Nitrogenous Compound Exposure in Unsanitary Rural Environments: A Case Study from Al Hoceima Province, Northern Morocco

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Abstract: Groundwater is a crucial drinking water resource for rural communities; however, the absence of adequate monitoring programs in these regions often results in uncertainties about groundwater quality. This study focuses on assessing the impact of nitrogen compounds from domestic wastewater on groundwater in rural communities within the province of Al Hoceima. The hydrochemistry of 33 groundwater samples was analyzed using various methods, including descriptive statistics, the Nitrate Pollution Index (NPI), the Chronic Health Risk Index (CHR), and a GIS-based spatial analysis. The investigation revealed significant contamination by nitrogen compounds in regions characterized by high population density. In these areas, nitrate (NO_3^-) and nitrite (NO_2^-) concentrations exceeded 50 mg/l and 0.2 mg/l, respectively, surpassing the WHO recommended limits. Notably, NO_3^- levels ranged from 0 to 89.63 mg/l, with 84.84% of groundwater samples contained more than 10 mg/l. The NPI values ranged from -1 to 3.48, with 33.33% of the samples were categorized as significantly and very significantly polluted. Additionally, CHR values ranged from 0 to 2.43 for adults, 0 to 2.03 for children, and 0 to 2.51 for infants. The CHR values exceeded 1 suggests that the contamination observed in the samples can be attributed to the widespread use of septic tanks in densely populated regions. Thus, to ensure the safety of rural communities, further assessments of health risks are mandatory.

1 Introduction

Groundwater constitutes almost half of the world's drinking water supply [1]. The quality of groundwater significantly influences human health. In regions with limited rainfall and scarce surface water, particularly in rural areas of developing nations like Morocco, groundwater serves as a crucial source for consumption. Recent years have witnessed a water resource shortage in the region due to declining rainfall, coupled with population growth intensifying the demand for drinking water. Consequently, the groundwater in the study area plays a pivotal role in meeting domestic water needs. However, previous investigations on salinity [2-3], and pollution [4-5] have raised concerns regarding potential health risks for consumers.

In a rural setting, the residents of the examined area utilize septic tanks to handle sewage. Despite its prevalence, this conventional method plays a pivotal role in contaminating groundwater, especially in areas where the water table is consistently shallow. This is the case in our study area, particularly in proximity to the coast, as observed in the Souani plain [6].

Nitrate poses a threat to human health due to its potential to form endogenous nitrosamines, known carcinogens [7]. Upon transformation into nitrite within the digestive system, it gives rise to methemoglobin, compromising the blood's oxygen-carrying capacity [8]. Several epidemiological investigations have provided evidence indicating a plausible link between prenatal exposure to nitrates in drinking water and the incidence of congenital malformations in offspring. These malformations include neural tube defects (NTDs) [9], anomalies in the central nervous system [10], and congenital heart abnormalities [11].

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As part of our research, the primary objective is to assess the potential risk of nitrogen compound contamination, particularly nitrates, associated with the use of septic tanks in the study area. This evaluation is conducted in rural communities within the province of Al Hoceima, using both the NPI and the CHR. The study seeks to understand the correlation between the use of septic tanks and the levels of nitrates, employing these indices as key indicators in our investigation.

2 Materials and methods

2.1 Study area

The depicted study area in **Figure 1** spans around 38 km^2 and is in the northeastern part of Morocco, within the eastern section of the Rif mountains. Its geographical coordinates range between latitudes 34° 42' and 35° 6' North and longitudes 3° 36' and 4° 4' West. Located east of Al Hoceima city, this region is linked to the Mediterranean Sea through a wide alluvial plain [12].

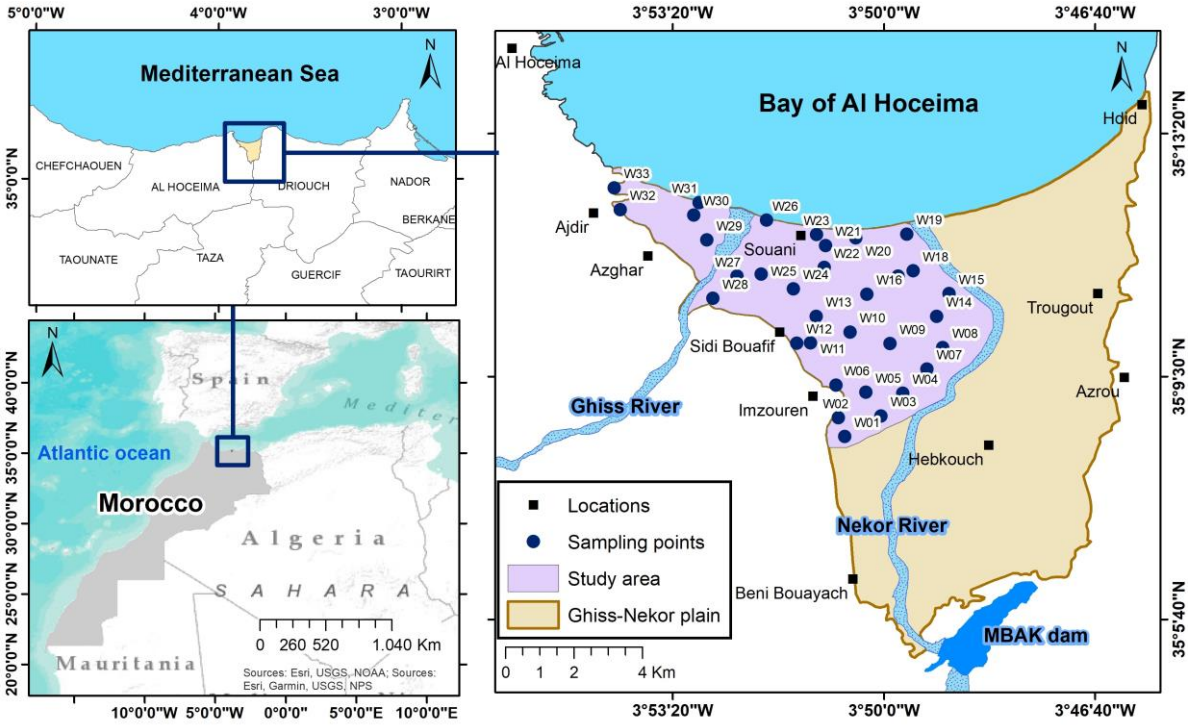

Fig. 1. Sampling Site Locations Within the Study Area

2.2 Collection and data processing

In February 2023, an extensive gathering of 33 shallow groundwater samples took place in the study area, as depicted in Figure 1. The sampling methodologies followed the recommendations specified in the 9th edition of the publication titled "Water Analysis" [13].

This study encompassed the measurement of fifteen physicochemical parameters, namely: pH, temperature, electrical conductivity (EC), and concentrations of ions, including potassium (K^+), ammonium (NH_4^+), sodium (Na^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), nitrates (NO_3^-), bicarbonates (HCO_3^-), chlorides (Cl^-), nitrites (NO_2^-), orthophosphate (PO_4^{3-}), and sulfates (SO_4^{2-}).

The PCE-PHD 1 Multimeter (PCE instruments) was employed for measuring temperature, pH, and EC. The Flame Photometer (Model: ELICO CL 378) with an accuracy of ± 0.5 ppm was used to determine Na^+ and K^+ levels. Ca^{2+} and Mg^{2+} concentrations were determined through titration using EDTA, while Cl^- levels were assessed via titration with 0.1 N silver nitrate. HCO_3^- levels were measured using titration with 0.1 N hydrochloric acid. For elements such as NO_2^-, PO_4^{3-}, NO_3^-, SO_4^{2-}, and NH_4^+, a colorimetric determination method was utilized, employing a UV-VIS spectrophotometer (Lange Hach DR-6000) with an accuracy of ± 1 nm. The detection limits for NO_3^-, NO_2^-, NH_4^+ and PO_4^{3-} are 0.01 mg/l, 0.03 mg/l, 0.002 mg/l and 0.09 mg/l, respectively.

The Nitrate Pollution Index (NPI) serves as a proficient indicator for assessing the extent of nitrate pollution in groundwater. Its calculation involves utilizing Equation 1:

$$NPI = \frac{Cn - Ci}{Ci} \quad (1)$$

Cn denotes the measured concentration of nitrate in the sample, whereas ***Ci*** signifies the allowable nitrate limit for human consumption, set at 10 mg/l.

The CHR evaluates the non-carcinogenic health hazards linked to the consumption of groundwater contaminated with nitrates. This evaluation particularly targets infants, children, and adults, as

affirmed by [14], and [15]. To accomplish this, the exposure through groundwater injection was computed using the formula outlined by [16] (Equation 2):

$$AD = \frac{IC*IR*ED*EF}{BW*ET} \quad (2)$$

In this context, ET indicates the average exposure time, BW stands for the average body weight., EF represents the frequency of exposure, ED stands for the exposure duration, IR denotes the ingestion rate, IC denotes the ionic concentration in groundwater, and AD represents the average daily exposure dose (expressed in mg/kg/day).

The values used as references for these parameters in the calculation are specified in **Table 1.**

Table 1. Health Risk Assessment Standards [15]

Parameters	Units	Infants	Children	Adults
IR	(l/day)	0,31	0,68	2,5
ED	(Years)	1	12	64
EF	(Days/years)	365	365	365
BW	(Kg)	6,9	18,7	57,5
ET	(days)	365	4380	23360

The computation of CHR is determined by Equation 3:

$$CHR = \frac{AD}{K} \quad (3)$$

Where K= 1.60 mg/kg/day, it represents the safe dose of NO_3^- for chronic oral exposure.

The gathered data underwent analysis through various approaches, encompassing descriptive statistics Accomplished with IBM SPSS Statistics, computation of the NPI, and CHR. The determination of the spatial distribution of the computed indices was carried out using ArcGIS 10.8 software.

3 Results and discussion

3.1 Descriptive statistics

The outcomes of the analysis of groundwater physicochemical parameters are detailed in **Table 2.**

Table 2. Statistical Evaluation of Groundwater Samples in the Study Region

	Units	Average	Min	Max	Norms of WHO (2011)	Moroccan standards 03.7.001 2006
pH	-	7.44	6.70	8.08	6.5-8.5	6.5-8.5
TDS		3223	1508.63	8289.80	-	-
EC		4095	2080.00	10650.00	1500	2700
Na^{2+}		507	233.00	1710.00	200	200
K^+		10.83	2.30	31.70	12	12
Mg^{2+}		149.01	57.60	367.68	150	150
Ca^{2+}		254.41	59.32	415.21	200	200
Cl^-	mg/l	817.25	354.53	3027.69	500	750
SO_4^{2-}		978.11	410.00	1592.25	250	400
HCO_3^-		358.98	152.50	512.40	500	300
NO_3^-		25.34	<DL*	89.63	50	50
NO_2^-		0.04	<DL	1.37	0.2	0.5
NH_4^+		0.02	<DL	0.14	0.2	0.5
PO_4^{3-}		0.04	<DL	0.61	0.5	0.5

*DL: Detection limit

The ammonium (NH_4^+) concentrations in all samples adhere to both Moroccan standards and WHO guidelines, noting values of 0.5 and 0.2 mg/l, respectively (**Figure 4 (a)**).

Nitrate (NO_3^-) concentrations display a range of variability spanning from DL to 89 mg/l, with an average of 34.16 mg/l (**Figure 4 (b)**). The contamination of groundwater with nitrate in the study area can be attributed either to agricultural activity, the excess of nitrates in the groundwater can result from the runoff of the fertilized soils [17], or to possible origins of untreated wastewater, given that the affected area lacks sewerage networks. It is crucial to emphasize that the consumption of water contaminated with NO_3^- can result in significant health problems, as emphasized by [18]. The heightened presence of NO_3^- in the bloodstream hinders the proper binding of oxygen by hemoglobin, contributing to

conditions such as "blue infant disease" or "methemoglobinemia" [19].

In the study area, 84.84% of the wells, specifically 28 out of 33, show undetectable levels of nitrite (NO_2^-). However, a single sample (W12) surpasses the Moroccan standards of 0.2 mg/l, recording a value of 1.37 mg/l **(Figure 4(c)).** This well, with a depth of 38 meters, is positioned near a densely populated area that lacks sufficient sewer networks for its residential structures. This situation implies the potential for contamination from the septic tanks employed by these households.

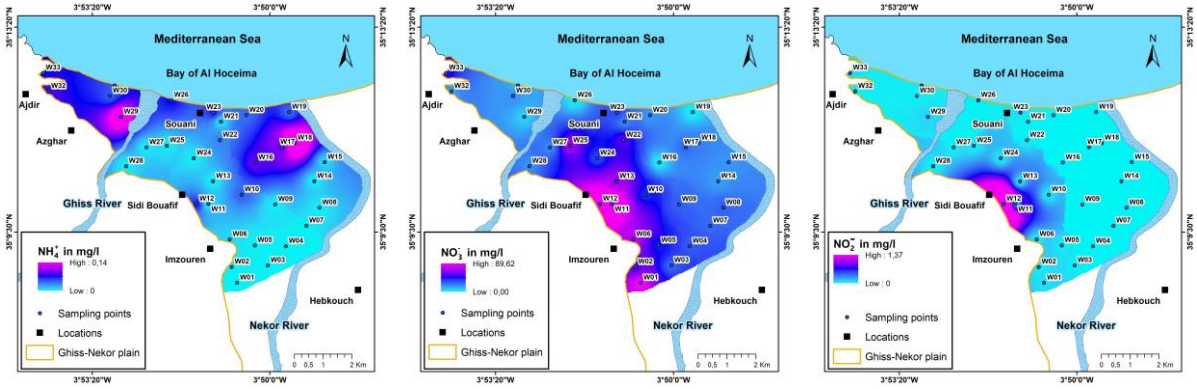

Fig. 2. Geographical dispersion of hydrochemical parameters.: NH_4^+ (a), NO_3^- (b), and NO_2^- (c)

3.2 Nitrate Pollution Index (NPI)

In this current study, the NPI values range from -1 to 3.48, with only 15.15% falling into the category of unpolluted, and 9,1% and 18,19% falling into the category of significantly polluted and very significantly polluted respectively.

Illustrated in **Figure 3,** the spatial arrangement of the NPI showcases interesting patterns. Six wells exhibit an NPI exceeding 3, signifying notable pollution. These samples are in areas marked by a high population density, with evident widespread usage of septic tanks.

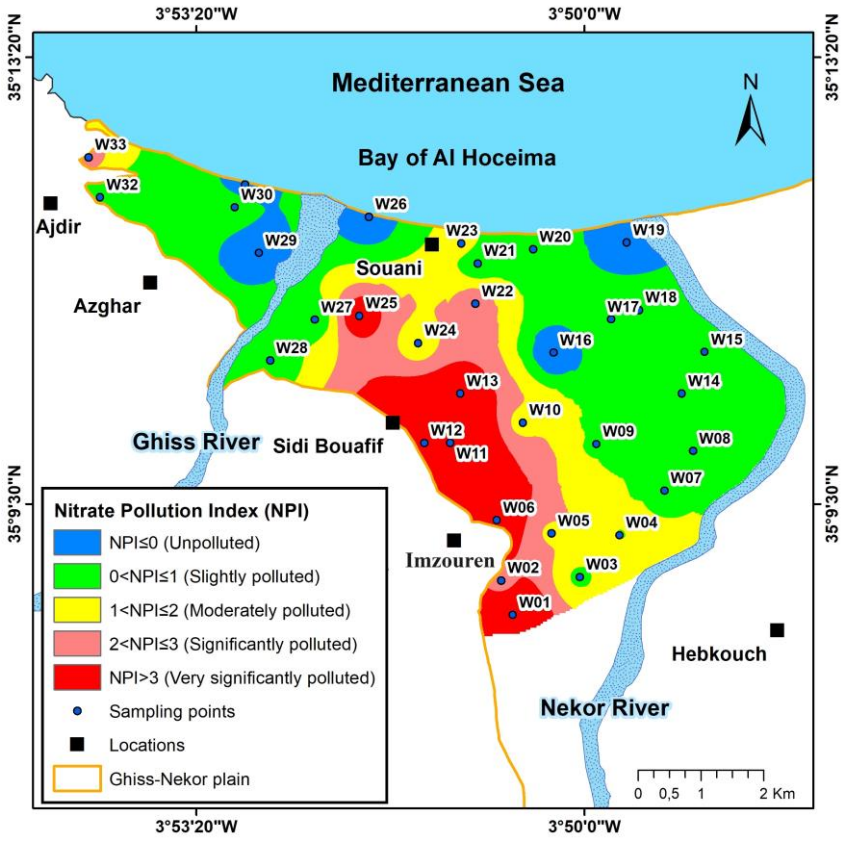

Fig. 3. Spatial Evaluation of Groundwater Quality in the Study region Using NPI

3.3 Chronic Health Risk Index (CHR)

The CHR was determined for three specific age categories, and the results regarding non-carcinogenic health risks are specified in the table 3. Noteworthy is

the CHR's range, which spanned from 0 to 2.43, with an average of 0.69 for adults. For children, the CHR values displayed variability within the range of 0 to 2.03, with an average value of 0.57. Infant CHR values range from 0 to 2.51, with an average of 0.71. **Figure 4** provides a visual depiction of the spatial distribution of CHR for infants, children, and adults. Areas posing health risks are concentrated between Imzouren and Sidi Bouafif, where CHR surpasses 1, signifying elevated health risks linked to the utilization of septic tanks and wells by the local population.

Table 3. Evaluation of Health Risks Linked to Nitrate Intake through CHR

CHR	Max	Min	Mean	N°	% of wells
Adults	2.43	0	0.69	7	**21.21%**
Children	2.03	0	0.57	6	**18.18%**
Infants	2.51	0	0.71	8	**24.24%**

N°= The number of groundwater samples exceeding the allowable limit for CHR=1.

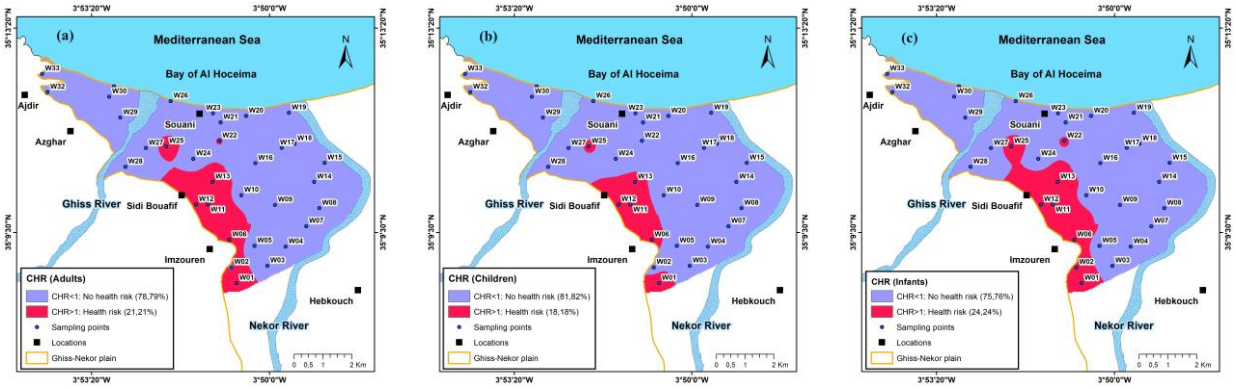

Fig. 4. Cartographic depictions illustrating health risks associated with carcinogens for adults (a), children (b), and infants (c)

4 Conclusion

The aim of this study was to assess groundwater quality and identify the risk of contamination by nitrogen compounds, especially nitrate, using the NPI and the CHR. The calculated NPI values, along with their spatial distribution, reveal anthropogenic pollution associated with nitrates in regions marked by high population density.

These findings serve as an alert to authorities and decision-makers concerning water resources. CHR values, whether for adults, children, or infants, indicate elevated risks in wells proximate to densely populated areas, suggesting potential contamination from unregulated septic tanks commonly used for domestic wastewater disposal.

In addition to the significant findings concerning health risks from contamination, it is crucial to incorporate supplementary assessments such as bacteriological evaluations, analyses of heavy metals, and a thorough examination of other physicochemical parameters. Additionally, it is strongly recommended to extend the study area to include a broader range of rural areas. Despite the ongoing efforts by Moroccan authorities, especially the "Loukkous Hydraulic Basin Agency", measures should be contemplated to safeguard groundwater heavily tainted with nitrogen. This approach aims to effectively mitigate health risks within the study area.

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