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DETERMINATION OF NITRATE AND NITRITE ORIGINS IN THE SOILS AND GROUND WATERS OF THE AREA BETWEEN MERSİN-TARSUS (TURKEY) USING GEOGRAPHIC INFORMATION SYSTEMS

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Abstract The study area is located east of the city of Mersin where both agricultural (especially greenhouse cultivation) and industrial activities are very intense. The aims of this study were to determine nitrate and nitrite levels in soil and ground water samples collected from the area and their spatial distributions using a Geographic Information System (GIS) and to find out their potential sources of pollution. For this purpose, 208 topsoil samples (from a depth interval of 0-15 cm) and 157 ground water samples were collected in August 2007 from the area between Mersin-Tarsus (Turkey). According to the results obtained from this study; nitrate concentrations in soil samples range between 10-1478 mg/L; whereas nitrite concentrations range between 0.0-9.6 mg/L. In ground water samples; however, nitrate concentrations range between 0-1834 mg/L; whereas nitrite concentrations range between 0.0-10.3 mg/L. Comparison of the spatial distributions of nitrate and nitrite in soils and ground water of the area using GIS revealed that their spatial distributions do not show a strong correlation. Examination of the thematic maps produced by GIS indicate that high nitrate and nitrite concentrations in ground water generally occur around settlement areas and industrial facilities; whereas, high nitrate and nitrite concentrations in soils of the area generally occur in places where agricultural activities are very intense.

Keywords: Geographic Information Systems (GIS), Mersin, nitrate, nitrite, pollution, Tarsus, soil, groundwater.

1. INTRODUCTION

The study area is restricted to the Deliçay Stream in the west, Tarsus River in the east, Mersin-Tarsus highway (D-400) in the north and the Mediterranean Sea in the south (Fig. 1). This study aims to determine the nitrate and nitrite contamination in both soil and ground water, and the spatial distribution of contamination by using the Geographic Information System (GIS) in the area between the cities of Mersin and Tarsus, where the agricultural (greenhouse, citrus, viticulture and garden agriculture) and industrial activities are dense and where there is interpenetration. A great number of contamination sources exist in the vicinity of the study area including a glass production plant, a soda/chromium processing plant, a cement production plant, fruit juice and fruit packaging plants, organized industry area, mining-marble processing plants and their storage areas, storage areas for oil and oil derivatives, greenhouse and other agricultural activities, and settlements. A land use map for the study area has been prepared by digitizing high resolution Quickbird satellite images to delineate industrial areas, citrus fruit orchards, greenhouse cultivation areas, forests and settlements (Fig. 1). The Mersin-Tarsus area has been an attraction center for the companies dealing with oil and oil derivatives over the last three decades due to mainly presence of the ATAŞ petroleum refinery in Karaduvar district. Many oil companies (some of them active, some currently being constructed) is currently being operated in this region.

Rapid development of energetics, industry, agriculture, transportation, and urbanization as well as constantly increasing population considerably changed balance in the environment (Dragićević, et al., 2010). There are a lot of environmental pollutants and one of the most harmfull them is probably nitrogen compounds.

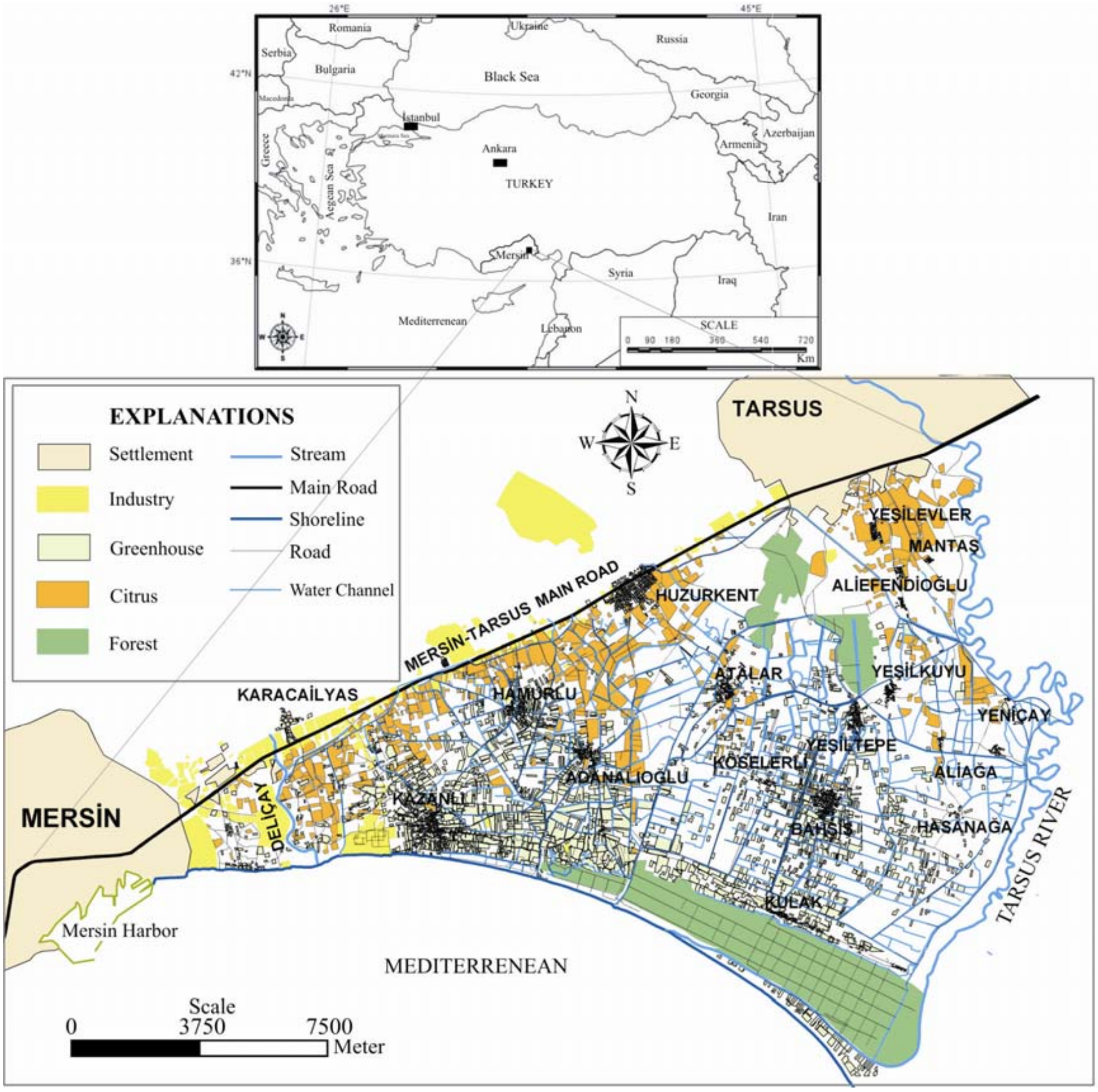

Figure 1. Location and land use map of the study region.

Nitrogen is inextricable part of the organic compounds, such as amino acids, proteins and nucleic acids. Approximately 98% of nitrogen in soil is organic nitrogen that is not taken by the plants. The rest of the nitrogen (2-3%) that may be used by plants is formed by nitrate (NO_3^-) and ammonium (NH_4^+) (Hope et al., 2005). Nearly 50-70% of the artificial nitrogen, which is supplied from the fertilizers, is consumed by plants, 2-20% of it evaporates and mixes into the atmosphere, 15-25% form compounds with organic materials in soil, and the remaining 2-10% is transported to surface and ground water. The main factors that control the spreading of nitrogen components in soil are soil structure, nitrogen demand of plants, speed of the biological decay, temperature, precipitation, quantity of fertilizer used, water content of soil, etc. (Antonopoulos & Wyseure, 1998; Akkurt et al., 2002).

Nitrogen components in water may originate from natural or anthropogenic sources. Natural nitrogen loads are the nitrogen compounds sourced from the micro-organisms in an aqueous environment, atmospheric precipitation and geologic materials. Anthropogenic nitrogen load may be derived from household garbage, wastewater from both households and industry, and cultivation activities. Nitrogen compounds in the ground water have two sources: agricultural and non-agricultural activities (Lerner, 2003). Agricultural contaminants include inorganic and organic fertilizers, sewage water used for agricultural irrigation, organic matter in soil, storage areas of animal food and manure, while non-agricultural contaminants are industrial waste and debris, solid waste storage areas, highways and sewage water (Lerner, 2003; Milanović et al., 2011; Karadavut et al., 2011). Contaminants sourced from agricultural, household and industrial activities may act separately; or in some cases, all of them together contaminate soil and ground water (Kaçaroğlu & Günay, 1997). Nitrogen load of soil, ground water and plants is steadily increasing due to the extensive use of fertilizers in agricultural activities and nitrogen from wastes (e.g., human, animal and industrial) (Kurt et al., 2008). Increased nitrogen loads of plants and water are transported directly via drinking water and indirectly via the food chain (plants) to the humans. It was determined that excess nitrate and nitrite compound cause acute and chronic poisoning in humans and even cancer (Aksoy et al., 1999). On the other hand concentration changes of nutrients, including nitrogen compounds, NH4-N and NH3-N, as they have harmful impact on aquatic organisms (Grabić et al., 2011). Protection of water resources is a major problem that has to be approached from the point of view of rational quantitative exploitation of sources and protection against human aggression in the worldwide circumstances of a growing demand for water (Gurzau et al., 2010).

2. DESCRIPTION OF THE STUDY AREA

The climate of the region is typically Mediterranean (i.e., hot and dry summers and mild and rainy winters) with a mean annual temperature of ~18°C. In the area, precipitation primarily occurs (as rainfall) between November and March with a mean value of ~610 mm/yr, whereas the mean potential evapotranspiration reaches 968 mm/yr. The topographic elevations in the area range from 0 to 30 m above mean sea level. Coastal part of the study area is mostly covered by well-sorted fairly loose recent eolian sand dunes that present an undulating topography in the area. The study area is represented by the Quaternary-Recent fluvio-deltaic sediments ranging in thicknesses from 30 m in the north and >300 m in the south. This unit mostly consists of recent deposits of the Deliçay, Tarsus, and Seyhan rivers. In most places, these deposits display a very heterogeneous character with laterally discontinuous layers that are mostly composed of clay with lesser amounts of silt, sand, and gravel.

Groundwater derived from the underlying Quaternary-Recent fluvio-deltaic coastal aquifer is mostly used for agricultural, industrial and domestic water demands. The hydraulic properties of the aquifer are highly variable in space, which is typical of highly heterogeneous deltaic systems of the region (Gürbüz, 1999). Reported saturated hydraulic conductivities of the surficial sediments range from 2.94×10^{-6} to 9.37×10^{-2} cm/s and gradually increase from north to south, which corresponds to a decrease in the percentage of clay- and silt-sized fractions (Güler et al., 2012). In the area depth to ground water range from 0.75 to 13.44 m and in the coastal part large areas become waterlogged during the wet winters (Güler et al., 2012). In the study area, average hydraulic gradient is ~2‰ and the general direction of groundwater flow is from NW to SE. Recharge to the aquifer takes place through direct precipitation, subsurface inflows from the northern side of the plain, seepages from the canal network and irrigation runoff, inflows from the Deliçay and Tarsus rivers, and the seawater intrusion near the coastal settlements such as Kazanlı and Kulak (Güler et al., 2012). Groundwater discharge; however, occurs primarily by groundwater abstraction via wells, evapotranspiration, and discharge from springs, seeps and open drainage canals (Fig. 2).

3. MATERIALS AND METHODS

In order to determine the nitrate and nitrite concentrations in the study area, 208 topsoil and 157 ground water samples were collected in August 2007. Topsoil samples were taken with Edelman hand auger (at 0-15 cm depth) then they were transported to the laboratory in plastic bags.

After the soil was dried in the air, it was disaggregated using a wooden hammer, and sieved through a 2 mm mesh. Textural properties of the soil samples were determined by hydrometer analysis using Bouyoucos method (Bouyoucos, 1951). Electrical conductivity (EC), pH and salinity of soil samples were measured in 1:5 (w/v) soil-pure water suspension (rested overnight) using the WTW Multi 340i/SET multi parameter device. Extraction of nitrate and nitrite from soil samples was carried out using a 2.0 N KCl solution (Keeney & Nelson, 1982). Nitrate and nitrite contents of the solutions obtained from the soil and ground water samples were measured by spectrophotometric methods. Nitrate concentrations were measured based on the cadmium reduction method, while nitrite values were determined using the diazotization method. Organic material contents of the topsoil samples were measured based on the Walkley-Black method (Walkley & Black, 1934). In order to determine cation exchange capacity of soil samples, sodium saturation method was used (Jackson, 1958; Chapman & Pratt, 1961; Hesse, 1972), and sodium concentrations of the solutions were determined with ICP-MS. All analysis results were recorded in dBASE IV format and transferred to GIS to prepare the distribution maps for each parameter. The parameter distribution maps were compared with the land use map, and the relationship between the nitrate and nitrite concentrations and the sources of contamination in the study area were investigated.

4. FINDINGS

According to the plots showing the distribution of textural composition of topsoil samples in the study area (Fig. 3); a 1-3 km wide zone extending along the Mediterranean coastline has a very high sand content (80-100%). The sand fraction decrease and the silt and clay fractions increase along the line stretching from south to north (Fig. 3). The pH values of the topsoil samples vary between 7.5–8.5, indicating an alkaline soil character. Salinity of the topsoils are generally low (Table 1), but it is significantly higher in the inner part, especially around the Kazanlı settlement. The reason for the high soil salinities around the Kazanlı can be attributed to seawater intrusion due to heavy ground water pumping for agricultural purposes.

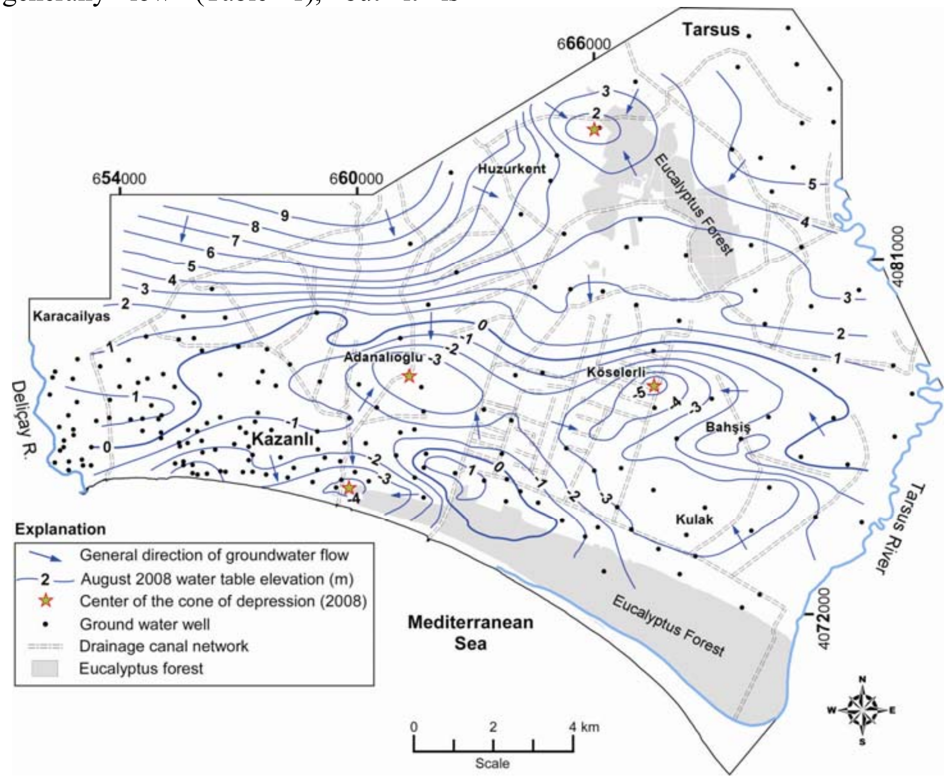

Figure 2. Map showing the ground water levels in the study area where water table elevations are in meters above mean sea level (modified from Güler et al., 2012).

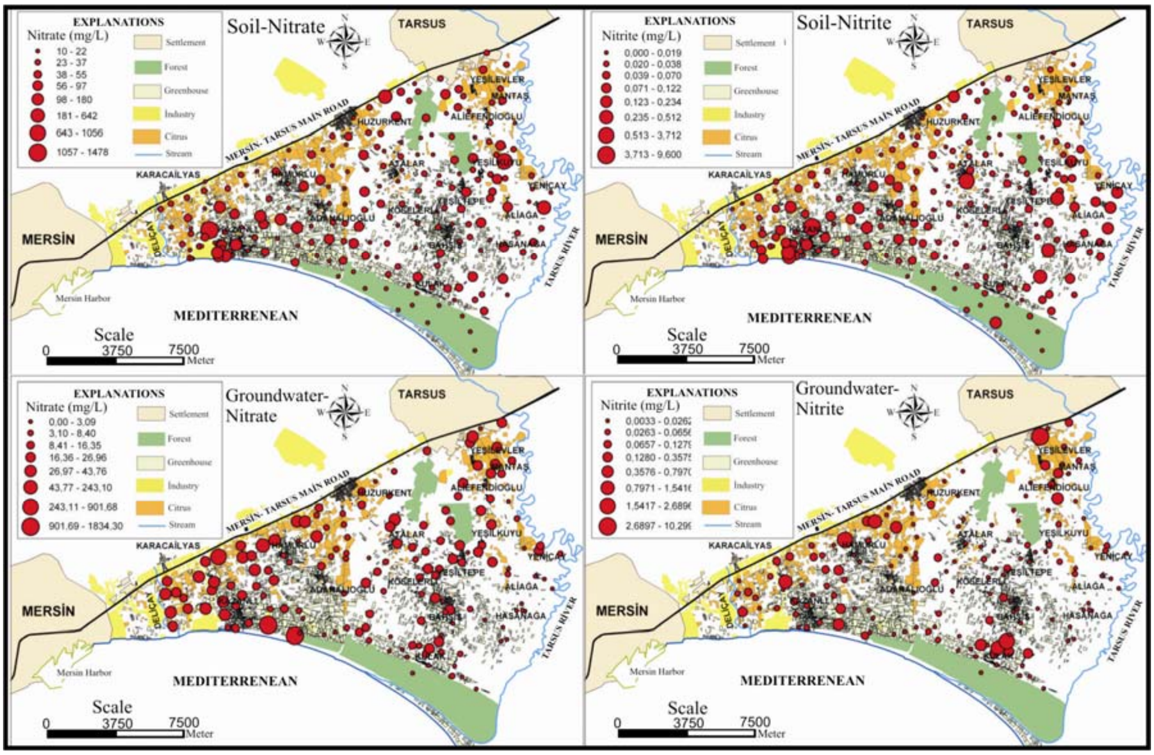

Figure 4. Distribution of nitrate and nitrite values of topsoil and ground water samples of the study area.

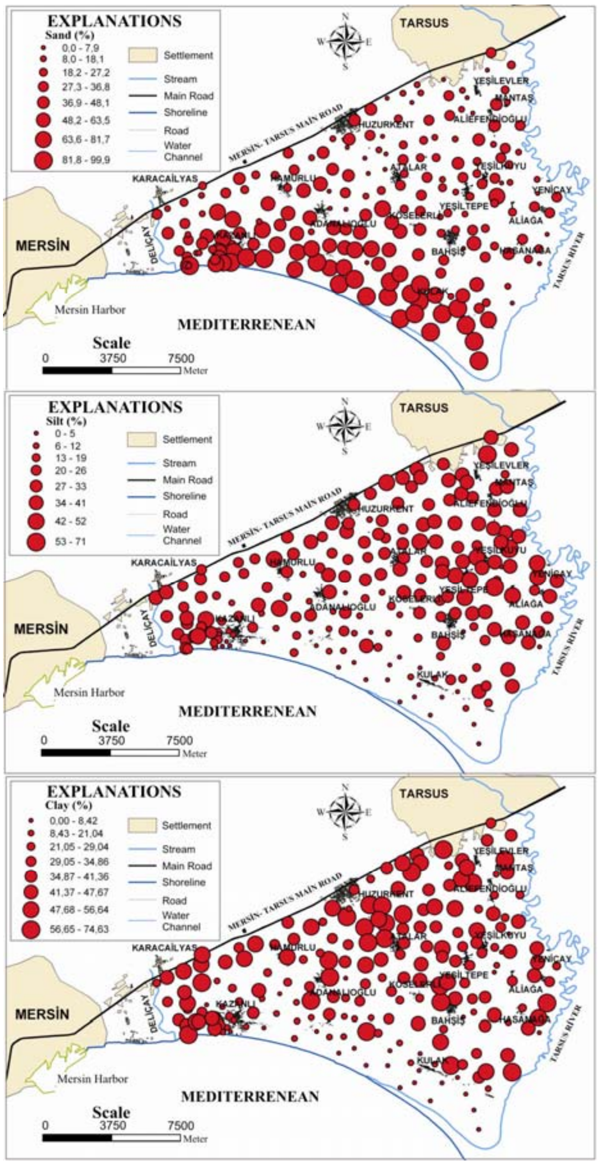

Figure 3. Spatial distribution of the grain size of topsoil samples of study area.

Distribution of nitrate and nitrite in soil and ground water were presented in Figure 4, along with the land use map. As shown in Figure 4, nitrate and nitrite values have similar spatial distributions, with locally very high nitrate and nitrite values in both soil and ground water. Results of this study have shown that nitrate and nitrite values were high in the section that is extending along the Mersin-Tarsus motorway between the towns of Kazanlı and Huzurkent, in the region between the Bahşiş and Kulak villages in the south of the Tarsus, and in and around the villages of Atalar, Yeşiltepe and Yeniçay (Fig. 4).

Organic material contents of topsoils is high in and around the forests, and in the middle and southern section where the greenhouse cultivation is observed, while it is low in the northern section where citrus orchards are present (Fig. 5). Cation exchange capacity (CEC) of the topsoil samples have a inverse relationship with organic material distribution. Soil CEC is high in the northern and central section, low in the southern section along the Mediterranean Sea (Fig. 5). In the area, generally topsoil samples with high CEC values present high clay contents, while topsoil samples with low CEC values present high sand contents. Maximum, minimum and average values of nitrate, nitrite, pH, electrical conductivity and salinity of 157 ground water samples and maximum, minimum and average values of nitrate, nitrite, pH, electrical conductivity, salinity, CEC and organic material of 208 topsoil samples are presented in table 1.

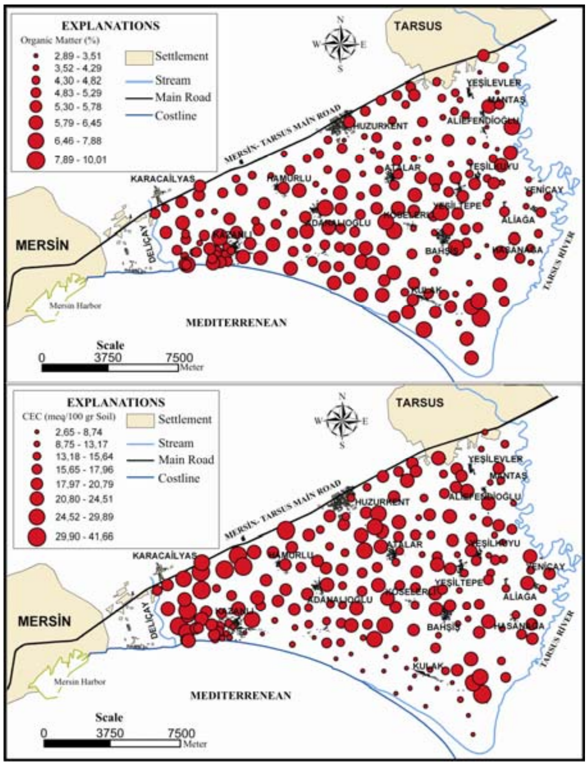

Figure 5: Spatial distribution of cation exchange capacity (CEC) and organic material contents of topsoil samples from the study area.

5. RESULTS

Urbanization and population density make it difficult to protect water sources especially in developing countries. Figure 6 indicates the ground water cycle in urban areas and in nature far away from the anthropogenic activities. Settlement areas create new contamination sources and can disturb the natural cycle of ground water and change the ground water levels. Cultivation activities, all underground transmission lines, sewage networks, rivers and streams, trade centers, industrial regions and waste disposal sites are the factors that change the natural composition of ground water (Fig. 6). Intense agricultural activities and settlements without proper sewage treatment facilities are the main reasons for the pollution of the ground water resources in the study area.

A great number of studies point out that most of the nitrate and nitrite of ground water is sourced from the agricultural activities (especially fertilizer applications). However, in the recent studies it is emphasized that sources of nitrate in ground water in urban and industrial regions are mainly domestic and industrial in origin (Ford & Tellam 1994; Lerner et al., 1999; Lerner, 2003; Wakida & Lerner, 2005; Wakida & Lerner, 2006). Plastic, textile, metal, woodwork and medicine industries are the main consumers of nitrogen compounds (Wakida & Lerner, 2005).

The nitrate and nitrite concentration distributions on the land use map of the study area show that concentrations are lower in agricultural areas, while the concentrations are higher near settlements and industrial regions (Fig. 4). For example; nitrate and nitrite level of ground water is low near the citrus orchards located in the towns of Huzurkent and Adanalıoğlu (Fig. 4). This observation clearly indicates that the high concentrations of nitrate and nitrite are sourced from settlements and/or domestic sources and not from agricultural activities. On the contrary, the high nitrate and nitrite values of two wells in an agricultural area in the east of Kazanlı town may point out to an agricultural origin.

Mueller et al., (1995) indicated that depth to ground water is one of the important factors controlling the pollution of ground water; if the ground water level is close to the surface, it has a higher contamination risk than the deep ground waters. Ground water level measurements in August 2008 indicated that ground water levels in the area are very close to the surface near the Mediterranean coast (0.75 m), while it deepens in the north, further away from the coast (13.44 m). Results of this study have shown that nitrate contents of ground water samples from four wells exceeded the 45 mg/L limit set by the Turkish Drinking Water Standard. Similarly, nitrite contents ground water samples from eight wells exceeded the drinking water limit value set by TS266 (0.5 mg/L). In the area, ground water samples with high nitrate concentrations also include high concentrations of nitrite. Nearly 8% of the ground water wells in the area have displayed very high nitrate and nitrite concentrations, which are deemed hazardous to human health.

Nitrate and nitrite contents of soil samples have similar distributions (Fig. 4), where they are high in the vicinity of Kazanlı, Adanalıoğlu and Hamurlu towns and in some parts of the Aliağa-Hasanağa-Yeşiltepe-Yeşilkuyu villages. Nitrate and nitrite concentrations are low in forestry areas (except nitrite concentration of one sample) and near citrus orchards. Low values of nitrate and nitrite concentrations in forestry areas and their high concentrations near greenhouses indicate an anthropogenic origin for these components. Lower concentrations of nitrogen components in citrus orchards also suggest a little or no fertilizer applications in these areas. Textural properties of soil are one of the most important factors that control the nitrate and nitrite contents of soil (Cameria et al., 2003). Clayey soil can contain more nitrogen components than sandy soils due to their high cation exchange capacity (Podgornik & Pintar, 2007; Gaines & Gaines, 1994). In our study area, soil texture is not directly related to the occurrences of high concentrations of nitrate and nitrite in the topsoil, but the main factors responsible for the high concentrations of nitrate and nitrite in the soil are the agricultural activities such as fertilizer and manure applications and settlements without proper sewage disposal facilities. Mirjat et al., (2008) found that nitrate and nitrite contents of soil are also affected by agricultural irrigation types. In their experimental study it was shown that using conventional irrigation methods (e.g., groove and pool) results in high nitrate concentrations throughout the soil profile, whereas when modern irrigation methods are applied (e.g., drip and rain) high nitrate levels only occurs at the surface of the soil. The highest nitrate levels in topsoil samples occur around the Kazanlı region and it is probably related to intense greenhouse cultivation activities here.

Table 1. Descriptive statistics of the physical and chemical properties of ground water and topsoil samples from the study area.

	Ground water (*n* = 157)		Soil (*n* = 2008)						
	Nitrate (mg/L)	Nitrite (mg/L)	Nitrate (mg/L)	Nitrite (mg/L)	pH	Electrical Conductivity (µS/cm)	Salinity (dS/m)	CEC[1] (meq/100 gr)	Organic Matter (%)
Maximum	1834.3	10.300	1478.4	9.600	8.92	3440	1.7	41.66	10.01
Minimum	0.0	0.003	9.7	0.000	7.50	151	0.0	2.65	2.89
Mean	52.7	0.200	50.9	0.113	8.16	546	0.1	17.42	5.15

[1]Cation exchange capacity.

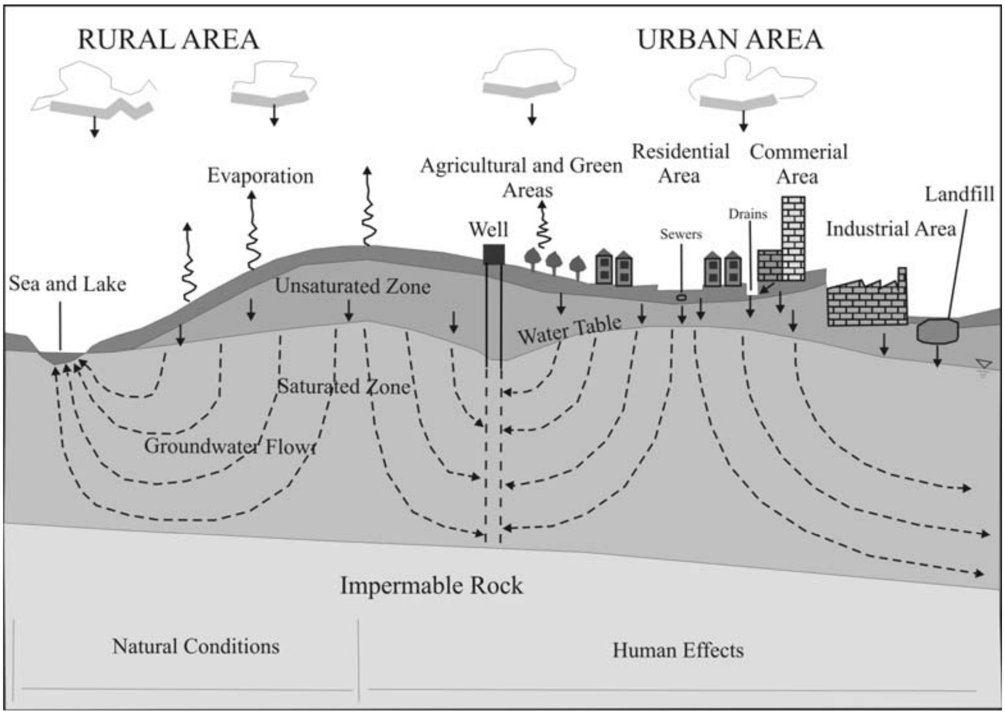

Figure 6. Cycles of ground water in urban and non-urban areas.

Figure 4 clearly shows that there is no reverse or straight relationship between the soil lithological properties and the nitrate/nitrite levels in topsoil samples. The distribution of nitrate and nitrite levels in the soils from the region is mostly related to agricultural activities, including nitrogen bearing fertilizer usage.

6. SUGGESTIONS

This study evaluated the nitrate and nitrite levels in the soil and ground water samples collected from the area between Mersin and Tarsus, where agriculture, industry and settlements are found side by side. Nitrate and nitrite distributions in topsoil are highly affected by agricultural activities, while nitrate and nitrite distributions in ground water are controlled by urban and industrial activities. In this study, distribution and origin of nitrate and nitrite components in soil and ground water samples were evaluated by GIS overlays. In recent studies (Feast et al., 1998; Mayer et al., 2001; Mayer et al., 2002) use of stable N isotopes ($\delta^{15}N$) have proven to be a successful method for the determination of the origin of nitrogen components, both in the ground water and soil.

Protecting our valuable ground water and soil resources is very important and necessitates careful use of fertilizers in agriculture and environmentally friendly industrial activities far from the agricultural areas (Riley et al., 2001; Kurt et al., 2008). Additional also, care should also be taken during site investigations for of settlement areas places that must not be planned situated close to agricultural areas and aquifer recharge regions. The results of this study has great implications for the human health, because the highest nitrate and nitrite levels occur in ground water wells located near Kazanlı town, whose drinking water is supplied from a well-field.

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