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Monitoring of nitrogenous compounds in Munzur and Pülümür River, tunceli, Turkey

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ABSTRACT

In this study the concentration of Nitrogenous compounds were investigated in 6 stations on Munzur (three stations) and Pülümür River (three station) which placed at the Eastern Anatolia of Turkey between 2006-2010. Water pollution was discussed according to the amount of nitrate, nitrite and ammonium values. The results showed that the concentration of nitrate depends on increasing of anthropogenic activities and discharges of waste waters from sewerage systems during the summer term in Munzur River. Regarding of Nitrogen compounds, the concentration of nitrate showed the highest values while the ammonium and nitirite ions measured at the low values in all stations for both river. Mostly the concentration of nitrate showed the highest values in all seasonal terms during the study time intervals in all sampling stations. One-way ANOVA and Duncan's tests were used to determine the differences between stations during the seasonal variations. According to the tests there were no significant differences for nitrate levels between stations during the study term. In this study we pointed out that the water pollution that occurred because of Nitrogenous compounds could be result of agricultural activities in Munzur and Pülümür River 2006-2010.

Introduction

Water is an essential resource for the existence and persistence of life. Water has been using in many activities such as irrigation, drinking and in aquaculture. Water directly affects people's lives as well as the quality of water as important as the presence of it. Given the rapidly increasing world population, food resources, and creation of new food supplies have been important, as well as by depletion of water resources, human being will be confronted of many problems including health subjects (Egemen and Sunlu 1996) in near future. Recently many researchers have been study on increasing water quality to increase the healthy usage of water.

According to UN, more than two billion people in 40 countries are faced with the problems of water scarcity. There are 1.1 billion people having no access to sufficient drinking water and 2.4 billion people have not wastewater services. As a result, diseases and health problems are increasing with engage in risk-sharing problems in food and water security. With the optimistic estimate; one in four people could not be reached to adequate drinking water in 2050. One of the most important factors that will determine humanity's future quality of life within the scope of the environmental pollution is water pollution, and it is updated day by day with more important.

Mostly water pollution is resulted from industry and agricultural activities in developing countries during the last century. Especially chemical fertilizers which used in agricultural production cause water pollution (Kaplan, et.al., 1999). Nitrogen exists as ions such as ammonia, nitrate and nitrite and can be involve in some chemical changes of organic compounds (Ayyildiz, 1983). Regarding as pollution from fertilizers is more emphasis the form of nitrate NO^{-3} on the waters. Because of increasing amounts of fertilizers applied to agricultural production NO^{-3} can be accumulated in the soil (Majumder et.al., 2008). Accumulation in varying amounts of this NO^{-3} is depending on the circumstances which act by washing the soil depth and reaches a section of underground and surface waters (Kaplan, et. al., 1999).

Protecting the quality of natural waters is a major challenge while considering with the global scale, surface and ground waters represents a significant part of the water resources used for drinking and domestic purposes. In recent decades, the contamination of natural water bodies by anthropogenic activities became disturbing in all over the world. Among the contaminants, nitrates, nitrites and ammonium occupy important roles. Nitrate contamination of water is a common problem of the modern world arising from diffuse reasons, intensive agriculture, unsewered of densely populated areas, sanitation, or from point sources, such as the irrigation of land by sewage effluents (Suthar et.al., 2009). Water pollution by nitrogen compounds in surface and groundwater streams can be resumed in a hydrodynamic mass transport accompanied by a mass transfer due to physical, chemical and biochemical processes (Marinov and Nicolescu, 2009). Entry of pollutants into shallow aquifers by percolation from the ground surface (disposal of wastes, agricultural fertilizers), from surface waters, through injection wells, sanitary septic tanks, sewer leakage and by saline water intrusion (Okafor and Ogbonna, 2003, Drolc and Koncan, 2010). Wastewaters from chemical manufacturing (fertilizers, explosives, etc.) and operations using nitrogen-containing products (e.g. corrosion-inhibitors), cleaners and metalworking (fluids) represent the basic industrial sources of nitrogen contamination. In drinking water treatment,

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microorganism's activity in the filtration elevation cause increasing of nitrate and nitrite concentrations which can also cause polluted media in the treated water. Natural sources of nitrate pollution are atmospheric precipitation, local mineral deposits (potassium nitrate), biomass decomposition, and activities of nitrogen-fixing bacteria. However the overall contribution instead of these natural sources, is negligible when compared to the anthropogenic activities (Yang and Cheng, 2007).

Nevertheless, the heavy use of nitrogenous fertilizers in cropping systems is the largest contributor to anthropogenic nitrogen in groundwater worldwide (Majumder et.al., 2008). Nitrogenous fertilizers rapidly convert NO^{-3} form in soils, which is readily available to plants, but is highly soluble and hence easily leachable to deep soil layers. The surplus of NO^{-3} totally adsorbed by soil particles could be noted, leaches out from the root zone by water percolating through the soil profile and ultimately accumulates into the groundwater (Kundu et. al., 2008). Moreover, NO^{-3} is a part of the nitrogen cycle in nature and it represents the most oxidized chemical form of nitrogen found in the natural systems. Also, it is an essential part of the building blocks of living organisms, ie proteins, the genetic material (DNA and RNA), vitamins, hormones and enzymes (Reddy et. al., 2008). Achieve a sufficient amount and quality of drinking water of people has been among the targets of the National Health. The 2000-2015 has been declared as a decade of 'Water for Life', by the international water-related issues which is planned more emphasis on cross-platform (Celebrating Water For Life, 2005). The "Water Pollution Control Regulations" for inland water sources was published by the Ministry of Environment and Forestry of Turkey on 31 December 2004 (Official No. 25687) and quality criterias were defined according to the classification of Water Quality. Parameters of pH, nitrite and nitrate on the quality classes were given. Consequently exposure to high nitrate levels for human health are great concern. Moreover greater NO^{-3} intake reduces the oxygen carrying capacity of the blood by binding hemoglobin which is causing a condition referred to as methemoglobinemia or "blue baby syndrome", which may cause mortality by asphyxiation especially in the newly born infants.

Material and Methods

Sampling Stations

The Eastern Anatolia region of Tunceli, 38°19'and 40°26' East Longitude and 39° 36'and 38°46' North Latitude, is one of the most important place which is at the West and North of the province of Bingöl Mountains and East of the province of Erzincan, South of the Keban Dam Lake and is surrounded by the province of Elazığ which has surface area of 7774 km^2, with altitude of 914 meters.

Table 1. The coordinates of the sampling stations

Sampling Stations	Coordinates	
	North (Y)	East (X)
1	37 544 809	43 28 301
2	37 553 184	43 29 028
3	37 559 818	43 38 630
4	37 592 802	43 31 687
5	37 531 383	43 50 038
6	37 501 307	43 53 713

Water samples taken from 6 different stations between 2006 to 2010. This study was carried out on the Munzur and Pülümür Rivers during the period of 4 years [2006-2010] and the concentrations of changes in nitrate, nitrite and ammonium values were observed. The three stations were selected on Munzur and Pülümür (Table 1) and the seasonal nitrogenous compounds values were obtained by spectrophotometric methods. The points of sample stations were selected as the represented of the nature of the river ecosystems which has been so close to the residential areas with the consideration of the factors of the total pollution. During the study period, 7000 Interface Photometer values were determined by measuring with a spectrophotometer device brand as seasonal samples from January 2006 to November 2010. The water quality measurements has been detected with a multi meters during the three-months periods (February, May, August and November) as determination of seasonal changes in the field. The pH and temperature of water, dissolved oxygen, potassium, sulphate, sulphite, ammonium, nitrite, nitrate, phosphate, and chlorine parameters were measured during the term.

Results

In order to monitor pollution of Nitrogenous compounds, the annual average of nitrate, nitrite and ammonium were detected. The findings were evaluated based on the data obtained from both side annually. The different amounts of nitrate concentrations were detected during the seasonal changes. Mostly the highest values were measured during the summer seasons for all sampling stations on Munzur River. Moreover the concentration of nitrate folded 6 times in first station during the summer term from 2006 to 2010. However the highest values of nitrate concentration observed for all station, the 2 station showed the highest value in fall term in 2008. Even though the nitrate values increased from 2006-2009, the concentration were decreased in summer season at the 3rd station in 2010. The results showed that the concentration of nitrate depends on increasing of anthropogenic activities and discharges of waste waters from sewerage systems during the summer term with the increasing of density of population for Munzur River.

The findings were evaluated based on the data obtained from Pülümür River as; the highest value was observed in spring term at the 4^{th} sampling station in 2009 annually for nitrate concentration. Mostly the concentration of nitrate showed the highest values in spring terms during study time intervals in Pülümür River. The pollution of nitrate occurred because of anthropogenic activities such as irrigations and climate changes between 2006- 2009 at the study area. Regarding of Nitrogen compounds, the concentration of nitrate showed the highest values while the ammonium and nitrite ions were measured at the low values in all stations for both rivers.

One-way ANOVA and Duncan's tests were also used to determine the differences between stations during the seasonal variations. According to the tests there were no significant differences for nitrate levels between stations during the study term (Table 2). There is no significant difference in the seasonal nitrate values for each stations (Table 3).The nitrate concentration suddenly increased in both station after 2008. The reasons could be increasing of anthropogenic activities parallel to the increasing of population. The Figure 1 showed the changes of nitrate concentration 2006-2010. Mostly the

concentration of nitrate showed the highest values in all seasonal terms during the study time intervals in all sampling stations. The Figure 2 showed the concentrations of all Nitrogenous compounds at the 4th station as the represented of all stations in 2010.

Table 2. The results of One-way ANOVA and Duncan Tests for nitrate values for seasonal variations

Season	Winter	Spring	Summer	Fall
	p = 0,866, p> 0.05	p = 0,796, p> 0.05	p=0.636, p>0.05	p = 0,809, p> 0.05

Table 3. The results of One-way ANOVA and Duncan Tests for each stations

Stations	1	2	3	4	5	6
	p=0,286, p> 0.05	p = 0,445, p> 0.05	p = 0,229, p> 0.05	p = 0,386, p> 0.05	p = 0.125, p> 0.05	p = 0,346, p> 0.05

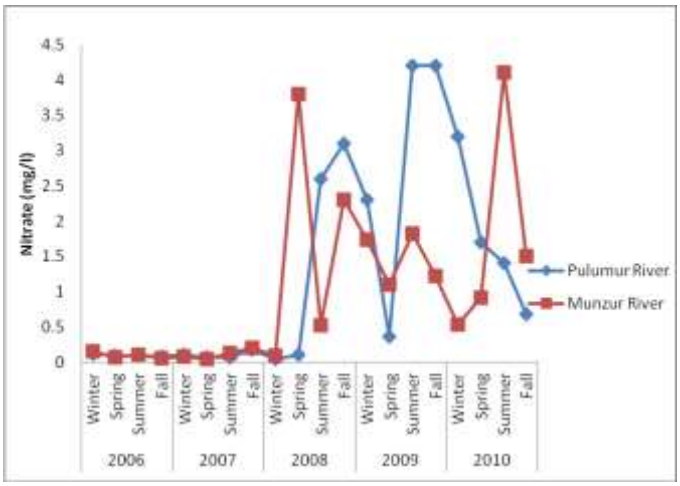

Figure 1. The Nitrate Concentration of stations 2006 to 2010

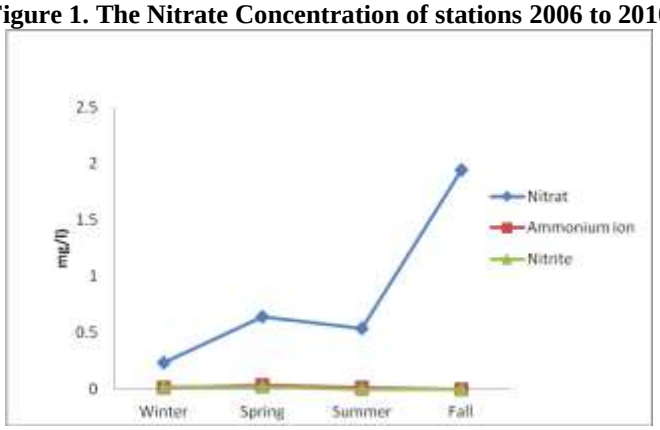

Figure 2. The concentration of Nitrogen compounds in Station 4 in 2010

Today surface and groundwater resources determine the fate of nations as one of the most important critical issue. Using the quality of drinking water has a close relationship between the public health. Individuals who wants to have the opportunity to consume healthy water which has quality become happier and more (Yu et. al., 2007, Puigagut, et.al. 2005). In our study, water samples were taken and examined from different regions of province of Tunceli. The results that obtained were compared with the Official Journal No. 25687 on 31 December 2004 where the "Water Pollution Control Regulations" arranged by Ministry of Environment and Forests.

Water contamination by Nitrogen compounds is one of the main problems associated with agricultural activities. This is mainly due to the fact that nitrates are highly soluble and migrate easily into groundwater. Overuse of fertilizers always increases the nitrate levels in water. There is a large nitrogen surplus in the agricultural soils of EU countries that can potentially pollute both surface and ground waters. It is nonetheless difficult to establish a link between nitrogen supply and water pollution. The main source of nitrate is the runoff and decomposition of organic matter from irrigation areas. The higher inflow of water and consequent land drainage cause high volume of nitrate (Thilaga et.al. 2005). However Nitrates can be denitrified by microbes, the leaching of nitrates could occur depends on geological, climatic and biological factors, particularly in porous rock aquifers and in wet climates Because of Nitrogen compounds stimulate eutrophication and can affect human health, the maximum admissible nitrate concentration limits have been set for drinking water. Directive of 98/83/EC on the quality of drinking water specifies a limit of 50 mg/l, which is matching the WHO guideline values. The directive also sets a guide level of 25 mg/l. Nitrates and ammonium are the most common forms of nitrogen in rivers, with nitrates alone accounting for over 80% of total Nitrogen. Over 65% of the rivers had average which exceeding 1 mg/l with annual nitrate concentrations for period of 1992-1996 in European Union. The concentrations of over 7.5 mg/l were also found in approximately 15% of cases during the same period with the highest concentrations are in Northwest Europe, where agriculture is intensive.

Agriculture remains the largest source of nitrogen in water, but industrial wastewater also contains nitrogen, particularly water discharged by manufacturers of fertilizer or explosives, metal processing and food-processing industries. The nitrate content of more than 100 mg/l impacts bitter taste of water and may cause physiological problem (Wolfhard and Reinhard, 1998). Drinking water which contains more than 50mg/l nitrate can cause methamoglobinemia in infants (Campos et. al., 2002). Nitrate causes the overgrowth of algae, which could resulted with fouls of population of other organisms in the water ecosystem. Epidemiological studies have predicted association between exposures to nitrate and gastric cancer because of the reaction of nitrate with amine in diet forming carcinogenic nitrosomoamines.

In order to diminish the risk of toxicity due to non-ionized ammonia and of oxygen consumption due to nitrification and of eutrophication; the concentration of total ammonium should not exceed values of the guide (G) and mandatory (M) for quality of inhabited by fresh water fish: salmonid and cyprinid waters. The data was interpreted from the quantitative analyses in regard to Regulation no. 4 on the quality of waters supporting organisms life such as fish and shellfish (Naydenova et.al., 2008).

As well as the study of Georgieva and his friends (Georgieva et al 2010) the concentrations of nitrate which we measured in all surface waters, agreed with the permissible standards that set by WHO and EPA for nitrates (measured as NO^{-3}) during the term between 2006-2010 in Munzur and Pülümür Rivers. The concentration of NO^{-2}–N could be classified as a potential pollutant which requires the effective removal by appropriate methods from the natural surface water bodies in all sampling points of Pülümür and Munzur River in Tunceli.

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