EEET ECOLOGICAL ENGINEERING & ENVIRONMENTAL TECHNOLOGY

Ecological Engineering & Environmental Technology, 25(12), 387–394
https://doi.org/10.12912/27197050/195114
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Received: 2024.10.08
Accepted: 2024.10.26
Published: 2024.11.01

Agricultural Nitrate Leaching into Groundwater – Case of Study in Apulia Region

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ABSTRACT

Nitrogen compounds, which are naturally present in the environment, are essential for the sustenance of life and for the growth of plants. However, to meet the needs of agricultural production and increase crop yields, they are often added in the form of fertilizers to the soil. These nitrogen compounds can then infiltrate deep soil layers, leach until they reach underground aquifers. Leaching of nitrates from soil is a serious environmental problem in modern agriculture as it can contaminate groundwater and degrade soil quality. Both nitrogen fertilization practices and irrigation methods contribute greatly to increased nitrate leaching. The present study aims to demonstrate the real impact of nitrate used in agriculture on groundwater comparing concentration of the chemical element between the soil and the aquifer at different depths. The case study involves a series of soil and groundwater sampling with the related analyses for the identification of nitrate concentrations. The sites considered as case of study have the same type of soil (lithology, texture) and the same land use (arable land with the same type of fertilization and irrigation). The experimentation carried out has shown that there is a correlation between the nitrate present in the soil and that present in the groundwater only for a limited distance from the emission point (<10m from the ground level), while for higher soil packages the correlation is absent as structures, such as vadose areas, intervene which intercept and accumulate nitrate leaching. This study demonstrate that a contamination of nitrate in the groundwater is correlated to the agricultural activities present in the impacting area only to a depth of 10 m and which therefore needs further investigation.

Keywords: nitrate leaching, groundwater, soil, correlation concentration of nitrate.

INTRODUCTION

The massive or incorrect use of nitrates in agriculture is one of the main factors of soil contamination and causes their leaching [Lu et al., 2021] and inefficient irrigation [Rath et al., 2021] also of aquifers [Patel et al., 2022].

The use of nitrogen fertilizers and manure has increased agricultural yield, simultaneously leading to an increase in nitrate concentrations in groundwater and surface water [Green et al., 2018]. High levels of nitrates in groundwater can cause eutrophication of surface waters [Korom, 1992], and once drinking water is contaminated with high levels of nitrates, it can increase the risk of diseases such as stomach cancer, childhood methemoglobinemia, non-Hodgkin lymphoma, and heart disease in humans [Mirvish, 1985; Knobeloch et al., 2000; Camargo and Alonso, 2006].

Nitrogen fluxes near the root zone are unstable due to ammonia volatility, nitrification, denitrification, and root nitrogen use. Of significant importance are the physical processes of nitrogen leaching, the transit time under the roots and the stable infiltration zone of the unsaturated zone in order to determine the impact of agricultural management on groundwater quality. In fact, several studies have demonstrated how the rate of mobility of nitrogen, and in particular of nitrates, is directly connected to the presence of physical processes in the soil, to the rate of recharge of groundwater, to the rate of evapotranspiration, to the transport and rate of leaching [Green et al., 2008; Liao et al., 2012; Robertson et al., 2017; Wang et al., 2019].

In order to study the leaching of nitrates of agricultural origin transported from surface soil into groundwater, several quantitative models were developed, which included different variables such as nitrogen fertilization and irrigation methods [Rath et al., 2021]. Nitrogen fertilization is one of the main elements affecting nitrate leaching by increasing the concentration of available nitrogen (Wang et al., 2019). At the same time, the types of irrigation that determine the quantity of water in the soil, increasing drainage and therefore leaching, are important [Yang et al., 2020].

Simulation models involve the evaluation of the various physical, chemical and biological (microbial) processes that determine the transport of contaminants in unsaturated and saturated zones, predicting their transport on both spatial and temporal scales. Among the different models used are the Hydrological Simulation Program-Fortran (HSPF), Integrated Nitrogen CAtchments (INCA-N) and Soil and Water Assessment Tool (SWAT) which determine the regional-scale characterization of groundwater recharge and transport vertical of nitrates in the unsaturated zone under different agricultural, pedo-climatic and climatic conditions [Ervinia et al., 2020; Xie et al., 2023; Kim et al., 2023]. These models simplify water and solute transport compared to models such as Hydrus, one-dimensional SIMWASER/STOTRASIM used in conjunction with groundwater simulation models [Zang et al., 2022].

Due to the different soil structure, the different types of crops, the different types of irrigation and fertilization, non-heterogeneous transport flows occur. Therefore, to accurately determine nitrate leaching, detailed information is needed. Turkeltaub et al. (2018) developed a regional-scale model that exploits a large database of soil properties derived from recent intensive soil profile sampling on the Loess Plateau of China (LPC).

Previous studies have verified that in order to identify areas vulnerable to nitrate leaching it is necessary to estimate water and nitrate fluxes from observations of deep unsaturated zones [Green et al., 2008; Machiwal et al. , 2018; Huan et al, 2013].

To date, however, it is very complex to determine leaching on the soil column despite the collection of data for the determination of the physical properties of the soil and the unsaturated hydraulic parameters [Huan et al., 2020]. In fact, the variability of landscape characteristics, the depth of the vadose zone, the properties of rocks and large-scale hydro geochemical processes also pose challenges for the assessment of regional nitrogen flux to groundwater [Turkeltaub et al., 2018; Huan et al., 2020].Therefore, the application of the different models generally requires a large amount of data.

Therefore, nitrate leaching requires mainly two main inputs: a significant amount of NO_3^- in the soil profile and sufficient rainfall or irrigation water to move the N beyond the root zone.

Leached nitrate is defined as the product of nitrate concentrations in the soil solution present in the water toward and moving toward the underlying aquifer. Heavy rainfall and excessive irrigation cause severe leaching of nitrates [Wang et al, 2019].

In order to study the movement of nitrates towards the aquifer, it is important to know the quantity of water present in the soil due to both precipitation and irrigation carried out. This parameter influences the leaching of nitrates with a relationship directly proportional to the quantity of water entering the soil [Chen et al. 1994; Xie et al. 2023]. At the same time, soil structure influences the movement and infiltration of water, affecting the retention of nitrates by the soil, with the least amount of nitrates absorbed by sand, followed by clayey sand, and the greatest amount by clayey sand. Sandy soils have low water holding capacity, which may promote leaching (Stenberg et al. 1999; Safadoust et al. 2024). This element becomes influential in the presence of cover crops (Quintarelli et al. 2022).

The main objective of the present study is to identify a possible correlation between the nitrate present in the groundwater and the nitrate in the soil. This correlation is based on monitoring a study area that has homogeneous characteristics regarding soil composition, rainfall, land use, fertilization and irrigation. Regarding the monitoring of the aquifer, four different wells were identified in the study area which fish at different depths of the same superficial aquifer.

MATERIALS AND METHODS

Study area

The study area is located in the province of Brindisi in the Fasano countryside. The area is a cultivated arable field. The study area presents a single sandy-gravelly lithological typology. Within the study area there are 4 different wells that tap the underlying aquifer at 4 different depths (Fig 1): A: 1m from campaign plan, B: 2m from campaign plan, C: 10m from campaign plan, D: 50m from campaign plan. In order to ensure that the wells were tapping from the same aquifer, tests were carried out with marking tracers which gave positive results and also highlighted that the aquifer has a speed of approximately 1 m per year. Therefore, the 4 sub-areas of investigations relating to the 4 wells were created.

Sampling activities

The collection of soil samples was carried out in accordance with the Soil Chemical Analysis methods issued by the Ministry of Agricultural and Forestry Policies, approved with the Ministerial Decree of 13 September 1999. For each site, one sampling was carried out upstream of the well and one downstream of the well (Fig. 2).

The two fronts have a distance from the well between 5 and 10m following the trend of the groundwater flow. Each front is characterized by five subsamples along the line perpendicular to the groundwater flow, which constituted our composite.

Each soil sample consists of soil collected at five different points within each sampling front. The soil samples were taken at a depth between 15 and 30 centimeters using a sterile spatula and excluding the first two centimeters with herbaceous vegetation. Those intended for chemical analysis were then homogenized and stored at 10 °C in sterile bags. Sampling consists of taking water from normally used wells. A purge equal to the volume of the water column was carried out to eliminate stagnant water in the well. At the end of the purge, water sampling was carried out following the APAT-IRSA methods. In particular, 5L of water was taken from each well, collected in sterile darkened PVC tanks.

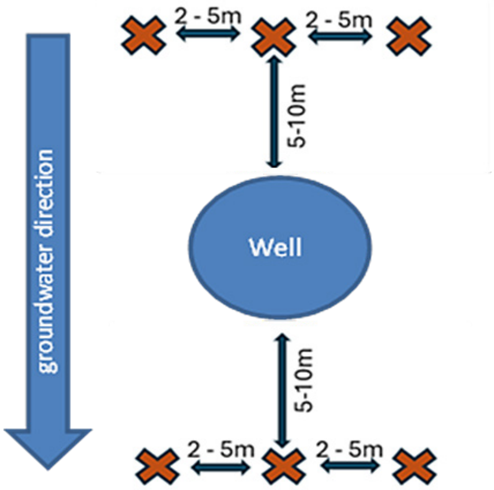

Figure 2. Soil sampling method

For the purposes of a real statistical analysis, sampling of the two matrices for each point was carried out approximately every 15–20 days for a total of 150 samples per well.

Chemical analysis nitrates

Soil

The chemical analyzes of the soil matrix samples were carried out according to

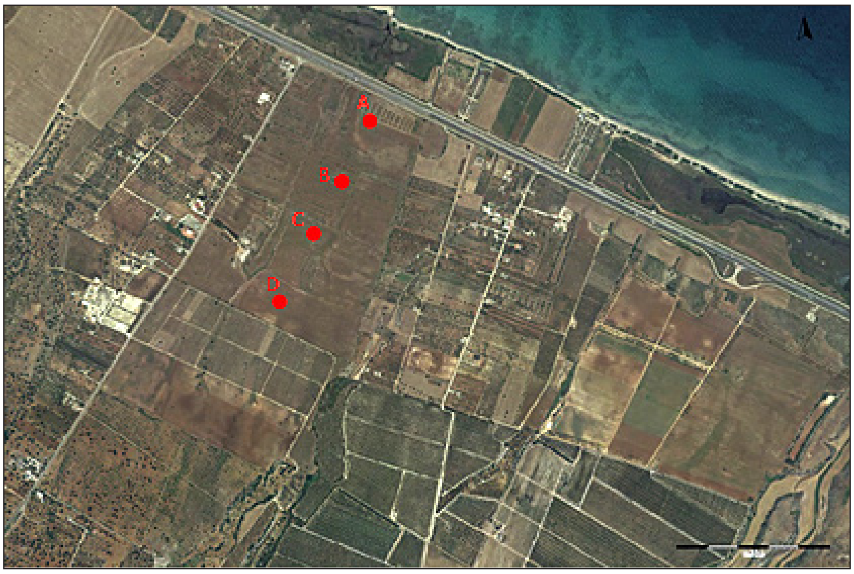

Figure 1. Identification of sampling points in the study area

the official methods of chemical analysis of soils (MUACS) as required by the Ministerial Decree. of 13 September 1999 issued by the Ministry of Agricultural and Forestry Policies (Gazz. Uff. Suppl. Ordin. n° 248 of 21/10/1999). For the determination of nitrate it was extracted from soil and brought into solution using the "method XIV.4 – extraction with potassium chloride solution" described in the document "Official Methods of Chemical Analysis of Soils (MUACS)" as required by the Ministerial Decree. of 13 September 1999 issued by the Ministry of Agricultural and Forestry Policies (Official Gazette Suppl. Ordin. n° 248 of 21/10/1999). The analysis is carried out according to official methods. Method XIV.9 – Determination of the nitrate ion content by ion chromatography.

Water

The chemical analyzes of the water matrix were carried out according to the "Analytical methods for water" APAT / IRSA-CNR". (APHA-AWWA-WEF, 1998).The determination of the nitric nitrogen concentration present in the water samples was carried out as described in chap. 4050 pp. 533-536 of "Analytical Methods for Water – Manual and Guidelines 29/2003–apat/irsa-cnr".(apha-awwa-wef, 1998; barnes & folkard, 1951; bendschneider & robins, 1952; epa, 1974; fao, 1975; irsa, 1986; kershaw & chamberlin, 1942; matsunaga & nishimura, 1974; shnn, 1941; strickland & parsons, 1968)

RESULT AND DISCUSSION

The analyzes carried out found a high correlation diversity between soil water and groundwater. In particular, the analyzes carried out on sub area A where the water table depth was equal to 1 m from the ground level revealed nitrate values in the soil with a minimum of 0.011 gN/Kg of soil and a maximum of 0.739 gN/Kg of soil . Regarding the concentrations of nitrate in groundwater, values were found with a minimum of 0.015 gN/L of water and a maximum of 0.87 gN/L of water. The statistical analysis in these case, with a distance from the input point of the contaminant to the aquifer equal to 1m, has shown that there is a high correlation between the nitrate present in the soil and that present in the water with u R^2 equal to 0.923 and a p-value<0.005 (Fig. 3)

The analyzes carried out on sub-area B where the water table depth was equal to 2 m from the ground level revealed nitrate values in the soil with a minimum of 0.018 gN/Kg of soil and a maximum of 0.752 gN/Kg of soil. Regarding the concentrations of nitrate in groundwater, values were found with a minimum of 0.019 gN/L of water and a maximum of 0.79 gN/L of water. The statistical analysis in these case, with a distance from the input point of the contaminant to the aquifer equal to 2 m, has shown that there is a high correlation between the nitrate present in the soil and that present in the water with an R^2 equal to 0.9048 and a p-value slightly <0.005 (Fig. 4) The analyzes carried out on sub area C where the water table depth was equal to

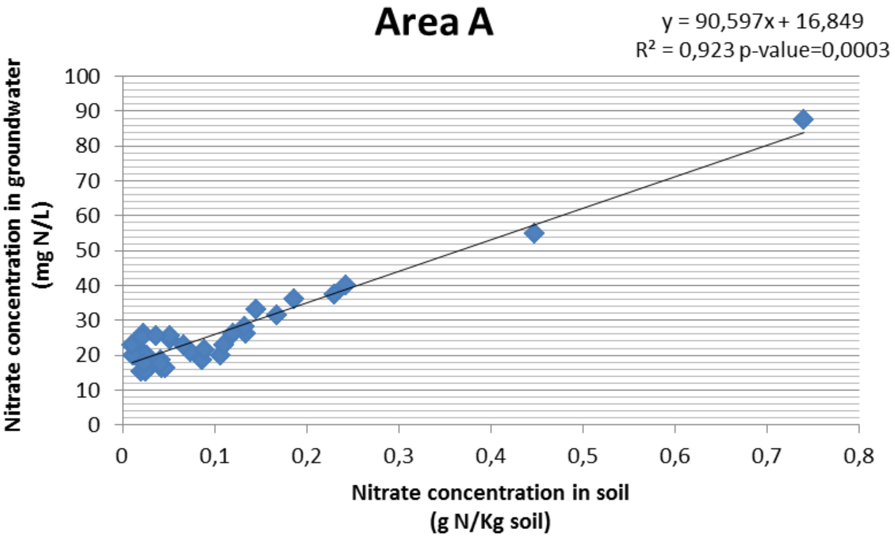

Figure 3. Correlation between concentration of nitrate in groundwater and concentration of nitrate in soil in the Area A, depth well is 1m from the campaign plan

10 m from the ground level revealed nitrate values in the soil with a minimum of 0.010 gN/Kg of soil and a maximum of 0.740 gN/Kg of soil. Regarding the concentrations of nitrate in groundwater, values were found with a minimum of 0.009 gN/L of water and a maximum of 0.84 gN/L of water. The statistical analysis in these case, with a distance from the input point of the contaminant to the aquifer equal to 10 m, has shown that there is a good correlation between the nitrate present in the soil and that present in the water with an R^2 equal to 0.825 and a p-value slightly <0.005 (Fig. 5) Finally, the analyzes carried out on sub area C where the water table depth was equal to 10 m from the ground level revealed nitrate values in the soil with a minimum of 0.015 gN/Kg of soil and a maximum of 0.86 gN/Kg of soil. Regarding the concentrations of nitrate in groundwater, values with a minimum of 0.01 gN/L of water and a maximum of 0.70 gN/L of water were found. The statistical analysis in these case, with a distance from the input point of the contaminant to the aquifer equal to 50 m, demonstrated the absence of a correlation between the nitrate present in the soil and that present in the water with an R^2 equal to 0.003 and a p-value equal to 0.455 (Fig. 6)

From the analysis of the data obtained in the monitoring carried out, it can be seen that a direct

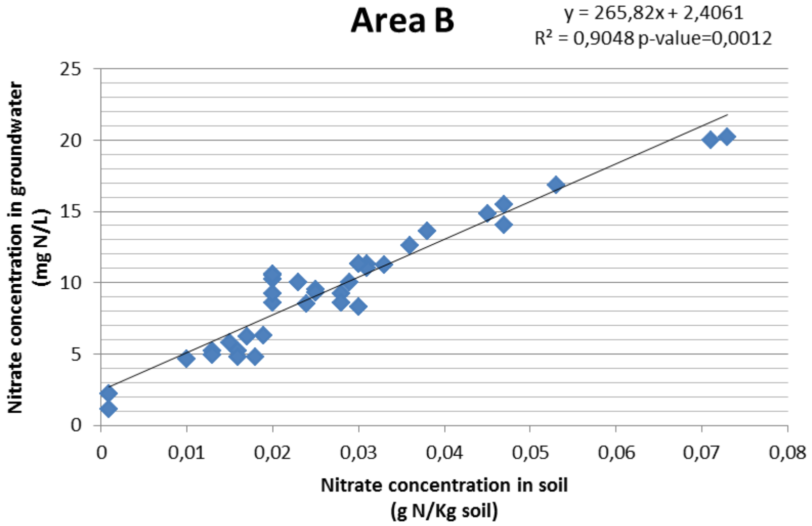

Figure 4. Correlation between concentration of nitrate in groundwater and concentration of nitrate in soil in the Area B, depth well is 2 m from the campaign plan

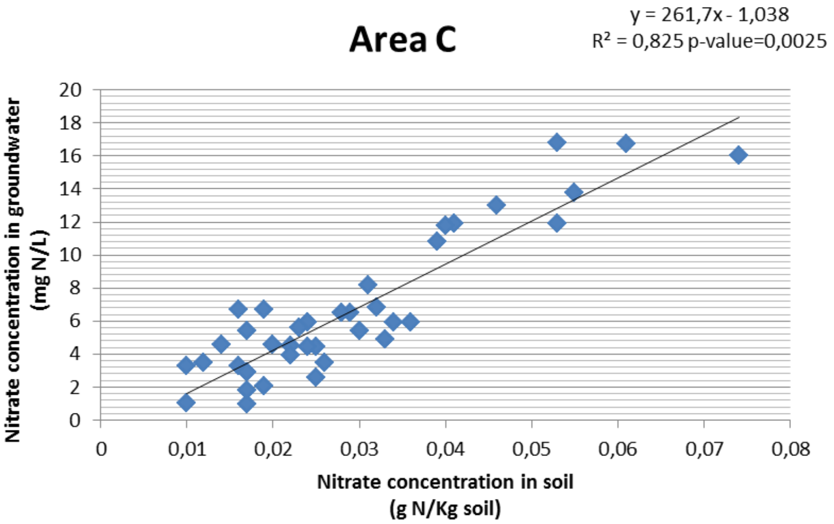

Figure 5. Correlation between concentration of nitrate in groundwater and concentration of nitrate in soil in the Area C, depth well is 10 m from the campaign plan

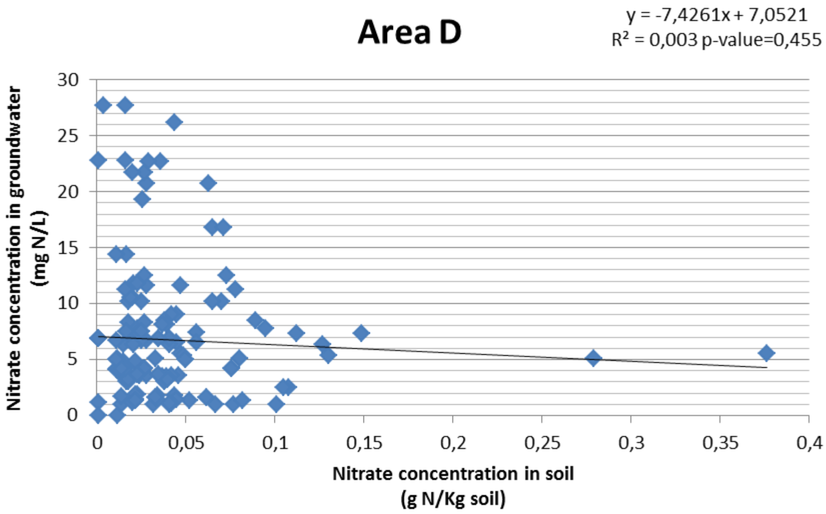

Figure 6. Correlation between concentration of nitrate in groundwater and concentration of nitrate in soil in the Area D, depth well is 50 m from the campaign plan

correlation is present between the nitrate concentrations in the soil and the nitrate concentrations in the surface groundwater up to a depth of 10m from the ground level. This characteristic therefore identifies in soils with these characteristics a leaching of the compound which occurs directly and therefore the transport of excess nitrates in the soil occurs directly. The vadose area is an important nitrate reserve that should be taken into consideration in future budgets for an effective elaboration of leaching dynamics. Nitrate storage in the vadose zone is substantial and increasing not only at national and basin scales (Worrall et al., 2009; Worrall et al., 2015; Meter et al., 2016; Ascott et al., 2016) but even on a global scale (Ascott et al., 2017). Nitrate storage per unit area is greater where dense vadose zones and extensive historical agriculture are present. With the increasing frequency of extremely heavy rainfall, nitrogen stored in the vadose zone will produce higher leaching rates that could threaten groundwater quality (Zhou et al., 2016; Zheng and Wang, 2021). Therefore, quantifying nitrogen accumulation and vadose zone fluxes is significant for protecting the groundwater environment.

CONCLUSIONS

The present study has demonstrated that in a real environment in the presence of homogeneous characteristics of land use and type, rainfall, type of fertilization and irrigation, so as to cancel out any variables that may influence the leaching of nitrates, the correlation of the concentrations of accumulated nitrates in the soil and those present in the groundwater is directly proportionate to the distance of the groundwater from the ground level. The greater the distance, the lower the correlation between the nitrate concentrations in the two matrices. Therefore, it will be possible, after ascertaining the characteristics of the soil and the activity carried out on it, to attribute any groundwater contamination by nitrates of agricultural origin to farmers who have their soil on a water table with a depth of less than 10m from the ground level. With regard to aquifers with greater depth, it will be necessary to carry out further studies to implement the knowledge of the leaching dynamics which have a notable influence not only on the part of the climatic aspects but also, as demonstrated, by the presence of vadose zones which determine a point of accumulation of nitrates and a release only following exceptional events such as heavy rainfall.

According to the nitrate legislation Directive 91/676/EEC, also known as the “Nitrate Directive”, the identification of nitrate contamination in groundwater must be directly attributed to the agricultural activity present in the area. The present study demonstrates how this correlation cannot be applied to all situations precisely because the impact of agricultural activities, in particular the introduction of nitrate, as can be seen from the study carried out, up to a depth of 10 m presents the characteristics of leaching a direct correlation between the input of soil nitrate and the nitrate present in the groundwater. The same study demonstrates that for greater groundwater depths there is a lack of clear correlation between the nitrate concentrations of the soil and the groundwater; this absence is due to the presence of particular soil structures, such as the Vadose areas, which directly interfere in the leaching of the nitrate. Therefore it is very difficult makes a directly correlation between the contamination of the aquifer and agronomic activities.

The present study opens up the possibility of carrying out further scientific research in order to identify in a much more precise manner the leaching dynamics in areas with groundwater depths greater than 10 m.

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