

# Determination of Different Forms of Phosphorus in Waters of the Wastewater Treatment Plant in Durres, Before and After Treatment

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**Abstract** - The purpose of this article is to present the results of a study on the water of the wastewater treatment plant in Durrës. For this, a study was conducted during the months of May, June and July 2021 which was based on the determination of the different forms of phosphorus in water, as one of the main nutrients, and responsible for the eutrophication of waters. Representative sampling was done before treatment, after treatment and in wetlands. Storage and transport of samples, based on recommended standard methods. Four different forms of phosphorus were identified (orthophosphate, total phosphorus, condensed phosphorus and organic phosphorus). The selection of standard analysis methods was made by APHA and DIN and for each of them the performance parameters of the method were defined (sensitivity, dictation limit and linear area of measurements). The results obtained were processed and compared with "On permissible discharge rates and zoning criteria for aquatic receiving environments", and EU Directive 91/271 / EEC. The results obtained from the study, showed the higher concentrations of different forms of phosphorus at the station before treatment, but only the values of total phosphorus concentration resulted outside the allowed norms. At the post-treatment station or in wetlands it is noticed that the concentrations of the studied of different forms of phosphorus are within the allowed norms, with the exception of the total phosphorus concentration. Therefore, for the reduction and recovery of phosphorus from water of wastewater treatment plants, the forms of phosphorus that are present must be considered.

**Keywords:** The different forms of Phosphorus, Wastewater, Durres, EU Directive 91/271 / EEC

## 1. Introduction

Eutrophication of surface waters is a major issue across the planet, with diffuse (agricultural) and point sources (wastewater treatment works, WwTW) being the main inputs. [1]

The difficulty in mitigating eutrophication lies partly in the fact that phosphorus is present nearly everywhere, in both organic and inorganic forms. It undergoes changes in form and solubility, becomes more or less bioavailable, gets transported and accumulated, though not necessarily where it is needed. [2] Phosphorus exists as inorganic orthophosphate (water soluble), polyphosphate (condensed phosphate), and organic phosphate.[3]

Organic phosphorus has taken a backseat to inorganic phosphorus in research, but in the last decades it has become apparent that it must be studied due to the prominent role it in the phosphorus cycle. [2] Particulate phosphorus—found in suspension or sediment—consists of plants, animals, phosphorus in minerals, and phosphate adsorbed on an iron oxyhydroxide mineral surface. [4]

Total phosphorus (TP) is a measure of all forms of phosphorus found in water. Dissolved inorganic P (DIP), in the form of orthophosphate, is easily exploited by primary manufacturers and is therefore the main available form of P, but also some dissolved organic species P (DOP) may find use. [5,6] The main sources of phosphorus in wastewater are human extracts, phosphorus contained in household detergents and some industrial and commercial discharges. Precipitation contributes very little to phosphorus in wastewater if combined sewage systems are implemented. [7] Phosphorus discharges into wastewater can come from the food and textile industry and from plant planting plants. The industrial and commercial contribution to phosphorus discharges into municipal wastewater can vary widely depending on local situations and is in the range of 10 to 40%. [8]

The treatment plant in Durrës is located in Porto Romano, about 2 km away from the city center of Durrës, at the former fishing company. The plant treats the polluted water of the sewage of the municipality of Durres as well as of some villages such as Bisht Pallë, Rrashbull, Arapaj, San Vlash and Shkallnur. The wastewater treatment plant in Durrës is biologically treated. The installed technology is "active sludge" and with advanced treatment for nitrogen and phosphorus reduction, while the gas obtained from sludge digestion will be used to produce electricity in such quantities as to meet the needs of the plant itself. In the plants it is prediction that a part of the treated water is used for purposes of protection in case of fire, rinsing of squares, irrigation of the vegetation around the plant Before the treated water is discharged into the sea it undergoes a chlorination process. The water treatment line in the plant consists of preliminary and primary treatment in which are being installed: mechanical grilles, pumping station, automatic grilles, collector and water distribution room depending on the number of ventilation basins, while the secondary treatment consists of the aeration basin and the secondary classifier. The tertiary water treatment will be performed through vegetation beds through which phosphorus will be reduced. [9]

The purpose of this article is to present the results of a study on the water of the wastewater treatment plant in Durrës. For this, a study was conducted during the months of May, June and July 2021 which was based on the definition of different forms of phosphorus in water, as one of the main nutrients, and responsible for the eutrophication of waters.

## Materials and Methods

### 2. Sampling

Samples for performing the analyzes were taken during the three expeditions from May to July 2021, at the wastewater treatment plant, Durres. Sampling, storage and conservation were performed in accordance with the recommended standard methods. The sampling stations for the study were: M1 before treatment; M2 after treatment at the plant; M3 in the wetland. Water samples were taken in 1Liter polyethylene bottles (care should be taken that the sampling and analysis equipment were cleaned with

phosphate free detergents) and transported to the laboratory in the refrigerator at 4°C. [7,10] Below are some photos from each sampling station for the wastewater treatment plant, Durres.



Figure 1. Pre - treatment sampling station



Figure 2. Post-treatment sampling station



Figure 3. Wet sampling station

Phosphorus species are typically defined by the technique used to extract and analyze the phosphorus. The orthophosphates analysis should be done immediately after sampling which is filtered immediately after sampling. [10,11] Wastewater samples were acidified to  $\text{pH} < 1$  using  $\text{H}_2\text{SO}_4$  4.5 M, before determination of total orthophosphate (dissolved particulate) to dissolve all the orthophosphates particulates. [7,12] Dissolved and total orthophosphate concentrations were measured immediately after sample collection. To measure condensed poly and organic phosphates, acid hydrolysable (ortho and condensed polyphosphates) and total (organic and condensed polyortho phosphates) phosphorus species had to be converted into orthophosphate. Acid hydrolysable phosphorus was converted to orthophosphate by acid digestion with 1 mL  $\text{H}_2\text{SO}_4$  4.5M [10,11] The total phosphorus was converted to orthophosphate by persulphate digestion [10, 11, 13 14, 15]. All phosphorus species, after the above specific treatments, were measured by colorimetry using the ascorbic acid method. All phosphorus forms shall be reported as P, mg/L.

## Results and Discussions

During the study, four different forms of phosphorus were studied: Orthophosphate, total phosphorus, condensed phosphate, and organic phosphorus, in the waters of the wastewater treatment plant in Durres. Chemical analyzes of concentrations of different forms of phosphorus were performed by standard methods obtained from APHA and DIN. The calibration curve, sensitivity, dictation limit and linear area of the measurements were also evaluated for chemical analysis.

Table 1. Calibration curve parameters

	Mean calibration curve	R <sup>2</sup>	Measurement zone	Work range
Condensed polyphosphates (P-PO <sub>4</sub> <sup>3-</sup> )	A = 0.7342x + 0.0042	0.9999	0 – 1mg/L	>0.02mg/L
Orthophosphates (P-PO <sub>43-</sub> )	A= 0.7349x +0.003455	0.9997	0 – 1mg/L	>0.02mg/L
P total	A=0.6999x + 0.007498	0.9983	0 – 1mg/L	>0,005 mg /L

The table shows that the values of the correlation coefficient ( $R^2$ ) for all calibration curves, turned out to be very close to the value 1; this shows that the dependence is very linear in the whole area of the concentrations of our measurements. The curve cutting values at the ordinate axis are quite small, indicating a very low level of white test for calibration solutions. Work area values corresponding to the concentration levels where the method can be applied are taken from the literature used.

Table 2 presents the results of statistical processing for the parameters studied using the Descriptive Statistics Method.

Table 2. Results of statistical processing for the parameters studied using Descriptive Statistics Method

	Mean			Median			Standard Deviation			Minimum			Maximum		
	M1	M2	M3	M1	M2	M3	M1	M2	M3	M1	M2	M3	M1	M2	M3
Orthophosphates (mg/L)	0.769	0.485	0.541	0.724	0.501	0.608	0.170	0.416	0.381	0.625	0.061	0.131	0.957	0.893	0.884
Total Phosphorus (mg/L)	6.633	2.102	2.000	4.430	2.358	2.568	3.877	1.734	1.459	4.358	0.254	0.343	11.11	3.693	3.090
Condensed polyphosphates (mg/L)	1.324	0.611	0.588	1.183	0.401	0.525	0.751	0.612	0.543	0.653	0.131	0.079	2.135	1.300	1.159
Organic phosphates (mg/L)	4.540	1.006	0.871	2.981	1.455	0.525	4.204	0.818	0.959	1.338	0.061	0.133	9.301	1.501	1.956

The figure 4 shows the mean, median, standard deviation, minimum and maximum of orthophosphates values ( $\text{PO}_4^{3-}$  P mg/L). The mean orthophosphates values ( $\text{PO}_4^{3-}$  P mg/L) range from 0.485 mg/L  $\text{PO}_4^{3-}$  for the M2 station to 0.769 mg/L  $\text{PO}_4^{3-}$  for the M1 station. It is noted that the highest orthophosphates values were measured at the M1 station, which belongs to the site of sampling at the plant entrance before treatment. These high values are followed by the M3 station and further the M2 station.

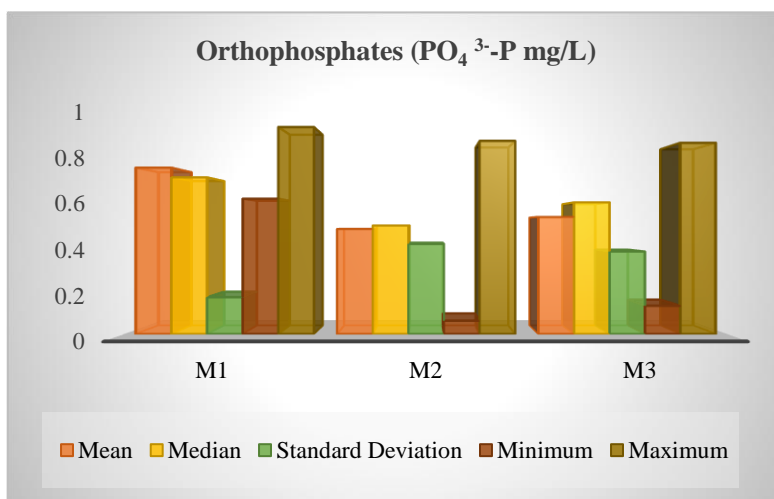


Figure 4. The mean, median, standard deviation, minimum and maximum values of Orthophosphates ( $\text{PO}_4^{3-}$ -P mg/L)

According to the established standards "For the allowed norms of wastewater discharges and the zoning criteria of the receiving aquatic environments", and the Directive of the European Union 91/271 / EEC [16, 17], that at the entrance of the plant before treatment the concentration of total phosphorus is allowed to be 5.8 mg / L  $\text{PO}_4^{3-}\text{P}$  and after treatment 2 mg/L  $\text{PO}_4^{3-}\text{P}$ , the found values of orthophosphate concentrations in the waters of the Wastewater Treatment Plant, Durres, meet these norms.

The figure 5 show the mean, median, standard deviation, minimum and maximum values of the total phosphorus.

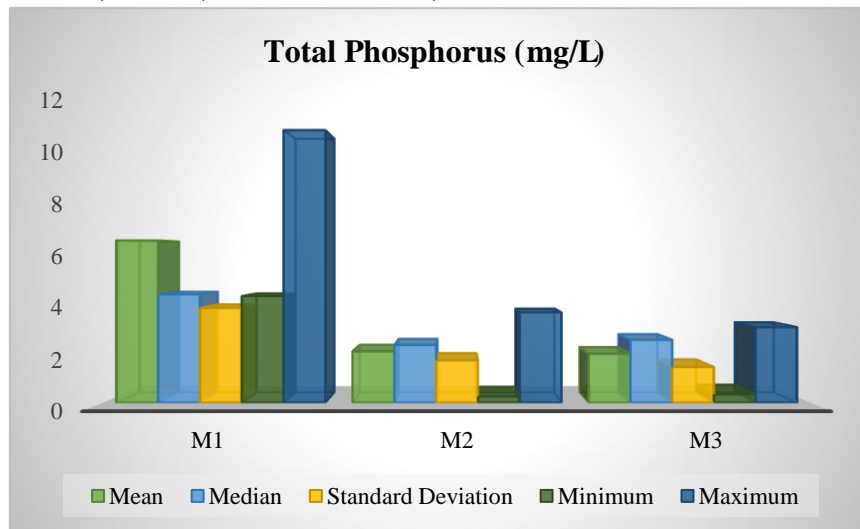


Figure 5. The mean, median, standard deviation, minimum and maximum values of Total Phosphorus (mg/L)

From these graphs, it is noticed that the highest values for the total phosphorus were measured at the M1 station (11,109 mg/L), which belongs to the sampling site at the entrance of the plant before treatment. These high values are followed by the M3 station (3,693 mg/L) and further the M2 station (3,090 mg/L). The mean values of the total phosphorus range from 2 mg/L for station M2 (after treatment) to 6,633 mg/L for the M1 station (before treatment). Compared to the established standards "For the allowed norms of wastewater discharges and the zoning criteria of the receiving aquatic environments", and the Directive of the European Union 91/271 / EEC [16,17], we say that the found values of total phosphorus in the waters of the wastewater treatment plant, Durres, before and after treatment, do not meet these standards, which means that it is necessary to improve the phosphorus treatment system by treating them according to specifications.

The histograms in Figure 6 show the mean, median, standard deviation, minimum and maximum of the Condensed Polyphosphates values ( $\text{PO}_4^{3-}\text{P}$  mg/L). It is observed that the condensed phosphates concentrations mean values range from 0.588 mg/L  $\text{PO}_4^{3-}\text{P}$  for the M3 station (Wetland) to 1,324 mg /L for M1 station (before treatment). Thus, the highest condensed phosphates values resulted in the M1 station. These high values are followed by M2 station and further M3 station. The concentrations values found are within the norms allowed by the standards for the water of wastewater treatment plants.

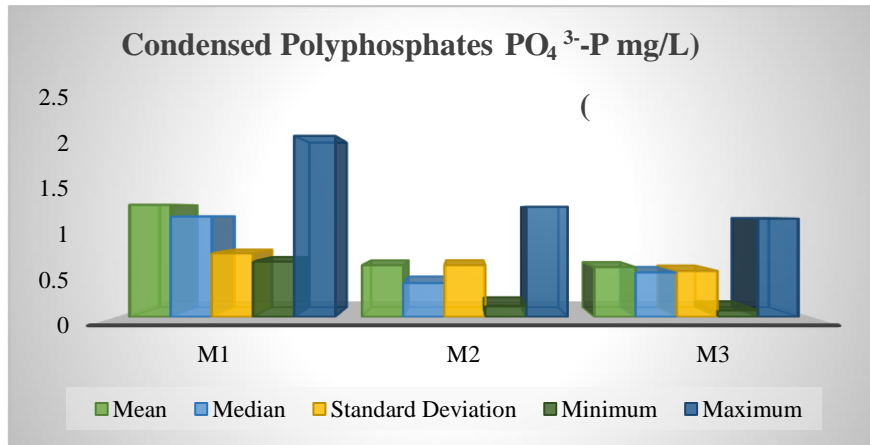


Figure 6. The mean, median, standard deviation, minimum and maximum values of Condensed Polyphosphates (PO<sub>4</sub><sup>3-</sup>-P mg/L)

The Figure 7 shows the mean, median, standard deviation, minimum and maximum of the Organic Phosphates values (PO<sub>4</sub><sup>3-</sup>-P mg/L). It is observed that the organic phosphates concentrations mean values range 0.871 – 4.54mg/L. Thus, the highest organic phosphates values resulted in the M1 station (pre- treatment). The organic phosphates concentrations meet the permitted values according to standards and norms.

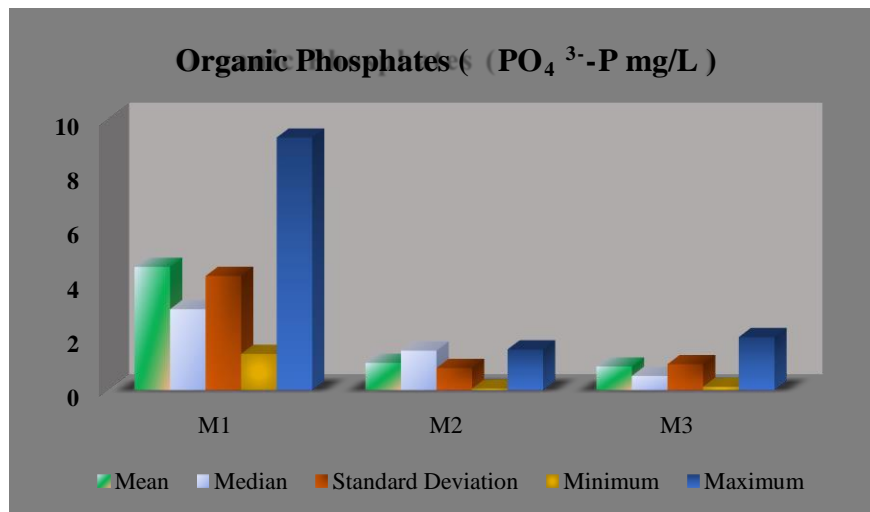


Figure 7. The mean, median, standard deviation, minimum and maximum values of Organic Phosphates (PO<sub>4</sub><sup>3-</sup>-P mg/L)

Figure 8 presents a comparison of the mean concentration values of each phosphorus species we studied. At all three stations, the total phosphorus concentrations were higher, and the orthophosphates concentrations were lower. Ranking starting from the species with the highest concentration is:

**the total phosphorus > the organic phosphates > the condensed phosphates > the orthophosphates**

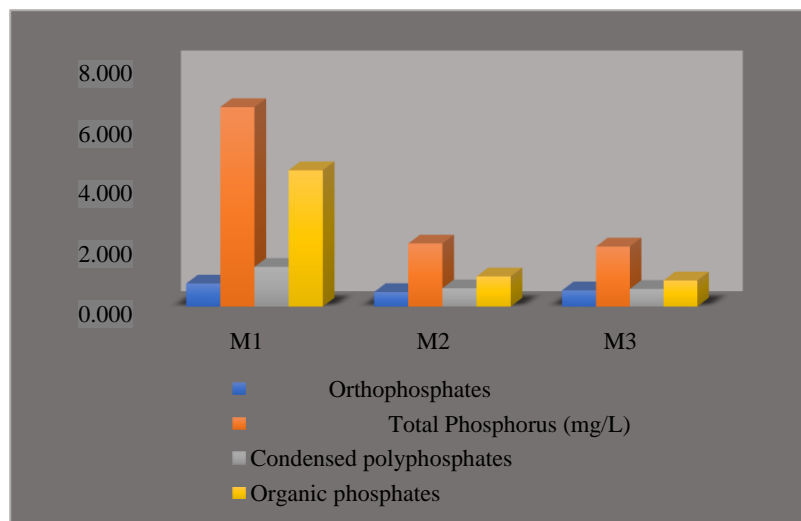


Figure 8. Comparison of the mean concentration values of each phosphorus species

### 3. Conclusions

From this study, we conclude that:

The mean results show a significant and sustainable impact of urban and industrial discharges on water quality. The results obtained from the study, showed the higher concentrations of different forms of phosphorus at the station before treatment, but only the values of total phosphorus concentration resulted outside the allowed norms. At the post-treatment or in wetland stations it is noticed that the concentrations of different forms of phosphorus are within the allowed norms, with the exception of the total phosphorus concentration. Therefore, for the reduction and recovery of phosphorus from water of wastewater treatment plants, the forms of phosphorus that are present must be considered.

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