

## **Evaluation of Critical Concentration of Nitrate and Phosphorus in Agricultural Soils of Guilan Province**

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**Abstract:** The quality of soil and arable land may be affected by the type of use as well as the long-term use of chemical fertilizers, and the washing of excess fertilizer chemicals causes concerns about the level of nitrate as well as phosphoric acid. Determining the concentration of these two elements in agricultural soils is important for many economic and environmental reasons. This research was conducted with the aim of determining the critical concentration of nitrate and phosphorus in gilly soils in Guilan province. In order to measure the quality and zoning of these two elements in terms of pollution and their spatial variation, 20 agricultural areas were sampled from 0 to 20 cm depth. Sampling and chemical analysis of soil samples were performed according to standard instructions. Then, using the obtained data, the correlation between the points of sampling by GS + software was performed and contamination was investigated by Kriging method for nitrate concentration and Olsen method for phosphorus concentration. Statistical analyzes were performed using SPSS software. The results show that the maximum concentration of nitrate measured in soil samples is 24 PPM and based on the critical limit of soil nitrate, which is 20-22 PPM, the concentration of nitrate in most samples is alarming but not reached the limit of its crisis. The maximum concentration of phosphorus measured in the studied soil samples, which was measured by the Olsen method, was 48.5 mg / kg soil, based on the critical limit of soil phosphorus by the method of 16 mg / kg, the concentration of phosphorus in most The samples are much higher than standard standards, meaning the concentration of phosphorus in these soils is critical. Pollination zonation shows that the highest concentration of nitrate in soil samples is related to areas that are used by farms and agricultural rivers to irrigate farms. Also, the highest concentration of soil phosphorus is related to the areas where fertilizers Chemical especially phosphorus fertilizers have been used.

**Keywords:** Zoning - Critical Concentration - Nitrogen - Phosphorus - Correlation

### **Introduction**

#### **Phosphor**

Phosphor among nutrients after nitrogen is the most important factor limiting agricultural production in most parts of the world and in Iran. Phosphorus resources are limited and can be completed (Salardini, 1995). Population growth and increasing per capita space for crops, especially rice, as well as the limited amount of rice cultivated land, use of chemical fertilizers to restore the intrinsic capacity of the soil to supply the nutrients needed by the plant It is essential. Rice yields about 2-3 kg of phosphorus per tonne per ton of product. (Sina & Coner, 2001; Salek et al., 2001)

When phosphorus compounds are added to the soil, they become slightly soluble or insoluble in form, thus reducing the potential for use by the plant. (Deylon & Doo, 1988) is the reason why phosphorus is unusable in the soil because of two processes of adsorption and sedimentation. It is believed that sedimentation occurs at high concentrations of phosphorus, and absorption occurs at low concentrations. Different soil components that contribute to phosphorus adsorption include iron and aluminum oxides, organic matter, calcium carbonate, and silicate minerals in soil. (Olsen and Khazana, 1980)

Many soil crops in Iran have been using phosphorus fertilizers for many years to have high amounts of available phosphorus (Karimian, 1998). The absorption of phosphorus in the early stages is rapid and then absorbed and phosphorus at this stage is called inorganic phosphate (with absorption capability Low for plant).

Over time, phosphorus is either ingested in or mined, or deposited on absorbing sites, but with high power, or in low solubility compositions. As a result, the amount of phosphorus extracted by the extractant

decreases (Javid & Rowl, 2002, Sue & Thompson 2000). The degree of phosphorus absorption depends on the amount of fertilizer in addition to environmental factors and soil characteristics.

### **Nitrate**

The nitrate is a colorless, odorless, and no taste that surrounds our surroundings (Drinking Handbook of Water Quality 2003). Nitrate is the ultimate product of nitrogen-based aerobic stabilization and is considered as the most stable oxidizing compound, which is highly soluble in water. Nitrate is the product of ammonium biochemical oxidation, in which nitrite is produced as intermediate product (nitrification) or directly (eg in the form of ammonium nitrate in chemical fertilizers). Nitrate is commonly found in water and soil, and it is one of the main forms of nitrogen in which plants obtain nitrogen from them. (Lord 1992). Nitrate can be rapidly converted to either NO<sub>3</sub> or NO<sub>3</sub>N. Considering the seven different nitrogen capacities, N<sub>2</sub>O<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> states of nitric acid and nitric acid play an important role in contaminating the environment. (Benton Franklin Healte District 1996)

The most important sources of nitrate pollution in the soil are nitrogen fertilizers and nitrogen fertilizers used in agriculture and for the cultivation of agricultural land. Nitrogen consumption higher than plant requirement may result in the accumulation of nitrate in a lower salinity than the developmental area of the plant root and thus cause nitrate leaching (Fallah and Tedin, 2009).

The critical limit of soil nitrate has been determined in various sources between 20 and 22 mg per kg of soil. (Rahmani 1385). In a study on the Tehran suburbs, nitrate concentrations of soils were measured even at a depth of up to 2.5 meters over 40 mg / kg (Melkoty 1378)

Many nitrate levels in the soil and the excessive absorption of this ion by plants and entering the food chain increase the likelihood of developing diseases such as cancer and threaten the health of individuals. Therefore, studying the concentration of soil nitrate and the use of useful methods to prevent the concentration of this ion to reach critical levels is very important.

### **Materials and methods for determining the concentration of soil phosphorus:**

In this study, Olsen extraction method was used to determine the concentration of phosphorus in soil. An extractant is a suitable extractor that can simulate root activity. In addition to the extract extract, it is also important to extract it. The ratio of soil to solution, the time of extraction and the speed of shaking are some of the factors that affect this stage. (Manter 1988)

Olsen's method is the most commonly used phosphorus extraction method in the world. This method is appropriate for a wide range of soils to predict the potential for phosphorus use for the plant. Olsen's method is more sensitive to buffering capacity than other methods (Menon et al. 1990). In soils where calcium phosphate is low and iron phosphate and aluminum phosphorus source are considered usable, Olsen's method is preferable. (PIRZINSKI 2000). Critical concentration of phosphorus can vary depending on laboratory conditions, physiological age, plant tissue, plant type and soil characteristics, plant management, and vegetation (Seynard and Tran 1993)

Investigating the different forms of phosphorus in order to determine and interpret the relationships between these forms and the results of soil phosphorous tests (Sharpley and Smith, 1985; Heilin Quar, 2000; Lopez-Pinerio and Garcia-Navarro, 2001; Salek et al., 2004) and adsorption And the phosphorus cycle in the soil (Halford & Meetingley, 1975; Sharpley, 1985; Ryan et al., 1985; Pena and Torrent; 1990; Bock Said and Duckmanjie; 1993; Sway and Thompson; 1999; Sway and Thompson; 2000; Van Lao, 2003; Akhtar et al., 2003) is also used. Beck and Sanchez (1994) and Coulaoul and Tian (2007) investigated the effects of organic matter on different forms of phosphorus in soil, as well as McGill and Cole (1981) and Griffin et al. (2003).

Different forms of phosphorus in soil can affect soil and phosphorus utilization. Melkoty and Kavousi (2004) stated that the critical limit of phosphorus used in rice fields was 12 mg / kg soil. The continuous withdrawal of phosphorus with low consumption or non-consumption of phosphorous fertilizers in the northern lands of the north of the country in recent years has led to possible changes and reductions in the storage of various forms of phosphorous in shalezir soils, and this is an assessment of the phosphorus storage status in the country's land cultivating soils It matters. Investigating different forms of phosphorus and making them aware of their state of affairs will be effective in optimizing the use of phosphorus fertilizer resources and reducing their environmental impacts.

In this study, 20 plots of land were planted before the beginning of the growing season, considering the appropriate distribution at the level of Guilan province. Samples were taken at a depth of 20 cm to 0 cm. After

drying in the air, a 2 mm sieve was carried out, then the critical concentration of phosphorus it placed. Extraction of soil samples for extraction of phosphorus absorption by Olsen method including extraction with sodium bicarbonate 0.5 molar in pH = 8.5 and 2.5 g soil with a ratio of 1.20 and a half hour of shaking (Olsen Et al., 1954). Descriptive statistics and statistical data analysis were performed using SPSS software.

#### **Soil extraction method to determine the concentration of phosphorus:**

To determine the concentration of phosphorus, soil samples were taken from a 2 mm sieve after drying in air. Chow and Jackson modified by Cove (1996) were used to isolate and determine the chemical forms of mineral phosphorus. Also, for other forms of phosphorus: 1- ammonium chloride 1 molar for soluble phosphorus extraction, and 2) Olson method for total phosphorus and organic phosphorus. Descriptive statistics compilation and analysis of data statistical relationships were performed using spss software package.

#### **Materials and Methods for Determination of Soil Nitrate Concentration:**

To determine the concentration of soil nitrate, the soil samples were transferred to the laboratory after collecting and passed through the 2 mm sieve after air drying and fuming. After sampling, the specimens were stored in polyethylene bottles and kept at 4 ° C until chemical analysis.

The nitrate ions react with brucin in a concentrated solution of yellow sulfuric acid, which is not a Brim Lambert's relativity, but the absorption light curve is uniform in relation to the nitrate ion concentration, and it is necessary for the test to be performed simultaneously with the test Standard solutions were also prepared and measured at 410 Nanometer. Also, the speed of color creation is directly related to heat, but the color intensity is inversely proportional to it.

#### **Intruder in measuring nitrate ion concentration:**

- 1- Oxidizing and potent oxidizing agents detect disturbance in the measurement of activity, which can determine the amount of oxidizing agents by orthotolidin, and eliminate chlorine interference by up to 5 mg / L by adding sodium arsenate.
- 2-The potential effect of concentrated sulfuric acid, as well as the high amount of organic matter in the test, may also increase the reading of light absorption at 410 nm. The intruder caused by these materials can be minimized by performing preliminary purification with aluminum hydroxide or activated carbon on the test specimen.
- 3-The nitrite interacting effect of up to 7 mg / L can also be eliminated by increasing the sulfanilic acid to the brucine agent.

For testing, we need a spectrophotometer or photometric filter to measure 410 nm in wavelength, with a light path of 1 to 5 cm.

#### **Soil extraction method for determination of nitrate concentration:**

To determine the concentration of nitrate, soil samples were extracted by sodium buffer buffer 1, sodium acetate (PH=4.5 -4.8 ) and photometric method. In this way, 12.5 g of soil was dried in air and weighed and prepared with 25 mg of buffer and extraction was carried out. To 5 ml of the subfiltration solution, 1 ml of Brucin-Sulfanic Reagent was added and mixed well with 10 ml of concentrated sulfuric acid at a density of 1.84 and placed in dark place for 10 minutes. After the color appeared, the solution was mixed with 10 ml of distilled water and placed again in dark place for 20-30 minutes. Then, the absorbance of the test specimen at 410 nm in the wake of the coping solution, it was done (with the exception of the addition of brucine solution - sulfanilic acid) by spectrophotometer. The concentration of nitrate ion in the test specimen was determined from the standard curve for the same sample in mg / liter.

#### **Results and discussion of the phosphorus concentration of soil samples**

The results of the physical and chemical analysis on the soil samples studied in Table (1) and the various forms of total phosphorus in Table (2) and the details of the method of comet extraction to determine the different forms of phosphorus in Table (3) it has been shown.

The results show that the best method for measuring the amount of extraction by using the Olsen method is.

Samii et al. (1987) and Laxminiryana (2003) reported the correlation between extracted phosphorus by Olsen method and relative yield of rice plant. In addition, the extraction of phosphorus by Olsen method shows a good correlation with plant responses in aerobic and anaerobic conditions (Chapto et al. 2003). Determination of the critical concentration of phosphorus extraction in the soils studied by the rice plant shows that in most of the soils where the extracted phosphorus is less, the relative function of the plant is also low. In most soils where extracted phosphorus is high, yield The relative height of the plant is high.

The results showed that the critical level of phosphorus by Olsen method is 16 mg / kg. Comparison of numbers shows that extractors that extract more phosphorus from the paste have a higher critical level and, conversely, extracts that extract less phosphorus have a lower critical level. Guerra et al. (1999) estimated the critical concentration of phosphorus by Olsen oyster extract for rice (6.90 mg / kg), Rehman et al. (1996). The critical concentration of phosphorus for rice plant was 14.9 mg / kg Kavousi (2004) reported the critical concentration of phosphorus by the Olsen ointment extract of 12 mg / kg. Table 4 shows the mean phosphorus extracted by Olsen method in soil samples.

Descriptive statistics of various forms of phosphorus from soil samples show that soluble phosphorus has the highest coefficient of variation among its different forms. The most skewness and elongation are found in soil phosphorus (Table 5). High skidding, elongation, and coefficient of variation indicate abnormal frequency distribution in the studied variable.

Based on the results obtained from different forms of phosphorus, mineral phosphorus with a range of changes of 60 -1427.5 and an average of 353 mg / kg, contains 62.42% of total phosphorus. Organic phosphorus, with a range of 25 -525 and an average of 211 mg / kg, contains about 37.30 % of total phosphorus.

The soluble phosphorus has a range of changes in the concentration of between 0 – 12.5 and 0.556 mg / kg of total phosphorus, which is not significantly reduced due to its low concentration (0.26).

Griffin et al. (2003) argue that although the increase of any phosphorus fertilizer source into the soil causes a rapid increase in soluble phosphorus, this element is not significantly altered due to easy access to the plant during the growing season.

Salek et al. (2004) stated that soluble phosphorus is an intermediate source for phosphorus absorption by plant and its concentration is low, and its average is not significantly different at different depths of rice soils. Salek and Creek (1995) evaluated the effect of chemical fertilizers and livestock manure on determining the different forms of phosphorus in Filipino saline lands showed that phosphorus had the highest mean among different forms of phosphorus. One of the possible reasons for the high concentration of this type of phosphorus in rice paddies in the studied area is the lower phosphorus absorption of this plant. Sealck and Crack (1995), in their study of the use of different forms of phosphorus as a potential phosphorus, emphasized that the induced flood and anaerobic conditions reduced the microbial activity of the phosphorus mineralization process and slowed down the process of organic phosphorus in Soil accumulates. According to McGill and Cole (1981), only the organic phosphorus mineralization process occurs when phosphorus is added to the soil. Sui and Thompson (2000) and Walter et al. (2003) investigate the effect of organic matter Soil on different forms of phosphorus indicated that the addition of organic matter or the inherent nature of organic matter in the soil in rice paddies increases the concentration of soluble phosphorus and organic phosphorus in these soils. Although this form of phosphorus is not directly available to the rice plant, it is biochemically active and can help to increase the phosphorus after mineralization. The researchers reason this effect on reducing the soil's ability to stabilize soil and keeping phosphorus in the soil, increasing large pores, and helping to move more phosphorous in soil and biological activity of living organisms in the sandstone field. The linear correlation between different forms of phosphorus with each other and with phosphorus It is shown in table (6). Given the critical level of phosphorous in the Guilan rice field, it seems that the reason for the high phosphorus available in most of the studied species is due to the fertilization of persistent phosphorus in the soil causing Increasing the amount of soil moisture in these areas, attributed to The title is a source of compensation for the plant's phosphorus. Salek and Creek (1995) stated that the concentration of available phosphorus in the land of mallow posts increases under saturated and flood conditions. These changes are due to the acidity of the soil around the root of the crop of rice. But since this plant cannot absorb all available phosphorus, these soluble and absorbable phosphorus can be absorbed by the diffusion phenomenon to the points far away from the root and produce a more uniform distribution. On the other hand, excessive use of phosphorus fertilizers in recent years has become an absorbable ortho phosphate in other forms. According to Cove (1996), no significant changes in the concentration of phosphorus in the soils of an area are not expected. In these soils, due to the different use of

phosphorus fertilizers and the rapid conversion of phosphorus-shaped forms into less soluble forms, different concentrations of phosphorus can be present in soil. Salt et al. (2004) showed that in younger Inspectorates, as compared with more mature soils, can be found more usable phosphorus, because in mature soils like low pH and low pH, they are converted into less soluble forms due to the abundance of Fe<sup>3+</sup> and Al<sup>3+</sup> phosphorus ions.

**Table 1**  
**Descriptive statistics of adsorption phosphorus concentration in studied soil samples**

Soil Sample	Phosphorus absorbable Mg/Kg	Soil Sample	Phosphorus absorbable Mg/Kg
1	48.50	11	17.80
2	45.10	12	16.70
3	36.20	13	15.80
4	27.80	14	14.20
5	25.30	15	13.80
6	23.80	16	13.50
7	22.50	17	11.40
8	22.30	18	11.10
9	19.80	19	10.90
10	18.80	20	6.50

**Table 2**  
**Descriptive statistics of various forms of total phosphorus**

Different forms of phosphorus	Percent of total phosphorus	Average	variation range
mg /kg Mineral phosphorus	60 – 1427.5	353	62.44
mg /kg Organic phosphorus	25 – 525	211	37.30
mg /kg Soluble phosphorus	0 – 12.5	0.556	0.26

**Table 3**  
**Detailed comet extraction method to determine the different forms of phosphorus**

levels	Shape of phosphorus	Stomach extract	Suspension ratio	Shaking time (min)
1	Soluble phosphorus	NH <sub>4</sub> CL 1 Molar	1:50	30
2	Organic phosphorus	H <sub>2</sub> So <sub>4</sub> 2Molar	1:25	1020

**Table 4**  
**Average extractable phosphorus extracted by Olsen method (mg /kg)**

Stomach extract	minimum	Maximum	Average
Olsen	6.5	48.5	21.63

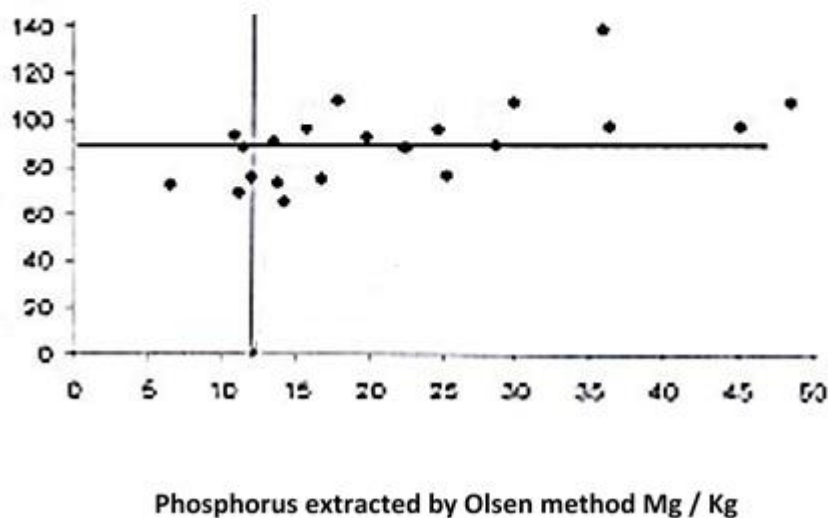
**Table 5**  
**Descriptive statistics of different forms of phosphorus in soil**

Shape of phosphorus	minimum	Maximum	Average	Skidding	Elongation	Coefficient of variation
Available phosphorus mg /kg	1.3	88.2	19.93	1.629	2.217	9.4
Organic phosphorus mg /kg	25	525	211	0.637	0.172	4.7
Soluble phosphorus mg /kg	0	12.5	0.556	3.822	19.968	27
Mineral phosphorus	60	1427.5	353	1.802	5.259	6

mg /kg						
Total phosphorus mg /kg	218	1677	563.70	1.602	5.232	4

Different forms of phosphorus mg /kg	Organic phosphorus	Soluble phosphorus	Available phosphorus
<b>Organic phosphorus</b>	<b>1</b>	<b>-0.139</b>	<b>-0.35</b>
<b>Soluble phosphorus</b>	<b>-</b>	<b>1</b>	<b>0.84</b>
<b>Available phosphorus</b>	<b>-</b>	<b>-</b>	<b>1</b>

figure 1  
Critical concentration of phosphorus extracted by Olsen method



### Results and Discussion of Nitrate Concentration of Soil Samples:

Summary descriptive statistics of nitrate concentration The soil samples studied before conversion are shown in Table (7). The average nitrate concentration in soil samples is 8.58 mg / kg, which does not exceed the limit of 20-22 mg / kg (Rahmani, 2006). The nitrate variance has high variance and standard deviation. Its elongation was also negative, indicating a further dispersion of this property around the mean. The number of skidding for the nitrate variable was positive and significant, indicating that it tends to be larger.

We will rotate the nitrate data to normalize. In this way, the number of data skewness decreases and the distribution of these variables in a straight line. Rodriguez-Martín et al., 2006) also stated that the distribution of heavy metals and organic matter had a high degree of skewness and, in order to balance variances in all subsequent statistical analyzes, transformed the data of these variables into their logarithms. (Table 8) The distribution table of nitrate in studied soil samples shows that all studied points are less than one point lower than 22 mg / kg. Table (9).

Considering that the limit of soil nitrate in various sources is 20 to 22 mg / kg (Rahmani 2006), it can be stated that although the onset of contamination has been observed in all soil samples, the concentration of nitrate in them is lower Is allowed. According to the soil samples experiment, although there were significant concentrations of nitrates in 98.46 % of the samples, these values have not yet reached the limit of

contamination. Certainly, the use of a large amount of nitrogen fertilizer fertilizers cannot be denied in increasing the amount of nitrate in cultivated land of Guilan. Table (10) summarizes the descriptive statistics of nitrate concentration and pH of soil samples studied.

Measurement of pH in studied soil samples:

The pH of the soil was measured using a potentiometric method (Paige et al., 1982). In this method, the concentration of dissolved hydrogen ion is measured by the potential difference created between the soluble ions and the special glass electrode. At first, suspensions of samples were prepared with a ratio of 2: 1/5 of water to water and stylized for half an hour, and then PH were sampled with pH meter. Regarding the pH data, its skewness is non-significant, and the median is close to the mean and has a normal distribution. Table (7) Sheikh Moghaddasi (2008) and Khzaee (2010) also showed that the pH of the soil is negative and non-significant. In contrast to the elongation of the PH is positive, which indicates the concentration of the data of these traits around the average and its dispersion is low. The number of PH slopes was negative and meaningless, indicating the tendency of this variable to be smaller.

**Table 7**  
**Statistical summary of nitrate content in soil samples before conversion**

Variable	Unit of measurement	number of samples	minimum	Maximum	Average	Standard deviation	Variance	Skidding	Elongation
NO3	PPm	20	1.11	24.1	8.58	5.78	33.58	0.52	<b>-0.72</b>
pH	-	20	5/89	7/94	7/33	0/40	0/18	-1/11	<b>1/34</b>

**Table 8**  
**Statistical summary of nitrate content in soil samples after conversion**

Variable	Unit of measurement	number of samples	minimum	Maximum	Average	Standard deviation	Variance	Skidding	Elongation
NO3	PPm	20	0	4.89	2.73	1.06	1.60	-0.13	<b>-0.78</b>
pH	-	20	-	-	-	-	-	-	-

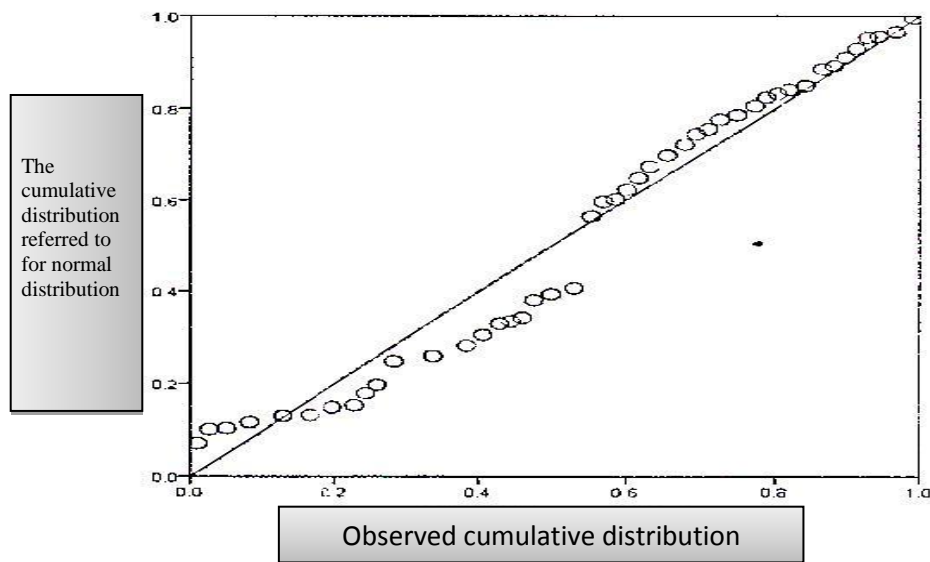
**Table 9**  
**Frequency of nitrate in studied soil samples**

Classes range ((ppm))	number of samples	Total number of samples	Percentage
0 – 10	12	20	<b>%60</b>
11 – 20	7	20	<b>%35</b>
21 - 30	1	20	<b>%5</b>

**Table 10**  
**Descriptive statistics of pH and nitrate concentration in soil samples**

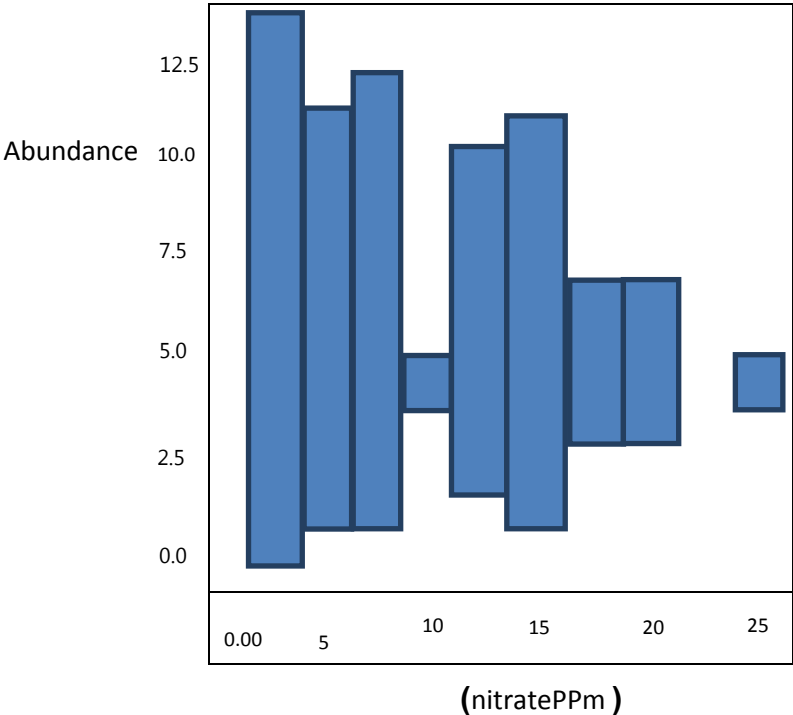
Soil Sample	PH	Nitrogen	Soil Sample	PH	Nitrogen
1	6.73	0.378	11	6.67	0.456
2	3.38	0.422	12	6.68	0.226
3	7.16	0.261	13	7.10	0.266
4	7.43	0.167	14	7.33	0.163
5	7.26	0.246	15	6.73	0.281
6	7.22	0.168	16	7.44	0.151
7	7.31	0.246	17	7.05	0.172
8	6.96	0.287	18	6.99	0.475
9	6.22	0.181	19	7.17	0.255
10	6.72	0.332	20	7.41	0.181

**Figure 2**  
**Cumulative distribution curve of soil nitrate**

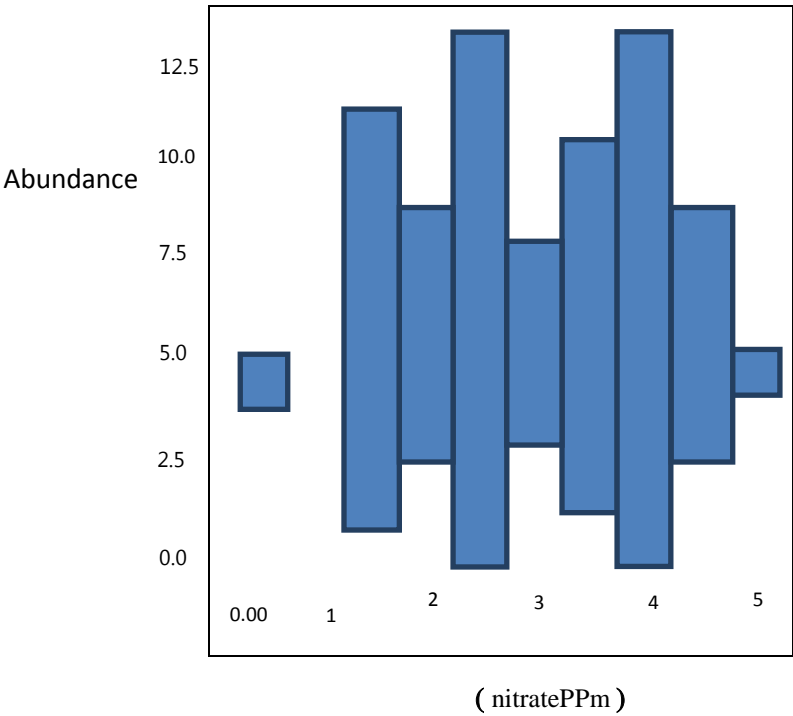




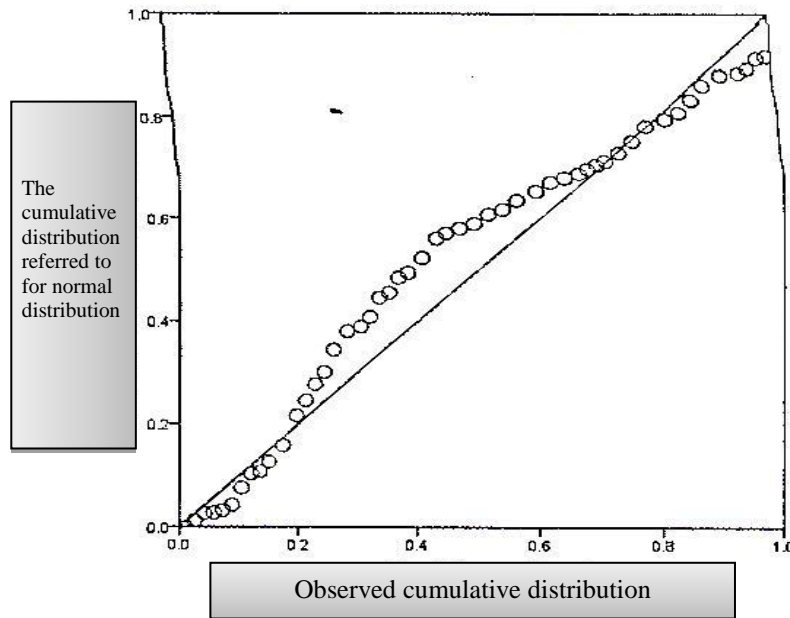
**Figure 3 Histogram of soil nitrate pre-conversion frequency**



**Figure 4 Histogram of the frequency of soil nitrate after conversion**



**Figure 5 Cumulative distribution PH curve of soil**



**Final conclusion:**

- 1- According to the results of this study, Olsen extraction method due to its extraction speed is economic and also the acceptable relation with relative yield of rice plant is recommended as the most suitable method for determining the critical level of phosphorus fertilizers. The amount obtained from the method The reference was also 16 mg / kg of soil.
- 2- According to the results, soils with higher levels of phosphorus than the critical level do not need to use phosphate fertilizer, and, unlike soils whose phosphorus content is lower than the critical level, they should be added to the soil test, phosphorus fertilizer. Most soils The study had a phosphorus higher than the critical level.
3. Based on the research, mineral phosphorus with an average of 353 mg / kg, contains about 62.6% of total phosphorus, and organic phosphorous with an average of 210 mg / kg, contains 37.4% of total phosphorus. The range of available phosphorus changes as well as the different forms of phosphorus in the studied soils was high. Linear correlation between available phosphorus and different forms of phosphorus was observed.
4. As observed in the zones, the maximum amount of soil nitrate in the eastern and north-eastern parts of the region is consistent. This suggests that there is a correlation between the excessive use of nitrogen fertilizers and the increase of nitrate in soil resources.
- 5 - Considering the total amount of total nitrate ion in the soil, it can be said that these sources have been impregnated with nitrate but the total amount of this ion in the soil resources of the study area is below the standard standard, but with the continuation of the process of disposal of various urban wastewater, Industrial and agricultural resources to surface water resources and due to the climatic conditions of the region and the transfer of these materials to aquifers and excessive use of fertilizers, there is a possibility of spread of pollution in the water resources of the region.

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