The Efficiency of Biological Total Phosphorus Removal Process

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This article investigates the efficiency of phosphorus removal in the municipal wastewater treatment plants in five counties of Romania from 2013 to 2017. This study focused on evaluation of the performance of phosphorus elimination using biological methods in order to respect the admissible effluent discharge limits. The yearly average of inflow total phosphorus varies from 3.64 mg/L to 4.22 mg/L comparing with 1.02 mg/ L and 1.59 mg/L the average of outflow. Chemical and biological methods are utilized to remove phosphorus. The efficiency of the numerous process available for the phosphorus removal is quite inadequate by comparing the effluent degree of purification and the removal cost.

Keywords: Biological phosphorus removal; eutrophisation; water pollution

Over the past decades, the phosphorus removal from wastewater has been recognized as a crucial task for municipal wastewater treatment plants with the purpose of limiting the input of phosphorus into river basins [1].

Existence of nutrients, notably nitrogen and phosphorus in wastewater effluents and their effects on natural water bodies are of major impact [2]. Different techniques for the elimination of total phosphorus from wastewater, based on chemical or biological methods, have been established and improved the water quality Biological phosphorus removal technique is frequent comparing with chemical means due to simplicity, economy and numerous environmental advantages [3].

Phosphorus is a limiting nutrient in aquatic ecosystems and it has a significant role for the growth of algae and vegetation of aquatic ecosystem, principally when it relates with fresh water [4]. Excessive quantities of phosphorus that are eliminated in fresh water bodies generate eutrophication and others complementary issues, that produces destructive effects for the aquatic life and the entire environment. Therefore, reducing phosphorus quantities in wastewater plant is obligatory before it is eliminated into water basins [5, 6].

Phosphorus is released to the ecosystems by diverse industrial sectors, agricultural and other activities. Despite the fact that many countries have approved rigorous effluent discharge limits for phosphorus by reason of accelerating concerns regarding the eutrophication, phosphorus pollution is still too high [7].

The full implementation of the Urban Waste Water Directive 91/271/ EEC Directive requires all Member States to use an adequate wastewater treatment infrastructure [8]. More than that, it designates a set of circumstances and contingencies, containing the dimensions of municipalities and depending on the sensitivity of the areas to require more stringent treatment. It has been established that the mitigation of point sources is an adequate method to minimize the quantity of nutrients discharged to the aquatic system, particularly for phosphorus [9]

The Water Framework Directive 2000/60/EC 2000 demands Member States to assure that whole surface and groundwater bodies are in favorable ecological and chemical conditions by 2015 [10].

Agriculture is still the principal source of diffuse pressure on water bodies, and dispersed nutrient pollution is still a significant threat to surface water, groundwater, lakes and transitional water quality. In compliance with EEA 2012 diffuse pollution from agriculture is a considerable pressure for, at least, 40 and 30% of rivers and lakes, respectively [11].

A significant percentage of pollution, in recent decades, has come from agricultural sources. This is a consequence of a reduction in the quantity of effluent resulting from industrial sources and human settlements into water bodies, in addition to an intensification of agriculture. Agricultural intensification consequences on water quality through the utilization of nutrients (like an effect of soil management and fertilizer treatment) and other chemicals (e.g. herbicides and pesticides) into the water environment, by biological pollution (e.g. from microbiological organisms in dung and droppings) and by soil being destroyed and washed off farmland [12].

The discharge of phosphorus from municipal wastewater is compulsory in order to reduce eutrophication in receiving water bodies, the Danube basin in this case.

Experimental part

The use of phosphorus is inefficient in certain stages of the life cycle, generating water contamination and waste at worldwide level, of associated resources. Five years datasets collected from municipal wastewater treatment plant (WWTP) from Giurgiu, Calarasi, Braila, Galati and Tulcea were studied in this paper.

The analyzed area, 26.345 km^2 and more than 1.65 million inhabitants is a predominantly agricultural being situated in the South and South Est part of Romania. The terrain is use predominantly for agricultural activities consisting of wheat, corn, barley, barley oats, sunflower and vegetables.

Water samples were collected from the five areas located in the Danube basin and were analyzed by the laboratory's municipal wastewater treatment plants. The dataset containing total phosphorus was measured from 2013 to 2017.

European standard EN ISO 6878:2004 is adopt for determination of phosphorus using the ammonium molybdate spectrometric method. This International Standard specifies the determination of the different forms

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of phosphorus compounds present in groundwater, surface water and waste water at variable concentrations, dissolved and undissolved. Concentrations in phosphorus between 0.005 and 0.8 mg/L can be determined without diluting the samples. A solvent extraction operation allows the determination of low phosphorus concentrations with a detection limit of about 0.0005 mg / L [13].

The basic principle consists in the reaction of orthophosphate ions with an acid solution containing molybdate and antimony ions to form the antimony-phosphomolybdate complex. The reduction of this complex is done using the ascorbic acid to form an intense blue complex of molybdenum. Measuring the absorbance of this complex is to determine the concentration of orthophosphates present. Polyphosphates and certain organophosphorus compounds are determined after transformation by hydrolysis with sulfuric acid into orthophosphates which react with molybdate. Numerous organophosphorus compounds are converted to orthophosphates by persulphate mineralization. Mineralization with nitric acid and sulfuric acid is used if a more vigorous treatment is required.

Determination of total phosphorus oxidation with persulfate (SR ISO 6878:2004)

Reagents. Analytical reagents having a recognized analytical quality and water with a negligible phosphate content shall be used during the analysis against the lowest concentration to be determined in the samples. For low phosphate content, it is recommended to use distilled water in a glass only appliance.

Sulfuric acid solution $c(H_2S0_4) = 4.5$ mol/L

Introduce 500 mL ± 5 mL of water into a 2-liter beaker. Subsequently, 500 ± 5 mL of sulfuric acid, p = 1.84 g / mL, is added cautiously with stirring and continuous cooling. Stir well and allow the solution to cool to ambient temperature.

Sodium hydroxide

Dissolve 80 g ± 1 g sodium hydroxide pellets in water, allow to cool and dilute to 1 liter with water.

Molybdate acid,

Add cautiously 230mL ± 0.5 mL of sulfuric acid to 70mL ± 5 mL of water, then cool. Dissolve 13 g ± 0.5 g of $[(NH_4)_6Mo_7O_{24} \times 4H_2O]$ ammonium hepta molybdate tetrahydrate in 100mL ± 5 mL of water. Add to the acid solution and mix thoroughly. Dissolve 0.35 g ± 0.05 g of potassium tartrate and semi-hydrated strontium $[K(SbO)C_4H_4O_6 \times 1/2\ H_2O)]$ in 100mL ± 5 mL of water. Add to the acid molybdate solution and mix thoroughly.

Turbidity and color compensation reagent

Mix two parts by volume of sulfuric acid and one part by volume of ascorbic acid.

Sodium thiosulfate pentahydrate, solution p = 12.0 g / L.

Dissolve 1.20 g ± 0.05 g of pentahydrate sodium thiosulphate ($Na_2S_2O_3 \times 5H_2O$) in 100mL ± 5 mL of water. Add 0.05 g ± 0.005 g anhydrous sodium carbonate (Na_2CO_3) as a conservation agent.

Potassium persulfate solution

Add 5 g ± 0.1 g of potassium persulfate ($K_2S_2O_8$) to 100 ± 5 mL of water and stir for dissolution.

Equipment. The spectrometer must be capable of measuring the absorption in regions of the visible spectrum and near the infrared. The most sensitive wavelength is 880 nm, but if sensitivity loss is allowed, absorbance can also be measured at 700 nm.

Sampling

Laboratory samples are preferably taken in glass bottles, polyethylene or polyvinyl chloride. In the case of low phosphate concentrations, glass vials are used. It is recommended to avoid the use of sampling vials as they may contain phosphorus. 100 mL borosilicate glass bottles with glass stoppers, hermetically sealed by means of metal clips (for determination of total phosphorus by persulphate method in the autoclave); polypropylene bottles or conical cups (with threaded plugs) may also be used. Prior to use, bottles or glasses are washed by adding about 50 mL of water and 2 mL of sulfuric acid. They are placed in an autoclave at a working temperature between 115°C and 120°C, cooled, then rinsed with water. Repeat this mode of operation several times and the vials are kept closed.

Results. The concentration in total phosphorus, ρ_p, was calculated, expressed in milligrams per liter (mg / L), using equation

$$\rho_P = \frac{A-A_0)V_{max}}{f*V_s} \quad (1)$$

where:

A is the absorbance of the sample;

A_0 is the absorbance of the blank sample;

f is the slope of the calibration curve, expressed in liters per milligram (L/mg);

Vmax is the volume of the quenched flask (50 ml), expressed in milliliters (ml);

Vs actual sample volume, expressed in milliliters (mL).

ArcGIS geo-statistical software, specifically, the Spline interpolation module was used to obtain a graphical image of pollutants diffusion. ArcGIS supplies a series of distinct tools for creating an estimated area from sample data points [14].

The Spline tool use an interpolation method that determine values applying a mathematical algorithm that minimizes general surface curvature, ensuing in a plain surface that passes precisely through the input points. Selection of the appropriate tool is dependent on the modeling needs, knowledge of how the tools function, and the sample data set. This technique is an excellent tool to create diverse surfaces like as elevation, water table heights, or pollution concentrations [15, 16].

The algorithm used for the Spline tool uses the following formula for the surface interpolation:

$$S(x,y) = T(x,y)\sum_{j=0}^{n} \lambda_j R(r)_j \quad (2)$$

where:

j = 1, 2, ..., N.

N is the number of points.

λ_j are coefficients found by the solution of a system of linear equations.

r_j is the distance from the point (x,y) to the j^{th} point.

T(x,y) and R(r) are defined individually, rely upon the selected option.

Results and discussions

Five years dataset measured from 2013 to 2017 was used to determine the total phosphorus concentration in Danube river basin. The annually average was illustrated in order to indicate the efficiency of municipal wastewater treatment plant, comparing the inflow and the outflow concentration of total phosphorus.

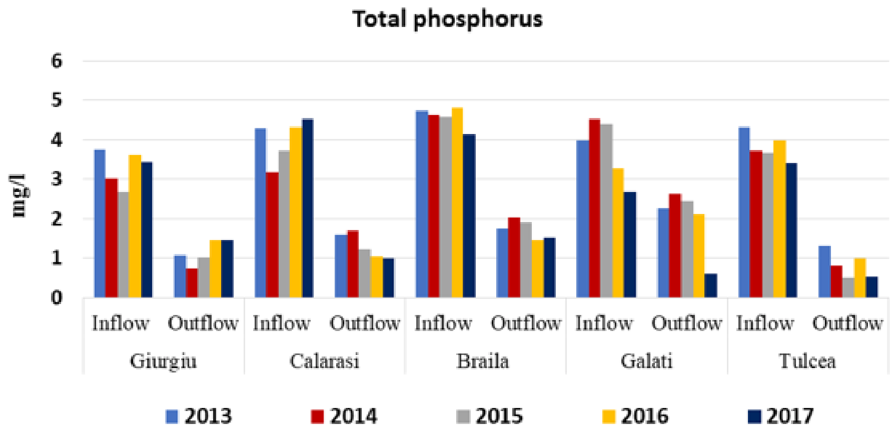

Fig. 1 The average values of 2013-2017 for total phosphorus, inflow and outflow

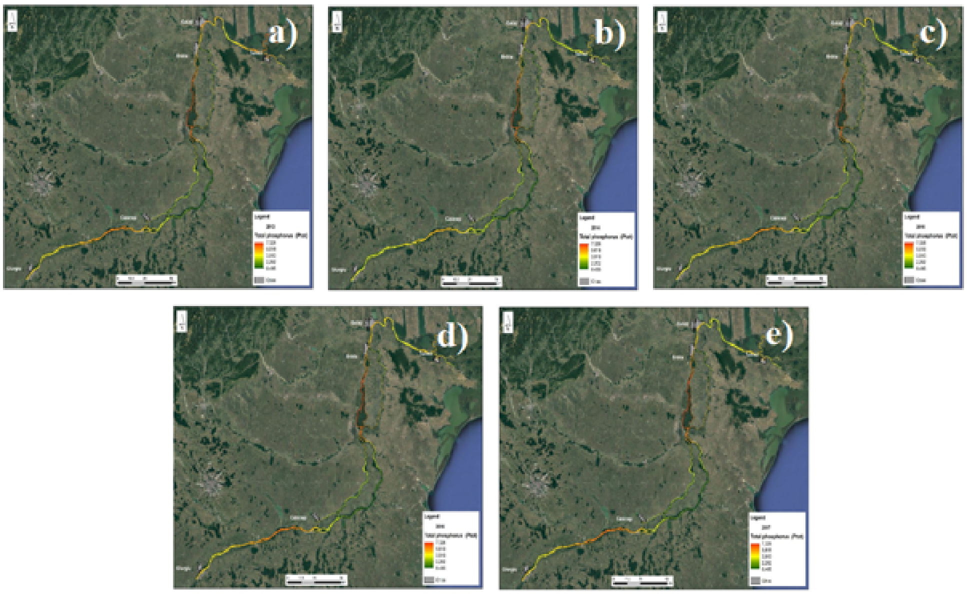

Fig. 2. Total phosphorus a) 2013; b) 2014; c) 2015; d) 2016 and e) 2017

Analyzing the total phosphorus measurements results these concentrations, in the whole region, are within the limits set by the European legislation.

Figure 1 indicate a higher value of inflow was 4.82 mg/L from Braila while 1.45 mg/L was the outflow effluent. 4.54 mg/L the highest average of 2017 from Calarasi, comparing with 4.52 mg/L average from 2014 from Galati. It should be revealed 2013 is the year when both the highest averages were calculated for Tulcea 4.33 and 3.75 mg/L for Giurgiu. The five years average of the difference between the total phosphorus inflow and outflow is 2.52 mg/L, which highlights the relevance of wastewater treatment before being discharged into the Danube basin.

Yearly maps of analyzed region were created in order to obtain a visual image of total phosphorus spreading. The geographical delineation of P_{tot} is valuable to accomplish an overview of the complete area and to estimate with a higher precision the influence of total phosphorus on the Danube river basin.

The largest concentration of P_{tot} is 4.22 mg/L is the average of 2013, while 3.64 mg/L is the lowest average from 2017. The most of the municipal wastewater plant had higher values in 2013. A visual observation highlights larger values of P_{tot} downstream the wastewater area (fig. 2)

The studied area in this paper is an agricultural one and it is evident that total phosphorus is applied on agricultural land as fertilizer. Except 2016, when the annual average of inflow P_{tot} was 4 mg/L, it can be said that the trend is a downward one. The lowest inflow average of P_{tot} for period 2013-2017, was measured in Giurgiu 3.30 mg/L, an average relatively similar with 3.77 mg/L from Galati and 3.83 mg/L from Tulcea. Higher average is 4.01 mg/L from Calarasi and Braila 4.85 mg/L.

Conclusions

The experimental results show that the removal of total phosphorus is imperative. As seen, the difference between inflow and outflow is very large. The five years average of analyzed region for inflow total phosphorus is 3.9 mg/L comparing with 1.38 mg/L the average of outflow.

Nutrient removal during wastewater treatment is vital to minimize the impact of nitrogen and phosphorus pollution on. Adopting a more sustainable mode of living is becoming a first concern. In these circumstances, the construction of wastewater treatments plants is a substantial advantage in respect of the removing of total phosphorus from wastewater, particularly from European's water bodies.

Inland water pollution issue with effects on both the drinking water supply of large municipal areas and on irrigation and ecosystems biodiversity is the current moment of the first commitment. In these conditions the required parameters functioning sewage treatment plants is a very relevant objective. There is a fast process of moving from disposal outright to the emissary to a series of increasingly complex and integrated wastewater treatment. This also from the perspective of progressively restrictive environmental regulations. Another important aspect is that farmers to reduce the use of phosphorus because of the negative repercussions the ecosystem

In Romania, inadequately purified waste water may be one of the important eutrophication elements in the Black Sea region.

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