



Geographic information system–based approach and statistical modeling for assessing nitrate distribution in the Mitidja aquifer, Northern Algeria

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Abstract The Mitidja alluvial aquifer in northern Algeria is an important drinking, industrial, and agricultural water source. Unfortunately, nitrate contamination has led to a decrease in water quality in several areas that benefit from this source. This study employed geographic information system and statistical modeling methods to evaluate the origin, evolution, and spatiotemporal distribution of groundwater nitrate in the aquifer and investigate the influence of different hydrogeological parameters on its extent. Control points were established across various regions of the Mitidja groundwater aquifer. A total of 1185 nitrate concentrations were measured at 316

sampling points between June 1985 and May 2015. The results showed variable rates, with the 50 mg/L nitrate consumption limit exceeded in 423 samples at 84 observation points. Statistical modeling showed that nitrate concentration was related to groundwater characteristics (aquifer nature, water table depth, and thickness of saturated zone) and human activities (land use, agricultural practices, and population density). Analysis of the nitrate distribution showed that the eastern and western watersheds experienced the greatest contamination. The significant nitrate concentrations in the eastern area were correlated with urban contamination, including uncontrolled urbanization, high population density, and industrial activity, while the primary origin of nitrate in the western area was correlated with agricultural activity, particularly fertilizers. The findings of this study can aid local government and water agencies in the development and implementation of regulations to help mitigate increases in nitrate concentrations.

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Abbreviations

ABH Agency of Hydrographical Basins
ANRH Agence Nationale des Ressources Hydrauliques (National Water Resources Agency)

DEA	Direction d'Environnement d'Alger (Environmental Direction of Algiers)
DEAH	Direction des Études et Aménagement Hydrauliques (Directorate of Hydraulic Studies and Facilities)
DEMRH	Direction des Études de Milieu et de la Recherche Hydraulique (Direction of Environmental Studies and Hydraulic Research)
GIS	Geographic information system
GPI	Grand Périmètre Irrigué (Large irrigated perimeter)
INSID	Institut National du Sol, Irrigation et du Drainage (National Institute for Soil, Irrigation and Drainage)
MADR	Ministère d'Agriculture et de Développement Rural (Agricultural and Rural Development Ministry)
MCL	Maximum concentration level (mg/L)
ONID	Office National d'Irrigation et Drainage (National Office of Irrigation and Drainage)
SEAAL	Société des Eaux et d'Assainissement d'Alger (Algiers Water and Sanitation Company)
UAS	Useful agricultural surface

Introduction

One of the most serious global environmental issues concerns the pollution of groundwater with nitrate (Erisman et al., 2013; Rodriguez-Galiano et al., 2018; Samantara et al., 2015; SEAAL, 2008; Zhang et al., 2014). This pollution can originate from several sources, including atmospheric deposition, wildlife, mineralization of organic matter, sewer and septic tank leakage, synthetic and organic agricultural fertilizers, leaching, effluent infiltration, industrial contamination, and other land uses (cemeteries, waste dumps, etc.) (Alabdula'aly et al., 2010; Almasri & Kaluarachchi, 2011; Ayadi et al., 2018; Bahri & Saibi, 2010; Boumans et al., 2005; Debernardi et al., 2008; Hudak & Sanmanee, 2003; Laftouhi et al., 2003; Menció et al., 2016; Samantara et al., 2015; SEAAL, 2008; Semar et al., 2013; Thangarajan, 2007; Zhang et al., 2014).

Groundwater nitrates are affected by complex physical and chemical processes within soils, subsoils, and

aquifers (Boumans et al., 2005). These processes mean that the vulnerability to pollution varies from one area to another (Tedd et al., 2014). To understand the occurrence and pathways of nitrate concentration requires an understanding of its sources and the factors that control its movement through the hydrogeological system (Burow et al., 2010; Tedd et al., 2014).

In soil and groundwater, the oxidation and reduction of organic and inorganic sources of nitrogen are accomplished by microorganisms (Fetter et al., 2017; Ward et al., 2018). Under oxidizing conditions, ammonia is converted to nitrite, which is then converted to nitrate. Nitrite is a very reactive ion and is almost immediately converted to nitrate; consequently, nitrite is not commonly found in the environment (Fetter et al., 2017). Under reducing conditions, nitrate can be biologically transformed to nitrogen gas through denitrification (Tedd et al., 2014; Ward et al., 2018).

In particular, nitrates are soluble and negatively charged and thus have high mobility and can potentially be removed from the unsaturated zone by leaching (Anayah & Almasri, 2009; Chowdary et al., 2005; DeSimone & Howes, 1998; Tedd et al., 2014). Any nitrates that are not taken up by plants or denitrified migrates to streams and into groundwater (Ward et al., 2005).

When nitrates reach groundwater, they can be attenuated by the processes of solute transport, including advection due to the groundwater flow velocity, dispersion, mixing (including molecular diffusion) (Almasri & Kaluarachchi, 2004, 2011; Anderson & Woessner, 1992; Carrera & Mathias, 2010; Delleur, 2016), dilution (Altman & Parizek, 1995; Debernardi et al., 2008; Jones et al., 2018; Lasagna et al., 2013, 2016), and denitrification (Korom, 1992; McAleer et al., 2017; Rivett et al., 2008; Seitzinger et al., 2006).

The concentration of nitrate in groundwater depends on the recharge, pollution loading, changes in meteorological conditions (i.e., precipitation and evaporation), groundwater flow and water table fluctuations, and the associated nitrate transport and mixing (Chowdary et al., 2005; Nas & Berkday, 2006; Wick et al., 2012).

Studies on the health effects related to nitrate exposure from drinking water have been the subject of great interest (Fan, 2019). Several studies on methemoglobinemia, reproductive and developmental effects, thyroid effects, and carcinogenicity have

reported positive associations with nitrate exposure (Fan, 2011, 2019; Ward et al., 2005, 2018). The World Health Organization's (WHO) guideline of 50 mg/L as the maximum concentration level (MCL) was promulgated to protect against methemoglobinemia, or "blue baby syndrome," to which infants are especially susceptible (Anayah & Almasri, 2009; Fan, 2011, 2019; Ward et al., 2005; WHO, 2004, 2016).

Studies across various countries and regions have described the spatiotemporal evolution of nitrate and the origins of its high concentrations in groundwater aquifers using various approaches, including statistical modeling, numerical modeling, geographic information system (GIS), and mapping, with the aim of mitigating nitrate pollution (Aksever et al., 2015; Arauzo & Martínez-Bastida, 2015; Burow et al., 2013; Calvi et al., 2020; Cellone et al., 2020; Cheong et al., 2012; Chitsazan et al., 2017; Darwishe et al., 2017; Ducci et al., 2020; Esmaili et al., 2014; Ki et al., 2015; Lasagna et al., 2016, 2018; Li et al., 2010, 2015; Martínez et al., 2014; Rina et al., 2014; Rock & Kupfersberger, 2019; Selek & Yetis, 2017; Soomro et al., 2017; Stamatis et al., 2011; Vystavna et al., 2017; Wang et al., 2013; Xi et al., 2015).

GIS is a powerful and promising tool for use in environmental problem-solving (Engel et al., 2016; Kennedy, 2013; Nas & Berktaý, 2006). Groundwater issues are spatially distributed and the use of modeling with GIS software has become essential (Goodchild et al., 1993; Longley et al., 2005). Moreover, statistical tests are widely employed in the water quality field to illustrate and measure associations between variables. The combination of GIS and statistical methods has been a successful approach to groundwater nitrate assessment (Nas & Berktaý, 2006). Many researchers have taken advantage of this approach to describe nitrate concentrations in groundwater in different countries (Anayah & Almasri, 2009; Arauzo & Martínez-Bastida, 2015; Arauzo et al., 2011; Hudak, 1999, 2000; Hudak & Sanmanee, 2003; Lee et al., 2003; Levallois et al., 1998; Nas & Berktaý, 2006; Tedd et al., 2014; Vinten & Dunn, 2001).

The Mitidja area in Algeria holds important socioeconomic significance. It is the nation's primary region of agri-food production, particularly arboriculture, and has experienced rapid urbanization, densification of industries, and population growth (Imache et al., 2011; INSID, 2011).

Sands and gravels are the most prevalent types of soil in the Mitidja (Sir M McDonalds & Partners Ltd et al., 1992; SOGREA, 2009). These are highly porous soils that possess a shallow water table that is very close to the surface in many regions. These types of aquifers have been termed vulnerable to pollution and are severely prone to the leaching and transport of contaminants (Fetter et al., 2017; Kim et al., 2009; Spalding & Exner, 1993).

Groundwater is the predominant water source for drinking, irrigation, and industry in the Mitidja area (ANRH, 1996; Mimouni & Mesbah, 2010; SEAAL, 2008). Unfortunately, the quality of water from this natural source has declined over the last several decades (Benlecheheb & Bouzid-Lagha, 2014). Previous studies found that Mitidja groundwater in distinct zones was contaminated with nitrate concentrations exceeding the 50 mg/L maximum concentration level (MCL) (Benlecheheb & Bouzid-Lagha, 2014; Hadjoudj, 2008; Hadjoudj et al., 2014; Khouli & Djabri, 2011; Messaoud Nacer, 1987; Mimouni & Chibane, 1989; Mimouni & Mesbah, 2010). Thus, the nitrate contamination of the Mitidja groundwater has recently emerged as a growing regional environmental problem, especially with the increasing demands of groundwater for drinking, industrial, and agricultural purposes.

The aims of the study were to document the nitrate pollution levels in Mitidja groundwater, to identify spatiotemporal trends, to analyze the effects of aquifer characteristics, and to determine the probable sources of contamination. For this purpose, we constructed an extensive and detailed panel dataset on the Mitidja aquifer situation that includes time series data on the nitrate concentration levels in groundwater, aquifer types, water table depths, the thicknesses of the saturated zones, the organic manure and mineral fertilizers used, land use data, and rainfall data for around 365 sampling points that covered the entire Mitidja area between 1985 and 2015. The temporal and geographical magnitude of our dataset is larger than in other studies.

GIS tools and statistical modeling were used for the analysis of nitrate concentrations measured in the Mitidja region between June 1985 and May 2015 and allowed for an investigation into the spatiotemporal evolution of nitrate pollution. This is the first study in the Mitidja area to employ these methodologies and use such a

comprehensive measurement database (30 years). The findings from this study are expected to provide valuable information regarding the water sources and areas vulnerable to nitrate pollution and can aid in the implementation of an action program to minimize nitrate contamination and restore water quality in this critical region.

Study area

The Mitidja study area is located in the northern center of Algeria and extends over the prefectures of Algiers in the north, Boumerdès in the east, Blida in the south, and Tipaza in the west (Fig. 1). This area covers 1195 km², is crossed by different Oued (Wadis)

flowing regionally from south to north, and includes 5 catchments, which, from east to west, are Coastal Cap Matifou, El Harrach, Mazafran, Oued Chiffa, and Oued Djer Bouroumi (Fig. 1). The area has a Mediterranean climate with dry summers (June–August) and rainy winters (December–February) (ABH, 2004). The climate becomes more humid, warmer, and more continental toward the southern reliefs. The average annual temperature varies from 16 to 18 °C. Precipitation represents the main source of recharge for the Mitidja groundwater with an average annual rainfall of 620 mm (ANRH, 2013; Mimouni & Mesbah, 2010).

The lithology and hydrodynamic parameters of the terrains allow for the identification of two main aquifer units (Fig. 2):

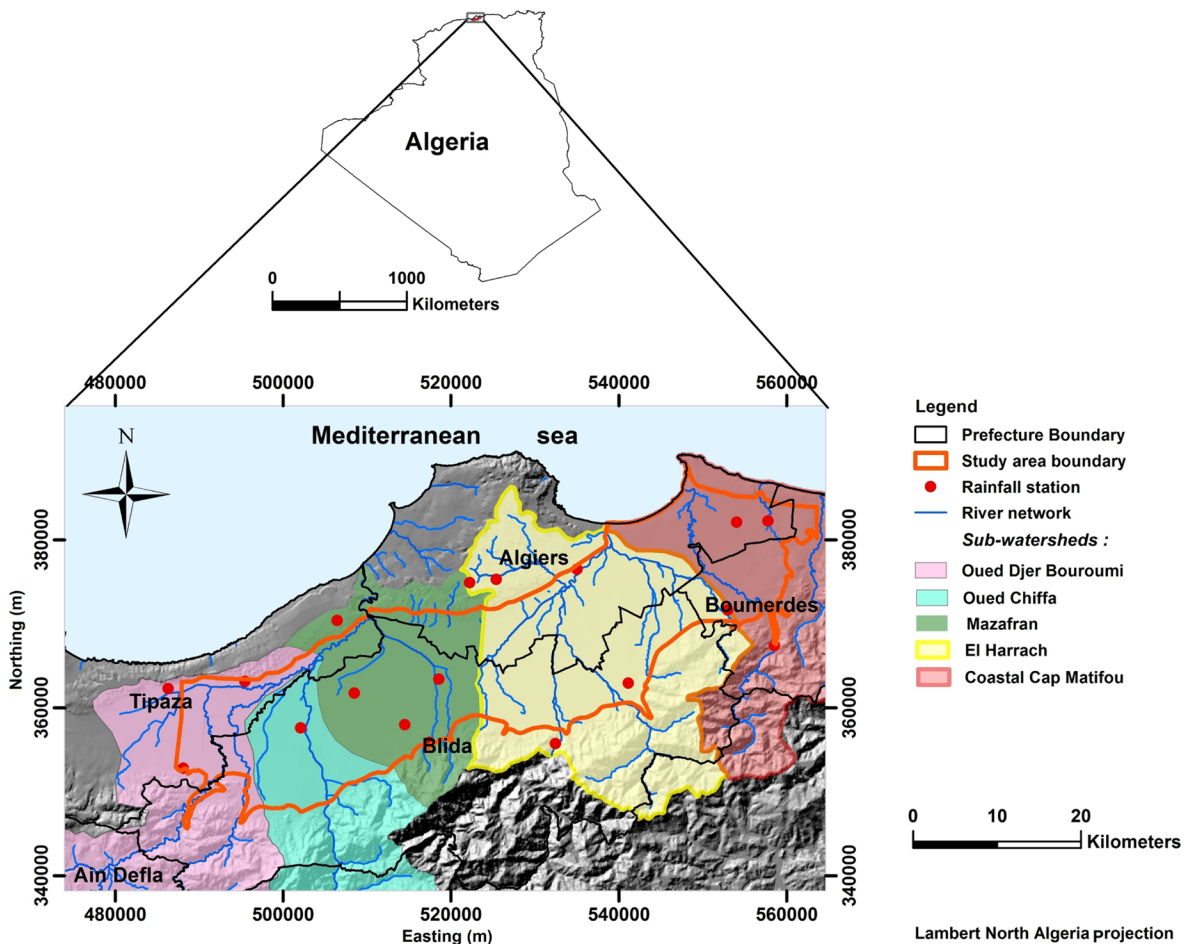


Fig. 1 Location, digital elevation, and hydrological map of the Mitidja study area

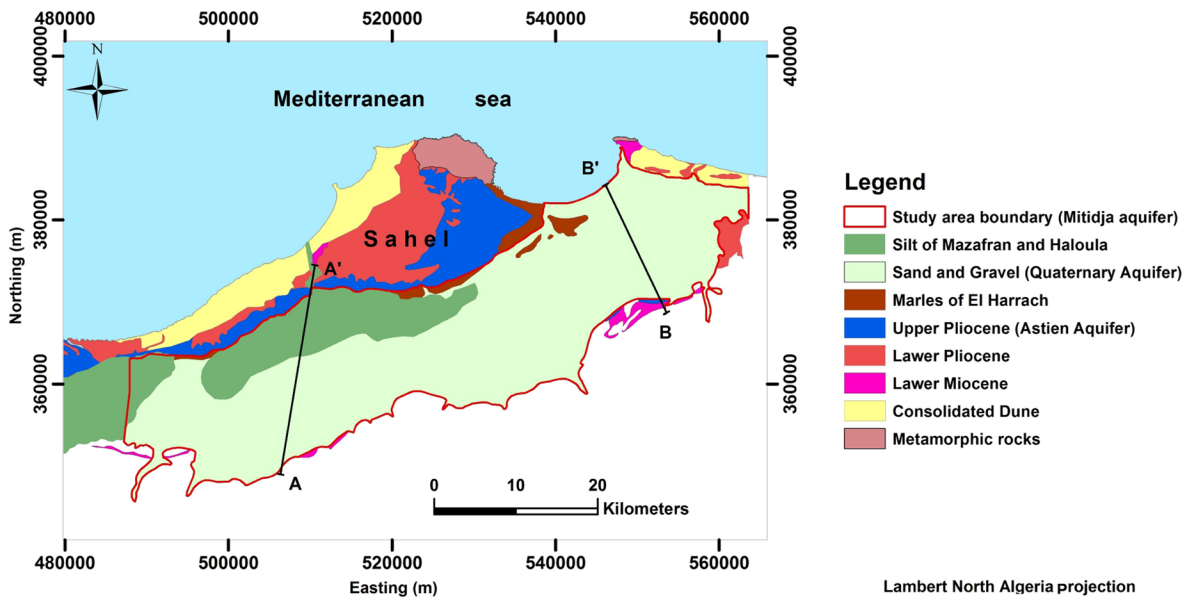


Fig. 2 Hydrogeological map of the study area

- The sandstone or sandstone-limestone Astian aquifer.
- Mitidja quaternary aquifers.

These two aquifers are separated by the yellow marls of the El Harrach over the majority of the area (Fig. 3; A-A' and B-B' cross-sections).

The deeper Astian aquifer consists of sandstone and sandstone-limestone formations with intercalations of clay. Although it is generally confined, it is not artesian and becomes free at the outcrop areas located in the Sahel, extending over most of the plain. The Astian aquifer is bounded by a clay substratum (Plaisancien marls) and El Harrach marl (Figs. 2 and 3). The average thickness of the aquifer is 100–130 m and is usually located at a depth of 250–300 m below ground level. However, the Astian formation can be found at shallower depths in the east with reduced thickness due to erosion. This aquifer is accessed in the Mitidja area through wells and at its outcrops. An increasing number of wells and boreholes draining this aquifer have been reported over recent years (Larbi, 2012; SOGREA, 2009).

The quaternary alluvial and shallow aquifer occupies the entire Mitidja plain and primarily consists of alluvium, sand, and gravel with intercalated silts and clays and predominately rests on the El Harrach marls.

The average thickness of the aquifer is approximately 100–200 m. The alluvial layer can be divided based on hydrodynamic behavior into a confined portion, located under the silts of Mazafran and Haloula, and a free water table residing over the remainder of the area (favoring the direct infiltration of rainfall), with the exception of areas presenting marls at the surface (DEMRAH, 1973; Larbi, 2012; Sir M McDonalds & Partners Ltd et al., 1992) (Fig. 2).

The quaternary aquifer is uniformly used as a water supply for drinking, irrigation, and industry (Sidi Moussa & Latrech, 2006). It is fed directly and primarily by rainfall infiltration, runoff from the wadis, lateral contributions by the Astian of the Sahel, and drainage and irrigation return (Benlecheheb & Bouzid-Lagha, 2014; GeoHydraulique, 1971; SEAA, 2008; Sidi Moussa & Latrech, 2006; SOGREA, 2009). Under average climatic conditions, the potential of the aquifer is estimated at 328 hm³/year (cubic hectometer per year), although the volume varies due to sensitivity to rainfall irregularities (ABH, 2004; Sidi Moussa & Latrech, 2006).

The Astian and alluvium are in direct contact in the eastern part of the plain, forming a unified aquifer with the quaternary. The two aquifers are separated throughout the remainder of the plain by the relatively impermeable yellow marls of the El Harrach,

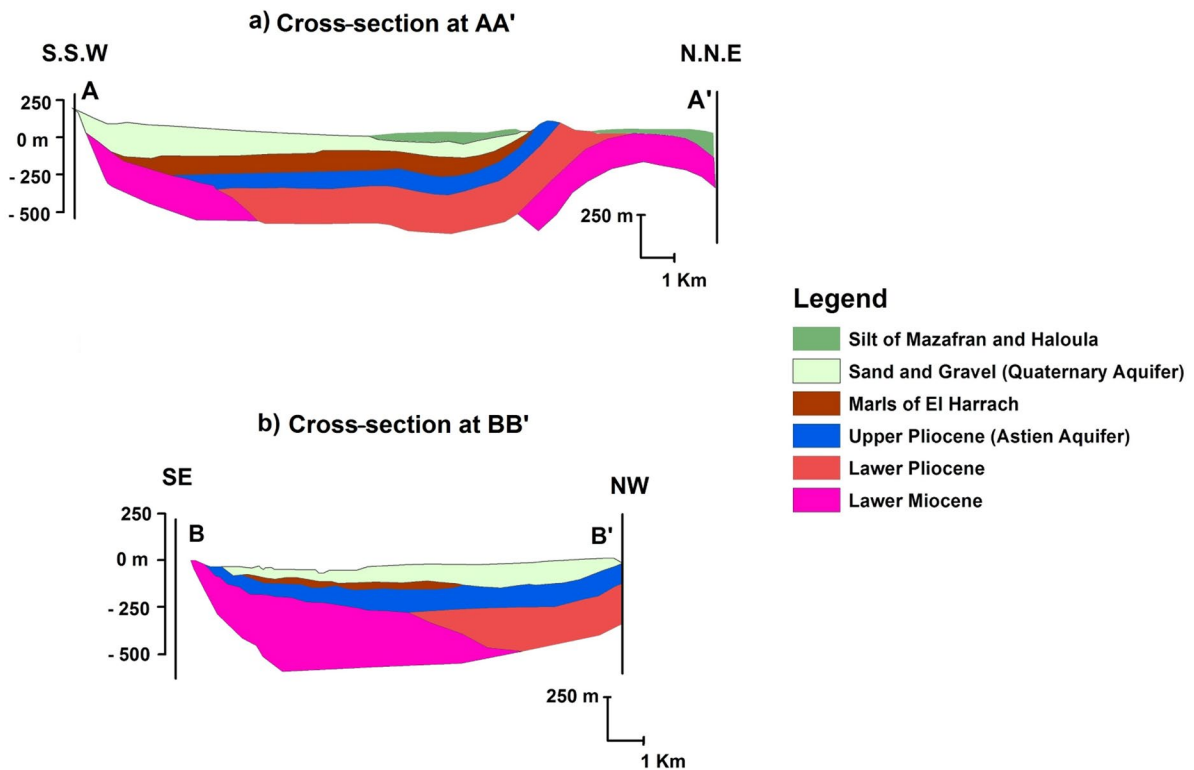


Fig. 3 Hydrogeological cross-sections

although vertical flow (hydraulic exchanges between the two aquifers) does occur at some points (Sidi Moussa & Latrech, 2006; SOGREAH, 2009).

The direction of Mitidja groundwater flow has undergone considerable change, originally moving from the south to the north with the Mediterranean Sea acting as an outfall at its northeastern limit. However, over-exploitation and climate change led to pluviometric poverty that altered this directionality, which is demonstrated by marine intrusion and the appearance of several depression zones, primarily in the pumping fields (Larbi, 2012; Mimouni & Mesbah, 2010; SEAAL, 2008; SOGREAH, 2009).

The Mitidja study area contains agricultural industries producing a wide variety of crops, including vines, citrus fruits, and annual and seasonal crops (Imache et al., 2011). Agricultural land accounted for the majority of the total area in 1971, with viticulture occupying approximately 27% of the total surface (DEAH et al., 2013). The majority of this important crop has now been replaced by citrus fruits (DEAH et al., 2013). The most recent land use maps

created by the National Institute of Soils, Irrigation and Drainage (INSID) in 2011 (Fig. 4) shows that 73% of the study area is agricultural: 39% arboriculture, 14% vegetable crops, 17% large dry crops, 2% viticulture, and 1% polyculture and olive cultivation. The remainder of the area is large population-dense urban agglomerations, rural lands, and unproductive lands, such as clearing and steppe-zones and water surfaces.

The majority of agricultural lands are irrigated with well water, with more than 2700 wells identified in 2008 (SEAAL, 2008), or from superficial resources through Grand Périmètre Irrigué (GPIs; large irrigated perimeters) operated by the Office National d'Irrigation et Drainage (National Office of Irrigation and Drainage; ONID). The eastern GPI was activated in 1966, the western GPI slice I in 1999 and slice II in 2004, and the center GPI in 2006 (Fig. 5).

Mitidja is the primary Algerian region for vegetable and fruit production, which requires heavy fertilization (DEAH et al., 2013; Imache et al., 2011). The study area, particularly the western region (part

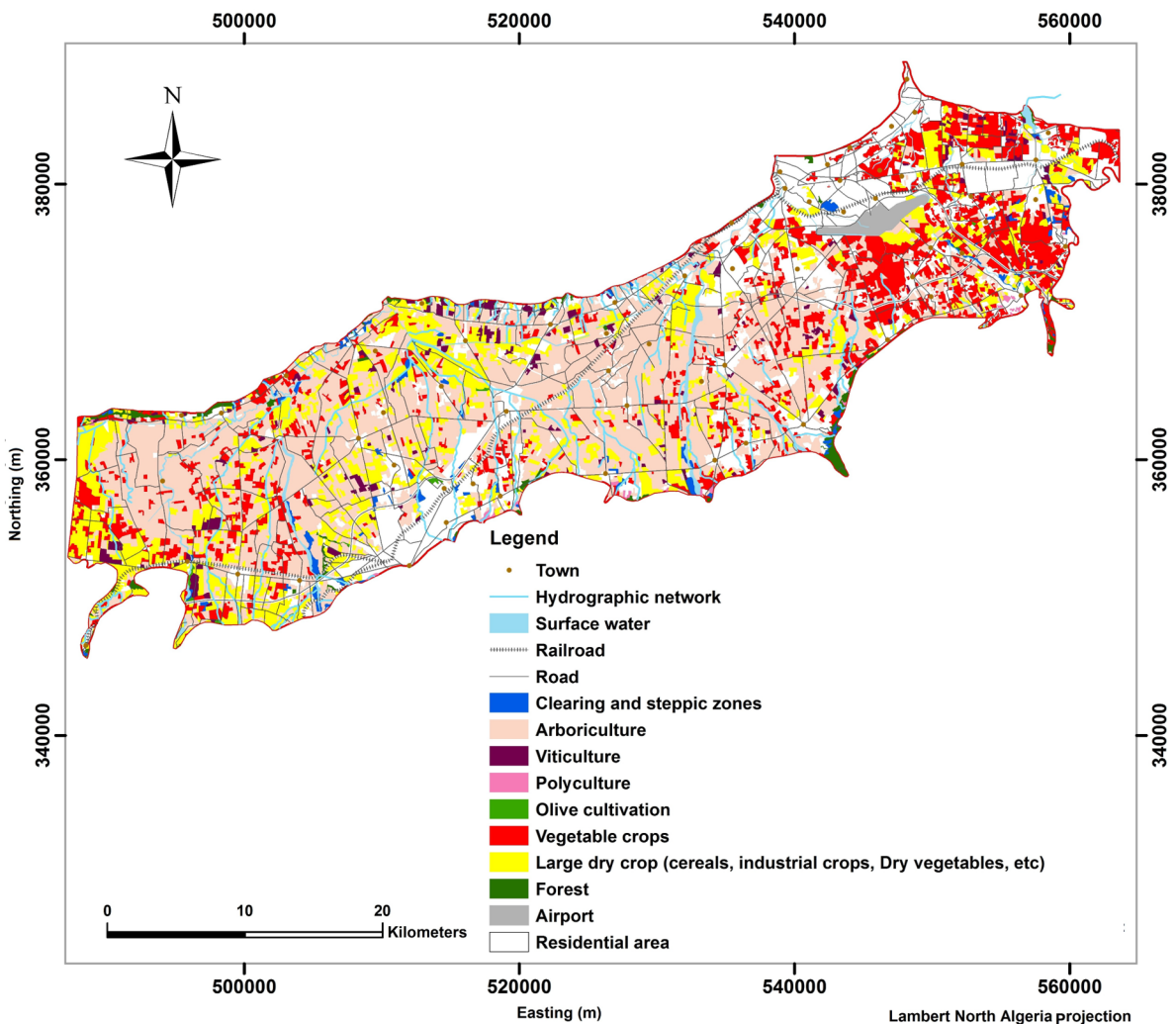


Fig. 4 Land use map of the Mitidja study area (INSID, 2011)

of Tipaza), is reported to be a large consumer of synthetic fertilizers (Hadjoudj, 2008). Mitidja has also experienced rapid urbanization over the last several decades, which, owing to a considerable increase in population, is often uncontrolled and detrimentally affects agricultural land. The 2008 census reported approximately 2 800 000 inhabitants, with a density of 2400 inhabitants/km² (values calculated from the RGPH General Population and Housing Census data) (RGPH, 1987, 1998, 2008). The study area also contains numerous industries, two classes of which can impact the quality of groundwater resources and, by extension, the quality of surface water:

- Small industry developed on the outskirts of Blida, particularly the agri-food industry
- Small and large industry to the east of Algiers, including metallurgical and agri-food industries

As the Mitidja plain is crossed by several rivers (oued Djer, oued Bouroumi, oued Chiffa, oued Djemmaa, oued Smar, oued Hamiz, and oued Reghaia), the dumping of liquid industrial effluents and domestic waste from the different industrial zones and households contribute to the observed water pollution in this region (ABH, 2004; Benlecheheb, 2010; DEAH et al., 2013; SEAAL, 2011).

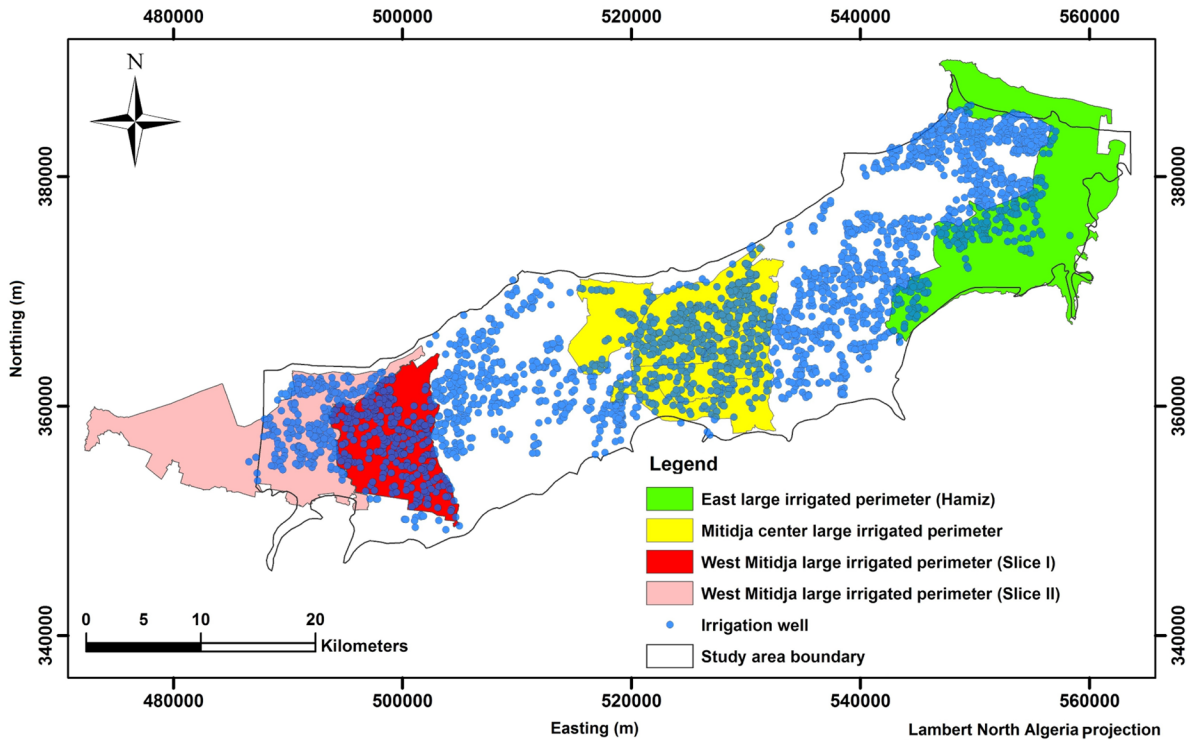


Fig. 5 Irrigation wells and large irrigated perimeters (GPIs) (DEAH et al., 2013; ONID, 2014; SEAAL, 2008)

Material and methods

This study used statistical analysis to assess the spatiotemporal distribution of nitrate in the Mitidja aquifer and investigate the response according to groundwater characteristics and human activities. All maps used in this study were digitized and a map database was established and registered as data layers with a common coordinate system (Lambert North Algeria) in Arc GIS 10.3 software (ESRI: Environmental Systems Research Institute, Redlands, CA, USA).

Nitrate data

The sampling network was composed of 316 points comprising 261 boreholes, 30 wells, and 25 piezometers (Fig. 6). A total of 1185 nitrate concentration measurements were obtained from June 1985 to May 2015. The control points for water quality and piezometric monitoring were managed and operated by the National Water Resources Agency (ANRH; 115 points with 902 samples) and the Algiers Water and Sanitation Company (SEAAL; 201 points with 283

samples). Two main sampling campaigns were performed, one following the rainy season (high water period: April–July) and the other after the dry season (low water period: September–November), corresponding to the periods when the water table depth reaches minimum and maximum values, respectively. The frequency of the readings varied across different points and between years because of security issues, especially during the period of terrorism known as the “black decade” (1992 to 1999), and because of technical hurdles.

Statistical analysis and modeling

Statistical modeling is a useful tool in the analysis of water resource data (Helsel & Hirsch, 1992). An appropriate statistical test is selected based on the type of analysis (comparison or correlation tests) and on the data itself (Helsel & Hirsch, 1992). In this work, box plots were used for the visualization of groundwater nitrate distribution (established by XL Stat 2014 and/or Arc GIS 10.3) as it presents a concise graphical display summarizing the distribution

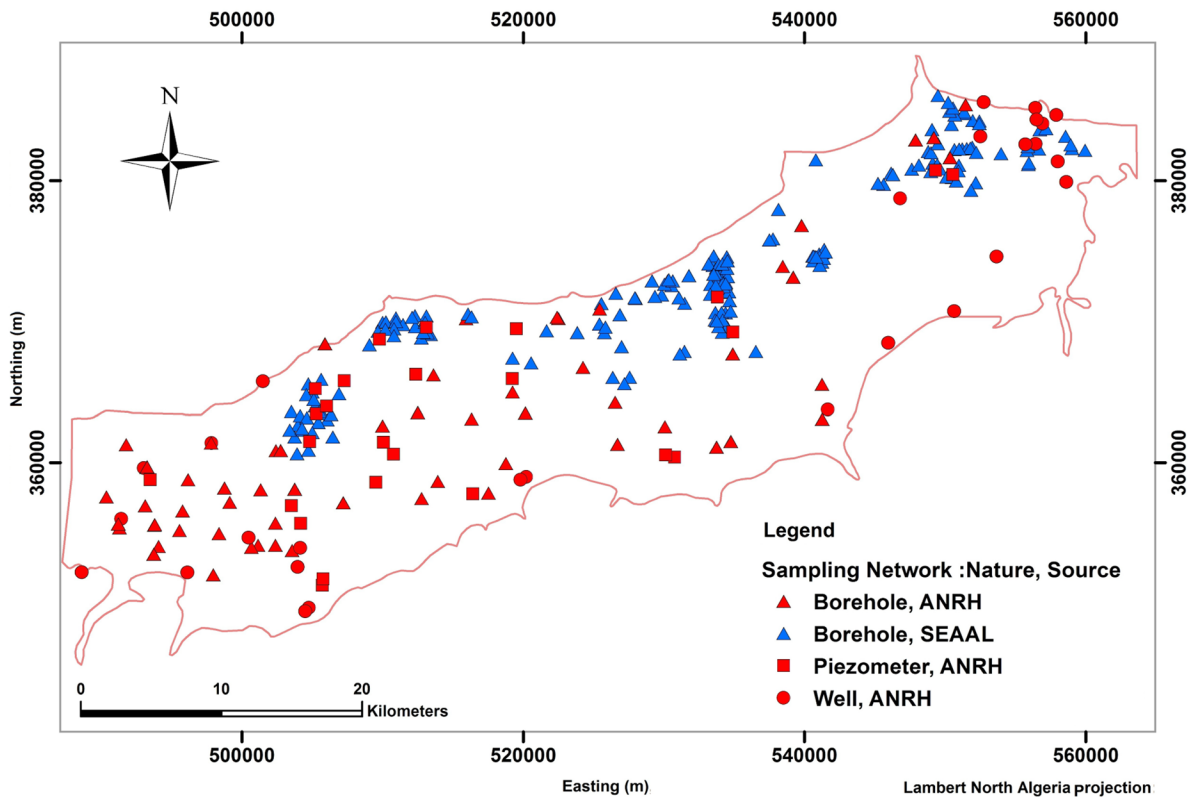


Fig. 6 Sampling network map from the Mitidja study area

of the dataset (Helsel & Hirsch, 1992; Tukey, 1977), including outliers and extreme values. Statistical modeling and tests were performed using the XL STAT 2014 package for EXCEL to assess the effects of specific factors (watershed location, seasonal variation, water table nature, saturated zone thickness, water table depth, and land use type) on groundwater nitrate concentration. The *p* values were calculated at the 95% significance level. The post hoc Conover-Iman test and Bonferroni correction were used for multiple comparisons. Groups marked by lowercase letters (a, b, and c) indicate significant differences at $p \leq 0.05$ or $p \leq p$ following Bonferroni correction for multiple comparisons.

Non-parametric tests have conventionally been advocated and are more appropriate for very small sample sizes and/or non-normally distributed data (Grech & Calleja, 2018). However, Table 1 describes the parametric tests used in this study and their condition of validity and proposes non-parametric test equivalents. Table 2 presents the conditions

of validity for the parametric and non-parametric tests.

Results and discussion

Spatiotemporal evolution of nitrate concentration

Maps of groundwater nitrate concentrations following both the dry and rainy seasons from 1985 to 2015 allowed for the analysis of spatiotemporal patterns of nitrate distribution. Nitrate concentrations above the MCL (50 mg/L) were detected at multiple locations throughout the 30-year measurement period (423 samples at 84 sampling points out of a total of 1185 measurements; 37.7% of the samples) (Fig. 7). Many measurements even exceeded 100 mg/L nitrate. Box plots revealed that median nitrate concentration readings exceeded the MCL at multiple locations (where >4 readings had been performed) and were highly variable with non-normal distribution (Fig. 8).

Table 1 Guidance for use of statistical tests (Grech & Calleja, 2018; Sheskin, 2011; Vickers, 2005)

Test type	Purpose	Data	Parametric test	Condition of validity	Minimum sample size requirement	Non-parametric equivalents
Compare locations*	Compare two observed means (independent samples)	Measurements of two samples	<i>t</i> test on two independent samples	- Samples have equal variances - Samples have normal distribution	> 15 for each sample	Mann–Whitney’s test
	Compare multiple observed means (independent samples)	Measurements of multiple samples	ANOVA		> 15 if 2–9 groups > 20 if 10–12 groups	Kruskal–Wallis test
Association tests	Test the association between two quantitative variables	Measurements of two quantitative variables from the same sample	Pearson’s correlation test	All variables are normally distributed	> 30	Spearman’s correlation test

*Means in parametric tests and mean ranks in non-parametric equivalents

Comparing nitrate concentration measurements from after the dry and rainy seasons indicated that there was no significant seasonal difference observed for either aquifer type (appropriate statistical test choice shown in Table 3; Mann–Whitney *U* test used for shallow water table samples and Student’s *t* test used for confined aquifer samples (Tables 4 and 5)). This could be due to recharge from precipitation during the rainy season or to recharge and leakage associated with the irrigation of agricultural lands from wells and GPIs during the dry season (Fig. 5). In addition, sewage networks and septic tanks provide a continuous source of pollution independent of season. Random fertilization practices and non-compliance with appropriate crop-specific fertilizer dosage and schedule have also been implicated in nitrate pollution (Ariouat, 1992; Benlecheheb, 2010; Benlecheheb & Bouzid-Lagha, 2014; Benouniche, 2007; DEAH et al., 2013).

Nitrate and groundwater (water table) characteristics

In addition to seasonal variation, the effects of water table characteristics, such as groundwater nature (unconfined/confined), thickness of the saturated zone, and water table depth, were analyzed. As the Kolmogorov–Smirnov’s normality test showed non-normal distribution, the Mann–Whitney *U* test was chosen to examine the effect of aquifer nature (unconfined and confined) on groundwater nitrate concentrations (Appendix 1). The test showed significantly higher concentrations ($p < 0.0001$) in the unconfined water table (Appendix 1 and Fig. 9). This could be due to the direct leaching of nitrate by infiltration and recharge processes across the unconfined aquifer, which consists of vulnerable components, such as alluvium, sand, and gravel, as opposed to the confined water table protected by the silt of the Mazafra.

Table 2 Conditions of validity for parametric or non-parametric tests (Grech & Calleja, 2018; Sheskin, 2011)

Test family	Purpose	Data	Statistical test
Tests on distributions	Test the normality of a series of measurements	Measurements on one sample	Kolmogorov–Smirnov’s test
Variance comparison	Compare several variances	Measurements on several samples	Levene’s test

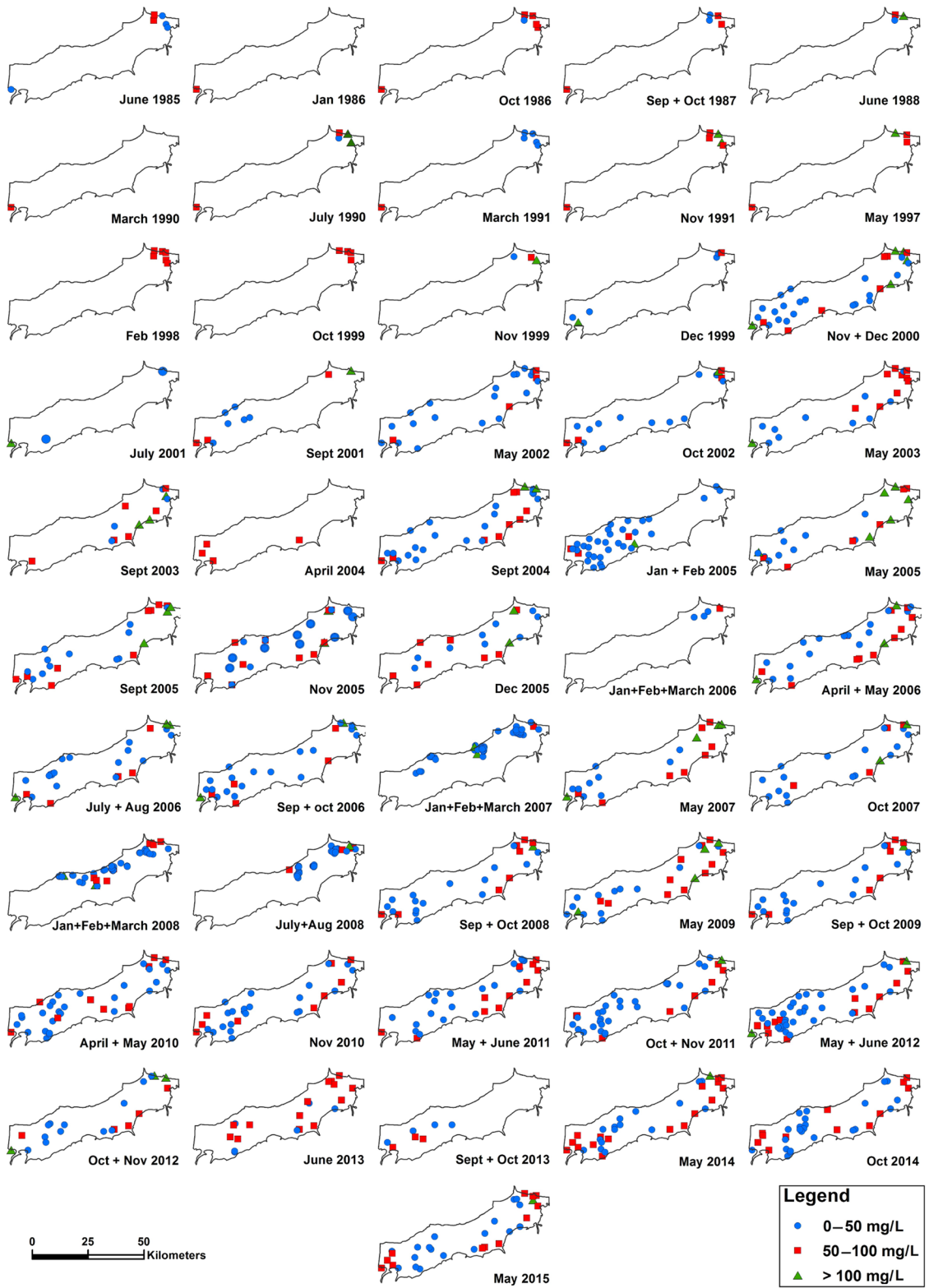


Fig. 7 Spatiotemporal variations in nitrate concentration in Mitidja groundwater from 1985 to 2015

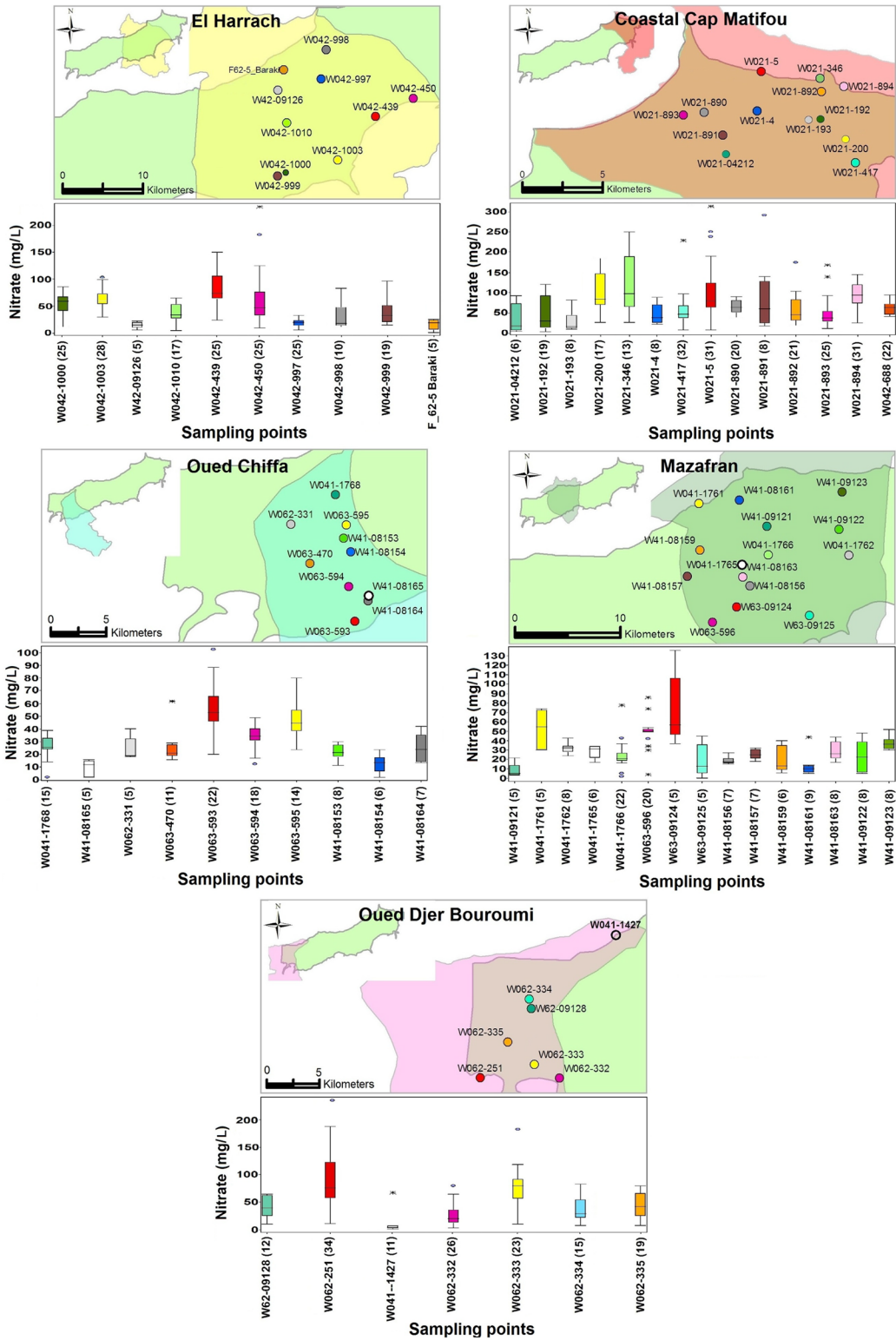


Fig. 8 Distribution of nitrate concentrations at sampling points having > 5 readings from 1985 to 2015. Number in parentheses indicates the number of readings

Table 3 Determination of appropriate statistical tests for seasonal variation of nitrate concentration in each aquifer type. Parametric tests (Kolmogorov–Smirnov’s normality test and

the Levene parametric test for equality of variances) were used to test the conditions of validity

Aquifer	Season	Samples	Kolmogorov–Smirnov’s normality test		Levene parametric test for equality of variances		Appropriate test
			<i>p</i> value	Distribution	<i>p</i> value	Variances	
Unconfined	Post-rainy	390	0.0011	Non-normal	/	/	Mann–Whitney
	Post-dry	379	<0.0001	Non-normal			
Confined	Post-rainy	52	0.1017	Normal	0.6300	Identical	Student’s <i>t</i> -test
	Post-dry	32	0.0857	Normal			

Table 4 Mann–Whitney *U* test to examine seasonal variation effect on nitrate in unconfined aquifer

Aquifer	Season	Samples	<i>p</i> value	Mean (mg/L)
Unconfined	Post-rainy	390	0.8341	51.55 ^a
	Post-dry	379		53.15 ^a

Table 5 Student’s *t*-test to examine seasonal variation effect on nitrate in confined aquifer

Aquifer	Season	Samples	<i>p</i> value	Mean (mg/L)
Confined	Post-rainy	52	0.2304	24.69 ^a
	Post-dry	32		19.17 ^a

The thickness of the saturated zone is defined by the piezometric level and the substratum of the aquifer. The Kruskal–Wallis test (Appendix 2) indicated that groundwater nitrate concentrations decreased significantly with increasing saturated zone thickness (Fig. 10). This may be due to the physical process of mixing and transport, and particularly dilution, which is the primary means of reducing nitrate concentration in the aquifer and depends highly on saturated zone thickness.

Water table depth is defined as the vertical distance from the ground level to the water level (Burkart &

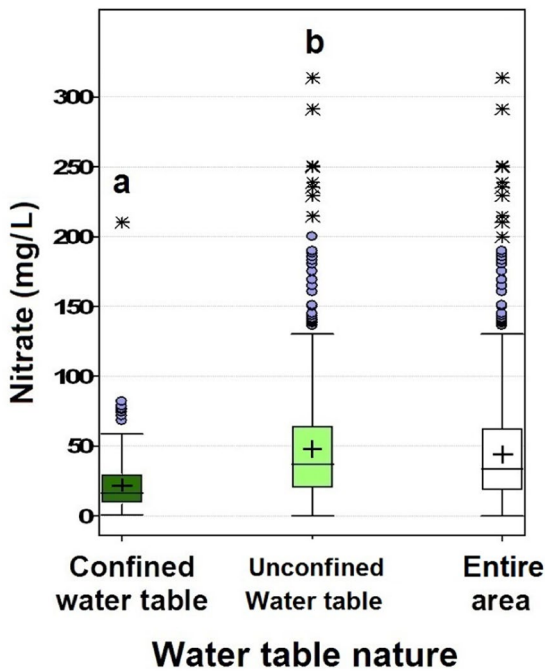


Fig. 9 Nitrate concentration in groundwater as a function of water table nature. Significant differences ($p \leq 0.05$) indicated by different letters as assessed by the Mann–Whitney *U* test

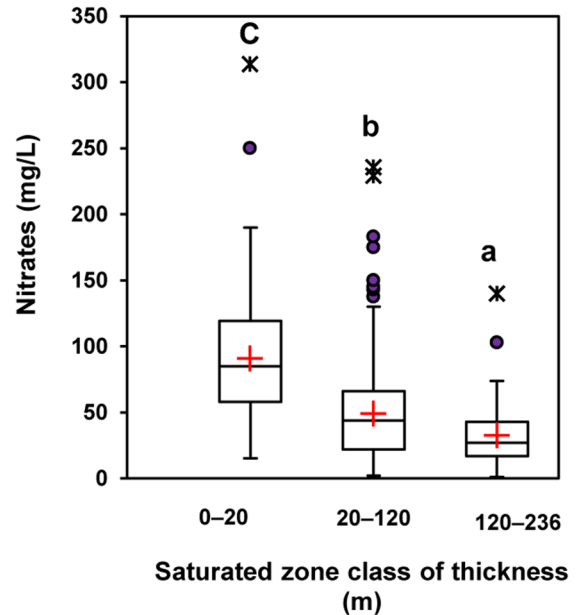


Fig. 10 Nitrate in the saturated zone partitioned by the Kruskal–Wallis test and post hoc Conover–Iman test with a Bonferroni-corrected significance level ($p = 0.0167$). Significant differences ($p \leq 0.0167$) indicated by different letters

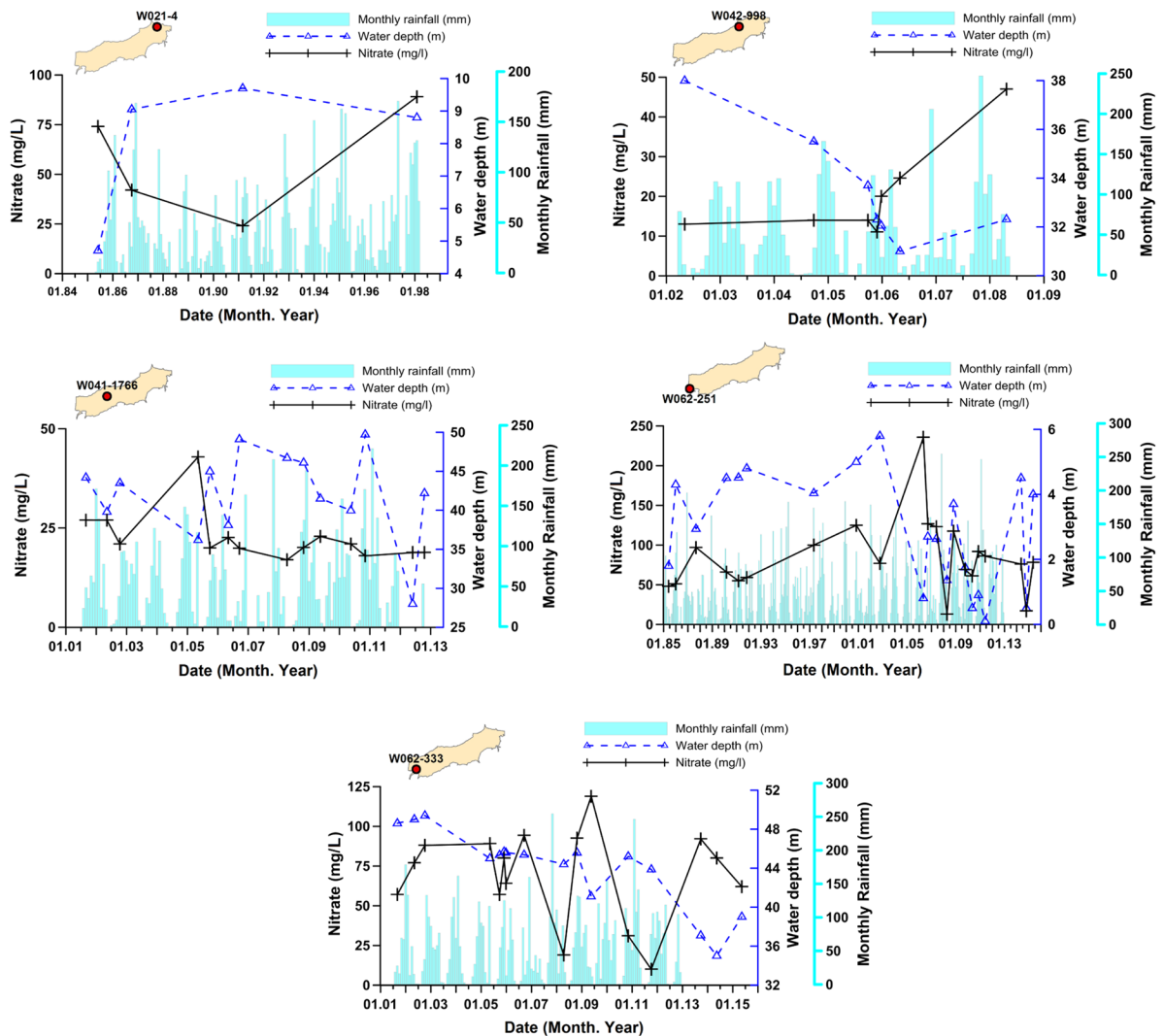


Fig. 11 Nitrate, rainfall, and water depth over time at selected sampling points

Kolpin, 1993) and represents the thickness of the unsaturated zone. Observing groundwater nitrate concentration over time as compared to the water table depth and rainfall at different locations indicated that nitrate concentrations were inversely related to water table depth (Fig. 11). When grouping water table depth into three classes (<5 m, 5–30 m, and >30 m), the Kruskal–Wallis test shows this inverse correlation to be statistically significant (Appendix 3 and Fig. 12). This phenomenon can be attributed to three main factors: denitrification, vertical groundwater movement, including direct leaching of nitrate from various sources, and nitrate transport and mixing. Aquifer depth is related to the time available to

transport, transform, or adsorb chemicals. For example, a high water table depth promotes denitrification in terms of the duration of exposure to the unsaturated zone and thus decreases nitrate leaching.

Nitrate according to the land use

Land use is typically classified into (1) residential, (2) agricultural (arboriculture, vegetable crops, viticulture, olive cultivation, polyculture, and large dry crops), and (3) other (forest, clearing, and steppe-zones). In this work, classifications were based on the 2011 land cover map from the National Institute for

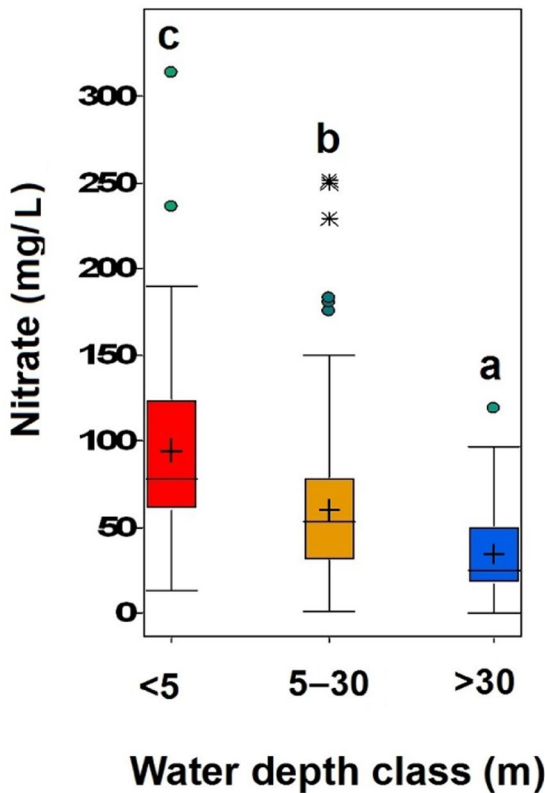


Fig. 12 Groundwater nitrate concentration as a function of water table depth partitioned by the Kruskal–Wallis test and post hoc Conover–Iman test with a Bonferroni-corrected significance level ($p=0.0167$). Significant differences ($p\leq 0.0167$) indicated by different letters

Soil, Irrigation, and Drainage (INSID) (Fig. 4) and analysis was restricted to nitrate measurements from 2009 to 2013 under the assumption that land use was essentially unchanged over this period.

The Kruskal–Wallis test was performed to investigate the effect of land use on groundwater nitrate concentrations, indicating that wells located in residential and agricultural areas were significantly more contaminated by nitrate than those in other lands (Appendix 4 and Fig. 13). Readings above 50 mg/L occurred in 41.43% of residential wells and 32.93% of agricultural wells, while only 10.00% of other wells registered such high nitrate levels.

In agricultural lands, the most likely source of elevated levels of nitrate is agricultural practices, particularly artificial fertilization. The Mitidja area is a large consumer of synthetic fertilizer, particularly in its western area (part of the Tipaza prefecture), reporting

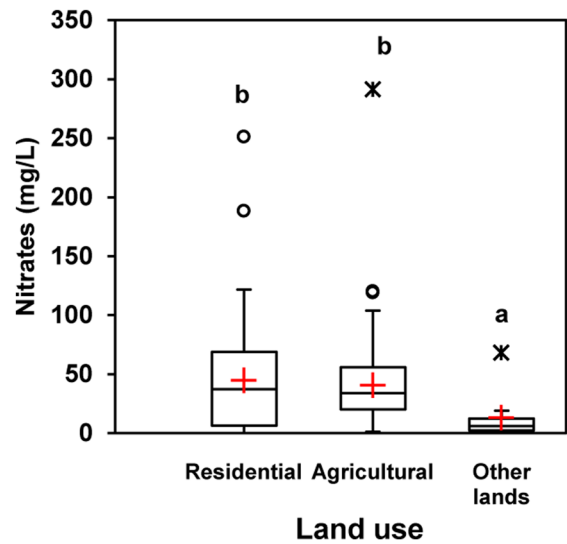


Fig. 13 Groundwater nitrate concentration as a function of land use partitioned by the Kruskal–Wallis test and post hoc Conover–Iman test with a Bonferroni corrected significance level ($p=0.0167$). Significant differences ($p\leq 0.0167$) indicated by different letters

the use of 70 kg N (nitrogen fertilizer) per hectare of useful agricultural surface (UAS) (data obtained from the Ministry of Agriculture and Rural Development (MADR) from 2005 to 2014). The second main source of nitrate in groundwater is from animal and livestock manure. Breeding of bovine, ovine, caprine, and equine species is actively performed in the Mitidja area according to MADR data from 2005 to 2014. The Nitrogen Livestock Unit (N-LU) is used to quantify water

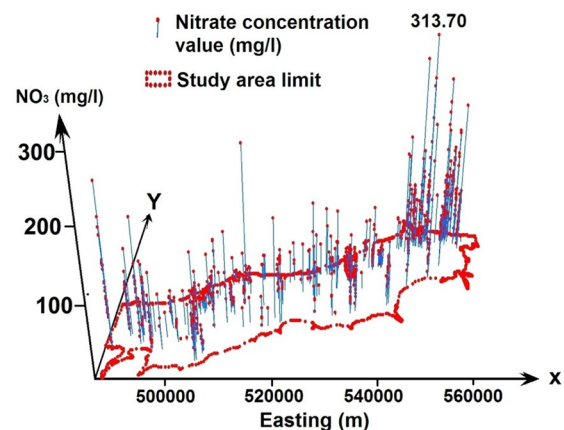
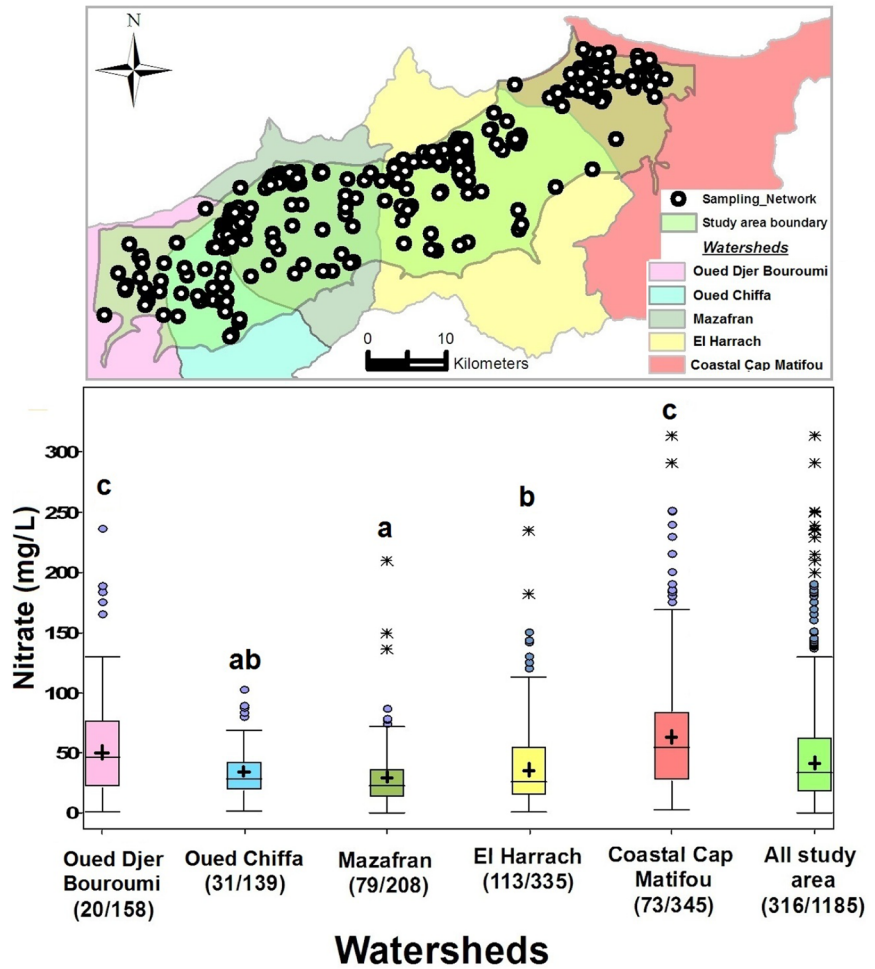


Fig. 14 Nitrate distribution trend from 1985 to 2015 (1185 samples from 316 sampling points)

Fig. 15 Nitrate concentrations across various watersheds. Kruskal–Wallis test and post hoc Conover-Iman test with Bonferroni correction were used to determine significant differences ($p \leq 0.005$), as indicated by different letters. Numbers in parentheses indicate number of sampling points and nitrate readings, respectively



pollution by nitrates and is calculated by multiplying the total number of animals with conversion factors that take into account “feed requirements” for the animal. An N-LU corresponds to 73 kg of nitrogen pollution/year from livestock manure (Corpen, 1999). The conversion factors for the study area have been documented (Chilonda & Otte, 2006; Corpen, 1999; FAO, 2003), allowing the total N for each species to be calculated: 1 cattle=0.7 LU=51.1 kg N/year, 1 sheep=0.1 LU=7.3 kg N/year, 1 goat=0.1 LU=7.3 kg N/year, and 1 horse=0.8 LU=58.4 kg N/year. The total nitrogen from agricultural activities (synthetic and organic) was calculated (MADR data from 2005–2014) and indicated a substantial contribution of fertilizing (nitrogen total (mineral+organic)/UAS) in western Mitidja with a maximum of 120 kg/hectare UAS used in 2006. Random fertilization practices have been reported

to result in high fertilization doses n(Ariouat, 1992; Benlecheheb, 2010; Benlecheheb & Bouzid-Lagha, 2014; Benouniche, 2007; BOUDI, 2005; DEAH et al., 2013). Septic tanks are an additional potential source of groundwater nitrate contamination in agricultural areas.

In residential areas, high levels of groundwater nitrate could originate from sewage (wastewater from the population and industries, particularly agri-food which is popular in the Mitidja area).

Nitrate distribution patterns in the Mitidja area

Nitrate distribution trends established using Arc GIS 10.3 (Fig. 14) showed that the eastern and western areas of the Mitidja were more polluted and contained a greater number of nitrate readings having maximum values and exceeding the MCL. The

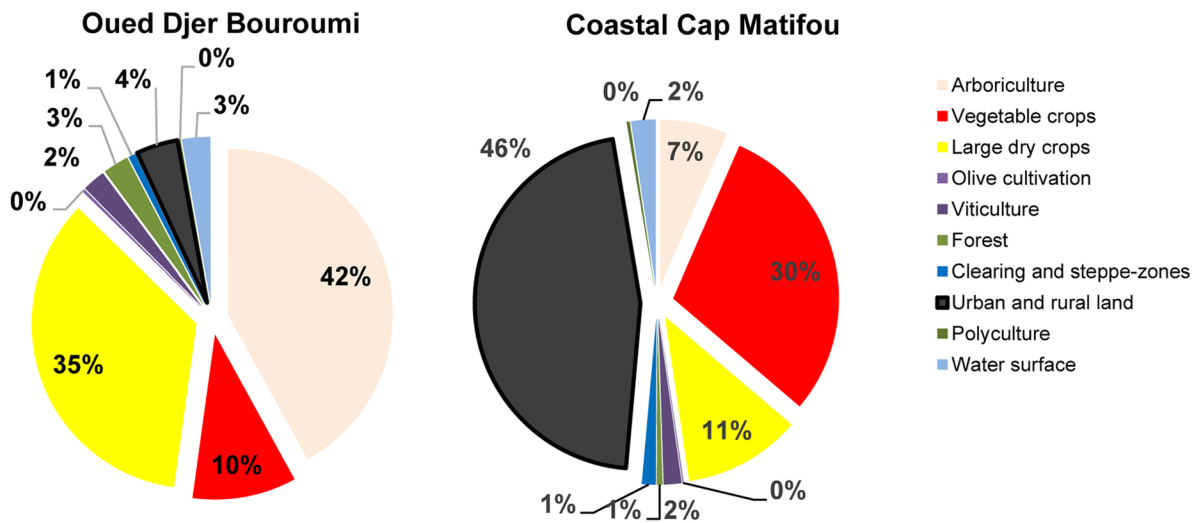


Fig. 16 Composition of land use in the eastern and western watersheds of the Mitidja (Coastal Cap Matifou and Oued Djer Bouroumi Watersheds) (2011 land use map)

observed differences between nitrate concentrations at the watershed catchments were confirmed by the Kruskal–Wallis test, which was chosen due to the non-normal distribution (Kolmogorov–Smirnov’s normality test) of each watershed (Appendix 5). The eastern and western areas, represented by Coastal Cap Matifou and Oued Djer Bouroumi watersheds, respectively, are significantly more contaminated by nitrate than other watersheds (Appendix 5 and Fig. 15). This pattern of nitrate contamination of the alluvial aquifer of Mitidja is likely due to the urbanization of the Coastal Cap Matifou in the east (46% of the area of the watershed) and the agricultural activity in Oued Djer Bouroumi in the west (42% of the surface is dedicated to vegetable crops, 10% to arboriculture, 35% to large dry crops, and approximately 2% to viticulture) (Fig. 16).

Conclusion

This study assessed the spatiotemporal distribution and evolution of nitrates in the Mitidja aquifer and evaluated their possible origin. The Mitidja area is characterized by intensive agriculture, massive industrial activity, and rapid urbanization, which are associated with increased vulnerability to pollution, particularly in zones consisting of a shallow water table and aquifer properties that promote rapid infiltration.

GIS cartographic mapping of different layers facilitated the visualization of nitrate concentrations at the geo-referenced locations throughout the sampling period. This survey revealed that nitrate contamination is a long-standing and widespread problem, observable from the first analysis in 1985 and throughout several zones. Statistical modeling and analyses of this data were used to identify aquifer characteristics that play a role in nitrate distribution in the Mitidja groundwater aquifer. Aquifer nature (unconfined/confined), thickness of the saturated zone, and water table depth were suggested to have a significant influence on groundwater nitrate contamination.

This study identified two primary areas highly polluted by nitrate and sought to determine the possible causes.

Eastern zone: This region has very high nitrate levels and is characterized by strong vulnerability to pollution owing to a shallow water table, highly permeable soil that promotes rapid and direct infiltration, and limited aquifer thickness. Intense urbanization, increasing population, and the presence of large and small industries, such as agri-food industries, in this zone also contribute to a high risk of nitrate pollution.

Western zone: This region has high to very high nitrate levels and is characterized by intense agricultural activity and excessive fertilizer use. In addition,

it shows similar water table vulnerability to the eastern area.

The remainder of the study area generally reported low to medium nitrate concentrations. As expected, these areas manifest fewer risk factors for nitrate pollution owing to decreased water table vulnerability arising from a protective layer of Mazafran silt over much of the aquifer. Water table depth and the thickness of the saturated zone also serve to mitigate nitrate pollution in these regions.

This study demonstrates the benefits of applying statistical analyses and GIS techniques to a long-term survey of nitrate concentration measurements over a widespread area to the understanding

of nitrate sources and spatiotemporal distribution. Such an approach can be used in many other regions and could aid in the control and mitigation of water pollution. Continuous monitoring of chemical concentrations of water contaminants is therefore highly recommended.

Appendix 1. Kolmogorov–Smirnov’s normality test and Mann–Whitney *U* test to examine the effects of aquifer nature (unconfined and confined) on groundwater nitrate concentration

Aquifer nature	Sampling points	Samples	Kolmogorov–Smirnov’s normality test		Mann–Whitney <i>U</i> test	
			<i>p</i> value	Decision	<i>p</i> value	Mean (mg/L)
Unconfined	235	1037	<0.0001	Non-Normal	<0.0001	40,28 ^b
Confined	81	148	<0.0001	Non-Normal		24,18 ^a

Appendix 2. Kruskal–Wallis test to examine the effects of saturated zone thickness (0–20 m, 20–120 m, and 120–140 m) on groundwater nitrate concentration. A post hoc Conover–Iman test with Bonferroni correction was used to determine the significance level ($p = 0.0167$). Significant differences ($p \leq 0.0167$) indicated by different letters

Saturated zone class (m)	Samples	Kolmogorov–Smirnov’s normality test		Kruskal–Wallis’s test		Conover–Iman’s test
		<i>p</i> value	Distribution	<i>p</i> value	Average rank (mg/L)	Groups
0–20	51	0.4060	Normal	<0.0001	334,03	c
20–120	304	0.0092	Non-normal		222,29	b
120–236	89	0.0552	Non-normal		159,31	a

Appendix 3. Kruskal–Wallis test to examine the effects of water table depth (< 5 m, 5–30 m, and > 30 m) on groundwater nitrate concentration. A post hoc Conover–Iman’s test with Bonferroni correction was used to determine the significance level ($p = 0.0167$). Significant differences ($p \leq 0.0167$) indicated by different letters

Water tables class	Sampling points	Samples	Kolmogorov–Smirnov’s normality test		Kruskal–Wallis’s test		Conover–Iman’s test Groups
			<i>p</i> value	Distribution	<i>p</i> value	Average rank (mg/L)	
< 5	5	41	0.2361	Normal	< 0.0001	345,06	c
5–30	41	203	< 0.0001	Non-normal		260,50	b
> 30	60	206	< 0.0001	Non-normal		167,22	a

Appendix 4. Normality on distribution test and Kruskal–Wallis test to examine the effects of land use (residential, agricultural, and other) on groundwater nitrate concentration. A post hoc Conover–Iman’s test with Bonferroni correction was used to determine the significance level ($p = 0.0167$). Significant differences ($p \leq 0.0167$) indicated by different letters

Land	Observations	Frequency > MCL (%)	Kolmogorov–Smirnov’s normality test		Kruskal–Wallis’s test		Conover–Iman test Groups
			<i>p</i> value	Decision	<i>p</i> value	Average rank (mg/L)	
Residential	70	41.43	0.0459	Non-normal	0.0024	163,41	b
Agricultural	246	32.93	0.0051	Non-normal		167,65	b
Other	10	10.00	0.2605	Normal		62,05	a

Appendix 5. Kruskal–Wallis test to examine the difference between nitrate concentrations unregistered at a catchment scale. A post hoc Conover–Iman test with Bonferroni correction was used to determine significant differences ($p \leq 0.005$), indicated by different letters

Watershed	Sampling point	Samples	Rate > MCL (%)	Kolmogorov–Smirnov’s normality test		Kruskal–Wallis test		Conover–Iman test Groups
				<i>p</i> value	Decision	<i>p</i> value	Average rank	
Coastal Cap Matifou	73	345	53.62	0.0006	Non-normal	< 0.0001	748,17	c
El Harrach	113	335	32.54	< 0.0001	Non-normal		526,78	b
Mazafran	79	208	13.46	< 0.0001	Non-normal		435,75	a
Oued Chiffa	31	139	17.99	0.1774	Normal		520,98	ab
Oued Djer Bouroumi	20	158	48.10	< 0.0001	Non-normal		664,95	c

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Data availability The dataset used during the current study are available from the corresponding author on reasonable request.

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