Nitrogen Compounds Distribution in Diyala River Opposite Al-Rustimiyah Sewage Treatment Plants

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ABSTRACT

The reach of Diyala River just before its confluence with Tigris River south of the capital city Baghdad was taken as a case-study. This segment of Diyala River is exposed to multiple points of treated and raw municipal wastewater discharges of Al-Rustimiyah wastewater treatment plants. Its pollution status was assessed with regard to nitrogen compounds levels.

The aquatic parameters: DO, TN, TKN NH_4-N, NH_3-N, NO_3-N, NO_2-N, pH, and temperature were monitored and measured at nine sites along the river reach for a period of one year to assess seasonal variations. The first and last sites were chosen at the downstream and upstream of the points of pollution flowing into Diyala River, while the second to eighth sites were located at the effluents of the WWTPs of Al-Rustimiyah. It was found that water at sites two, seven, and four, respectively, were the most polluted points among all duo to the presence of the bypasses from the WWTPs at these sites.

With regard to NH_4-N, NH_3-N, and TN concentrations, the river was found to be heavily polluted with untreated wastewater at site two and between low to medium strength at other sites, except for site one. On the other hand, NO_3-N and NO_2-N concentrations categorized the river water as an effluent rather than a stream according to Iraqi standard classification.

Reversed relations were found between the DO concentrations and some of the nitrogen compounds and temperature. A statistical model relating TN concentration to DO, NH_3-N, and temperature was derived. It was proved to be accurate.

Keywords: Diyala River, TN, NO_3-N, NH_3-N, DO, Temperature

INTRODUCTION

One of the most important problems facing mankind nowadays is water pollution. Water quality deterioration in surface water is the impact of anthropogenic activities due to rapid industrialization [1]. Major sources of surface water contamination are construction, municipalities, agriculture, and industry [2].

Wastes are most often discharged into receiving water bodies with little or no regard to their assimilative capacities [3]. Monitoring the parameters of a receiving water body should be essential in order to obtain its capacity to accommodate wastes. Physico-chemical properties such as pH, dissolved oxygen and others can be used to determine the water ecosystem integrity [4].

The dissolved oxygen (DO), for example, measures the amount of dissolved or free oxygen present in water; therefore, it represents the capacity of water to assimilate the pollution load. Dissolved oxygen in rivers results from combined impact of aeration and oxidation of organic matters [5]. If organic wastes were to be discharged into streams without treatment, the DO concentrations would deplete in the receiving water body [6].

Nitrogen compounds, on the other hand, contain one of the biggest groups of natural and drinking water contaminants [7]. These compounds could be oxidized or reduced by organisms

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[8]. Nitrogen loads in rivers has different sources, such as deposition from the atmosphere, the direct discharging from industrial, residential or agricultural residuals, and others [9].

Nitrogen's most common compounds are the ammonium (NH_4-N), ammonia (NH_3-N), nitrate (NO_3-N), nitrite (NO_2-N), Total Kjeldahl nitrogen (TKN), and Total nitrogen (TN). Ammonia is toxic to aquatic life. It occurs in nature duo to the degradation of organic nitrogen compounds in water. High ammonia concentrations in surface water create a large oxygen demand owing to the ammonia conversion to nitrate. High ammonium concentrations motivate algal and plants growth. Their subsequent death and decomposition may produce anoxic conditions [10].

NO_3-N is considered as the most oxidized forms of nitrogen found in wastewater. It has a serious and sometimes fatal effect on infants [11]. As for nitrite, one of the oxidation states of nitrogen, it occurs both in the reduction of nitrate and the oxidation of ammonia into nitrate. It occurs in low concentrations in both surface water and wastewater duo to its rapid oxidation to nitrate, however it is extremely toxic to most types of fish and other aquatic species [11].

The TN is approximately the sum of TKN and the NO_xN [10]. The TKN is defined as the sum of the ammonia nitrogen and organic nitrogen, the organic nitrogen contains proteins, urea, peptides, and other organic matters [12].

In spite of what was mentioned above, Nitrogen is regarded as a necessary nutrient in aquatic life. It significantly influences the growth of algae and other plants in freshwater [13]. The overloads of some of its compounds in surface waters is what concerns environmental researchers.

The point and nonpoint sources of different pollution in small rivers, as like NH_3, NO_3, and others, has an important role in the river's behavior as much as the self-purification of the rive itself [14]. Several studies have been done to identify different types of nitrogen compound pollution loads in rivers around the world [7, 9, 15-22].

The aim of this research was to study the pattern of different nitrogen compounds distribution along the reach of interest of the river Diyala within Baghdad city and the effect of the effluents from the wastewater treatment plants of Al- Rustimiyah on this pattern.

Materials and Methods

The study area

Diyala River is one of the tributaries of Tigris River. In the past, it contributed in about 11% of river Tigris's total water income. Unfortunately, know it is considered an effluent receiving water body.

The current study was carried out on the reach of the river Diyala just before its confluence with the Tigris River in about 15 km, located within the capital city of Baghdad, Iraq.

This segment of Diyala River is exposed to multiple points of treated and raw municipal wastewater discharges. These are represented by the outfalls and bypass of three wastewater treatment plants (WWTP) of Al-Rustimiyah, R3, R2, R01. The WWTPs mentioned above are over loaded with influent that exceeds their operational capacities which in turn, affects the aquatic life of the receiving river represented by the river Diyala.

Figure 1 illustrates the zone of the study area and the locations of the WWTPs in the vicinity as well [23]. Several studies have been done on the river Diyala [24-28], in which none of them reported the nitrogen compounds distribution in the river reach and their relation to other parameters.

Figure (1) The study area and the locations of the WWTP's along the reach[23]

Field Sampling

The river reach taken in this study was about 7 km long. It was divided into nine sites according to the points of pollution entering Diyala River. The first site was located upstream of all three WWTPs while further sites were located after each point of pollution submitted to the river, in an adequate distance to insure the mixing of pollutant with the river water. The final and ninth site was located downstream the last point of pollution were no other point inters the river till it pours into Tigris river. The location of each site was identified by the use of the GPS device. Figure 2 shows the locations of the sampling sites and their profile in kilometers along the river reach, with an indication to the position of the most polluted point among all. Table 1 illustrates the description and coordinate of each point.

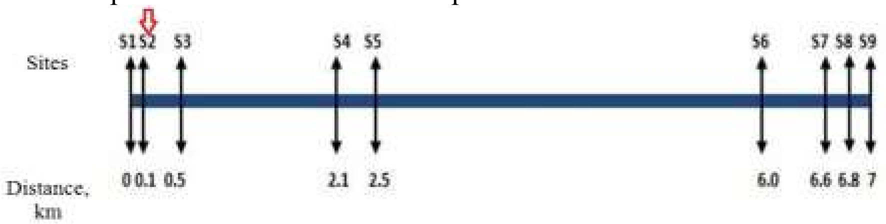


Figure (2).Sampling profile in kilometers along Diyala River in Baghdad

Table (1). The description and coordinates of the nine sampling sites

Site No.	Description	Coordinates
S1	Upstream point	33º 17' 31.77" N 44 º 32' 16.66" E
S2	Bypass R3	33º 17' 29.18" N 44 º 32' 16.42" E
S3	Outfall R3	33º 17' 19.33" N 44 º 32' 15.95" E
S4	Bypass R2	33º 16' 27.87" N 44 º 32' 16.21" E
S5	Outfall R2	33º 16' 16.32" N 44 º 32' 2.08" E
S6	Outfall R01	33º 16' 25.83" N 44 º 31' 42.68" E
S7	Bypass R01	33º 16' 39.04" N 44 º 31' 43.00" E
S8	Army Channel	33º 16' 47.68" N 44 º 31' 36.55" E
S9	Downstream point	33º 16' 46.71" N 44 º 31' 34.23" E

The field sampling was carried out during a whole year starting from April 2014 till March 2015 in order to cover all seasonal variation that may occur in the region.

A polyethylene bottle was used to collect the samples of nitrogen compounds, DO and other tests. All bottles were rinsed with de-ionized water before usage. During sampling, the bottles were rinsed with the river water at points of collecting samples three times before taking any sample. Afterwards, all samples of nitrogen compounds tests were preserved at a temperature of 4˚C and transferred to laboratory.

Field analysis and lab measurements

The measurements were classified into two categories; Field and laboratory measurements. The field measurements were represented by DO, pH, and Temperature. On the other hand, the laboratory measurements were TN, TKN, NH_4-N, NH_3-N, NO_3-N, and NO_2-N. Field measurements were conducted on site immediately after each sample taken in order to prevent any error in the results due to their sensitivity to time and location. Devices such as DO meter, and pH meter were taken each trip to conduct the measurements onsite. The DO, and temperature measurements were done by the use of the WTW DO meter which adopts standard methods number 4500-O of DO measuring and number 2550 for temperature measuring, used in the APHA [12]. The pH measure was done by the use of the pH meter (pH 200) Lovibond. This device adopts the standard method number 4500-H^+ of pH measuring used in the APHA [12]. The laboratory measurements were carried out at The Environmental Research Center, University of Technology, Baghdad, Iraq. The TN test is done by the WTW photo lab S12 device, which adopts the standard method number 4500-N-C of TN measuring, used in the APHA [12]. NH_4-N, NH_3-N, NO_3-N, and NO_2-N tests were done by the C200 Multiparameter Bench photometer device. This device adopts the Nessler method number D1426-92 of NH_3-N and NH_4-N measuring used in the ASTM Manual of Water and Environmental Technology [29], the Cadmium Reduction method of NO_3^--N measuring and the Ferrous Sulfate method of NO_2^--N measuring used in the ASTM Manual of Water and Environmental Technology [30]. The TKN was calculated from relations in literature [10].

Results and Discussion

DO

The field results of DO in mg/l for a whole year along the river reach was illustrated by Figure3. This clears that the general approach of DO trend was almost similar, with a slight variation during different months of sampling. It can be seen that the DO concentration increases during cold seasons for all sites, while it decreases in certain sites during different seasons. The most critical site during the year was site number two. This in line with the site monitoring, were the bypass of R3 WWTP was continuously pouring into the river and it polluted the river tremendously. However, one can summarize these results by Figure 4, in which the average value of DO concentration, for each site, was taken for the results of the whole period of study in order to simplify the display. The results indicated that DO concentration gave its highest levels at site one, upstream from all the outfalls and bypasses of the WWTPs.

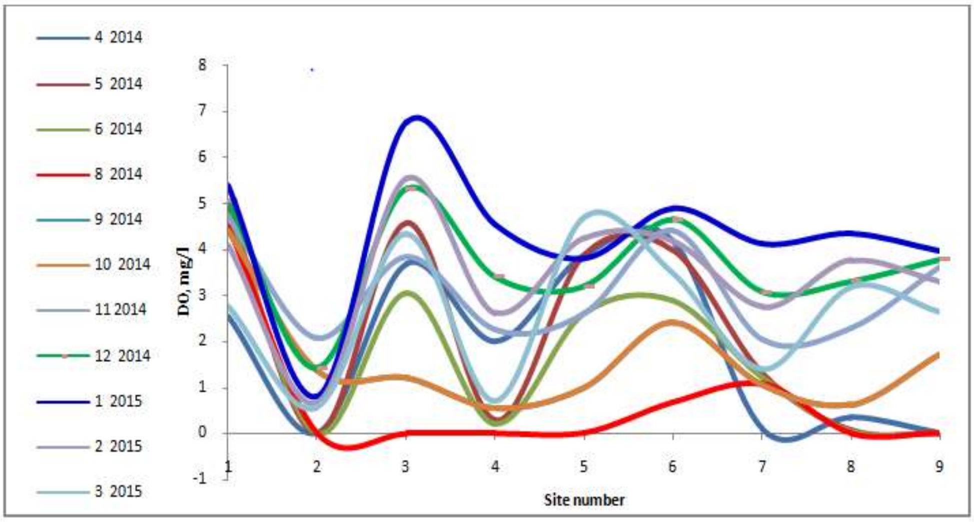


Figure (3) Dissolved Oxygen (DO) trend for a whole year along the river reach in mg/l

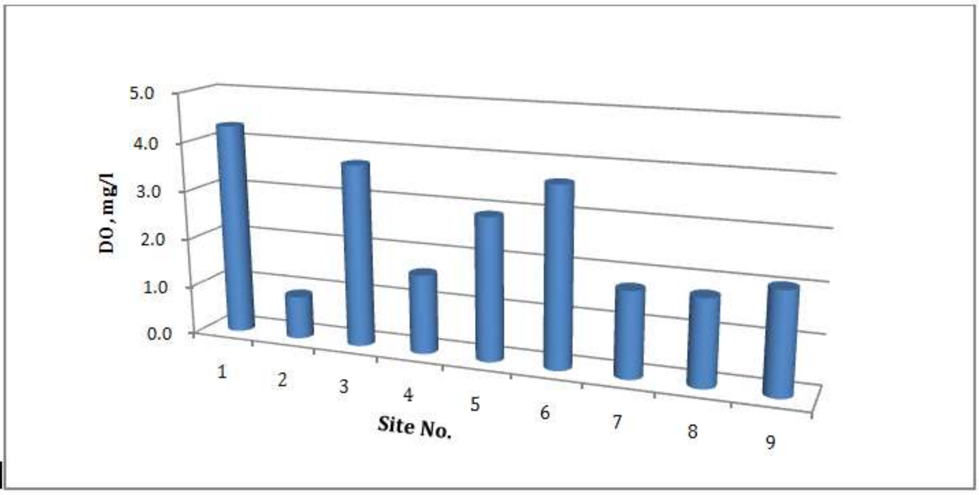


Figure (4) Average DO values for a year along the river reach in mg/l

Nitrogen Compounds

The nitrogen compounds, measured in this study, varied along the river reach, as depicted in Figure 5. The highest concentration among all four compounds of ammonium, ammonia, nitrate, and nitrite was the ammonia followed by ammonium, while the nitrite and nitrate concentrations were rather low. The nitrate and nitrite concentrations increased, in small portions, at the sites where the ammonia and ammonium decreased, which compiles the natural cycle of nitrogen compounds transformation.

NO_2-N and NO_3-N concentrations had a minimum value of zero, at some site, during winter and a maximum value of 4.2 and 5.8 mg/l respectively, during the summer. Both were within the Iraqi effluent standard, but not within the Iraqi stream standard, taken from the Iraqi rivers protection act number 25 [31]. This indicates that the water at the river reach was rather an effluent than a stream.

The minimum concentrations of NH_3-N and NH_4-N were 2.16 and zero mg/l respectively, while their maximum concentrations were 46.8 and 32.9 mg/l respectively. When compared to the typical compositions of untreated domestic wastewater shown in literature [11], the water should be classified as untreated wastewater of high strength at site two and between low and medium strength at other sites except for site one.

The TN concentrations gave their lowest values at site one, like others, but its highest average levels occurred at sites nine, two, and seven, as illustrated in Figure 5. This may be attributed to the additional components in the total nitrogen, such as protein, DNA, urea and benzalkonium [10]. The maximum individual TN concentration was 114 mg/l, which was measured at site two during summer season. When comparing the TN concentrations with the typical compositions of untreated domestic wastewater shown in literature [11], the river could be classified as highly strengthen untreated wastewater during summer at site two, seven, and nine and between low and medium strength at other sites except for site one, which almost matches the classification obtained above with respect to ammonia concentrations. The TKN average trend shows an identical pattern with the TN. The small, almost undetected, difference between TN and TKN indicates the absence of NO_x-N compounds in the river reach which matches the measurements. The difference between the TKN curve and the NH_3-N curve indicates the presence of organic nitrogen in the river reach especially at sites nine, seven, and two. The high levels of NH_3-N at sites two and four might indicate the beginning of organic nitrogen transformation, in which ammonia is the first stage of the organic nitrogen degradation.

In general, site one gave the lowest values of all nitrogen compounds compared to the rest, while sites two, four, and seven were high in some of the nitrogen compounds levels. This can be attributed to the presence of the bypasses of AL-Rustimiyah WWTPs at these sites, as depicted in Table 1. Finally, site nine gave high concentrations of TN and TKN only; this might be attributed to the presence of the fresh raw sewage discharged temporarily into the river at this site during the last four months of monitoring which increased their average values. This also means that the organic nitrogen was at its highest levels and its degradation has not started yet at this site.

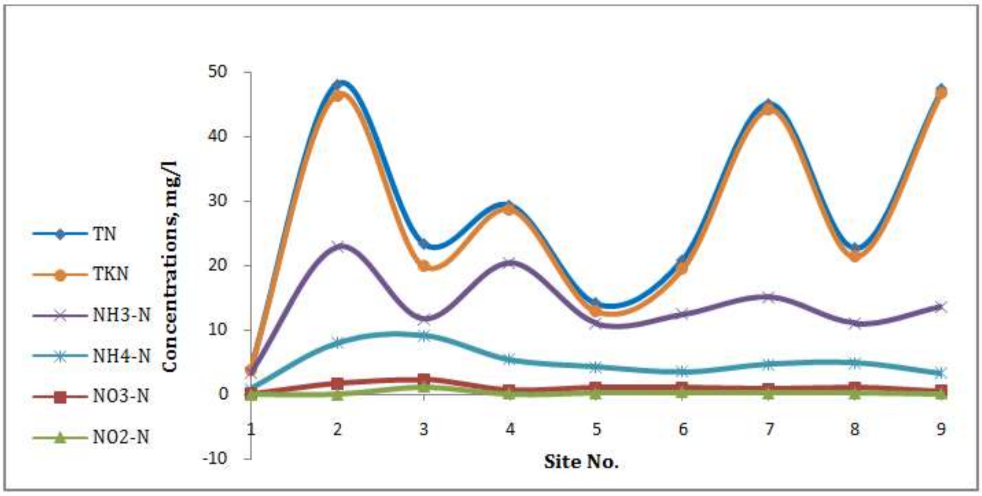


Figure (5) Average nitrogen compounds concentrations along the river reach

pH

The pH levels were almost constant during different seasons and among all sites. Its range lies within 6.9 to 8.6.

Temperature

Temperature was almost constant along the river reach during the same site visit. It differed around the year of course. Temperature had indirect effect on most of the parameters, as will be illustrated later.

DO – Nitrogen compounds relations

The relation between DO and the nitrogen compound measured in this study was found to be reversed for most of them. This could be explained simply as follows; the presence of high concentrations of NH_3-N, for instance, consumes the available DO during oxidation. Figure 6 showed the relations between the average values of the TN, TKN, NH_3-N and NH_4-N concentrations along the river reach and the corresponding average DO concentrations. The same trend was found for all of them, with a difference in their values, having the TN with the highest curve and NH_4-N the lowest. No real relations were found relating the NO_x-N concentrations with DO. This could be attributed to the low values of NO_X-N measured for most of the winter season readings.

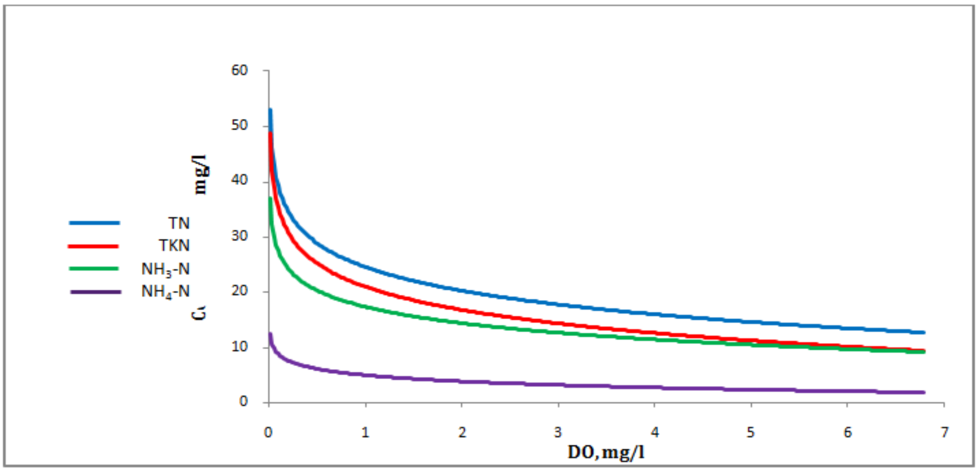


Figure (6) DO relations with TN, TKN, NH_3-N, and NH_4-N

DO – Temperature relation

The obtained relation between temperature and DO was found to be reversed, as illustrated in Figure 7, which commensurate with the literature in this regard, that is higher temperatures revels lower DO concentrations [11]. The R^2 of this relation did not exceed 0.80, which indicates that temperature is not the only parameter that affects the DO concentrations.

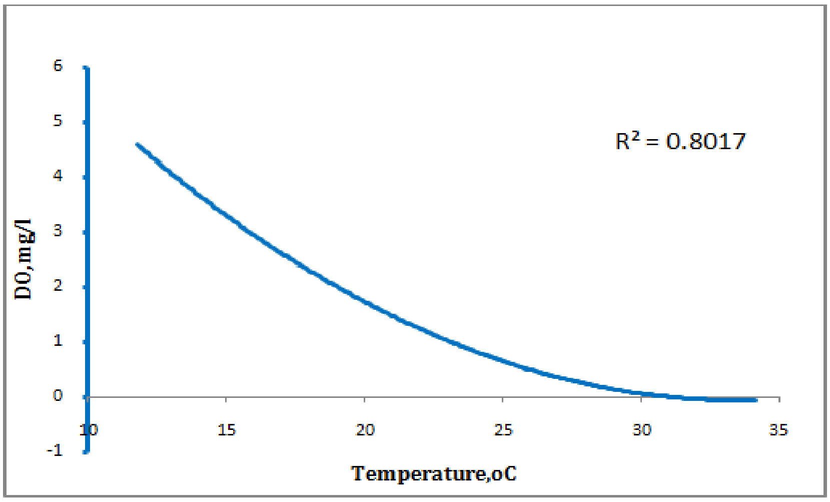
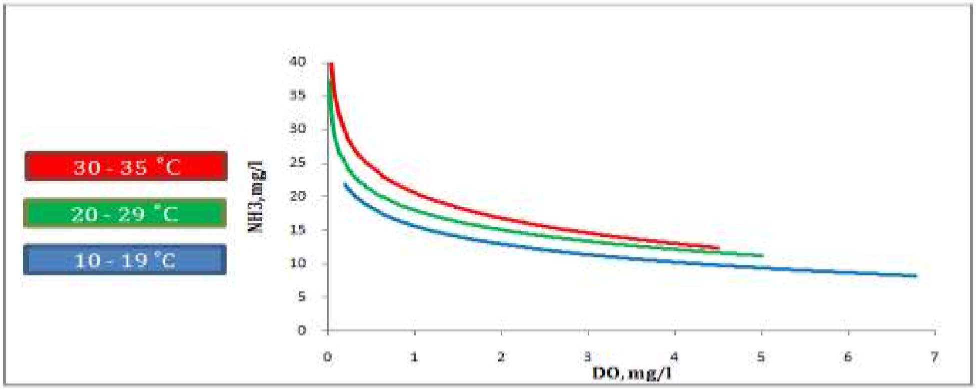


Figure (7) DO relations with temperature

DO – Nitrogen compounds relations with temperature

The relation between NH_3-N and DO among different temperature ranges was found to be reversed, as depicted in Figure 8. Higher temperatures revels higher NH_3-N and lower DO concentrations, and vice versa.

The same trend was found for most of the nitrogen compounds tested. That is a positive relation with temperature and a reversed relation with DO concentrations.



Figure(8) The relation between DO, NH_3-N, and temperature

Statistical Analysis of Results

A statistical model was obtained for the measured data using the SPSS version 20 program. In the model, the total nitrogen (TN) in mg/l was adopted as the dependent variable (DV) and all other parameters as the independent variable (IV).

The individual relations between the DV and IV's were found to be linear for the data of the given period. For that a multiple linear regression analysis was conducted using the stepwise method.

The final relation was illustrated by equation (1):

$$TN= 4.572+ 0.66\ Temp + 0.566\ NH_3N - 2.164\ DO \quad ....(1)$$

Where:

TN: The total nitrogen concentration at the point of interest in mg/l.

Temp: The water temperature at the point of interest in ºC.

NH_3N: The ammonia by nitrogen concentration at the point of interest in mg/l.

DO: The Dissolved Oxygen concentration at any point in mg/l.

It can be concluded from equation (1) that NH_3-N, temperature, and DO were the only significantly affecting variables on TN concentrations among all other parameters measured in this study. The rest of the parameters, NH_4-N, NO_3-N, NO_2-N, TKN, and pH, were eliminated by the stepwise method duo to their insignificance.

Equation (1) has a value of R^2 =92%, and a p-value less than 0.05 for all terms, which categorizes the model as significant.

The measured TN concentrations, which represents the actual values, were plotted verse the predicted TN concentrations, from equation (1), as shown in Figure 9. The relation gave a valuable regression among the actual and predicted concentrations, R^2 =0.93. Furthermore, the accuracy of the obtained statistical model was established.

The statistical analyses of the measured parameters were summarized in Table 2.

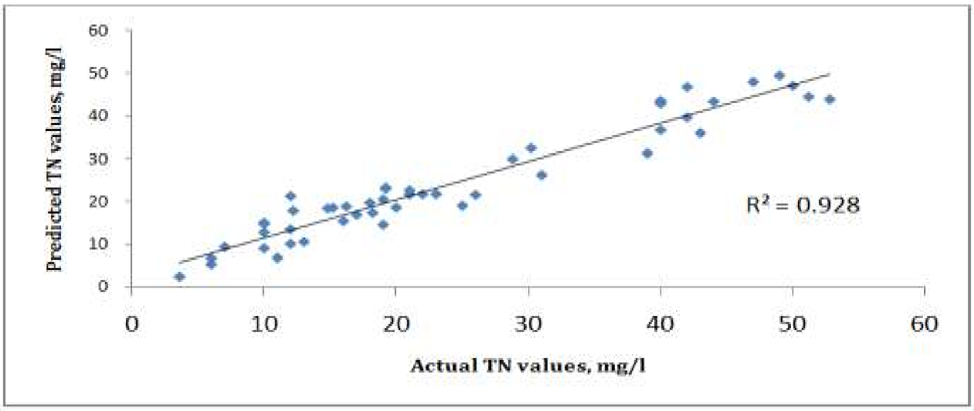


Figure (9) Actual and predicted TN concentrations' regression

Table (2) Statistical analysis of the studied parameters

Parameter	Unit	Min	Max	Mean	Standard Deviation	Variance	Range	Standard Error
pH	—	6.9	8.6	7.6	±0.34	0.11	1.7	0.034
Temp.	˚C	11.8	34.1	22.2	±6.06	36.77	22.3	0.61
DO	mg/l	0.01	6.78	2.51	±1.76	3.1	6.77	0.18
TN	mg/l	2.7	114	27.21	±21.16	447.8	111.3	3135.2
TKN	mg/l	2.68	113.96	25.81	±22.00	484.4	111.28	3391.44
NH_4-N	mg/l	0	32.9	5.48	±25.99	675.55	32.9	4872.32
NH_3-N	mg/l	2.16	46.8	17.73	±12.99	168.83	44.64	1205.91
NO_3-N	mg/l	0	5.8	1.08	±1.12	1.253	5.8	9.04
NO_2-N	mg/l	0	4.2	0.25	±0.61	0.37	4.2	2.66

CONCLUSIONS

Diyala River at its last reach opposite Al-Rustimiyah WWTP's was monitored. Several tests such as DO, TN, TKN, NH_4-N, NH_3-N, NO_3-N, NO_2-N, pH, and temperature were measured. The river reach of interest was found heavily polluted. It can be concluded that the pollutants were at their highest levels at sites 2, 4, and 7 which lied downstream the bypasses of the three WWTPs, afterwards the concentrations varied along the river reach depending on the location of sites taken. The converse can be said on DO levels were its highest concentrations occurred at site 1 before any pollution from the WWTPs fallen into the river, while the lowest concentration of DO was monitored at site 2 which had the highest concentration of pollutants among all.

As for the nitrogen compounds' concentrations, the river reach could be classified as untreated wastewater of high strength at site two and between low and medium strength at other sites except for site one.

The relations between DO concentrations and some of the nitrogen compounds taken in this study with addition to temperature were found to be reversed. For the same parameter of nitrogen compound taken, higher temperatures reflected higher concentrations of the parameter and lower DO levels.

A statistical model relating TN concentration to other parameters was established. It was proved to be accurate.

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