

## Statistical variation of nutrient concentrations and biological removal efficiency of a wastewater treatment plant

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**Abstract:** The treatment plant of "AINEIA", which is situated near the touristic area of N. Michaniona (Northern Greece), was considered as a pilot wastewater treatment plant to evaluate the respective trends. Moreover, an attempt was made to identify a possible relationship between the variation of influent concentration levels and the nutrient removal efficiency. The data collection was based on regular measurements of total nitrogen and total phosphorus concentrations in the influent and effluent streams, during the period March 2014–February 2015. The statistical analysis was performed by the implementation of SPSS software statistical package. The first step was a closer insight into the data obtained by the application of certain descriptive statistical tests. Then, the statistical analysis was performed by the application of Shapiro-Wilk and Levene tests for the determination of normality and homogeneity of the collected data. Subsequently, the mean values of nitrogen and phosphorus concentrations were used for the calculation of one-way ANOVA (analysis of variance) and Kruskal-Wallis test for the data presenting normal or asymmetric distribution, respectively. The statistical results demonstrate whether the mean values are statistically different or not at the significant level of 0.05. The results showed that nitrogen concentrations in influent and effluent streams differed significantly in almost all seasonal time periods throughout the year. However, this intense variation in nitrogen loading did not reduce its removal efficiency, which was found to be constantly very high (>80%). Regarding the seasonal distribution pattern of phosphorus, the influent concentrations were not significantly different, whereas the variability in spring was found significant, when compared to the other seasons, due to additional nutrient loads. With respect to the effluent concentrations, they were found to differ significantly only during the summer period. Finally, the range of phosphorus removal was found between 25-84% and the trend of removal efficiency was associated with the phosphorus loading in the influent, having a relatively strong linear correlation.

**Key words:** statistical analysis; wastewater treatment plant; nutrients (nitrogen and phosphorus); seasonal variation; removal efficiency (biological)

### 1. INTRODUCTION

A number of external variables, such as nutrients, season and flow regimes, may greatly influence the structure and function of aquatic ecosystems. However, urbanization and agricultural intensification have caused phosphorus in particular, to switch from being the limiting nutrient for plant growth, to being present occasionally in excessive amounts, especially in freshwaters, causing 'stress' to aquatic ecosystems through the eutrophication process (Howell, 2010). This can create aesthetic issues, as well as several water quality problems, regarding specific water uses, especially those relevant to domestic and recreational purposes. In addition, the high solubility of ammonia in water can lead to increased concentrations and may negatively influence the aquatic life, especially the fish reproduction. The phenomenon of eutrophication, leading to the presence of excessive Natural Organic Matter concentrations, can also affect negatively the performance of disinfection process during drinking water treatment, e.g., with the application of chlorination, increasing the risk for various diseases. Thus, it is necessary that wastewater should be appropriately treated, prior to discharge into the environment (Pirsaheb et al., 2014).

In an attempt to reduce the several nutrient impairments, especially the point-source sewage treatment dischargers have been enforced to receive more stringent effluent limits regarding nitrogen and phosphorus maximum allowable concentration levels (MALs). To achieve these new,

lower effluent nutrient limits, wastewater treatment facilities have begun to examine innovative treatment technologies (U.S. EPA, 2007). As stricter effluent quality standards are imposed, the complexity of wastewater treatment plants (WWTPs) tends to increase in order to meet the new standards. Generally, in Europe the main focus in many countries regarding wastewater treatment is related to the construction of new and the upgrading of existing WWTPs to include also nitrogen and phosphorus removal. Consequently, the efficient control of nutrient removing processes will remain an important issue (Jeppsson et al., 2002).

The assessment of wastewater treatment system efficiency showed that nutrient removal variation are very important issues in view of good maintenance and effluent quality promotion (Pirsaheb et al., 2014). Therefore, it would be helpful to know, whether high (“peak”) nutrient concentration values are following a significant distribution pattern, or they occur accidentally. For example, if higher nutrient concentrations are noticed in the influent of a wastewater treatment plant, then this plant may be overloaded and appropriate (temporary) changes in the operating conditions may be needed to apply. More specifically, if phosphorus is removed, e.g., via phosphate precipitation, then higher chemical addition dosage may be necessary, as it is common practice to regulate the dosage of chemicals on the influent composition. In addition, by obtaining such knowledge, a specific relationship between the variation of influent nitrogen/phosphorus concentration levels and the respective removal efficiency could be found. For the estimation of this variance, certain statistical procedures and tests can be used to determine the statistical significance of a set of data/measurements.

SPSS software has been used widely as a useful statistical tool for analysis, concerning the wastewater treatment plants. Khambete and Christian (2014) presented the correlation between Waste Water Quality Index (WWQI) and the different parameters, such as TDS, SS, BOD, COD etc. of treated wastewaters from Anjana Treatment Plant in Surat city with the help of SPSS. Bozdogan and Sogut (2013) determined the effect of reuse of treated urban wastewaters by a pilot-scale subsurface flow constructed wetland in Karaisali-Adana on the irrigation of rosemary (*Rosmarinus officinalis* cv. Abraxas) and lavender (*Lavandula officinalis* cv. Bella Purple) fields; all data, pH, EC and plant nutrition, were collected and evaluated statistically by SPSS. In the modelling of Konya wastewater treatment plant, SPSS was also used to compare the performance of this model, regarding pH, temperature, COD, TSS and BOD (Tumer and Edebali, 2015). Hoa et al. (2003) used a synthetic wastewater in SBR treatment and performed multiple regression analysis by the SPSS software to assess the effect of different variables on nutrient operational conditions and especially on the EPS (Extra-Cellular Substances) production and on sludge properties (Hoa et al., 2003).

In this study, the origin of the wastewater data comes from WWTP “AINEIA”. It is a conventional treatment plant and its effluent quality meets the current local discharge MALs. According to the statistical analysis performed, the annual fluctuations of nutrient concentration in the influent and effluent streams were determined. In addition, the possible relation between the variations in the incoming wastewater nutrient loading and the respective nutrient removal efficiency was also investigated. Considering the increasingly stringent nutrient effluent limits, this study provides statistical results and observations that could be a useful tool for not only the monitoring of plant operation, but also for directing any possible future modifications of the plant, in order to satisfy the upcoming (stringent) regulations.

## 2. MATERIALS AND METHODS

### 2.1 Wastewater treatment plant

The wastewater treatment plant of “AINEIA” is considered as a rather conventional one. It receives about  $8 \times 10^3$  m<sup>3</sup>/d of influent, of which  $7 \times 10^3$  m<sup>3</sup>/d is municipal wastewater and  $1 \times 10^3$  m<sup>3</sup>/d

is domestic septage waste. The plant consists of a combination of preliminary, primary and secondary (biological) treatment and ozone disinfection. One of the primary tanks is used for the equilibration/ homogenization of domestic septage waste. The effluent from the primary (screening, sedimentation) treatment is further treated by aerobic biological processes (oxidation ditch configuration) and after the secondary settling, the treated wastewater is subjected to ozone disinfection and discharged into the nearby sea (Thermaikos Gulf). The primary and the secondary (biomass) sludges are thickened, stabilized by anaerobic digestion and dewatered by a belt filter press before appropriate disposal. The main operational parameters of this wastewater treatment plant are presented in Table 1.

Table 1. Main parameters of "AINEIA" wastewater treatment plant (mean annual values).

Parameter	Units	Range
Volume of reactors (V)	m <sup>3</sup>	10,500
Volume of settling tanks (V <sub>s</sub> )	m <sup>3</sup>	5,760
Hydraulic detention time (θ <sub>s</sub> )	hour	10-21
Food to microorganism ratio (F/M)	kg BOD <sub>5</sub> /kg MLSS	0.03-0.11
Mean cell-residence time (θ <sub>c</sub> )	day	20-55
Dissolved oxygen (DO)	mg/L	1.7-2.5
MLSS (X)	mg/L	4.1-6.8
MLVSS (X <sub>v</sub> )	mg/L	3.3-5.3

## 2.2 Wastewater analysis

Wastewater samples received from the influent and effluent streams of this wastewater treatment plant were analyzed (among several other parameters) for total nitrogen and total phosphorus concentrations. The samples were collected three times per week for total nitrogen analysis, and on weekly basis for total phosphorus analysis. All measurements were performed according to the respective Standard Methods (APHA, AWWA, WEF, 1992).

Influent and effluent water streams were surveyed for the period between March 2014 and February 2015 to determine whether there was a seasonal variation of nutrients concentrations. The number of data samples was not considered as big enough, however, they were representative and adequate for the estimation of concentration trends. Moreover, the correlation between the total nitrogen and total phosphorus influent concentrations and the respective removal efficiency of the WWTP was carried out.

## 2.3 SPSS Statistics for data evaluation

First, the raw data were presented in a more meaningful way through the descriptive statistics, used to describe the basic features of available data sets. Then, the statistical analysis was performed by the implementation of SPSS software package.

The parametric statistical analysis assumes a certain distribution of examined data, usually the normal distribution. However, when the assumption of normality is violated, then the interpretation and inference of these data may not be reliable or valid. Therefore, it is important to check this assumption before proceeding with any relevant statistical procedure. Shapiro and Wilk test was originally restricted for data sizes of less than 50 and it is able to detect departures from normality, due to either skewness, kurtosis or both (Razali and Wah, 2011). Moreover, these issues need to be based on the *homogeneity of variances*. For this purpose, the Levene's test for checking the homogeneity of variances between the data was used. If the distribution was not normal, then the data values were further parameterized and the homogeneity was controlled by the non-parametric Levene's test.

If the data satisfy the aforementioned assumptions, then the one-way ANOVA can be selected for their statistical analysis to determine whether there are any significant differences between the

means of two or more independent groups. However, if the group variances were not statistically equal, then the Brown-Forsythe test was used, which is an ANOVA performance test, based on the transformation of the response variable. On the other hand, if the data present an asymmetric distribution, then the Kruskal-Wallis is the appropriate statistical test to be performed, which is considered as a non-parametric version of standard one-way ANOVA, in which the data are replaced by their ranks (de Smith, 2015).

Correlation is considered as a measure of the degree of linear relationship between two variables. It expresses the extent to which two variables vary together towards the same direction, or to the opposite one. Correlation coefficients reveal the magnitude and the direction of these relationships. A correlation can have a value ranging from -1 to 1. Values that are closer to the absolute value 1 indicate that there is a strong positive linear relationship between the variables being compared, whereas values closer to 0 indicate that there is no linear relationship between the examined variables (Khambete and Christian, 2014). For real-valued data, the most widely used correlation coefficient is the Pearson coefficient for the normally distributed data and the Spearman coefficient, which is a form of rank correlation coefficient, for the non-parametric data (de Smith, 2015).

### 3. RESULTS AND DISCUSSION

#### 3.1 Nitrogen and phosphorus concentrations

Table 2 demonstrates the average total nitrogen and total phosphorus concentrations in the influent and effluent streams, respectively. These measurements have been used as input data for the statistical analysis, which follows. The observed higher total nitrogen and total phosphorus concentrations for the months April, May and January are attributed to additional influent loading of unknown (possibly of not urban wastewater origin). The effluent quality complies absolutely with the current local wastewater discharge nutrient limits and regulations, which are 15 mg/L for total nitrogen (Council Directive, 1991) and 12 mg/L for total phosphorus (Joint Ministerial Decision 13059/1992) (Figure 1).

Table 2. Influent and effluent total nitrogen and total phosphorus concentrations (monthly averaged values).

	Total Nitrogen		Total Phosphorus	
	Influent (mg/L)	Effluent (mg/L)	Influent (mg/L)	Effluent (mg/L)
March 2014	62.2	3.4	8.8	2.1
April 2014	82.5	3.0	10.9	1.8
May 2014	88.5	3.8	15.2	4.5
June 2014	68.2	2.8	9.4	7.0
July 2014	63.2	3.7	8.2	6.6
August 2014	61.1	8.4	8.4	5.1
September 2014	59.3	3.3	7.3	4.6
October 2014	62.8	7.4	8.2	5.4
November 2014	61.7	8.1	9.3	5.1
December 2014	54.8	7.9	7.5	4.3
January 2015	75.1	12.8	11.6	5.2
February 2015	67.9	11.5	8.5	4.6

#### 3.2 Descriptive statistics

Table 3 presents the descriptive statistics of total nitrogen concentrations for the time period March 2014 - February 2015 in the influent and effluent streams. The comparison between the mean and the median values show intense differences for the influent stream during April and May, indicating a deviation from the normal distribution. Considering the standard deviation and the variance in combination with the range of data, relatively larger data spread was observed for the influent stream during the months April, May, December and January, as well as for the effluent

stream during February. The distributions for March, October and January for the influent stream and for March, June and February for the effluent stream are intensively platykurtic, which means that most data are away from the mean, following a flat-topped curve, according to the calculated kurtosis coefficients.

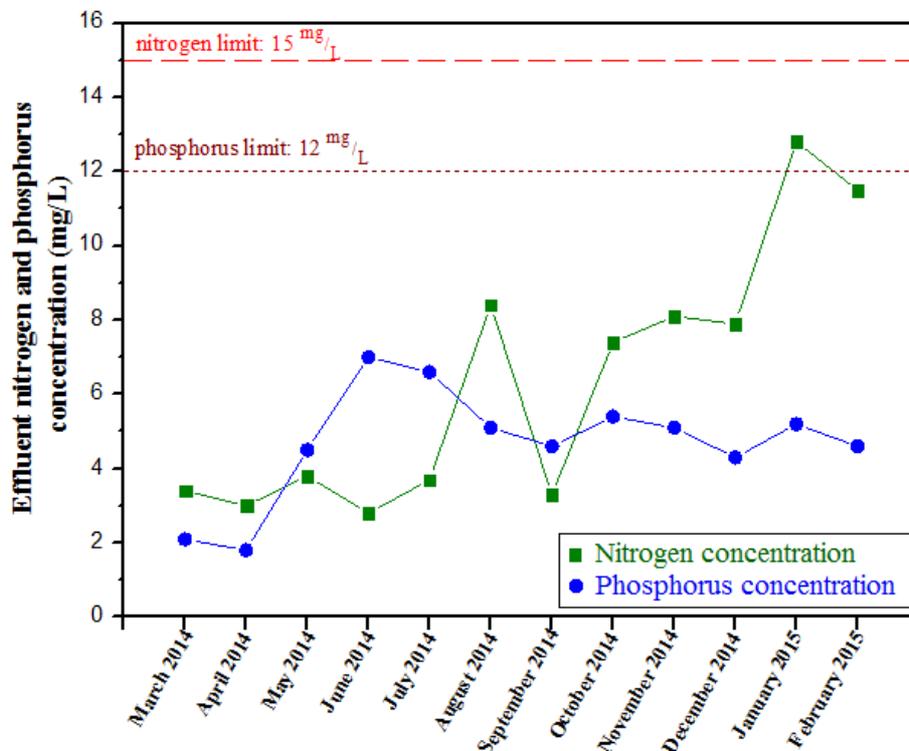


Figure 1. Total nitrogen and total phosphorus mean concentration of the effluent stream and the respective regulatory discharge limits.

Table 3. Descriptive statistics of total nitrogen concentrations (mg/L) in the influent and effluent streams for the months March 2014-February 2015.

	March 2014		April 2014		May 2014		June 2014		July 2014		August 2014	
	inf	eff	inf	eff	inf	eff	inf	eff	inf	eff	inf	eff
Mean	62.8	3.4	85.0	3.2	87.6	3.8	68.2	2.8	63.3	3.8	61.5	3.2
Median	62.0	2.7	70.9	2.9	94.9	3.4	69.0	2.5	64.0	4.0	62.6	3.3
Mode	64.3	2.7	45.8	2.7	61.6	3.0	57.2	2.4	55.7	2.8	66.4	2.1
Range	22.7	7.3	95.5	3.6	53.4	3.9	21.9	3.0	14.3	2.7	13.3	2.8
SD*	5.0	1.9	32.8	1.0	20.4	1.2	5.6	0.8	5.0	0.9	4.4	0.9
Variance	25.2	3.8	1077.0	1.0	416.6	1.5	31.6	0.6	25.1	0.8	18.9	0.9
Skewness	0.97	2.41	0.56	1.23	-0.14	0.83	0.11	1.86	-0.23	0.03	-0.56	-
Kurtosis	4.29	6.25	-1.08	1.12	-1.75	-0.35	0.68	3.72	-1.55	-1.50	-0.70	-
	September 2014		October 2014		November 2014		December 2014		January 2015		February 2015	
	inf	eff	inf	eff	inf	eff	inf	eff	inf	eff	inf	eff
Mean	59.8	3.3	63.1	7.4	63.1	8.2	54.9	8.4	75.9	12.7	61.5	69.0
Median	59.7	3.2	65.0	7.0	63.1	7.5	52.0	7.8	72.4	12.7	62.6	67.4
Mode	54.0	1.9	66.0	1.8	53.0	5.0	33.1	6.0	63.6	11.7	66.4	60.2
Range	12.5	3.1	18.9	11.5	20.3	8.1	64.9	10.3	54.1	4.8	13.3	20.0
SD*	3.3	0.9	4.9	3.3	6.1	2.8	18.2	3.4	13.8	1.5	4.4	5.6
Variance	11.0	0.9	23.8	11.2	37.7	7.9	330.2	11.5	189.3	2.3	18.9	31.1
Skewness	0.44	0.35	-1.95	0.12	-0.12	0.67	1.17	0.55	2.73	-0.27	-0.56	0.43
Kurtosis	0.41	-0.33	4.43	-0.33	-0.44	-0.80	1.49	-0.96	8.24	-0.84	-0.70	0.15

\*SD: Standard deviation

Table 4 presents descriptive statistics of total phosphorus concentrations for the time period March 2014-February 2015 in the influent and effluent streams. In all groups of data, the median

values did not deviate extensively from the mean values. The spread of phosphorus concentration values within this period of months can be estimated by the standard deviation, the variation and the range. As an example, the values corresponding to the influent and effluent phosphorus concentrations during May can imply a distribution deviated from the normal pattern. The coefficients of skewness and kurtosis show the degree of symmetry and peakedness/flatness in the phosphorus concentration distribution, respectively. The effluents concentrations in April are indicative of negatively skewed and platykurtic distribution, showing that the respective data deviate from the mean towards higher values, whereas those calculated for December were found to be positively skewed and showed a leptokurtic distribution, describing that these data tended to the lower values and with a high peak.

Table 4. Descriptive statistics of total phosphorus concentrations (mg/L) in the influent and effluent streams for the months March 2014-February 2015.

	March 2014		April 2014		May 2014		June 2014		July 2014		August 2014	
	<i>inf</i>	<i>eff</i>	<i>inf</i>	<i>eff</i>	<i>inf</i>	<i>eff</i>	<i>inf</i>	<i>eff</i>	<i>inf</i>	<i>eff</i>	<i>inf</i>	<i>eff</i>
Mean	9.0	2.1	11.6	1.7	15.2	4.5	9.4	7.0	8.7	6.5	8.3	5.1
Median	9.0	2.1	12.3	2.0	15.1	5.1	9.1	6.5	8.7	6.6	8.2	5.1
Mode	8.6	0.8	7.6	1.0	8.8	0.8	9.1	6.3	7.4	5.5	7.9	4.1
Range	0.7	2.8	8.7	1.4	13.1	6.4	2.8	2.4	2.5	2.2	1.1	2.1
SD	0.3	1.2	3.8	0.6	6.0	2.8	1.2	1.2	1.0	0.8	0.5	0.9
Variance	0.1	1.5	14.4	0.4	36.3	8.0	1.4	1.4	1.1	0.6	0.2	0.8
Skewness	-0.94	0.20	0.01	-0.45	0.07	-0.90	1.20	1.95	-0.14	0.11	1.60	-0.02
Kurtosis	1.50	-2.54	-2.21	-2.43	-3.50	-0.08	2.32	3.85	0.78	0.37	2.87	-0.13
	September 2014		October 2014		November 2014		December 2014		January 2015		February 2015	
	<i>inf</i>	<i>eff</i>	<i>inf</i>	<i>eff</i>	<i>inf</i>	<i>eff</i>	<i>inf</i>	<i>eff</i>	<i>inf</i>	<i>eff</i>	<i>inf</i>	<i>eff</i>
Mean	7.3	4.6	8.1	5.2	9.1	4.9	6.2	4.2	11.6	5.2	8.5	4.6
Median	7.6	4.6	7.9	5.1	9.1	4.6	6.7	3.8	9.7	5.3	8.5	4.9
Mode	7.6	4.1	7.1	4.2	7.2	4.2	3.4	3.6	7.9	4.4	8.5	3.1
Range	2.5	1.1	3.0	3.0	5.2	1.9	4.1	2.5	11.3	1.4	0.3	2.4
SD	1.0	0.5	1.2	1.1	1.7	0.6	1.6	1.1	5.2	0.6	0.1	1.1
Variance	1.1	0.2	1.4	1.2	2.9	0.4	2.6	1.1	26.6	0.3	0.0	1.1
Skewness	-1.41	-0.04	1.71	1.44	1.29	0.88	-1.71	2.14	1.80	-0.79	-	-1.34
Kurtosis	2.65	-2.67	3.35	2.79	2.47	0.28	3.07	4.69	3.3	1.77	2.23	1.33

### 3.2 Tests of Normality

Tables 5 and 6 present the results from the Shapiro-Wilk tests (normality tests) for the nitrogen and phosphorus concentrations in influent and effluent streams during the period between March 2014 and February 2015, respectively. The significance (Sig.) values indicate the normality of data distribution. If the Sig. value of the Shapiro-Wilk test is greater than 0.05, then the respective data is considered as normally distributed. If it is lower than 0.05 then the data significantly deviate from the normal distribution. Regarding the influent stream, normal distribution was not observed during March, September, October and January for the total nitrogen concentrations, as well as during April and May 2014, considering the total phosphorus concentrations. The Sig. value of effluent data is below the significance level during March, June and February for total nitrogen concentrations, as well as during April, May, June and December for total phosphorus concentrations. Except for the numerical method, normality was estimated also graphically. In order to determine normality graphically, the output of a normal Q-Q plot was used. Four of the monthly Q-Q plots are shown in Figure 2 as examples of this approach. In the plots of Figures 2a and 2c, the data points are close to the diagonal line, therefore, these data are normally distributed, whereas in the plots of Figures 2b and 2d the data points are not following the diagonal line in an obvious non-linear fashion and the respective data are not normally distributed.

Table 5. Shapiro-Wilk tests of Normality for total nitrogen distribution in influent and effluent streams (significance level 95%).

	March 2014	April 2014	May 2014	June 2014	July 2014	August 2014
Influent Sig.	0.035	0.152	0.050	0.671	0.196	0.179
Effluent Sig.	0.001	0.065	0.119	0.003	0.330	0.525
	September 2014	October 2014	November 2014	December 2014	January 2015	February 2015
Influent Sig.	0.823	0.004	0.840	0.167	0.000	0.770
Effluent Sig.	0.715	0.924	0.194	0.214	0.692	0.035

Table 6. Shapiro-Wilk tests of Normality for total phosphorus distribution in influent and effluent streams (Significance level 95%).

	March 2014	April 2014	May 2014	June 2014	July 2014	August 2014
Influent Sig.	0.734	0.000	0.001	0.374	0.972	0.235
Effluent Sig.	0.808	0.033	0.001	0.015	0.994	1.000
	September 2014	October 2014	November 2014	December 2014	January 2015	February 2015
Influent Sig.	0.265	0.132	0.260	0.141	0.091	0.406
Effluent Sig.	0.820	0.277	0.463	0.005	0.677	0.344

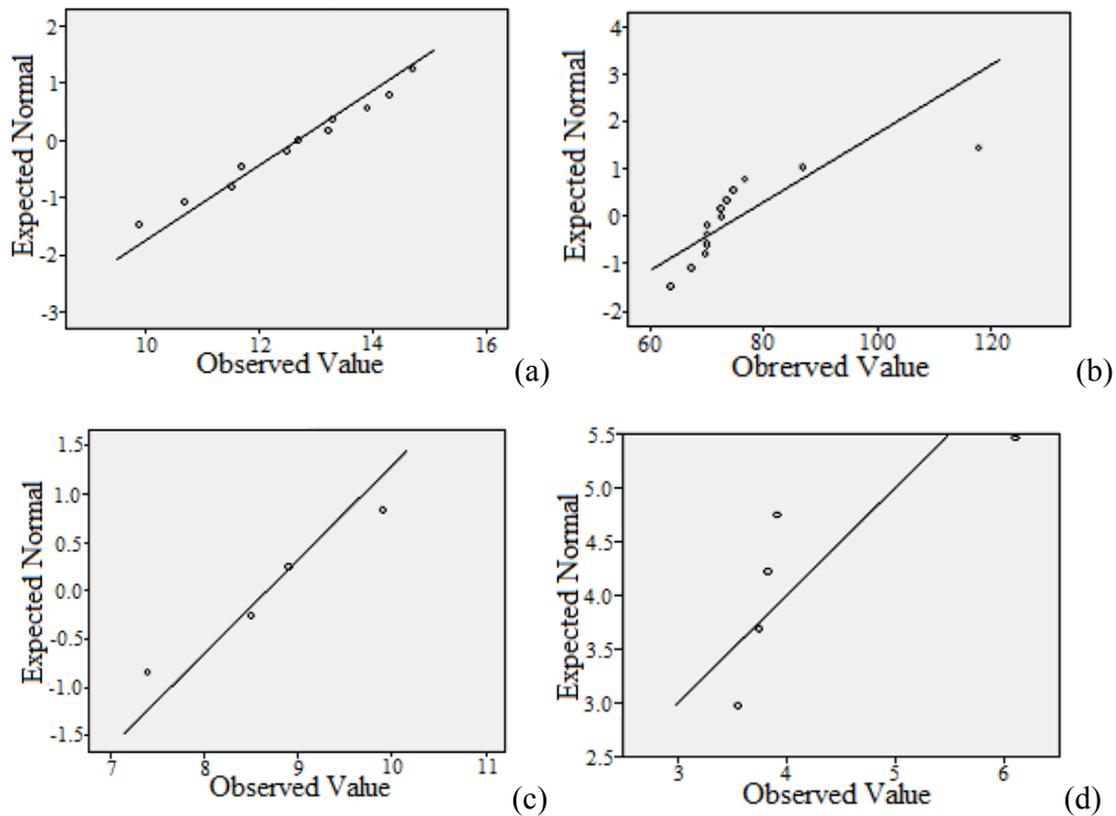


Figure 2. Examples of Normal Q-Q plots for normal (a,c) and asymmetric (b,d) distribution. (a) January 2015 effluent-total nitrogen, (b) January 2014 influent-total nitrogen, (c) July 2014 influent-total phosphorus, (d) December 2014 effluent-total phosphorus.

### 3.3 Seasonal trends

#### 3.3.1 Total Nitrogen

Table 7 presents the output of seasonal variation analysis of nitrogen concentrations in influent and effluent streams during the period between March 2014 and February 2015. Regarding the

seasonal variation of nitrogen, significant difference was found in the influent concentrations during all months (throughout the year) and in the effluent concentrations during the summer, autumn and winter months, as the respective Sig. values did not exceed 0.05. As a result, the seasonal variation of nitrogen concentrations in influent and effluent streams is intense almost the whole year. The differences are presented within the respective seasons as a whole. The multiple comparisons (Tables 8 and 9) between the groups of months that differ significantly, can offer more specific results about which months mostly denote the observed difference. Statistically different were found the pairs of months that present Sig. values lower than 0.05. The multiple comparison results of Kruskal-Wallis tested groups of months show the exact percentage of difference regarding the seasons and the months as well.

Table 7. Seasonal variation of total nitrogen in influent and effluent streams (Significance level 95%).

	Homogeneity	Test	Sig.	Significant difference
Spring 2014 influent	Non-parametric Levene's test (Sig. 0.010)	Kruskal - Wallis	0.016	Yes
Summer 2014 influent	Parametric Levene's test (Sig. 0.659)	One-way ANOVA	0.004	Yes
Autumn 2014 influent	Non-parametric Levene's test (Sig. 0.529)	Kruskal - Wallis	0.044	Yes
Winter 2015 influent	Non-parametric Levene's test (Sig. 0.609)	Kruskal - Wallis	0.001	Yes
Spring 2014 effluent	Non-parametric Levene's test (Sig. 0.446)	Kruskal - Wallis	0.173	No
Summer 2014 effluent	Non-parametric Levene's test (Sig. 0.568)	Kruskal - Wallis	0.017	Yes
Autumn 2014 effluent	Parametric Levene's test (Sig. 0.006)	Brown-Forsythe	0.007	Yes
Winter 2015 effluent	Non-parametric Levene's test (Sig. 0.144)	Kruskal - Wallis	0.004	Yes

Table 8. Multiple comparisons within the one-way ANOVA tested groups: Summer 2014 influent and autumn 2014 effluent data (Significance level 95%).

	Sig.
<b><i>Whole group – Summer 2014 influent</i></b>	
<i>June – July – August 2014</i>	0.004
<b><i>Within the group</i></b>	
<i>June – July</i>	0.053
<i>June – August</i>	0.005
<i>July - August</i>	0.605
<b><i>Whole group – Autumn 2014 effluent</i></b>	
<i>September – October – November 2014</i>	0.007
<b><i>Within the group</i></b>	
<i>September – October</i>	0.010
<i>September – November</i>	0.044
<i>October – November</i>	0.884

Table 10 shows the annual variation of total nitrogen on seasonal basis in influent and effluent streams and Table 11 the performance of multiple comparisons within the seasons' data. The total nitrogen variability was found more intense during autumn for the influent stream, which occurred because during this period the respective concentrations were lower than the rest of the year. In this case, the variability in the effluent stream was found significant, except for the period from spring to summer. This could be attributed to the higher nitrogen removal, due to the higher seasonal temperatures (higher nitrification rates).

### 3.3.2 Total Phosphorus

Table 12 shows the output of the seasonal variation analysis of phosphorus concentrations in influent and effluent streams during the period between March 2014 and February 2015. According to the calculated Sig. values, there is statistically significant difference (i.e.,  $p = 0.042 < 0.05$ ) in the effluent phosphorus concentrations during the summer months. The results also showed that there is significant difference among all examined months. In order to determine which of specific months differ from the previous statistical pattern, multiple comparisons between them were also carried out. The results in Table 13 show that intense differences were observed during June and August,

while July and August differ only slightly. The phosphorus variance in the effluent stream for June and July appear approximately similar. Conclusively, significant variability with respect to the phosphorus concentrations in the effluent stream was found only during the summer.

Table 9. Multiple comparisons within the Kruskal-Wallis tested groups: Spring 2014 influent, autumn 2014 influent, winter 2015 influent, summer 2014 effluent and winter 2015 effluent data (significance level 95%).

	Difference Percentage (%)	Sig.
<b><u>Whole group – Spring 2014 influent</u></b>		
March – April – May 2014	21	0.016
<b><u>Within the group</u></b>		
March – April	10	0.112
March – May	38	0.002
April – May	0	0.701
<b><u>Whole group – Autumn 2014 influent</u></b>		
September – October – November 2014	15	0.044
<b><u>Within the group</u></b>		
September – October	20	0.015
September – November	12	0.069
October – November	0	0.854
<b><u>Whole group – Winter 2015 influent</u></b>		
December – January – February 2015	37	0.001
<b><u>Within the group</u></b>		
December – January	40	0.002
December – February	34	0.004
January – February	12	0.092
<b><u>Whole group – Summer 2014 effluent</u></b>		
June – July – August 2014	21	0.017
<b><u>Within the group</u></b>		
June – July	31	0.004
June – August	8	0.158
July – August	8	0.158
<b><u>Whole group – Winter 2015 effluent</u></b>		
December – January – February 2015	30	0.004
<b><u>Within the group</u></b>		
December – January	40	0.002
December – February	15	0.060
January – February	12	0.086

Table 10. Annual variation of total nitrogen in influent and effluent streams (Significance level 95%).

	Test	Sig.	Significant difference
Influent	Kruskal - Wallis	0.004	Yes
Effluent	Kruskal - Wallis	0.009	Yes

Table 11. Multiple comparisons within the seasons' total nitrogen influent and effluent data (significance level 95%).

	Difference Percentage (%)	Sig.
<b><u>Whole group</u></b>		
Spring-Summer-Autumn-Winter Influent	9	0.004
<b><u>Within the group</u></b>		
Spring - Summer	4	0.068
Spring - Autumn	11	0.003
Spring - Winter	1	0.301
Summer - Autumn	4	0.069
Summer - Winter	3	0.101
Autumn - Winter	10	0.006
<b><u>Whole group</u></b>		
Spring-Summer-Autumn-Winter Effluent	54	0.009
<b><u>Within the group</u></b>		
Spring - Summer	0	0.765
Spring - Autumn	22	0.000
Spring - Winter	70	0.000
Summer - Autumn	26	0.000
Summer - Winter	72	0.000
Autumn - Winter	32	0.000

Table 12. Seasonal variation of total phosphorus in influent and effluent streams (significance level 95%).

	Homogeneity	Test	Sig.	Significant difference
Spring 2014 influent	Non-parametric Levene's test (Sig. 0.723)	Kruskal - Wallis	0.334	No
Summer 2014 influent	Parametric Levene's test (Sig. 0.472)	One-way ANOVA	0.329	No
Autumn 2014 influent	Parametric Levene's test (Sig. 0.782)	One-way ANOVA	0.172	No
Winter 2015 influent	Parametric Levene's test (Sig. 0.023)	Brown-Forsythe	0.156	No
Spring 2014 effluent	Non-parametric Levene's test (Sig. 0.348)	Kruskal - Wallis	0.359	No
Summer 2014 effluent	Non-parametric Levene's test (Sig. 0.723)	Kruskal - Wallis	0.042	Yes
Autumn 2014 effluent	Parametric Levene's test (Sig. 0.548)	One-way ANOVA	0.492	No
Winter 2015 effluent	Non-parametric Levene's test (Sig. 0.881)	Kruskal - Wallis	0.360	No

Table 13. Multiple comparisons within the summer 2014 effluent data (significance level 95%).

	Difference Percentage (%)	Sig.
<b>Whole group</b>		
June – July – August 2014	52	0.042
<b>Within the group</b>		
June – July	3	0.624
June – August	76	0.021
July - August	48	0.050

Table 14 shows the annual variation of total phosphorus on seasonal basis in the influent and effluent water streams, and Table 15 presents the performance of multiple comparisons within the seasonal data. Observing the total phosphorus trends during the whole year, significant variability was detected in the spring months for the influent stream, which is attributed to additional loading occurred during that period, as well as in spring and summer months for the effluent water stream, due to slightly lower and higher concentrations than the average values, respectively.

Table 14. Annual variation of total phosphorus in influent and effluent streams (significance level 95%).

	Test	Sig.	Significant difference
Influent	Kruskal - Wallis	0.017	Yes
Effluent	Kruskal - Wallis	0.000	Yes

Table 15. Multiple comparisons within the seasons' total phosphorus influent and effluent data (significance level 95%).

	Difference Percentage (%)	Sig.
<b>Whole group</b>		
Spring-Summer-Autumn-Winter Influent	19	0.017
<b>Within the group</b>		
Spring - Summer	15	0.057
Spring - Autumn	25	0.008
Spring - Winter	25	0.010
Summer - Autumn	5	0.227
Summer - Winter	5	0.241
Autumn - Winter	0	0.809
<b>Whole group</b>		
Spring-Summer-Autumn-Winter Effluent	44	0.000
<b>Within the group</b>		
Spring - Summer	51	0.000
Spring - Autumn	37	0.001
Spring - Winter	28	0.008
Summer - Autumn	33	0.002
Summer - Winter	45	0.001
Autumn - Winter	0	0.661

### 3.4 Fluctuation of total nitrogen and phosphorus influent and relation to removal efficiency

Figure 3 demonstrates the mean nitrogen concentration values from March 2014 to February 2015, in relation to the respective nitrogen removal efficiency of the wastewater treatment plant. The total nitrogen concentration in the wastewater influent varied between 60 and 90 mg/L, without affecting the removal efficiency. The nitrogen removal percentage was found almost stable and at high levels, indicating the efficient and appropriate operation of the treatment plant. The slightly lower removal percentages during autumn and winter months can be explained by the lower temperatures, which affect negatively the denitrification rate. As a result, the higher nitrogen concentration in the raw wastewater is not expected to influence adversely its subsequent removal by increasing accordingly its concentration in the effluent stream. This is in agreement with the correlation analysis (Table 16). The Sig. value of 0.215 confirms the “null hypothesis” that influent nitrogen concentration is not associated with the removal efficiency. The same observation with respect to the total nitrogen concentration of the influent and its influence to the effluent quality has also been made by de la Torre et al. (2013) for two WWTPs at Utiel and Corbera-Llauri. Since the total nitrogen concentration in the influent stream was not found to affect the corresponding concentration in the effluent, this was an indicator that the plants operated correctly and could be even oversized.

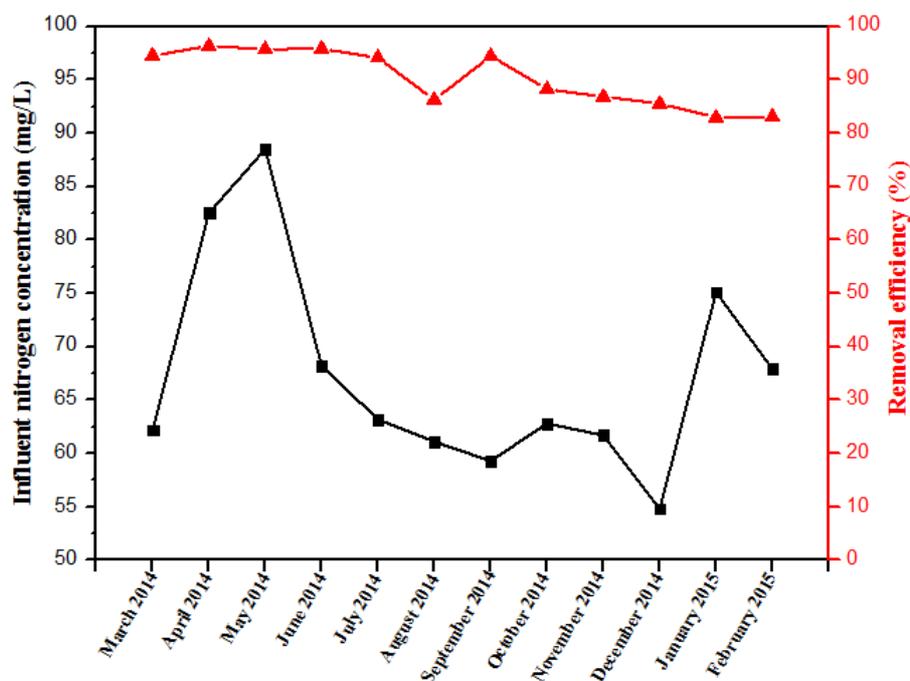


Figure 3. Nitrogen concentration of the influent stream and nitrogen removal efficiency during the period between March 2014 and February 2015.

Table 16. Spearman correlation test between nitrogen concentration of the influent stream and nitrogen removal efficiency (significance level 0.05).

Parameter	Value
Correlation coefficient	0.386
Sig. (2-tailed)	0.215

Figure 4 shows the mean phosphorus concentration values from March 2014 to February 2015, in relation to the phosphorus removal achieved throughout the wastewater treatment. The fluctuation in phosphorus concentration and the respective removal efficiencies indicate that they follow the same pattern during autumn and winter months. However, during spring and summer months, concentrations and their removals do not relate in a specific way. In this period, a deviation

from the normal distribution of data was observed. It may be due to additional wastewater loads, or temporary operating disturbances of the treatment plant. Similarly, the correlation analysis (Table 17) shows that there is significant correlation ( $p$ -value = 0.038) between phosphorus concentration of the influent stream and phosphorus removal efficiency. The observed positive linear relation between them is considered as medium to strong, due to the respective correlation coefficient's value (60%).

Table 17. Spearman correlation test between phosphorus concentration of the influent stream and phosphorus removal efficiency (significance level 0.05).

Parameter	Value
Correlation coefficient	0.602
Sig. (2-tailed)	0.038

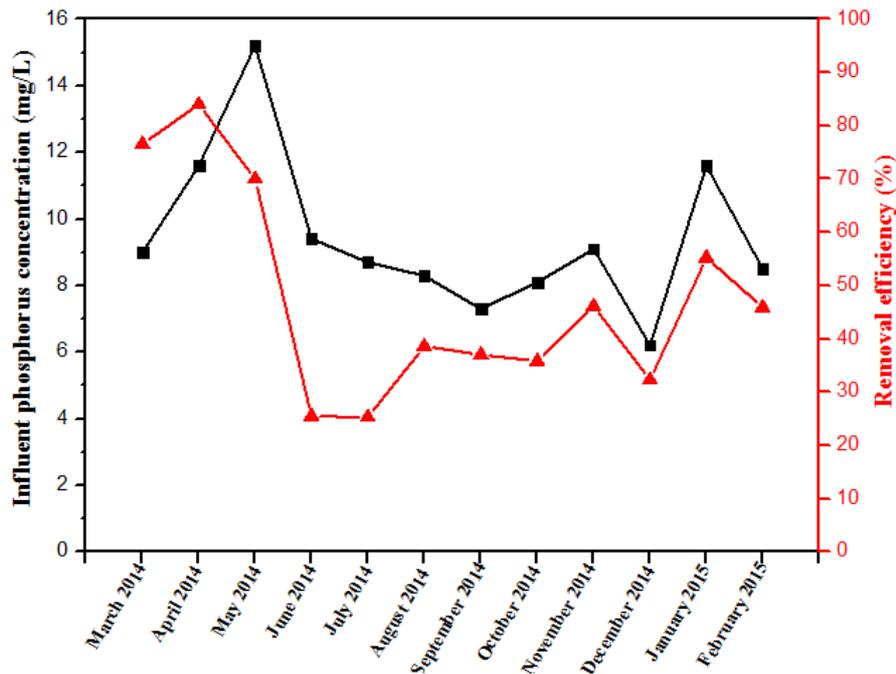


Figure 4. Phosphorus concentration of the influent stream and phosphorus removal efficiency during the period between March 2014 and February 2015.

#### 4. CONCLUSION

A statistical survey of nutrient concentrations and their relations with the respective removal efficiency has been conducted for the wastewater treatment plant “AINEIA” near Thessaloniki, Greece. The data were collected from the influent and effluent wastewater streams. The outstanding influent nutrient concentrations during April, May and January months were ascribed to additional loads with non-urban wastewater origin. Hypothesis testing for symmetric and asymmetric distributions (ANOVA and Kruskal-Wallis) revealed that in almost all seasons there were significant differences between the mean values, or ranks for the nitrogen concentrations, while phosphorus concentrations differed significantly only during the summer months. The annual variation of total phosphorus on seasonal basis showed that influent loading during spring months differed from the rest of the year, due to additional loading. The concentrations during spring and summer months for the effluent water stream varied accordingly, as well.

The possibility that the variations of influent concentration levels and the respective nutrient removal efficiency be related in a specific manner was subsequently statistically examined. Nitrogen concentrations varied throughout the year without any noticeable effect on their removal percentage efficiency, which was constantly high. However, a rather stable relation occurs for

phosphorus concentrations during the autumn and winter months, but no systematic trend could be observed for the spring and summer months, while approximately 60 % phosphorus removal efficiency was observed.

A good proposal for eliminating the effluent phosphorus concentration in order to meet the upcoming lower regulation standards could be the application of phosphate removal process from re-circulated side-streams by chemical precipitation. The sludge treatment side-streams return to the headwork of the plant and carry a significant nutrient load. This load could be reduced by side-stream treatment via struvite (magnesium ammonium phosphate) precipitation – recovery. Moreover, struvite precipitation reduces also the re-circulated nitrogen concentration as well. As a result, although nitrogen initial load and respective removal are not strongly correlated, the suggested side-stream treatment could contribute to even lower nitrogen effluent concentration, without changing significantly the plant's operating conditions.

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## REFERENCES

- APHA, AWWA, WEF, 1992. Standard Methods for the Examination of Water and Wastewater, 18<sup>th</sup> ed. American Public Health Association, Washington DC, USA.
- Bozdogan E. and Sogut Z., 2013. Determination of reuse potential of treated wastewater at Urban Green Area. In: ICOEST 2013 – Cappadocia, Urgup, Turkey, June 18-21, 2013.
- Council Directive, 1991. Council Directive of 21 May 1991 concerning urban waste water treatment (91/271/EEC). Official Journal of the European Communities, 135: 40-52.
- de la Torre M.L., Sanchis J., Grande J.A., Valente T., Santisteban M., Fernandez J.P., 2013. Comparative analysis of different types of wastewater treatment plants: application of statistical methods to large data sets of effluent quality parameters. In: International Multidisciplinary Scientific GeoConference SGEM, Albena, Varna, Bulgaria, 16-22 June, 2013.
- Hoa P.T., Nair L., Visvanathan C., 2003. The effect of nutrients on extracellular polymeric substance production and its influence on sludge properties. Water SA, 29(4): 437-442.
- Howell J.A., 2010. The distribution of phosphorus in sediment and water downstream from a sewage treatment works. Bioscience Horizon, 3(2): 113-123.
- Jeppsson U., Alex J., Pons M.N., Spanjers H., Vanrolleghem P.A., 2002. Status and future trends of ICA in wastewater treatment – a European perspective. Water Sci. Tech., 45(4-5): 485–494.
- Joint Ministerial Decision 13059/1992 on the approval of the environmental terms concerning the wastewater treatment plant in the touristic area of Thessaloniki (Prefecture of Thessaloniki and Prefecture of N. Michaniona).
- Khambete A.K. and Christian R.A., 2014. Statistical analysis to identify the main parameters to effecting WWQI of sewage treatment plant and predicting BOD. IJRET, 3(1): 186-195.
- Pirsaheb M., Fazlzadehdavil M., Hazrati S., Sharafi K., Khodadadi T. and Safari Y., 2014. A survey on nitrogen and phosphorus compound variation processes in wastewater stabilization ponds. Pol. J. Environ. Stud., 23(3): 831-834.
- Razali N.M. and Wah Y.B., 2011. Power comparisons of Shapiro-Wilk, Kolmogorov-Smirnov, Lilliefors and Anderson-Darling tests. J. Stat. Model. Anal., 2(1): 21-33.
- Smith M.J., 2015. Statistical Analysis Handbook. Digital edition, online at: <http://www.statsref.com>.
- Tumer E. and Edebali S., 2015. Prediction of wastewater treatment plant performance using multilinear regression and artificial neural networks. In: INISTA 2015 – International Symposium on Innovations in Intelligent Systems and Applications, Madrid, Spain, 2-4 September, 2015, doi:10.1109/INISTA.2015.7276742.
- U.S. EPA, 2007. Biological Nutrient Removal Processes and Costs. United States Environmental Protection Agency.