New Methodology for the Identification of Nitrate Contamination from Agricultural Sources

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***Abstract*— Modern agriculture appears to have a very diversified impact on the soil not only for the crops used but also for the type of fertilizer used. One of the least studied impacts is that on the soil microbiome. Maintaining a stable soil microbial community structure is crucial in preserving soil production potential and overall soil health. Various nitrogen (N) addition strategies induced changes in soil physicochemical properties which are correlated with alterations in microbial community structure and partial microbial abundance, thereby displaying differences in carbon and nitrogen use efficiencies. Therefore it becomes important to analyze how the microbiology of the soil and the effects of the fertilizers used can vary.**

The current European legislation (Directive 91/676/EEC) and national legislation (Legislative Decree no. 152/2006) set the limits for contamination of groundwater without determining a very precise methodology on how to analyze these compounds and how to identify their actual source.

The analysis system presented is an absolute innovation as it allows two different types of integrated analysis (punctual and spatial) through the processing of chemical and microbiological data of both groundwater and soil.

The identification of the source of contamination occurs following the complete analysis of all processing phases through the Bottom-up methodology, first identifying the sites and the nitrogenous form that determines groundwater contamination, continuing with the analysis of the different information layers and the analysis of the data collected including microbiological verification.

The spatial analysis is processed by the system at the conclusion of the specific investigation. The system creates correlations between the different sites analyzed on the basis of the possible groundwater interrelationships of the points and following the direction of the groundwater and the speed of movement of the groundwater (preset data).

The System also allows a temporal analysis of the contamination in order to be able to define whether the contamination is more or less recent.

Keywords—Nitrate, source of contamination, new methodology, styling, insert *(key words)*

I. Introduction

With the introduction of the European Directive 91/676/EEC, the control of nitrates in groundwater resulting from agricultural contamination began.

The Water Framework Directive (2000/60/EC) complements the Nitrates Directive by aiming to achieve "good ecological status" for all groundwater resources by 2015. This includes maintaining nitrate concentrations within legal limits.

Data from the European Environment Agency (EEA) reveals concerning levels of nitrate contamination in European groundwater. In 2003 [1], a significant portion of groundwater bodies exceeded a benchmark of 25 mg/L of nitrate ions (NO_3^-). Countries like Spain, the UK, Germany, France, and Italy faced particularly high levels, while Scandinavian and Baltic states had a lower percentage exceeding the limit.

This issue is not limited to Europe. Elevated nitrate concentrations have also been documented in other parts of the world, including Australia [2] and North America[3,4].

Addressing nitrate contamination presents a significant challenge due to its long-term, widespread, and ongoing nature [5,6]. Current mitigation strategies primarily focus on two approaches: continued implementation of land-use controls, this involves establishing protection zones around vulnerable water sources. These zones aim to reduce nitrate infiltration into the subsurface through various management practices [7] and relying on natural attenuation processes, this strategy leverages natural mechanisms in the environment that can break down or transform nitrate before it reaches groundwater sources.

Groundwater ecosystems [8] stand out from surface soil and aquatic environments due to the absence of photosynthesis and limited fresh, readily available organic carbon. These factors shape the microbial communities within aquifers, dominated by heterotrophs adapted to thrive in the nutrient-poor (oligotrophic) conditions.

With legislative decree n. 152/99, Italy gave the first national transposition of Directive 91/676/EEC, establishing the procedures for the approval, by the Regions, of their Action Programmes, pursuant to Article 5 of the directive itself. Legislative decree no. 152/99 was subsequently repealed by the legislative decree of 3 April 2006, n. 152, which also substantially reconfirmed the guidelines. We therefore refer the discussion of the salient points to the in-depth analysis of the subsequent legislative decree of 2006.

The entry into force of the Nitrates Directive, therefore, obliged Member States to carry out checks on the concentration of nitrates in fresh water, to designate "vulnerable areas" and establish action programmes, to establish codes of good agricultural practice, to prepare programs for the training and information of farmers. “Vulnerable areas” are defined as areas already affected by nitrate pollution or which could become polluted in the future.

Monitoring of nitrate concentrations in water must be carried out in order to identify polluted waters and designate vulnerable areas. The criteria for identifying polluted waters are the nitrate content exceeding 50 mg/l in surface fresh waters, in particular those intended for the production of drinking water or the possibility of exceeding this limit if action programs are not adopted and the eutrophication of natural freshwater lakes, other fresh waters, estuaries, coastal and marine waters or the possibility of eutrophication if no action is taken.

To date, however, all regulations do not identify a system or an operational method for identifying the source of contamination from nitrates of agricultural origin, leaving a lot of freedom of action and interpretation of the data.

This work identifies a unique method for identifying nitrate contamination in groundwater and the possibility of identifying the source of contamination thanks to the data spatialization system.

II. ANALYSIS SYSTEM

The analysis system developed is an absolute innovation as it allows two different types of integrated analysis (punctual and spatial) through the processing of chemical and microbiological data of both groundwater and soil.

Top-down and bottom-up models are information processing and knowledge management strategies. Generally speaking, they are methodologies used to analyse problematic situations and build hypotheses providing a resolution to a practical/operational problem.

In the top-down model, an overall vision of the system is initially formulated. Each part of the system is subsequently refined (decomposition, specialization and specification or identification) by adding more design details. Each new part thus obtained can then be refined again, specifying further details, until the complete specification is detailed enough to validate the model. The top-down model is often designed with the help of black boxes that simplify filling but do not allow understanding the elementary mechanism.

In contrast to the top-down model is bottom-up design, in which individual parts of the system are specified in detail, and then connected together to form larger components, which are then interconnected to create a complete system. Strategies based on bottom-up information flow appear potentially necessary and sufficient, as they are based on knowledge of all the variables capable of influencing the elements of the system.

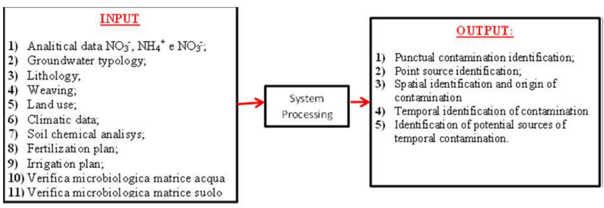

Fig. 1: System scheme of analyses

For these reasons the System has developed a Buttom-UP System which takes shape from the starting point (bottom) or from the initial situation; considers the final objective, leads to the construction of a sequential path organized in successive steps in which the anchoring between intermediate objectives and the final objective is generally sought in an intuitive (heuristic) way.

A. General description

The system for the analysis and identification of contamination sources uses a mixed geo-spatial and analytical analysis.

The identification of the source of contamination occurs following the complete analysis of all processing phases through the Bottom-up methodology, first identifying the sites and the nitrogenous form that determines groundwater contamination, continuing with the analysis of the different information layers and the analysis of the data collected including microbiological verification.

The System therefore requires the inclusion of all the information and analytical layers in order to be able to provide a timely, spatial and temporal output at the end of the processing as in the scheme figure 1.

III. DATA PROCESSING MATRIX

A. Fase 1

The System processes the chemical analysis data, it will be carried out on the basis of current legislation, relating to the sampling carried out in the groundwater. A specific analysis is performed with a subsequent determination of the concentration of nitrate nitrogen on the basis of the legal limits, identifying three different classes:

1) GOOD STATUS if the Nitric Nitrogen concentration is less than 40 mg $NO_3^- L^{-1}$

2) STATE OF ATTENTION the concentration of Nitric Nitrogen is between 40 mg $NO_3^- L^{-1}$ and 50 mg $NO_3^- L^{-1}$

3) STATE CONTAMINED BY NITRATE if the concentration of Nitric Nitrogen is equal to or greater than 50 mg $NO_3^- L^{-1}$.

B. Fase 2

The System analyses the presence of other forms of nitrogen present in particular by analysing the concentrations of Ammonia Nitrogen and Nitrous Nitrogen.

Based on the analysis of PHASE 1 and the results of this phase, the system determines two different states:

1) GOOD ENVIRONMENTAL STATUS if total absence of overcoming, total absence of exceedances (input Phase 1= good condition and absence of other types of contamination)

2) Possible contamination (if even one exceedance of the three forms of nitrogen is identified)

The system therefore in case 1 signals the point as NOT CONTAMINATED, in case 2 it moves on to the procedure for verifying the origin of the contamination

C. Contamination's origine procedure

The procedure for verifying the origin of the contamination is made up of two different data processes:

1. Direct analysis of contamination spread

2. Microbiological verification

The direct analysis of diffusion of contamination consists of a cascade system that carries out an analysis of possible diffusion of nitrates from the surface until reaching the aquifer.

The System processes the information that is entered through a System for identifying the characteristic and processing the nitrate diffusion data based on known scientific knowledge. For each step, a certain output is produced which varies based on the possibility of diffusion in the matrix of the chemical compost under examination.

The first procedure consists in identifying the type of aquifer in question, in particular whether a phreatic aquifer or an artesian aquifer.

This allows us to identify the points where the probability of the nitrate leaching and the consequent reaching of the groundwater is greater. This step thus excludes those points where there is no direct communication between the surface and the aquifer since it will hardly be possible for the leaching nitrate to reach these waters. In fact, on the basis of their classification [9]. An aquifer is said to be phreatic if all the soil above it, up to the atmosphere, is permeable (i.e. semi-permeable, with capillary vessels). If the aquifer, due to the underground flow of water, is between two impermeable layers, it is called artesian.

The System moves on to the analysis of the lithology of the site under examination. One of the main influences of soil lithology is the speed of transport of the chemical element from the surface to the groundwater. The diversity of the component of the soil matrix in fact significantly influences not only the speed with which the element can reach the underlying aquifer but also the possibility that it reaches the underlying aquifer.

Based on the lithological characteristics of the site in question, the system produces five different classifications:

1) Absence of leaching;

2) Almost zero leaching

3) Low Leaching

4) Medium leaching

5) High leaching

These will provide four outputs:

1) Zero probability of contamination coming from the surface layer;

2) Low probability of contamination coming from the surface layer;

3) Average probability of contamination coming from the surface layer

4) High probability of contamination coming from the surface layer.

The System will therefore provide two distinct indications:

1) Absence of contamination coming from the surface layer only for output 1

2) Presence of possible contamination coming from the output 2-3-4 surface layer

Case 1 will be reported as good status in relation to the origin of the contamination from the surface layer, excluding the sites from potential impact points, while case 2 will continue with the analysis of the System, moving on to next step.

A fundamental element for understanding the transport of nitrate contamination in the groundwater with leaching is texture. The diversity of this characteristic determines at a more detailed level than lithology the possibility of transport of the chemical element from the superficial layer of the soil to the deeper layer [9].

Based on the lithological characteristics of the site in question, the system produces five different classifications:

1) Absence of leaching;

2) Almost zero leaching

3) Low Leaching

4) Medium leaching

5) High leaching

In this step the system identifies four nutrient retention classes based on the previous characteristics:

1) High nutrient retention;

2) Medium-High nutrient retention

3) Average nutrient retention

4) Low nutrient retention.

These will provide four outputs:

1) Zero probability of contamination coming from the surface layer;

2) Low probability of contamination coming from the surface layer;

3) Average probability of contamination coming from the surface layer

4) High probability of contamination coming from the surface layer.

The System will therefore provide two distinct indications:

1) Absence of contamination coming from the surface layer only for output 1

2) Presence of possible contamination coming from the output 2-3-4 surface layer

Case 1 will be reported as good status in relation to the origin of the contamination from the surface layer, excluding the sites from potential impact points, while case 2 will continue with the analysis of the System, moving on to the next step.

The last step is the identification of land use. This parameter identifies the possible correlation of the contamination found in the groundwater with activities of agricultural origin.

D. INTEGRATED ANALYSIS

In order to understand the cause of the potential contamination, the resulting contaminating points are subjected to the study of the activities present.

In particular, all those factors that can potentially induce an accumulation and consequent leaching of nitrate in the groundwater are analysed, and in particular:

1) WEATHER AND CLIMATE EVENTS, identifies whether the contamination may have been caused by an exceptional event which resulted in greater leaching of nitrate into the groundwater, thus excluding the point as a possible source of anthropic origin or incorrect agricultural use.

2) CHEMICAL ANALYSIS OF THE SOIL MATRIX, the chemical analysis of the soil matrix allows us to identify which nitrogenous form is present in the matrix and understand the real source of contamination and possibly whether it is due to excess fertilization and possibly identify which fertilizer is contaminating in order to minimize the contribution and/or replace it. Chemical analyses will be carried out on the basis of current legislation

3) FERTILIZATION PLAN, determines the quantities of fertilizer introduced into the soil and the type useful for reworking the input based on the chemical analyses of the matrix under examination, minimizing the impacts.

4) IRRIGATION PLAN, allows for the calculation of any savings in water use and at the same time provides useful information for identifying the transport of nitrate in the aquifer. Its reprocessing thus allows the reduction of nitrate transport in the aquifer without ignoring the water needs of the crops present.

E. MICROBIOLOGICAL VERIFICATION ANALYSIS

The Microbiology verification, carried out through biomolecular analyses, consists of comparing the results of the water matrix and the soil matrix. Performs two different types of analysis for each matrix. The first is the verification of the presence and relative quantity of nitrifying and denitrifying agents. Their presence and different concentrations determine the identification of the origin of the nitrates. In particular, based on the studies carried out [10], it examines the presence of the growth substrate, thus determining whether the nitrate present is the product of microbial activity (nitrification by nitrifying bacteria) or is itself the growth substrate (presence of denitrifying agents). The second analysis identifies the relevant target species, both nitrifying and denitrifying, by carrying out the same analysis previously indicated[11,12].

The analyzes on the two matrices of the microbiological presence end in a mathematical matrix which analyzes and provides certain data identifying the point as a source of nitrate contamination of agricultural origin or as a non-source of contamination of agricultural origin.

IV. POINT ANALYSIS

At the end of the analysis using the previously described method, the system provides a single output indicating whether the aquifer analyzed has nitrate contamination of agricultural origin, with activity present on the site above the aquifer or not.

V. SPATIAL ANALYSIS

The spatial analysis is processed by the system at the conclusion of the specific investigation. The system creates correlations between the different sites analyzed on the basis of the possible groundwater interrelations of the points and following the groundwater direction and the speed of movement of the groundwater (present data).

This investigation therefore allows us to identify what could be the hypothetical spatial trends of nitrate contamination (or other nitrogenous chemical compounds), in particular by creating the correlation between the results of the direct analysis and the results of the microbiological verification and therefore creating a trend of concentrations and outlining those areas that are vulnerable to nitrates of agricultural origin.

The analysis constraint exists in the number of sampled sites which must not be less than 12 sites and their geolocation, in particular the sites must be selected in such a way as to be able to cover the direction of the water table. It is also important to know and enter the distance between the sites into the system, which should possibly not exceed the interval of 5/6 km.

VI. TIME ANALYSIS

The System also allows a temporal analysis of the contamination in order to be able to define whether the contamination is more or less recent.

The constraint for this analysis is to have an analytical set that includes a time interval of at least three years from the first sampling (with at least 1 sampling per year).

The calculation system carries out an initial precise analysis of the individual annuities. Subsequently, a detailed analysis of the trend in the concentrations of nitrogenous compounds is carried out.

Simultaneously the System carries out the microbiological verification for single years and also in this case for each site it carries out the temporal processing of the microbiological presence.

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