Groundwater Pollution by Nitrates

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Groundwater pollution by nitrates from agricultural sources is a common environmental issue. Surpluses from nitrogen fertilization are leached and they reach groundwater.

Keywords: nitrogen requirement ; hazard index ; hazard map ; Nitrogen Input Hazard Index ; Nitrate Vulnerable Zone

1. Introduction

From an environmental perspective, surface and groundwater pollution caused by anthropogenic activities is one of the most common issues across the world [1][2][3]. In the past fifty years, the expansion of human activities, such as urbanization, industry and agriculture, has increased the pressure over water resources, and the consequences may endanger water quality both for human and natural uses [4][5].

The intensification of agriculture has been supported by the use of nitrogen fertilizers [6], which are relatively cheap and allow a significant crop increase. However, contamination from agricultural sources is mainly caused by the use of fertilizers and manure. Organic and mineral nitrogen are commonly used for fertilization, but the application of nitrogen fertilizers above the plants' needs usually means that the nitrogen and salt surpluses leach into groundwater bodies [7][8]. Nitrogen usually reaches groundwater bodies in varying forms, such as organic nitrogen, ammonium or nitrate, (NO_3^-) with several sources of recharge, such as nonpoint recharge from rainfall or irrigation, lineal recharge from streams or rivers, and areal recharge from lagoons and lakes [9].

Whereas lineal and punctual sources are relatively easy to control and mitigate, diffuse pollution is difficult to prevent and estimate. Agricultural lands are considered as the main source of diffuse pollution [10] and it has a wide range of environmental impacts related to changes in water quality, which directly influences biodiversity, and animal and plant communities [11]. Since nitrogen is a nutrient that results in a significant rise in plants' productivity, excessive nitrogen in aquatic environment enhances an intensive algal growth, limiting the oxygen in water for other organisms [12]. Additionally, high nitrate concentration in drinking water has been related to several pathological conditions in humans [13].

With the aim to control high nitrogen concentrations in surface and groundwater, several countries and supranational institutions have proposed programs and measures of protection and mitigation [14][15]. In the European Union, the Water Framework Directive [16] is the backbone of water protection directives, which include the Nitrate Directive [17] and the Groundwater Directive [18].

Following the Nitrate Directive, the member states have to control and reduce the water pollution by nitrates from agricultural sources. The correct implementation of the EU directives is based on the promotion of sustainable agricultural practices and on the protection of vulnerable areas, known as Nitrate Vulnerable Zones (NVZ). In these areas, Codes of Good Agricultural Practice are implemented to decrease and control nitrogen leaching [19]. However, the NVZ declaration has shortcomings and drawbacks and does not necessarily improve groundwater quality [20][21].

For an accurate implementation of measures related to the mitigation of water pollution, several tasks are required, such as the quantification of the anthropogenic pressures, the estimation of nutrient leaching and the identification of the potential sources of pollution [22]. In relation to these tasks, hazards and risk assessments can be considered as useful tools to quantify hazard and risk levels. Risk has been commonly defined as the result of the combination of a hazard and the vulnerability of the elements exposed [23][24][25][26], whereas hazard is a phenomenon, process, or activity that may be harmful and damaging to the society and the environment [27]. Therefore, risk assessments are holistic analyses which include hazard, vulnerability and exposure factors, while hazard assessments are restricted to the analysis and classification of the potential hazards within an area. Following this approach, several groundwater hazard indexes have been developed (e.g., the Danger Contamination Index (DCI) [28]; the Pollutant Origin Surcharge Hydraulically (POSH)

[29]; and the Hazard Index (HI) [30]. These hazard indexes are designed to be applied in a variable set of areas, so they take into account a wide range of land uses and activities that could be potential sources of groundwater pollution.

Given the wide variety of pollution sources considered by traditional indexes and the relevance of pollutants from agricultural sources, especially nitrates, some authors developed specific methodologies for assessing groundwater nitrate pollution [31][32][33]. Shaffer and Delgado [34] provide a three-tiered nitrate leaching index assessment tool. They also used a qualitative approach to separate leaching potential levels, and they used the vulnerability to contamination to target the level of protection of aquifers at risk. In 2005, Birkle et al. [35] proposed the Nitrogen Leaching Hazard Index (NLHI), with the aim of providing information for farmers to reduce potential nitrogen contamination of groundwater in California. This index identified the areas of highest intrinsic vulnerability by classifying the soils, crops and irrigation systems. It was later corrected and updated by O'Geen et al., [36], who created a new data-driven Nitrate Hazard Index (NHI).

However, both traditional and specific indexes have some weaknesses that could be addressed. The specific agricultural indexes usually include vulnerability criteria in their hazard analysis, so according to the basic risk equation, where risk is defined as the combination of hazard, vulnerability and exposure, they should be considered as risk indexes instead of hazard indexes. On the other hand, the traditional hazard indexes tend to undervalue the potential pollution of agricultural sources, especially the nonpoint ones which provide a constant flux of pollution [37], and are recognized as the most common source of nitrogen pollution. Additionally, they do not follow a clear criterion when rating the potential sources nor do they relate the pollutant supply and the impact of the amount of pollutant to groundwater quality, that is, the real groundwater body level of affection. The result is a dimensionless parameter that is difficult to relate to the reality, which raises questions on the calibration of the methods.

2. Efectiveness of the Nitrogen Input Hazard Index (NIHI)

The NIHI has an interval delimitation basis, exclusively based on the nitrogen fertilizer requirements of the crops. The use of the nitrogen fertilizer requirements allows its application in a wide range of areas, since the method is flexible and adaptable to the agro-hydrological parameters of each place. Thus, a crop can have different NR and be classified in a hazard level depending on the study area.

When developing a hazard index or a risk methodology based on a quantitative approach, and one easy to map and reproduce, it is recommended to use a measurable parameter which may help to establish the thresholds between hazard intervals. This process should be preferential compared to indexes that establish levels of hazard based on arbitrary criteria. In the case of nitrate pollution, nitrate concentration has proved to be appropriate in different scenarios [32][38]. In this research, this parameter was used to create thresholds between hazard categories. Even though concentration can be used to calibrate the index, nitrate concentration is not a valid indicator of good versus bad agricultural management [39] (i.e., good agricultural management may also produce a high nitrate concentration in groundwater). The relationship between nitrogen supply and nitrate concentration may be weak due to several parameters related to intrinsic vulnerability. These reasons should be deeply analyzed when a risk assessment is being carried out. However, in a hazard assessment, those parameters related to vulnerability should not be considered. In any case, it must be highlighted that the aim of the index is to offer a better approach for interval delimitation, based on a measurable parameter instead of using arbitrary criteria.

The use of nitrate concentration to establish thresholds between intervals is also supported by the fact that it is the parameter used by water authorities to implement protection measures in groundwater bodies.

The ultimate objective of a hazard index is to develop a hazard map that could be useful for developing management and control measures to mitigate the negative effects of groundwater pollution and to improve the effectiveness of the environmental measures. To do so, when categorizing hazard intervals, the categories should be used to distinguish measurable levels of pollution of water bodies. The weakness of some indexes that consider vulnerability factors, or that rank hazards on a non-measurable basis, is that the intervals lack a realistic validity [35]. In the NIHI, the intervals estimate, in an approximate but measurable way, the potential effect of a certain crop on the groundwater quality. That is, a high hazard level means that the amount of nitrogen required in a plot would lead to the legal nitrate concentration threshold of 50 mg L^{-1} being exceeded.

Regarding the hazard maps, they usually establish thresholds on an arbitrary basis (e.g., regular intervals based on the data range), but they do not relate the real hazard influence over pollution of the aquifer. For this reason, other indexes classify most of the study area in the low or moderate hazard level [21], even though pollution is very high. Those maps could be considered as unsuccessful hazard maps.

As stated by De Girolamo et al. [22], the most suitable spatial unit for estimating diffuse pollution is the basin scale. However, by working on a plot scale within the basin, the level of detail of the hazard map increases. The plot scale may be considered as the management unit to control pollution, since it eases the delimitation of areas of significant hazard due to high nitrogen fertilizer requirements. The delimitation of those areas may be useful for establishing specific measures related to fertilization rates and dates. Those measures could be included in the action programs implemented in the Nitrate Vulnerable Zones. These programs have to be followed on a mandatory basis, but their effectiveness has been frequently questioned [40][41]. The lack of effectiveness of those programs can be related to the wrong conception of the most vulnerable zones. The term is used to define polluted zones without considering their intrinsic or specific vulnerability, and they are delimited using administrative units (e.g., municipalities), which have nothing to do with natural water boundaries.

3. Conclusions

Currently, risk analyses are usually carried out once an area has been polluted, and it requires mitigation and control measures. However, these types of environmental analyses are useful either when the area is polluted or if it is at risk. Hazard mapping must be based on measurable and comparable parameters, and the use of hazard maps when establishing mitigation and control measures in groundwater is highly recommended, especially in the current climate change scenario, when water scarcity may be recurrent.

The NIHI is a powerful hazard index that can be used to estimate the environmental consequences (NO_3^- concentration in groundwater) of agricultural activities, based on its characteristics and nitrogen fertilizer requirements (NR). The index provides advantages for hazard analysis and mapping: compared to previous methods, which may be confusing, it allows independent assessment of hazard factors and the hazard intervals are based on the relation between nitrogen input and the level of groundwater pollution. In addition, the method is adaptable so it can be easily applied to a wide range of scenarios.

Our results in the GGB showed that most of the study area presents a high hazard level. The hazard classification displayed in the hazard map is in line with the high NO_3^- concentration observed in the GGB since the late 1970s. The NIHI map provides a more realistic hazard map compared to previous hazard indexes, which underestimate hazard levels and classified most of the study area in the low and moderate hazard levels.

The hazard map obtained by the NIHI application may be used for future risk assessments and, eventually, as a tool to apply specific control measures in certain areas that are potentially at risk of increased nitrate pollution. In the GGB, the control programs implemented during the past decades have proven failures due to the lack of appropriate criteria when delimiting the Nitrate Vulnerable Zones, and recurrent stoppages in water supply due to high NO_3^- concentration have affected some of the villages in the area. Therefore, any tool that may improve the implementation of more accurate spatial measures, together with a better understanding of the hydrogeological dynamics, would lead to a recovery of groundwater quality in a more effective and rapid way.

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