Effect of Fertilizers and Irrigation Water on Accumulation Nitrates and Nitrites in Tomatoes Produced from Greenhouse

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Abstract

Elevated concentrations of nitrates and nitrites in food and water pose significant risks to human health and the environment. This study aims to evaluate the levels of nitrates and nitrites in greenhouse-grown tomatoes in the coastal region of Syria. One hundred tomato samples were randomly collected from 50 greenhouses (two samples per greenhouse) across ten villages in Sahil Akkar, Tartous, Syria. A detailed information card was prepared for each greenhouse, documenting the greenhouse area, the types of fertilizers used, and the irrigation water source. Water samples were analyzed using a colorimeter, and nitrate and nitrite concentrations in the tomato samples were measured using a spectrophotometer. The findings revealed that the highest nitrate concentration was recorded in samples from Riyaf (307.87 mg/kg), while the lowest was detected in samples from A. Zibdi (101.26 mg/kg). Similarly, the highest nitrite concentration was observed in Riyaf (0.058 mg/kg), whereas the lowest was found in Dkaiki (0.066 mg/kg). The elevated nitrate and nitrite levels in the greenhouse samples may be attributed to the use of irrigation water containing high concentrations of these compounds, combined with the excessive application of mineral and organic fertilizers.

Keywords: Nitrates, Nitrites, Tomatoes, Fertilizer, Greenhouse

Introduction:

One of the primary strategies to enhance soil quality is the application of fertilizers, including phosphorus, nitrogen, and potassium., the global consumption of these fertilizers increased dramatically from 14 million tons in 1950 to 137 million tons by 1996 (Shuxuan *et al*., 2005; Lin *et al.,* 2003). However, excessive fertilizer use often leads to residual amounts in water, with significant quantities being absorbed by plants (Abu-Dayeh *et al*., 2006).

Additionally, the cultivation of tomatoes in greenhouses has grown significantly due to the higher yield compared to traditional field farming methods (Luo *et al.,* 2022).

The primary natural source of nitrates originates from atmospheric deposition, biological nitrogen fixation, and rainfall (Cancer, 2010; Brender, 2020), Unnatural sources of nitrates include sewage systems, open drainage pipes, industrial waste, explosives, and certain food preservatives (Rousta *et al*., 2010). The overuse of nitrogen-based fertilizers contributes to soil contamination, as large quantities persist in the soil and water, ultimately accumulating in the roots, leaves, and fruits of plants (Zhang and Fang, 2007).

Previous studies have shown that high concentrations of nitrates and nitrites can have adverse effects on human health. The initial symptoms of nitrate and nitrite poisoning include dizziness, headache, tachycardia, and hypotension. Additional symptoms such as nausea, vomiting, and abdominal pain may also occur (Robson, 2007), Disturbances in thyroid gland function and the nervous system have been reported as other potential side effects (Chung *et al.,* 2011).

Approximately 5–7% of ingested nitrates are converted into nitrites, a percentage that can exceed 12% in children due to their higher levels of stomach acid. The resulting nitrites can enter the bloodstream within a few hours (WHO, 2017).

The majority of ingested nitrate (70–95%) is eventually excreted in the urine as ammonia, urea, or nitrate, with fecal excretion being negligible (Campbell and Dunn, 2000). However, nitrates that remain in the body convert red hemoglobin into dark-brown methemoglobin (metHb), which is incapable of transporting oxygen to tissues. When metHb concentrations reach 10% or more of normal hemoglobin levels, methemoglobinemia occurs, leading to cyanosis and, at higher concentrations, asphyxia (Epley et al., 1992; Bryan, 2006).

Nitrites directly alter the blood's properties, preventing it from performing its primary function of oxygen transport from the heart to other parts of the body (Umah et al., 2003). Notably, methemoglobin poses additional risks to pregnant women, increasing the likelihood of miscarriage, birth defects, and thyroid disorders (Awad, 2003). Certain inflammatory conditions and illnesses may also elevate nitrate levels in the body (Rodica et al., 2010).

Men with a deficiency in the glucose-6-phosphate dehydrogenase enzyme are more prone to methemoglobin formation. When methemoglobin levels reach 50%, death becomes inevitable (Speijers and Van den Brandt, 2003). Inside the human body, nitrates may transform into nitrosamines and nitrosamides, both of which are classified as carcinogenic. Nitrite ions react with amino acids naturally present in living organisms to form nitrosamines, which are known to contribute to certain cancer cases (Simion *et al.,* 2008). Nitrosamines have been observed to negatively affect protein synthesis and glycogen storage in the liver. They have also been found to increase the production of glutamic transaminase in plasma and ornithine carbamyl transferase even before the appearance of any symptoms. In some cases, nitrosamines elevate bilirubin levels in the blood and impact the levels of vitamins and thyroxin (Blot *et al.,* 1999).

Nitrosamines can be formed in the production and preparation of food. Nitrosamines are also produced in the stomach of mammals. When given to animals, Nitrosamines caused brain tumors, and these brain tumors are considered number one death causing cancer in children. They are also known to cause colon cancer and esophagus and lymphatic nodes in humans (Griciute, 1976; Jakszyn and González, 2006).

It was observed that Nitrosamines in pregnant women, who were given vitamins C and E during the period of pregnancy, were not very effective. It was also observed that there is a link between stomach cancer and the Nitrites and Nitrosamines found in vegetables and smoked foods (EFSA, 2008), and a link between Nitrites and diabetes, causes of abortion and certain birth defects (Speijers and Van den Brandt, 2003). It was also found that the amount of Nitrates is 36-58% lower and the amount of Nitrites is 82-98% lower in vegetables which are very well cooked (Speijers and Van den Brandt, 2003).

According to the World Health Organization (WHO) and the Food and Agriculture Organization (FAO), the daily permissible levels of nitrates and nitrites are 3.7 mg/kg and 0.06 mg/kg of body weight, respectively (Deb *et al*., 2007).

The primary objective of this study is to assess the concentration of nitrates and nitrites in greenhouse-grown tomatoes and the water used for irrigation in the Sahil Akkar region, located in the coastal province of Tartous, Syria. This region was selected for the study due to its high number of greenhouses dedicated to tomato cultivation. Additionally, the area faces significant environmental challenges, including inadequate sewage systems, a proliferation of industrial activities, and the overuse of fertilizers. Ultimately, the goal of the study is to compare the nitrate and nitrite concentrations in the sampled tomatoes and irrigation water with the permissible limits set by WHO and FAO.

Materials and Methods:

One hundred samples of greenhouse tomatoes (in their green state) were randomly collected from 50 greenhouses (2 samples per greenhouse) in ten villages in Sahil Akkar, Tartous. The villages included in the study are Arzona, Madihli, A. Zibdi, B. Shofan, Shas, Riyaf, Zahid, Dkaiki, Habroun, and T. Sunoun. Five greenhouses were selected from each village. Samples were collected during the first quarter of 2024. The samples were then placed in polyethylene bags, and water samples were stored in sterilized plastic bottles until they were analyzed.

A special information card was prepared for each greenhouse, documenting the area of the greenhouse, the types of fertilizers used, and the source of water used for irrigation.

Water samples were analyzed using two colorimeters: the DR 1850 Colorimeter by HACH and the DATALOGGING Colorimeter used by the Drinking Water Institution in Syria. The water was tested using specific programs designed to measure Nitrates (NO_3-N) and Nitrites (NO_2-N). The methodology followed was based on the HACH system. A blank sample was prepared in the same manner as the test samples.

To extract the levels of nitrates and nitrites in the tomato samples, each sample was thoroughly washed, completely dried, finely chopped, and then soaked in hot water following the method described in the reference (Yash and Kalra, 1998).

To measure the nitrate content in the tomatoes, a Spectrophotometer was used, applying the Cadmium Reduction Method (Yash and Kalra, 1998). A sample of the prepared tomatoes was placed in a quartz cell, and absorption was measured at wavelengths of 220 nm and 275 nm. The difference between the two readings represented the nitrate absorption.

To determine the nitrite content in the tomatoes, a Spectrophotometer was used with the Colorimetric Method (Yash and Kalra, 1998). A 50 mg sample of the prepared tomato filtrate was taken, and 2 mg of the nitrite color tester was added. The sample was allowed to stand for a minimum of 10 minutes and a maximum of 2 hours to achieve the appropriate color change. Absorption was then measured at a wavelength of 543 nm.

Results:

The mean concentrations of nitrates and nitrites in the examined irrigation water and tomato samples, along with the quantities of organic and mineral fertilizers used per 100 square meters of greenhouse area, are presented in **Table 1**. Additionally, **Table 2** shows the mean values, standard deviations, and the minimum and maximum levels for each sample. The types of fertilizers used were also measured and compared among the samples. Furthermore, **Table 3** presents Pearson's Correlation Coefficient for nitrates and nitrites in both irrigation water and tomato samples.

In **Figure 1** and **Figure 2**, the percentages of nitrates and nitrites in the irrigation water are shown, respectively. **Figure 3** presents the mean quantities of organic and mineral fertilizers used per 100 square meters. Finally, **Figure 4** and **Figure 5** show the concentrations of nitrates and nitrites in the tomato samples, respectively

Discussion:

According to our study, the highest nitrate concentration in the irrigation water of greenhouses was observed in Shas (34.75 mg/L), while the lowest concentration was recorded in Dkaiki (5.7 mg/L). Conversely, the highest nitrite concentration in the irrigation water was detected in Madihli (0.041 mg/L), whereas the lowest concentration was found in Habroun (0.019 mg/L). These variations may be attributed to the use of mineral fertilizers and the reliance on groundwater for irrigation in Shas.

The study also revealed that the mineral fertilizers used in the examined greenhouses comprised 36.82% P_2O_5, 30.12% urea, and 33.06% potassium. The highest application rate of mineral fertilizers was recorded in the tomato greenhouses in Riyaf (27 kg/100 m²), while the lowest rate was observed in Madihli (4.46 kg/100 m²).

Regarding organic fertilizers, the composition included 48.18% poultry manure, 37.85% cow manure, and 13.97% sheep manure. The highest application rate of organic fertilizer was recorded in Riyaf (374.99 kg/100 m²), whereas the lowest rate was observed in Arzona (108.8 kg/100 m²).

Furthermore, the highest nitrate concentration in tomato samples was detected in Riyaf (307.87 mg/kg), while the lowest concentration was found in A. Zibdi (101.26 mg/kg). Similarly, the highest nitrite concentration in tomato samples was also observed in Riyaf (0.58 mg/kg), with the lowest concentration recorded in Dkaiki (0.066 mg/kg). These results demonstrated a statistically significant difference in nitrate and nitrite levels across the examined areas ($P = 0.000$).

The elevated levels of nitrates and nitrites in the tomato samples from Riyaf can be attributed to the excessive use of organic and mineral fertilizers, particularly those rich in nitrogen, such as urea and poultry manure. Previous research indicates that the nitrogen content in poultry manure is the highest compared to other types of organic fertilizers (Sulaiman and Salman, 2013; Martin and Restani, 2003).

Additionally, the fertilizers used in this study contained 46% nitrogen in urea, 46% phosphorus in P_2O_5, and 46% potassium in potassium fertilizer, as reported by the Syrian Fertilizer Company. The lowest concentrations of nitrates and nitrites in the tomato samples from A. Zibdi and Dkaiki can likely be attributed to the limited use of mineral fertilizers and the reliance on cattle manure. This finding suggests that vegetables grown with mineral fertilizers exhibit higher contamination levels compared to those cultivated using natural methods (McKnight *et al.,* 1999).

In general, greenhouse-grown vegetables contain higher concentrations of nitrates and nitrites compared to those cultivated in open fields and normal agricultural areas. This disparity can be attributed to reduced daylight intensity in greenhouses and the higher levels of nitrogen applied during cultivation. Additionally, these concentrations tend to be higher in winter compared to other seasons (Amr, 2000; Shahlaei *et al.,* 2007; Sulaiman and Salman, 2013).

Irrigation water in the study was sourced equally from surface water (50%) and groundwater (50%). The nitrate and nitrite concentrations in surface water were lower compared to groundwater. This difference is attributed to rainfall, which washes nitrates and nitrites from the soil and directs them into surface water sources (Zhang and Fang, 2007).

A comparison was conducted between the standard permissible levels of nitrates and nitrites in tomatoes, as established by the World Health Organization (WHO), and the concentrations found in the tomato samples. According to WHO guidelines, the allowable limit is 300 mg of nitrates per kilogram and less than 1 mg of nitrites per kilogram (Chung *et al.,* 2003; Rousta *et al.,* 2010; WHO, 1978). The nitrate concentrations varied across the samples, with the highest level (60%) detected in Riyaf, followed by 20% in B. Shufan and Habroun, and 10% in Arzona, Zahid, Dkaiki, and Madihli. However, no nitrate contamination was observed in the samples from A. Zibdi, Shas, and T. Sunoun. Overall, the percentage of nitrate contamination in all greenhouses was 14%. Conversely, the nitrite

levels in all tomato samples remained within the standard limits set by the World Health Organization (WHO) (Chung *et al*., 2003; Rousta *et al*., 2010).
Results also showed that the Mean of Nitrates in all tomato samples was 177.57 mg/kg. When comparing these results with other studies done in different regions of the world, our results were higher than the ones reported in the study done in Toul Karm, Palestine (16.95 mg/kg), in Hong Kong (57 mg/kg), in Shanghai (58 mg/kg), in Romania (114.57 mg/kg) in addition to the results reported in China (4.57 mg/kg) (Abu-Dayeh *et al.,* 2006; Chung *et al*., 2011; Simion *et al*., 2008; Speijers and Van den Brandt, 2003). While the Mean of our results is lower than the study done in Shiraz, Iran (942 mg/kg), and that reported in China (856 mg/kg) in addition to the study done in Ahwaz in Iran (544 mg/kg) (Shahlaei *et al*., 2007; Rousta *et al*., 2010; Speijers and Van den Brandt, 2003).
As for the Mean of Nitrites in our study was 0.019 mg/kg, lower than the one done in Toulkarm, Palestine (0.14 mg/kg), in Romania (0.37 mg/kg), in Ahwaz in Iran (6.20 mg/kg) (Abu-Dayeh *et al*., 2006; Simion *et al*., 2008; Shahlaei *et al*., 2007).
Based on Pearson's Correlation Coefficient, the results show that the strongest correlation was between Organic fertilizer and the Nitrites in Tomatoes (r=0.7695), and the weakest correlation was between the Nitrites of the irrigation water and the nitrates found in tomatoes (r=0,0148). It is well-known that the closer the correlation coefficient is to number one, the stronger the correlation (Petrie and Watson, 1999).

Conclusions:

There is a statistically significant difference between the levels of Nitrates and Nitrites in the studied samples (P=0.000). Nitrates and Nitrites were higher in the samples of the greenhouses where water with high levels of Nitrates and Nitrites is in addition to excess amounts of mineral and organic fertilizers are used. Moreover, Nitrates levels were higher than the permitted limits reported by WHO, whereas the levels of Nitrites were within the standard levels reported by WHO. This requires a review of the process of consumption and the technologies of farming. In addition to that; linking the contaminated areas with environmental maps should be done in many countries including Syria.

Table (1): The Mean for Nitrates and Nitrites in the tomato (mg/kg), and irrigation water samples (mg/l), and the fertilizers used (kg/100m^2).

Type / Village	Analysis of TS		Analysis of IW		Fertilizer used	
	Nitrites	Nitrates	Nitrites	Nitrates	Organic Fert. Per 100 m^2	Mineral Fert. Per 100 m^2
Arzona	0.0716	198.34	0.0804	11.02	108.806	12.994
Madihli	0.1761	198.1	0.4172	15.08	193.06	4.464
A. Zibdi	0.165	101.26	0.0992	15.1	245.714	7.072
B. Shofan	0.308	202.01	0.0634	33.026	338.886	7.616
Shas	0.1214	112.19	0.0882	34.752	118.166	18.85
Riyaf	0.583	307.87	0.047	9.08	374.996	27
Zahid	0.2515	153.26	0.0378	7.1	323.338	9.464
Dkaiki	0.0663	150.12	0.0232	5.7	172.576	5.986
Habroun	0.076	211.88	0.0198	10.86	210.474	13.6
T.sunun	0.1099	140.66	0.075	24.88	292.402	14.614
Mean	0.19288	177.569	0.09512	16.6598	237.8418	12.166

Table (2): Statistics Analyses of Nitrates and Nitrites in Tomato and water samples, and the used fertilizers

Samples	comp	Number of samples	SD ± MEAN	min - max	Lo 95% CI-UP 95% CI
Tomatoes	Nitrates	(100)	177.57± 60.009	101.26-307.87	220.5–134.64
	Nitrites	(100)	0.1586± 0.1929	0.0663-0.583	0.3063–0.0793
Water	Nitrates	(50)	16.66 ±10.552	5.7- 34.75	24.208–9.111
	Nitrites	(50)	0.0951±0.1164	0.0198-0.4172	0.1784–0.0119
Fertilizer	Mineral Fert.	(50)	12.166 ± 6.87	4.46-27	17.08–7.25
	Organic Fert.	(50)	237.84±92.71	108.80-374.99	304.16–171.52
p=0.000					

Table (3): Pearson's Correlation Coefficient in Nitrates and Nitrites in irrigation water and in Tomato samples.

Samples	Nitrite in IW	Nitrates in IW	Nitrates inTomatoes	Organic Fert.	Mineral Fert.
Nitrates in Tomatoes	0.0148	0.3106		0.4139	**0.4922**
Nitrites in Tomatoes	0.0569	0.0524	0.6852	0.7695	**0.5312**

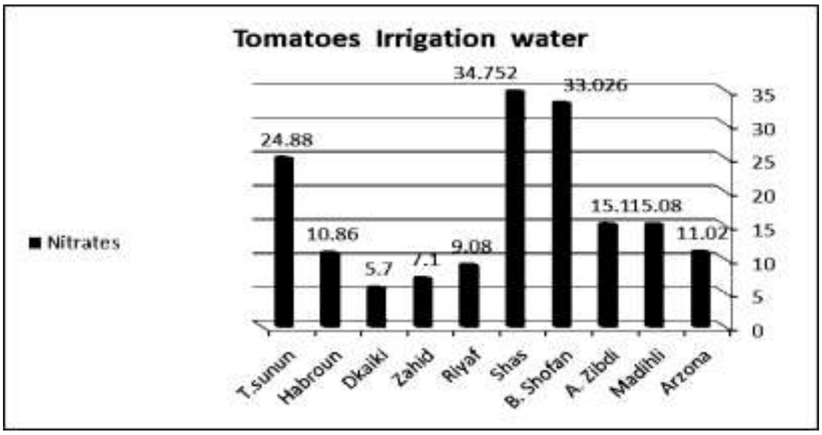

Fig (1): Nitrates levels in irrigation water in mg/l.

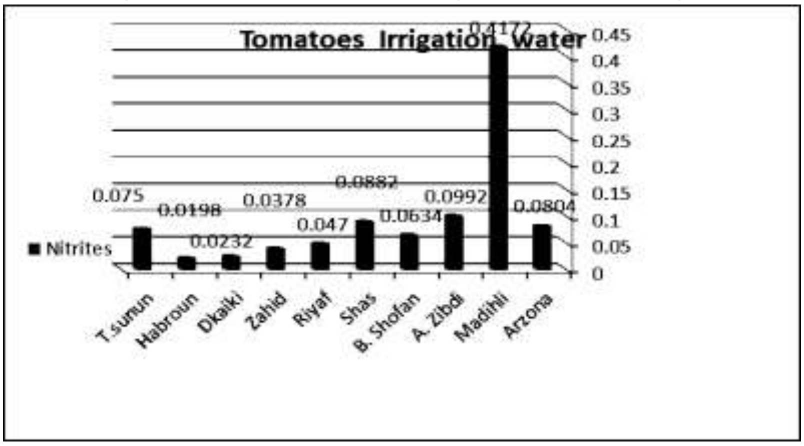

Fig (2): Nitrites levels in Irrigation Water in mg/l.

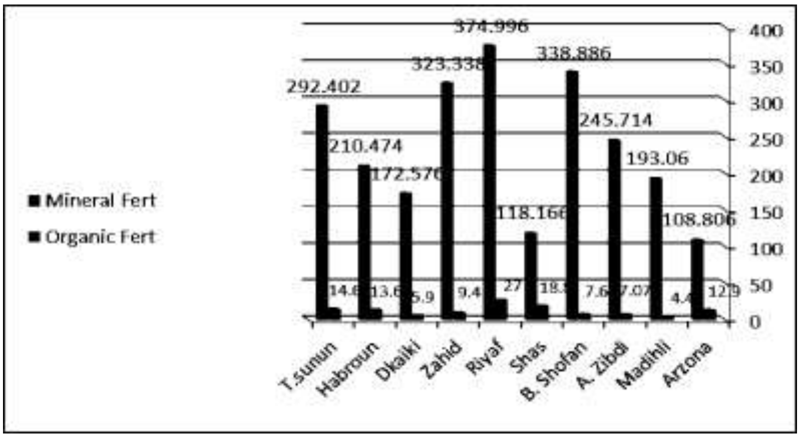

Fig (3): The mean of OF (Oragnic Fert) and MF (Mineral Fert) used in each 100 square meters.

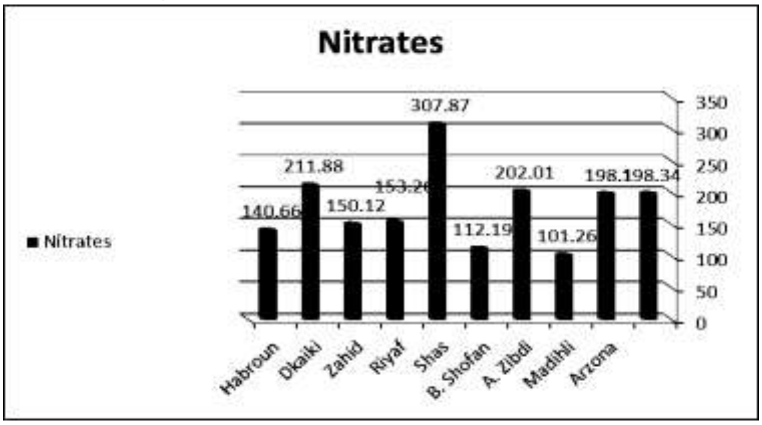

Fig (4): Nitrates levels in tomato samples in mg/Kg.

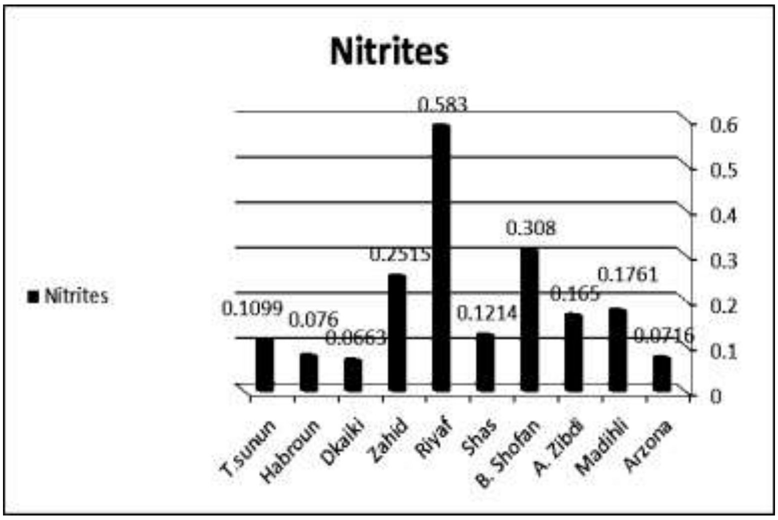

Fig (5): Nitrites levels in tomato samples in mg/Kg.

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تأثير الأسمدة ومياه الري على تراكم النترات والنتريت في البندورة المنتجة من البيوت البلاستيكية

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الملخّص

تشكل التركيزات المرتفعة من النترات والنتريت في الغذاء والماء مخاطر كبيرة على صحة الإنسان والبيئة. تهدف هذه الدراسة إلى تقييم مستويات النترات والنتريت في البندورة المزروعة في البيوت البلاستيكية في المنطقة الساحلية من سوريا. تم جمع مائة عينة بندورة بشكل عشوائي من 50 بيتاً بلاستيكياً (عيّنتان من كل بيت بلاستيكي) موزعة على عشر قرى في سهل عكار، طرطوس، سوريا. تم إعداد استمارة معلومات مفصلة لكل بيت بلاستيكي، توثق مساحة البيت البلاستيكي، وأنواع الأسمدة المستخدمة، ومصدر مياه الري. تم تحليل عينات المياه باستخدام جهاز colorimeter، وتم قياس تركيزات النترات والنتريت في عينات البندورة باستخدام جهاز spectrophotometer. كشفت النتائج أن أعلى تركيز للنترات سُجّل في العينات من قرية رياف (307.87 ملغ/كغ)، في حين تم الكشف عن أدنى تركيز في العينات المأخوذة من قرية عين الزبدة (101.26 ملغ/كغ). كما لوحظ أعلى تركيز للنتريت في قرية رياف (0.058 ملغ/كغ)، بينما وُجد التركيز الأدنى في قرية الدكيكة (0.066 ملغ/كغ). قد تُعزى المستويات المرتفعة من النترات والنتريت في عينات البيوت البلاستيكية إلى استخدام مياه ري تحتوي على تركيزات عالية من هذه المركبات، إلى جانب الإفراط في تطبيق الأسمدة المعدنية والعضوية.

الكلمات المفتاحية: النترات، النتريت، البندورة، الأسمدة، البيت البلاستيكي.