0.701** | 0.737** | 0.326** | 0.501** | 1 |

The strongest correlations exist between BOD and all the chemical parameters from the data set. TSS showed significant correlations with the chemical parameters. Sulfates were less correlated as compared to other chemical parameters such as nitrites, nitrates, ammonium, phosphates, chlorides and detergents.

## Exploratory factor analysis

The purpose of the multivariate analysis was to obtain a reduced number of factors that might account for most of the variability encountered in the data set of the 13 water parameters, both physical and chemical. The input matrix was 259 objects (number of measurements) by 13 variables (effluent physicochemical parameters).

Three factors have been extracted, since the scree plot of the eigenvalues highlighted three eigenvalues meeting the Kaiser criterion (>1). Together they accounted for 66.27% of the variability in the data (Table 4). The first extracted factor explained almost half of the total variance (47.2%) with a significant eigenvalue of 6.13. Rotation was performed using the Varimax method, which is an orthogonal rotation of factors that redistributes the variance, accounted within the pattern of factor loadings. This has facilitated the explanation of the factors.

The latent factors content based on the corresponding values of the significant factor loadings estimated by FA (Table 5) had the following structure: Factor 1 (TSS, BOD, COD, Nitrites, Nitrates, Ammonium, Phosphates, Sulfates, Chlorides and Detergents), Factor 2 (ESOS and Temperature) and Factor 3 (pH).

*Table 4*

Factorial analysis: Total variance explained; PCA extraction method based on Eigenvalues

| Component | Initial Eigenvalues | | |
|---|---|---|---|
| | Total | % of Variance | Cumulative % |
| 1 | **6.136** | 47.203 | 47.203 |
| 2 | **1.397** | 10.745 | 57.948 |
| 3 | **1.082** | 8.322 | 66.270 |
| 4 | .905 | 6.958 | 73.228 |
| 5 | .675 | 5.190 | 78.418 |
| 6 | .574 | 4.415 | 82.833 |
| 7 | .510 | 3.924 | 86.757 |
| 8 | .429 | 3.297 | 90.054 |
| 9 | .358 | 2.757 | 92.812 |
| 10 | .317 | 2.441 | 95.253 |
| 11 | .255 | 1.965 | 97.217 |
| 12 | .194 | 1.492 | 98.709 |
| 13 | .168 | 1.291 | 100.000 |

*Table 5*

Factorial analysis of physicochemical data set: component extraction

| Component | Component Matrix Extraction Method: PCA (3 components extracted) | | | Rotated Component Matrix Extraction Method: PCA Varimax with Kaiser Normalization (Rotation converged in 6 iterations) | | |
|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 1 | 2 | 3 |
| Temperature | 0.200 | **0.811** | -0.324 | 0.237 | **0.622** | -0.599 |
| pH | 0.348 | -0.207 | **0.738** | 0.310 | 0.089 | **0.778** |
| TSS | **0.786** | 0.120 | 0.030 | **0.787** | 0.115 | 0.021 |
| ESOS | -0.010 | **0.752** | 0.359 | -0.004 | **0.833** | 0.042 |
| BOD | **0.892** | 0.056 | 0.055 | **0.890** | 0.064 | 0.075 |
| COD | **0.807** | 0.115 | 0.037 | **0.807** | 0.112 | 0.031 |
| Nitrites | **0.870** | 0.010 | 0.079 | **0.866** | 0.031 | 0.114 |
| Nitrates | **0.686** | -0.139 | -0.018 | **0.682** | -0.142 | 0.072 |
| Ammonium | **0.836** | -0.020 | -0.028 | **0.836** | -0.038 | 0.024 |
| Phosphates | **0.785** | -0.078 | 0.082 | **0.778** | -0.049 | 0.145 |
| Sulfates | **0.454** | -0.262 | -0.442 | **0.465** | -0.416 | -0.285 |
| Chlorides | **0.648** | -0.073 | -0.296 | **0.658** | -0.187 | -0.212 |
| Detergents | **0.861** | 0.014 | 0.005 | **0.860** | 0.006 | 0.044 |

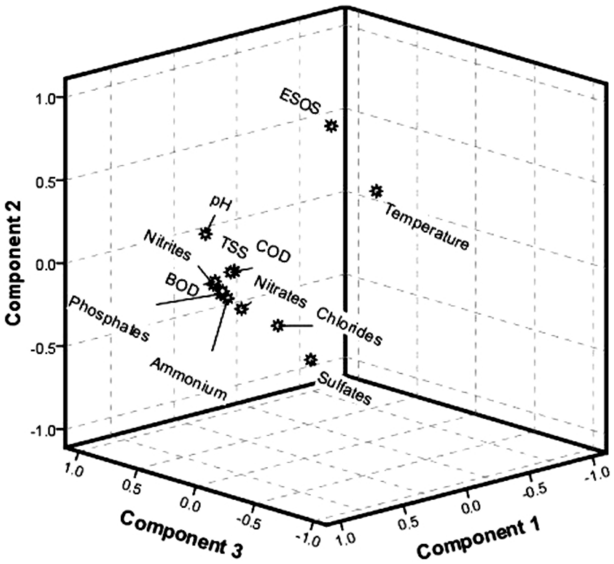


Fig. 2 – Component plot in rotated space based on component score coefficient matrix of the effluent parameters.

Varimax with Kaiser's normalization computed the rotated component matrix, which provided the same structure of the latent factors (Table 5). Sulfates had the weakest factor loading in component 1 being constant after rotation.

The 3-D graph (Fig. 2) presents the relationship between component scores coefficients, highlighting in a graphical manner the grouping of variables in three components as follows: the first group is the chemical factor (contamination factor), the second one is the seasonal factor (thermal factor) and the last group is the efficiency factor (water treatment factor).

The main variability in the original data was accounted in Factor 1. The second latent factor (Factor 2) explained 10.74% of the data set variability.

## CONCLUSIONS

Interpreting the water quality or the effluent composition data is a complex task requiring computing tools for assessing the differences in composition of contaminants in the water samples. Factor analysis based on the principal component approach facilitates the understanding of multivariate data generated by the WWTP effluents' monitoring by extracting the variation between samples and the correlation between effluent variables from the constructed data matrix. The correlation matrix of 13 variables showed the presence of high statistical significant correlations, most of associations being positively correlated. The first factor formed by the contamination variables is responsible for pollutant load of the effluent, temperature is the extrinsic seasonal factor, while pH can be regarded as an efficiency factor of the water treatment process. ESOS is an independent variable with little influence on the other variables from the data set. The presented technique can provide an assessment framework of the monitoring sites highlighting the interactions between effluent parameters, which evaluate more accurately the water treatment efficiency.

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