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## Comparative Study of Methods used for the Determination of Nitrate and Nitrite Pollutants in Well, Ground Water and Soil in Al-Hassa Area, Saudi Arabia

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**Abstract:** Concentrations of  $\text{NO}_3^-$ -N and  $\text{NO}_2^-$ -N that constitute the main source of ground water and soil contamination, were determined in well and ground water as well as soils in Al-Hassa Oasis. Three analytical procedures were used to determine the concentrations of  $\text{NO}_3^-$  and  $\text{NO}_2^-$ . There were no significant differences in the analytical results of the methods followed. However, the concentration of  $\text{NO}_2^-$  was lower than that of  $\text{NO}_3^-$ . Overall, the concentration of  $\text{NO}_3^-$  was higher than the critical limits established for plant growth, human health and animal uses. The differences in concentration of these anions were due to differences in the depth of water bearing aquifer and to human activities in the area. The  $\text{NO}_3^-$  content in the soil depended on the type of nitrogen fertilizer used. Organic manure and urea fertilizer increased the  $\text{NO}_3^-$  in the soil.  $\text{NO}_3^-$  increased with increasing soil depth, but was less in the second layer (25-50 cm) of the soil than the upper layer (0-25 cm).

**Key words:** Nitrate, nitrite, pollutants, well, ground water, soil

### INTRODUCTION

Since there are no perennial streams to provide a dependable water supply, most of the water being used in Saudi Arabia is ground water or desalinated water from the Red Sea or the Arabian Gulf. Pollution significantly alters the quality of ground water often creating critical health hazards. Three aquifers (Neogene, Dammam and Umm er Radhuma) are the main sources of water in Al Hassa Oasis. Water samples of Neogene aquifer in Al Hassa contain high concentrations of nitrate<sup>[1]</sup>. Extensive use of organic and inorganic nitrogen fertilizers in agriculture were identified as important sources of  $\text{NO}_3^-$ -N pollution contaminating both ground and surface water<sup>[2,3]</sup>. Some of the applied nitrate fertilizers may be leached down the soil profile into the deeper aquifers. It was reported that 20-60% of the applied N is taken up by arable crops and 40-80% by grass<sup>[4]</sup>. At citrus sites in west central Florida, USA, high  $\text{NO}_3^-$ -N concentrations (20-40 mg  $\text{NO}_3^-$ -N.l<sup>-1</sup>) were found in the surficial water table (located 2- 4 m below the soil surface). This zone of  $\text{NO}_3^-$ -N accumulation commonly, extends 2 to 3 m downwards before  $\text{NO}_3^-$ -N concentrations decline to less than 10 mg.l<sup>-1</sup><sup>[5]</sup>. Five days after application of nitrogen fertilizer (2.24 kg.ha<sup>-1</sup>) in June to sugarcane planted in Mississippi River alluvial soil in southern Louisiana, USA,  $\text{NO}_3^-$ -N appeared in its highest concentrations (5-11 mg l<sup>-1</sup>) in the drain water and almost 50% of the applied  $\text{NO}_3^-$ -N was leached by the 75th day into the subsurface drains<sup>[6]</sup>.

The importance of nitrate and nitrite stems from their effects on human health. Nitrate itself is not toxic, but nitrite originating from the reduction of nitrate induces methaemoglobinemia in infants. Nitrous acid may dissociate into  $\text{OH}^-$  and  $\text{NO}^+$ . The latter radical oxidizes the  $\text{Fe}^{2+}$  of the hemoglobin to  $\text{Fe}^{3+}$ , which in oxidized form is unable to adsorb  $\text{O}_2$ <sup>[1]</sup>. It is generally accepted that the critical level of  $\text{NO}_3^-$ -N concentration of drinking water is 10 ppm for human, 25 ppm for chickens<sup>[8]</sup>.

The most popular methods used for  $\text{NO}_3^-$  and  $\text{NO}_2^-$  determination are the reduction of  $\text{NO}_3^-$  to  $\text{NH}_3$  followed by steam distillation<sup>[9,10]</sup>, reduction to  $\text{NO}_2^-$  and its determination by the Griess-Ilosvay method<sup>[9,10]</sup>, ion electrode<sup>[11]</sup>, ultraviolet spectrophotometry<sup>[12]</sup> and the colorimetric measurement of the nitration product formed by  $\text{NO}_3^-$  with phenoldisulfonic acid<sup>[13]</sup>. These  $\text{NO}_3^-$  methods, although adequate for determination of  $\text{NO}_3^-$  in water, have certain disadvantages and limitations that hinder their performance.

Reduction of  $\text{NO}_3^-$  to  $\text{NO}_2^-$  using Cd and the resulting  $\text{NO}_2^-$  determined by the Griess-Ilosvay method have been used extensively because of no interferences and its great sensitivity<sup>[14,9]</sup>. The disadvantage of this method is the small dynamic range and the problem is found in the reduction step<sup>[14,9]</sup>.

The strong absorption band of the  $\text{NO}_3^-$  ion at 203 nm<sup>[15]</sup> has been used for the determination of  $\text{NO}_3^-$  in alkaline earth carbonates<sup>[15]</sup>, in natural waters<sup>[16,17]</sup> and in soil solution<sup>[12]</sup>. Analysis of  $\text{NO}_3^-$  by UV

spectrophotometry usually encounters interferences from non-nitrate substances such as  $\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{Fe}^{3+}$  and organic matter that absorb in the wavelength range of the  $\text{NO}_3^-$  band. Some UV methods either measure<sup>[6,17]</sup> or eliminate the absorbance from these interfering species<sup>[2]</sup>. Two of these methods<sup>[17]</sup> designed primarily for  $\text{NO}_3^-$  determination in water samples, correct only for organic matter interference. This correction is accomplished by measuring the absorbance of the sample at the  $\text{NO}_3^-$  band (210 or 220 nm) and at 275 nm where  $\text{NO}_3^-$  no longer absorbed. Since organic matter compounds absorb strongly at 275 nm and overlap the  $\text{NO}_3^-$  band, a correction for the interference due to the organic matter is then obtained by subtracting a multiple of the absorbance at 275 nm band. Since organic matter absorbs at the wavelength of the  $\text{NO}_3^-$  band, this method of correction is justified only if the organic matter content is small, which is generally not the case.

The main purpose of this study was to compare three methods of  $\text{NO}_3^-$  determination, two are based on ultraviolet spectrophotometer technique and the third is a colorimetric method for determining  $\text{NO}_3^-$  and  $\text{NO}_2^-$  in ground water collected from different depths in different locations of Al Hassa Oasis. Furthermore, the study investigates the effect of urea-nitrogen and organic manure fertilization on the quality of ground water of different aquifers as well as soil.

## MATERIALS AND METHODS

The Eastern Province of Saudi Arabia, has two major oases, namely Al-Hassa and Al- Qatif, and small oasis in Harad and Wadi Al- Miyah. Al-Hassa oases is situated some 60 km in land of the Gulf coast between 25°5' and 25°40' N and 49°10' and 49°55' E and covers an area of approximately 20000 ha. The oasis is L shaped and sloped with a very low gradient towards the Gulf coastal plain. East of the Oasis is the flat Al-Jafura desert floor while west of the oasis is a desert strip. The escarpment of the Assumman plateau rises to an altitude of 270 m above sea level<sup>[8]</sup>. The water of Al-Hassa oasis discharges from the Neogene aquifer belonging to the Umm-er-Raduma formation. This stratum occurs at a depth of some 280 m with a thickness of approximately at 320 m<sup>[8]</sup>. There are 32 main springs in Al- Hassa oasis.

Two locations were selected to collect ground water samples to study the impact of fertilizer application on the quality of ground water. The first location was the Veterinary and Agricultural Research and Training Station, King Faisal University, where the soil was cultivated with citrus and date palm and affected by the application of urea (750 g N/tree/year) and organic manure (0.19 m<sup>3</sup>/tree/year). Some chemical properties of the organic manure, according to Montensen<sup>[9]</sup>, are as follows: N (0.48), P (0.20), K (0.53), Ca (0.71), Mg (0.18),

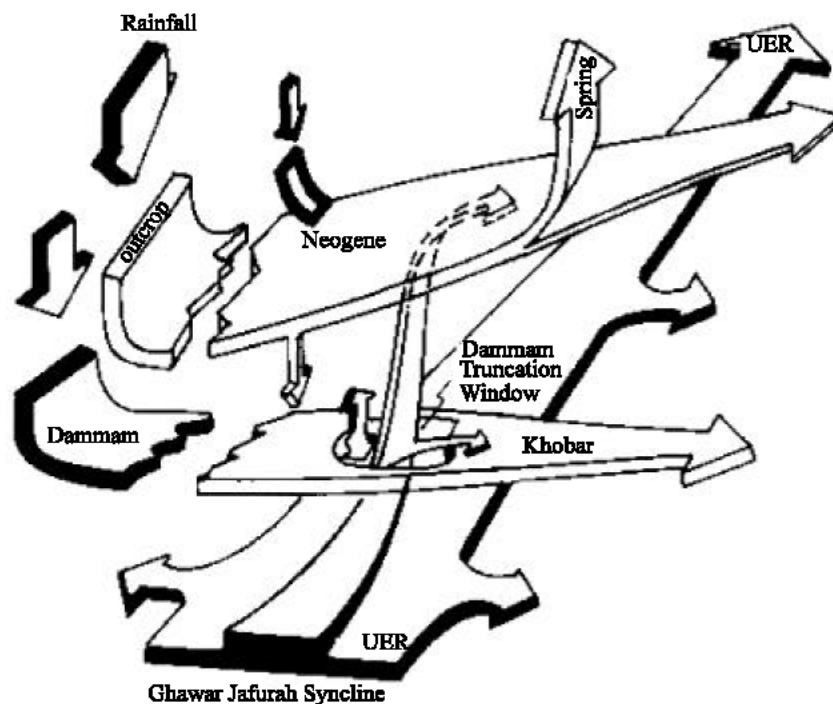


Fig. 1: The interactive aquifer system of Al-Hassa diagrammatic sketch. Cited from Al-Hassa Irrigation and Drainage Authority, Al-Hassa, Saudi Arabia

S (0.09%), Zn (6.16 ppm), Fe (7.6 ppm) and Mn (5.28 ppm). The main sources of irrigation water in this station are eight wells from the three aquifers (Fig. 1). The second one was from an agricultural farm in Al-Hassa oasis. In this site, farm yard manure was used as the only source of fertilizer. Table 1 summarizes the depth, aquifer name and some chemical properties of the collected water samples. They were collected from the pump outlet of the wells while ground water samples were collected from digs (1×2×3 m) under the trees. Samples were filtered in the field through a Whatman No. 42 filter paper in polyethylene bottles that had been washed with diluted HCl and thoroughly rinsed with <2 uL dm<sup>-1</sup> water. Plastic bottles were filled with water samples, capped and stored in an ice chest for analysis.

The soil samples were collected from different fields at El Hassa area at three depths (0-25, 25-50, 50-75 cm) to study the effect of organic manure and urea fertilizer on the nitrate content of the soils. The soil samples were grouped according to the source of nitrogen fertilizer into 4 types; no fertilizer (virgin soil), organic manure, urea and urea+organic manure.

Three methods were used to determine NO<sub>3</sub><sup>-</sup>-N and NO<sub>2</sub><sup>-</sup>-N in wells water samples. According to the method of Norman *et al.*<sup>[20]</sup>, 1 mL of the sample was diluted with distilled water to 25 mL in a volumetric flask. One mL of 2% w/v sulfamic acid was added to the diluted sample and swirled to dispel the NO<sub>2</sub><sup>-</sup> before determining NO<sub>3</sub><sup>-</sup>. The absorbance of the resulting solution was measured at 210 nm (A1) and 270 nm (A2). The concentration of NO<sub>3</sub><sup>-</sup> © was calculated using the following equation:

$$C = D [(A_1 / S) - R (A_2)]$$

D = a dilution factor of water samples

Where: R = A<sub>3</sub> / A<sub>4</sub>

S = the slope of the standard curve (0.117 cm<sup>2</sup> µg<sup>-1</sup> NO<sub>3</sub><sup>-</sup>-N) which was calculated by the preparation of a series of standard solutions (0 to 10 ppm NO<sub>3</sub><sup>-</sup> (KNO<sub>3</sub>) from diluted 100 ppm NO<sub>3</sub><sup>-</sup> and then from every concentration, 1+1 ml of 2% w/v sulfamic acid in 25 ml distilled water was taken to measure the absorbance values at 210 nm. R is the mean value of an individual empirical factor used to calculate the absorbance of non-nitrate species at 210 nm. It is determined by measuring the absorbance of diluted water samples (1/100) in the absence of both NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup>, according to the following procedure: Into an unstoppered 25 mL volumetric flask, 0.3 g of Raney Nickel catalyst powder, 1 ml of diluted sample (which was treated with 1 ml 2% sulfuric acid) and 0.5 ml of 20% v/v H<sub>2</sub>SO<sub>4</sub> were added and the flask was placed in an oven at 58°C for 35 min. The

solution was filtered in a 5 mL funnel tube using 9 cm diameter filter paper (Whatman No. 42) and then 1 mL of the filtrate was transferred to another volumetric flask and diluted to 25 mL with distilled water and the absorbance was measured at 210 nm (A3) and 270 nm (A4).

According to the second method described by Armstrong<sup>[16]</sup>, 0.1 mL of hydrazine sulphate solution (2% w/v in water) was added to a 10 mL water sample in a 150×20 mm stoppered test tube, and to the mixture, 10 mL sulfuric acid (98%, 1.84 sp.gr. of this acid was heated to boil for 15 min. cooled and stored in a glass stoppered bottle) was added. Another water sample (10 mL) was placed in another test tube and mixed with 10 mL of the sulfuric acid (boiled and cooled as described above). The tubes were cooled in running water; mixed and cooled again. The absorbance was measured at 230 nm. The difference in the two readings is proportional to the nitrate concentration. A slope factor for the calculations was obtained by using samples with known nitrate concentration. A Perkin Elmer Lamde 3 UV-VIS spectrophotometer with path length 1 cm<sup>3</sup> was used in the two methods.

The third method (the chemical- kit colorimetric method) depends on using cadmium metal NitraVer 5 Kit to reduce nitrates present in the sample to nitrite. The nitrite ion reacts in an acidic medium with sulfonic acid to form intermediate diazonium salt. This salt couples to gentisic acid to form an amber-colored product. This reacts with chromotropic acid to produce a pink colored complex directly proportional to the amount of nitrite. The color was measured at 507 nm.

## RESULTS AND DISCUSSION

Some chemical analyses of collected water samples from two locations and from different aquifers at different depth at Al-Hassa oasis are depicted in Table 1. In general the EC values and the concentrations of cations and anions decreased with the increase in depth of the samples in the two locations. The concentrations of cations and anions were in the following order Na<sup>+</sup>>Ca<sup>2+</sup>>Mg<sup>2+</sup> and Cl<sup>-</sup>>SO<sub>4</sub><sup>2-</sup>>HCO<sub>3</sub><sup>-</sup>. The data revealed that salt concentrations in location I was higher than salt concentrations in location II.

Table 2 shows the effect of nitrogen fertilizer type (inorganic and organic) on pollution of ground water. The results revealed that in location I, where inorganic and organic fertilizers were added, the NO<sub>3</sub><sup>-</sup>-N concentration ranged between 4.8 and 407 ppm according to the aquifers and depth of the sample, while in location II which received only organic manure, NO<sub>3</sub><sup>-</sup>-N concentration varied from 1.8 to 227 ppm. The high NO<sub>3</sub><sup>-</sup>-N concentration

Table 1: Depth, aquifer name and some chemical properties of water samples collected from location I at King Faisal Univ. and location II at different farms in Al-Hassa oasis (crops were treated with inorganic and organic and organic fertilizers, respectively)

Location	Depth (m)	Aquifer name	pH	EC dS/m	m.mol/m <sup>3</sup>					
					Cl <sup>-</sup>	HCO <sub>3</sub> <sup>-</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	SO <sub>4</sub> <sup>2-</sup>
I	3		8.39	5.10	16.0	4.5	10.3	18.7	17.5	1.3
I	3		6.69	6.69	15.0	7.0	21.8	23.1	22.5	1.3
I	3		7.97	18.45	17.5	9.5	125.7	49.2	90.0	2.5
I	3		8.00	1.00	5.0	2.0	7.0	7.0	6.0	2.0
I	3		8.21	9.80	22.2	4.6	72.2	37.6	60.5	2.1
I	3		8.61	10.96	26.7	13.5	65.9	33.7	75.6	2.3
I	3		8.40	13.04	23.2	13.4	93.8	46.1	80.5	3.8
I	250	Dammam	7.15	1.89	2.5	2.4	8.9	5.2	8.0	0.1
I	250	Dammam	7.38	2.13	2.3	0.3	15.3	7.1	7.0	0.1
I	450	UER*	7.29	1.74	1.4	1.4	12.2	4.3	8.8	0.3
I	450	UER	7.71	1.30	3.0	2.0	1.5	3.9	5.2	0.1
I	80	Neogene	7.49	2.84	7.4	4.8	15.7	13.1	16.0	0.1
II	3		7.81	6.33	13.5	5.9	18.3	19.5	20.4	1.0
II	3		8.01	6.18	32.1	9.5	23.1	31.1	29.2	2.0
II	3		8.06	6.28	15.1	10.2	45.3	29.1	33.2	2.2
II	3		8.00	7.57	11.7	14.5	47.9	10.5	57.0	8.2
II	3		7.33	5.18	4.8	8.2	37.0	7.1	36.3	6.8
II	3		7.62	7.15	17.2	12.5	43.1	39.8	3.8	31.0
II	3		8.03	7.95	5.6	4.3	67.7	25.5	49.0	4.8
II	260	Dammam	7.82	0.53	1.5	0.9	2.6	1.4	1.69	1.7
II	260	Dammam	7.77	0.99	4.0	3.3	2.0	1.2	5.60	2.4
II	450	UER	7.81	0.66	1.5	1.9	2.9	1.0	2.40	2.4
II	480	UER	7.74	3.09	6.3	4.6	19.7	10.2	16.8	4.4
II	120	Neogene	7.85	2.91	2.8	7.0	18.8	16.5	6.8	5.4
II	25	Neogene	7.08	3.05	2.6	5.5	23.7	6.8	18.8	4.1
II	30	Neogene	6.89	3.15	3.9	4.9	22.3	5.5	20.9	4.7
II	35	Neogene	7.06	2.32	2.8	4.0	15.8	3.8	15.3	3.8
II	40	Neogene	7.38	2.64	3.1	4.1	17.9	1.8	20.6	3.9
II	135	Neogene	7.18	3.88	4.3	5.2	23.1	6.3	22.5	4.3
II	150	Neogene	7.33	2.74	2.6	6.9	17.3	6.2	16.5	3.9

\* UER: Umm er Radhuma aquifer

in the two locations was in the upper ground water samples (3 m below the soil surface), but the highest concentrations of NO<sub>3</sub><sup>-</sup>-N at the same 3 m depth were found in location I. The means of NO<sub>3</sub><sup>-</sup>-N concentration at the depth (3 m) were 378 and 206.9 ppm in the two locations, respectively. However, the NO<sub>3</sub><sup>-</sup>-N concentration decreased with the increase in the depth of the ground water (120-420 m). These concentrations ranged from 4.8 to 22 ppm with a mean value of 14.1 ppm in location I and from 1.8 to 4.0 ppm with a mean value of 2.8 ppm in location II. These results revealed that the ground water of the soil fertilized with urea N fertilizer and organic manure was more polluted with NO<sub>3</sub><sup>-</sup>-N than the ground water of the soil fertilized with only organic manure. These results agreed with<sup>[2,21]</sup> who reported a decrease in nitrate concentration in the surface water due to a decrease in the amount of applied inorganic nitrogen fertilizers.

Data in Table 2 show that NO<sub>2</sub><sup>-</sup>-N concentration was less than the concentration of NO<sub>3</sub><sup>-</sup>-N. Generally, NO<sub>2</sub><sup>-</sup>-N decreased as the depth increased, and the upper aquifer (Neogene) was polluted more than the lower aquifer (Dammam and Umm er Radhuma). Table 2 also shows that there is no difference in the NO<sub>2</sub><sup>-</sup>-N concentration due to

the type of fertilizers in the two locations. This result means that NO<sub>2</sub><sup>-</sup>-N levels do not depend on the type of fertilizer but it may depend on other factors such as oxidation-reduction states of system. Stuart *et al.*<sup>[22]</sup>

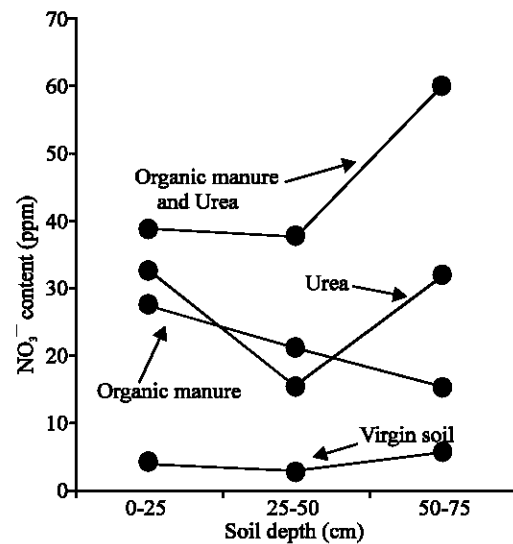


Fig. 2: The NO<sub>3</sub><sup>-</sup> content (ppm) at different depth of the soil collected from Al-Hassa area

Table 2: Effect of nitrogen fertilizer type (inorganic and organic) on NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> concentration in groundwater samples collected from two locations

Location I				Location II			
Aquifer Name	Depth (m)	NO <sub>3</sub> <sup>-</sup> N (ppm)	NO <sub>2</sub> <sup>-</sup> N (ppm)	Aquifer Name	Depth (m)	NO <sub>3</sub> <sup>-</sup> N (ppm)	NO <sub>2</sub> <sup>-</sup> N (ppm)
SGW*	3	407	1.7	SGW	3	227	1.40
SGW	3	363	1.6	SGW	3	181	1.80
SGW	3	181	1.5	SGW	3	227	2.80
SGW	3	265	1.9	SGW	3	198	1.40
SGW	3	358	2.04	SGW	3	200	1.20
SGW	3	420	2.75	SGW	3	240	1.60
SGW	3	342	1.7	SGW	3	219	1.20
Neogene	80	64	0.23	Neogene	25	44.3	0.05
				Neogene	30	24.4	0.27
				Neogene	35	18.2	0.15
				Neogene	40	14.2	0.27
				Neogene	65	18.2	0.19
				Neogene	120	19.9	0.08
				Neogene	135	21.7	0.15
				Neogene	150	16.4	0.05
				Neogene	150	17.7	0.07
Dammam	250	22	0.122	Dammam	260	1.8	0.04
Dammam	250	17.7	0.042	Dammam	280	3.1	0.08
Dammam	250	20.1	0.080				
UER **	450	12.0	0.269	UER	420	2.2	0.05
UER	450	4.8	0.053	UER	450	0.9	0.01

\* SGW : Surface ground water samples at about 3 m depth.

\*\* UER : Umm er Radhuma aquifer.

Table 3: NO<sub>3</sub><sup>-</sup>-N concentration (ppm) in some groundwater samples determined by three spectrophotometric methods

Analysis Methods			Means	Standard
I	II	III	Means	deviation
44.3	42.9	45.3	44.2	±1.21
4.0	4.7	5.1	4.6	±0.56
17.7	17.9	18.3	18	±0.31
14.2	16.5	14.8	15.2	±1.19
24.4	25.3	25.1	24.9	±0.47
19.9	21.2	20.5	20.5	±0.65
21.7	21.8	24.4	22.6	±1.53
16.4	18.2	14.8	16.5	±1.70
17.7	17.5	19.4	18.2	±1.04
17.7	18.9	19.0	18.5	±0.72

showed that the general lack of wells water contamination might be the result of agricultural practices used in the region and/or the effect of denitrification of nitrogen fertilizers.

The NO<sub>3</sub><sup>-</sup> contents in the soil samples are shown in Fig. 2. The results revealed that NO<sub>3</sub><sup>-</sup> ion content in the second depth of the soil (25-50 cm) was lower than in the other two depths (0-25 and 50-75 cm). The low values in the second depth may due to the activity of the root system. The C/N ratio of the soil was lowest in the third depth. The NO<sub>3</sub><sup>-</sup> content was in the following order with regard to treatments: organic manure and urea>urea>organic manure>virgin soil. Drozd and Weber<sup>[23]</sup> showed that native humus would be expected to have a lower C/N ratio than most undecayed plant residues. The decay process is accompanied by

conversion of organic form of N to NH<sub>3</sub> and NO<sub>3</sub><sup>-</sup>; and the soil microorganisms will utilize part of this N for synthesis of new cells. Kristensene and McCarty<sup>[24]</sup> reported that the fate of mineral forms of N in soil is determined to some extent by nonbiological reaction involving NH<sub>4</sub><sup>+</sup>, NH<sub>3</sub> and NO<sub>2</sub>.

The concentrations of NO<sub>3</sub><sup>-</sup>-N in groundwater samples determined by the three spectrophotometric methods summarized in Table 3, show that there are no significant differences in the values among the three methods. The standard deviation ranged between 0.31 and 1.70 for all samples. Generally, these methods were rated as reliable for the determination of NO<sub>3</sub><sup>-</sup>-N in water samples without serious interferences from non nitrate or organic species. However, method I was found to be simpler, more rapid, sensitive and reliable than the other two methods even in the presence of interfering non nitrate and organic species.

According to this study, NO<sub>3</sub><sup>-</sup>-N content of groundwater decreased with increasing depth. Also, groundwater of soil fertilized with urea N fertilizer and organic manure was more polluted with NO<sub>3</sub><sup>-</sup>-N than that of soil fertilized with organic manure alone. Where NO<sub>2</sub><sup>-</sup>-N level was found to be independent of both depth and type of fertilizer factors. The three spectrophotometric methods used for the determination of NO<sub>3</sub><sup>-</sup>-N in water samples were being reliable without any serious interferences from non nitrate or organic species. However, method I was simpler, more rapid, and sensitive than the other two methods.

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