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Research Article

Investigation of Nitrate, Nitrite Pollution Levels and Organic Matter Amounts of Artesian Waters of Aydın Region

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ABSTRACT

Among the pollutants that can spread over large areas, nitrate, nitrite and organic matter are considered as an important indicator of pollution of the environment. It is known that there is a high connection and relationship between agricultural activities and nitrate contaminations. This study was carried out to determine the amount of nitrate, nitrite and organic matter, which are important indicators of water pollution, in artesian waters taken from various districts of Aydın. The artesian waters used in the study were obtained from randomly selected artesian wells close to the settlements of 9 districts of Aydın province (Germencik, Çine, Kuşadası, Bozdoğan, Efeler, Köşk, Söke, Yenipazar, Koçarlı) in September 2019. Nitrate and nitrite analysis in waters by colorimetric method; organic matter analysis was performed by titrimetric method. Underground water resources in Aydın are generally used for agricultural irrigation and to meet the water needs of farm animals. In the water samples taken in the study, nitrate and nitrite amounts were determined below the upper limit determined by TSE. Despite this, the amounts of organic matter were found in all samples; It is above the limit values of 0.1-2 mg/L for groundwater. It is thought that this contamination due to organic matter may have been caused by domestic contamination.

Keywords: *Aydın, nitrate, nitrite, organic matter, water analysis*

Aydın Bölgesi Artezyen Sularının Nitrat, Nitrit Kirlenme Düzeyleri ve Organik Madde Miktarlarının Araştırılması

ÖZET

Geniş alanlara yayılabilen kirleticiler arasında nitrat, nitrit ve organik madde çevrenin kirletilmesinde önemli bir gösterge olarak kabul edilmektedir. Tarımsal faaliyetler ve nitrat kirlenmeleri arasında yüksek bir bağlantı ve ilişki olduğu bilinmektedir. Bu çalışma, Aydın iline bağlı çeşitli ilçelerden alınan artezyen sularında su kirliliğinin önemli belirteçlerinden olan nitrat, nitrit ve organik madde miktarlarını belirlenmek amacıyla yapılmıştır. Çalışmada kullanılan artezyen suları, 2019 yılı Eylül ayında Aydın ilinin toplam 9 ilçesinden (Germencik, Çine, Kuşadası, Bozdoğan, Efeler, Köşk, Söke, Yeni Pazar, Koçarlı) yerleşim yerlerine yakın rastgele seçilmiş artezyen kuyularından temin edilmiştir. Sularda nitrat ve nitrit analizleri kolorimetrik metotla; organik madde analizi titrimetrik yöntemle yapılmıştır. Aydın'daki yeraltı su kaynakları genellikle tarımsal sulama ve çiftlik hayvanlarının su ihtiyaçlarını gidermek için kullanılmaktadır. Yapılan çalışmada alınan su örneklerinde nitrat ve nitrit miktarları TSE'nin belirlediği üst limitin altında tespit edilmiştir. Buna rağmen organik madde miktarları tüm örneklerde; yeraltı suları için belirlenen 0,1-2 mg/L limit değerlerin üzerindedir. Organik maddeye bağlı bu kirlenmenin evsel kirlenmeden kaynaklanmış olabileceği düşünülmektedir.

Anahtar kelimeler: *Aydın, nitrat, nitrit, organik madde, su analizi*

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Introduction

Water is an indispensable substance that plays the most important biological and chemical role in the universe. It is of vital importance for all known living forms and for us humans. In addition to these, it is one of the cornerstones of the life cycle not only for living things and people, but also socially and eco-systemically. If the oceans, seas and polar glaciers remain on one side, only 3.5% of the existing water in the world is usable (Kılıç, 2008).

A large part of the water used in daily life is obtained from underground sources. In recent years, pollution from industrial and domestic wastewater and the use of numerous chemical fertilizers in agricultural systems have caused pollution in groundwater. Pollution is an important issue in environmental sustainability and a serious environmental problem for the world (Zhang et al., 2018).

The excessive use of nitrogen fertilizers in agriculture has been one of the primary sources of high nitrate in groundwater. Nitrogen is applied in the forms of ammonium (NH_4+) and amide (NH_2-), which are converted to nitrate in the soil system through very rapid mineralization in tropical and subtropical soils. Due to its high solubility in water and low retention by soil particles, nitrate is prone to leaching into subsoil layers and eventually groundwater if not taken up by plants or denitrified to N_2O and N_2 (Majumdar and Gupta, 2000; Burkut, 2018). The rate of infiltration is governed by the soil properties and the amount of water present in the soil system. The use of nitrogen fertilizers, excessive application of irrigation and abundant precipitation can increase the transfer of nitrate to groundwater. Animal farms, barns, septic tanks, animal and human contamination are other important sources of high nitrate contribution to groundwater. Nitrite ion is formed as a result of nitrate oxidation or more nitrate reduction during chemical and biological processes (Mikayilov and Acar, 1998; Atay and Pulatsu, 2000; Şanlı, 2002; Atılgan et al., 2007).

The importance of nitrates and nitrites in terms of environmental toxicology is evaluated in relation to acute and chronic nitrate and nitrite poisoning caused by dose intake in humans and animals. Nitrates, which are taken into the body through food and water, are reduced to hydroxylamine and ammonia, partly by microorganisms in the intestinal flora and partly by some other factors (Lundberg et al., 2018). In the acid medium, this reduction product of nitrate reacts with amines and amides to form N-nitroso compounds. These compounds are known to have carcinogenic effects in humans and animals (Tricker and Preussman, 1991; Weyeret al., 2001; Çakmak et al., 2009). To protect public health from hazards associated with high nitrate concentration, WHO determined that nitrate is 50 mg/L and nitrite, 3 mg/L in drinking water (WHO, 2017).

High nitrate concentration in drinking water increases the risk of disease and health effects such as methemoglobinemia, diabetes, spontaneous abortion, thyroid disease and stomach cancer (Havelaar and Melse, 2003; Kobayashi, 2018; Ward et al., 2018; Carlström et al., 2020). Depending on the amount of nitrate taken with water, acute and chronic poisoning is seen in animals. Water containing more than 500 ppm nitrate can cause anoxic convulsions, cyanosis of the mucous membranes and non-pigmented parts of the skin, unconsciousness, coma and acute poisoning causing death; long-term consumption of nitrate waters higher than 125 ppm causes respiratory distress, vasodilation, tachycardia, mydriasis, cyanosis, decreased milk secretion, abortion, avitaminosis, deterioration in thyroid gland functions, and decreased thyroxine, triiodotronin and somatomedin levels (Kaya et al., 1998; Ateşşahin and Servi, 2017).

Therefore, the identification of nitrate sources is crucial for planning effective nitrogen pollution reduction strategies and ensuring the sustainability of water resources. Understanding the nitrate contamination situation and determining the source of nitrate pollution is key to pollution control.

One of the most important parameters for understanding the quality of water is the amount of organic matter. If the amount of organic material in the water is too large, serious results may occur. Organic substances found in natural waters are composed of naturally occurring organic substances in the aquatic environment; it arises from the substances that come out during the treatment, disinfection and distribution of water, or from the pollutants that arise as a result of the pollution of water resources by industrial and agricultural activities. Pollutants mixed with industrial and domestic wastewater and agricultural fields are important polluting sources that affect water quality. An increase in the amount of organic matter is a sign of water pollution. Organic substances cause bacteria and fungi to grow in water (Alaş and Çil, 2002). It is undesirable for the amount of organic matter in drinking water to be over 3.5 mg/L (Varol et al., 2008).

This study was carried out to determine the amount of nitrate, nitrite and organic matter, which are important indicators of water pollution, in artesian waters taken from various districts of Aydın.

Materials and Methods

The artesian waters, which are the study material, were collected from 9 districts of Aydın province (Germencik, Çine, Kuşadası, Bozdoğan, Efeler, Köşk, Söke, Yenipazar, Koçarlı) randomly selected from artesian wells close to settlements in September-October 2019, with aluminum foil taken in coated plastic bottles as 1 liter. Analyzes were performed immediately without waiting for samples.

Determination of nitrite in water samples using a nitrite reagent containing tartaric acid, α-naphthylamine and sulfanilic acid at a wavelength of 543 nm was done spectrophotometrically. The nitrite amounts were determined from the calibration curve created with 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8 and 1 mg nitrite standard solutions prepared with $NaNO_2$ (Anonymous, 2013).

Brucine method is one of the most used methods in the chemical determination of nitrate ion in water. The basis of the method is to read the absorbance values of the yellow color formed in the reaction between brucine and nitrate in the spectrophotometer and to compare these values with standard solutions. 2 ml of water samples were taken, 1 ml of brucine sulfanilic acid solution and 10 ml of sulfuric acid were added. The prepared mixtures were kept in the dark for 10 minutes. Then, 10 ml of distilled water was added to them and mixed. After cooling for 20-30 minutes in the dark, measurements were made in the spectrophotometer at a wavelength of 410 nm. Concentrations were calculated from the calibration curve (Anonymous, 2013; Baltacı, 2000).

Organic substances can enter waters from a variety of sources, including plants, humans and animals. One of the methods used in the determination of organic matter in water is the titration method. It is based on the oxidation of organic substances in water by using permanganate solution in an acidic environment. The amount of potassium permanganate spent in oxidation by back titration is determined and the amount of organic matter is calculated from there.

25 ml samples were taken into 250 ml flasks. 2.5 ml of sulfuric acid solution and 2.5 ml of standard potassium permanganate solution were added and kept in a boiling water bath for 30 minutes. After waiting, 2.5 ml of sodium oxalate was added to it and titrated with potassium permanganate until pink color appeared in hot state, and the consumptions were noted. With the help of the formula, the amount of organic matter in the sample was calculated (Anonymous, 2013).

$$OM = \frac{S}{m} \times 1000 \times 0{,}0125 \times 8$$

OM: Organic matter amount (mg/L)

Q: Amount of $KMnO_4$ used (ml)

m: Sample amount (ml)

Results

The nitrite amounts of the samples, the absorbance values read at 543 nm, were calculated according to the graphic formula (y = 0.8438x; r^2=0.998) of the calibration curve created from the standard solution series.

Calibration curve graphic formula of standard solutions with nitrate varying between 0-50 mg/L; found as (y = 0.8438x; r^2=0.998). By replacing the read absorbance values in this formula, the concentrations of the samples were determined. The nitrate and nitrite amount of the water samples taken from the districts are presented in Table 1. The amounts of organic matter in the samples determined by the titration method are given in Table 1.

The highest nitrite amount is in the water sample taken

Table 1. Nitrite, nitrate and organic matter results of water samples

Districts	Nitrite Amount (mg/L)	Nitrate Amount (mg/L)	Organic Matter Amount (mg/L)
Germencik 1	0.012	0.069	6.4
Germencik 2	0.003	0.216	6
Germencik 3	0.0008	0.40143	6
Germencik 4	0.0034	2.417	6
Germencik 5	0.0042	0.2239	5.8
Germencik 6	0.0802	1.5748	5.8
Efeler	0.0118	0.06176	6
Kuşadası	0.0017	2.1075	6
Bozdoğan	0.0017	0.1698	6.4
Söke 1	0.016	0	6
Söke 2	0.0178	0.03088	7.8
Köşk	0.0135	1.7215	6
Koçarlı	0.027	0	6
Işıklı(Efeler)	0.0135	0.04632	6.2
Umurlu(Efeler)	0.0397	1.25061	6
Yenipazar	0.1173	0.17756	5.4
Çine	0.3502	0	5

from Çine district, the nitrate amount was determined in the samples taken from Germencik 4 and Kuşadası. The amount of organic matter in all samples was found to be between 5-7.8 mg/L.

Discussion

The biggest cause of groundwater pollution is the discharge of domestic and industrial wastes to the receiving environments without treatment. After solid, liquid and gaseous wastes are given to the receiving environment; depending on the climatic situation, the structure of the soil, the shape of the land, the type of waste and time, it mixes with groundwater. In addition, excessive and unconscious use of agricultural struggle drugs is an important cause of pollution. Where there is no sewage system, dirty waters leaking from toilet pits and fertilizers are mixed with groundwater to pollute ground water.

Nitrate among pollutants that can be spread across large areas is considered an important indicator of pollution in the environment. Many studies on this subject show that there is a high correlation and relationship between agricultural activities and nitrate pollution (Olhan and Ataseven, 2009). According to the drinking water standard TSE 266, nitrate concentration was determined as 45 mg/L (Sağlam, 2000).

In a study conducted around Karabük Eskipazar district, nitrate pollution in discharged waters was investigated and high nitrate concentration was encountered. Nitrate values were found to be minimum 1.2 mg/L and maximum 135 mg/L and the mean value was 48 mg/L (Ekemen Keskin, 2010). In Manisa (Eryurt and Sekin, 2001), which depends on fertilization and agricultural activities; In the vicinity of Urla and Menemen (Aslan and Akkaya, 2001), high rates of nitrate contamination have been detected in groundwater.

In the study of Ekşi (2005) in Samsun province, 9 water samples were analyzed. In addition to having a very high value in well water, it has been reported that it is lower than the limit value (45 mg/L) in mains water. According to the results of the monitoring study conducted on the basis of nitrate parameter at 15 selected groundwater sampling points in Eskişehir between October 2005 and July 2006, it was observed that the nitrate concentrations ranged from 13 to 360 mg/L and the standard value (50 mg/L) was exceeded at 6 groundwater sampling points (Çakmak, 2007). The amount of 243.61 mg/L nitrate and 0.63 mg/L nitrite (Özdemir et al.,2004) was found in the Afyon region well waters. Nitrate levels in the well waters of Van center and its districts are 24.7-35.5 ppm; nitrite levels were determined below 0.1 ppm (Ağaoğlu et al., 2007). In the province of Bitlis, nitrate and nitrite amounts in natural spring waters used for human consumption were found to be below 0.5 mg/L (Urgan and Koç, 2020).

In the studies where the seasonal evaluation of nitrate pollution in groundwater in İzmir was carried out, different nitrate values were determined according to the regions; It has been observed that nitrate levels in the waters tend to decrease in winter and increase in summer (Polat et al., 2007; Tayfur et al., 2008). In a similar study, Esmeray and Gökçekli (2020) determined nitrate concentrations in 22 groundwater sources in Karabük province from 2.50 to 44.20 mg/L in the rainy season; they reported a slight increase in the dry season, ranging from < 0.45 to 50.5 mg/L.

In the artesian waters of Aydın province, 1.11–158.9 ppm in winter and 1.2–96.87 ppm in summer nitrate were detected. While 1.26 ppm nitrite was detected in artesian waters in winter only in two settlements, nitrite was not found in other places. It has been determined that the residential areas where the nitrate level of the water samples is determined to be 40 ppm and above in winter and summer months are on flat plains and are places where intensive agriculture and animal husbandry are made (Uçmaklıoğlu, 2011).

There are around 15000 wells, most of which are for irrigation purposes, that have been drilled throughout the province of Aydın. As a result of the researches carried out by the DSI Regional Directorate in 2010, ammonia, nitrite, nitrate was found in various purpose wells drilled in Aydın city center and throughout the province, and an average of 40 mg/L pollution was detected in the measurements (Arslan and Şenol, 2010). The nitrate results of underground (geothermal) waters taken from different stations in Aydın province were 0.063-42.22 mg/L; nitrite was found between 0.008 and 43.624 mg/L. The highest nitrate-nitrite amount was determined in Alangüllü town, which is rich in geothermal waters (Özdoğan et al., 2016).

In this study, which was carried out in the artesian waters of Aydın center and its districts, the average nitrate and nitrite levels were found to be lower than the average values reported by many researchers. It was observed that the nitrate level of artesian waters remained below 45 ppm, which is the permissible level determined in drinking water for humans. According to TSE 266, nitrite is not required in drinking water, while nitrite is allowed up to 0.05 ppm in drinking water according to the Regulation Concerning Water Intended for Human Consumption of the Ministry of Health (Sağlam, 2000). While the nitrite level was below 0.05 ppm in the analyzed samples, it was found to be high in the water samples taken from Yenipazar, Germencik 6 and Çine.

The determination of total organic matter is the measurement of reducing substances present in the minimum amount of water. Total organic matter can be correlated with the natural color of the water or with some organic waste from industrial wastes or sewers. An increase in the amount of organic matter indicates that there is pollution in the water. Atasoylu et al. (2006) were determined the amount of organic matter above 3.5 mg/L in 154 of 4410 drinking water samples by Aydın provincial public health laboratory. The nitrate and nitrite amount in the water samples taken in the study were determined below the upper limit determined by TSE. Despite this, the amount of organic matter in all samples; It is above the 0.1-2 mg/L limit values determined for groundwater.

It is thought that this pollution due to organic matter may have resulted from domestic pollution.

Conclusion

Groundwater management is key and ensuring the sustainable use of groundwater resources is a major challenge. For this reason, water analysis in terms of water pollution should be repeated from time to time, taking into account seasonal changes.

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Conflict of Interest

The authors declare that they have no conflict of interest in this study.

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