# A cost-effective method for assessing groundwater well vulnerability to anthropogenic and natural pollution in the framework of Water Safety Plans

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**Abstract:**

Water abstraction is a key aspect when performing drinking water risk assessment within the scope of Water Safety Plan (WPS). In this context, evaluating aquifer vulnerability could be not exhaustive. Care must be taken to consider the well structure and dynamic behavior that can determine different water quality and vulnerability than those of the tapped aquifer. Here, a methodological approach to assess well vulnerability to natural and anthropogenic pollution is proposed. A data-driven hydrogeochemical conceptual modeling was performed through cluster analysis, supporting the identification of the main features determining well vulnerability. Well vulnerability was then assessed through a semi-quantitative method based on a well-specific analysis of the tapped aquifer type, water table depth, vadose zone permeability, natural redox conditions, and qualitative classification of the tapped groundwater age, considering evidence of mixing processes induced by the well dynamic behavior. Each feature was categorized into several classes, and a score was associated with each class according to the vulnerability induced by that specific condition. The method was applied to a dataset of ~200 wells, in northern Italy. Each well was classified, and its vulnerability was assessed. The method was validated by analyzing the distribution of wells affected by natural or anthropogenic pollution in each of the vulnerability classes. Results of the chi-square test showed that the distribution of the polluted wells was associated with vulnerability classes, which is evidence of the robustness and reliability of the proposed method. This method was developed exploiting only hydrogeological information and raw water quality data, largely available to water managers from routine monitoring, which makes this approach widely applicable and cost-effective.

**Keywords:** Groundwater quality, Safe water, Multivariate analysis, Risk assessment, Groundwater hazardous events

# 1 Introduction

The Human Right to Water and Sanitation (UN General Assembly, 2010) states that everyone has the right to sufficient, continuous, and safe water for personal and domestic use. The Water Safety Plan (WSP) approach, introduced by WHO (2004), is increasingly used around the world as a way to guarantee healthy water for human consumption, and it is now mandatory within the European law framework (Directive (EU) 2020/2184, 2020; Gunnarsdottir et al., 2020; Kumpel et al., 2018; String and Lantagne, 2016). The WSP approach consists of a detailed risk assessment of the whole water supply chain, from abstraction to consumption (Bartram, 2009; Davison et al., 2005).

Water abstraction is the first component of the water supply chain therefore, it has a fundamental role in the risk assessment of the whole supply chain. Groundwater is often used as a source of water supply, thus the risk assessment of groundwater abstraction is key to many WSPs.

The WHO guidelines for WSP (Bartram, 2009; Davison et al., 2005) require the identification of each hazard and hazardous event that could result in a compromised, contaminated or interrupted water supply. Every phase of the supply chain needs to be analyzed, including abstraction, treatment and distribution. For each identified hazardous event, a risk assessment is then required. A semiquantitative risk assessment method is suggested, based on a risk factor matrix with two inputs: likelihood/frequency and severity/consequence. Considering groundwater abstraction, for hazardous events related to chemical contamination, the likelihood is considered as the likelihood of groundwater pollution and represents the quantification, in probability terms, of the pollution potential (Schmoll et al., 2006). The pollution potential is defined as the combination of 1) the pollutant load applied to the subsurface, related to the land use and all the possible pollution sources, and 2) the aquifer vulnerability (Foster and Hirata, 1988).

Aquifer vulnerability has received great scientific attention in the hydrogeologic literature. Related studies are mainly aimed at the production of maps (Wachniew et al., 2016) to assess the spatial distribution of groundwater vulnerability in a specific aquifer. Methods for the aquifer vulnerability assessment are mainly classified into index-based, process-based, and statistical methods (Machiwal et al., 2018). Index-based methods, often referred to as subjective or parametric, combine various physical factors whose choice and ratings are defined for each method based on a priori hydrogeologic knowledge (Barbulescu, 2020; Dassargues, 2000; Shirazi et al., 2012). The most widely used index-based methods are DRASTIC (Aller et al., 1987), SINTACS (Civita, 1994; Civita and Maio, 2004), accompanied by a wide variety of applications, integrations, and modifications (Jhariya, 2019; Kong et al., 2019; Nadiri et al., 2018; Nazzal et al., 2019; Noori et al., 2019; Oke, 2020). The statistical approaches aim at predicting contaminant concentrations correlating them with aquifer and sources characteristics, thus closer to specific vulnerabilities (Boy-roura et al., 2013; Masetti et al., 2009; Sorichetta et al., 2012). Process-based methods, mainly involving simulation models, are often associated with specific vulnerability incorporating various physical, chemical, and biological (microbial) processes dictating the fate and transport of contaminants in unsaturated and saturated zones (Machiwal et al., 2018). Most recent studies attempted at incorporating the timescale within the vulnerability assessment, by determining travel time in unsaturated or saturated deposits through models or environmental tracers (Eberts et al., 2012; Neukum and Azzam, 2009; Newman et al., 2010; Popescu et al., 2008; Sinreich et al., 2007).

In the scope of the risk assessment related to groundwater abstraction and in the framework of WSP, a change of focus seems to be required, shifting from aquifer vulnerability to well vulnerability. Recent studies (Eberts, 2014; Eberts et al., 2013) highlighted that public-supply-well vulnerability to pollution is not the same as aquifer vulnerability: while aquifer vulnerability mostly depends on contaminant sources, contaminants mobility and persistence and intrinsic susceptibility of the aquifer (Focazio et al., 2002), well vulnerability is also related to design, location, manufacture, operation, and maintenance of the well.

While aquifer vulnerability is essential in the scope of environment protection, well vulnerability is more directly linked to public health even though, of course, the two cannot be decoupled. To the best of the authors' knowledge, only a few studies focusing on well vulnerability exist. Some of these studies associated well vulnerability with wellhead protection zones through the application of numerical models (Clark et al., 2006; Frind et al., 2006; Huan et al., 2015; Molson and Frind, 2012;

Soriano et al., 2020). Mendizabal and Stuyfzand (2011) quantified well vulnerability towards anthropogenic impacts using groundwater and surface water quality data, isotopic analysis, wellhead protection areas boundaries, and land use. Eberts (2013) associated well vulnerability with its recharge sources, geochemical conditions, groundwater-age mixtures, and preferential flow pathways.

The above-mentioned studies on well vulnerability provided a detailed and well-grounded assessment, but they were based on a broad set of data and on detailed knowledge of every individual well (e.g., groundwater age, wellhead protection zones, recharge areas, land use, presence of preferential flow pathways) which are rarely available in the ordinary management of water supply worldwide, and challenging to collect within the time frame of risk assessment (Eberts, 2014).

Furthermore, scientific literature mostly focuses on aquifer vulnerability to anthropogenic impacts, ignoring natural pollution, which may also affect groundwater quality, raising public health risks. The main examples are natural arsenic or fluoride pollution affecting many regions around the world (Coomar and Mukherjee, 2021; Van Halem et al., 2009). Indeed, the WSP approach highlights the importance of considering all the possible hazards in water for drinking purposes, thus both anthropogenic and natural pollutants. While WSP is an increasingly trending topic (Aali et al., 2021; Barrow et al., 2021; Dettori et al., 2022; Pundir et al., 2021), a standardized methodology on how to assess well vulnerability in the scope of WSP remains a scientific gap, which this work aims to address.

This work proposes an approach for assessing well vulnerability, which can be used in the scope of the WSP risk assessment, subject to the following requirements. Firstly, it focuses on well vulnerability rather than aquifer vulnerability, by considering structural data and dynamic behavior of the wells; secondly, it considers natural and anthropogenic impacts jointly for a complete risk assessment; finally, it is cost-effective since it is based on data that are regulated in most countries worldwide drinking water legislation (WHO, 2021) and, therefore, it does not require specific field campaign, which makes this method widely applicable. To develop a method that could be easily replicable also by water suppliers, based on routine monitoring data, well vulnerability was here assessed through an index-based method. Furthermore, index-based methods are particularly appropriate in the WSP framework, where the complete risk assessment is based on a semiquantitative categorical approach. The proposed approach is a workflow in which the first step is the elaboration of a conceptual model of the area and the identification of the main pollution sources (i.e. in this area anthropogenic pollution and natural pollution related to red-ox processes). The subsequent step is the identification and categorization of the main processes influencing the vulnerability of the wells to a specific pollution, reaching, in the end, a well-specific analysis and classification of each well according to the identified parameters.

As a first step, data-driven hydrogeochemical conceptual modeling was performed through multivariate statistical analysis, which has been proven to be a successful tool in supporting hydrogeochemical characterization (Blake et al., 2016; Zanotti et al., 2019). Then, the main aspects characterizing the system were parametrized and inserted in a semiquantitative index to classify the well vulnerability of each well. The method was applied and validated on a wide dataset of ~200 wells, serving 65 municipalities in northern Italy, supplying about 240.000 consumers.

# 2 Materials and methods

## 2.1 Study area

The study covered an area of ~4000 km$^2$ in the Lombardy region of northern Italy (Fig.1). It included three distinct geographical and hydrogeological settings: an Alpine mountain area in the northern part, the morainic hills of Lakes Iseo and Garda, two major Italian subalpine lakes, and a Po Plain area in the southern part (Marchetti, 2002).

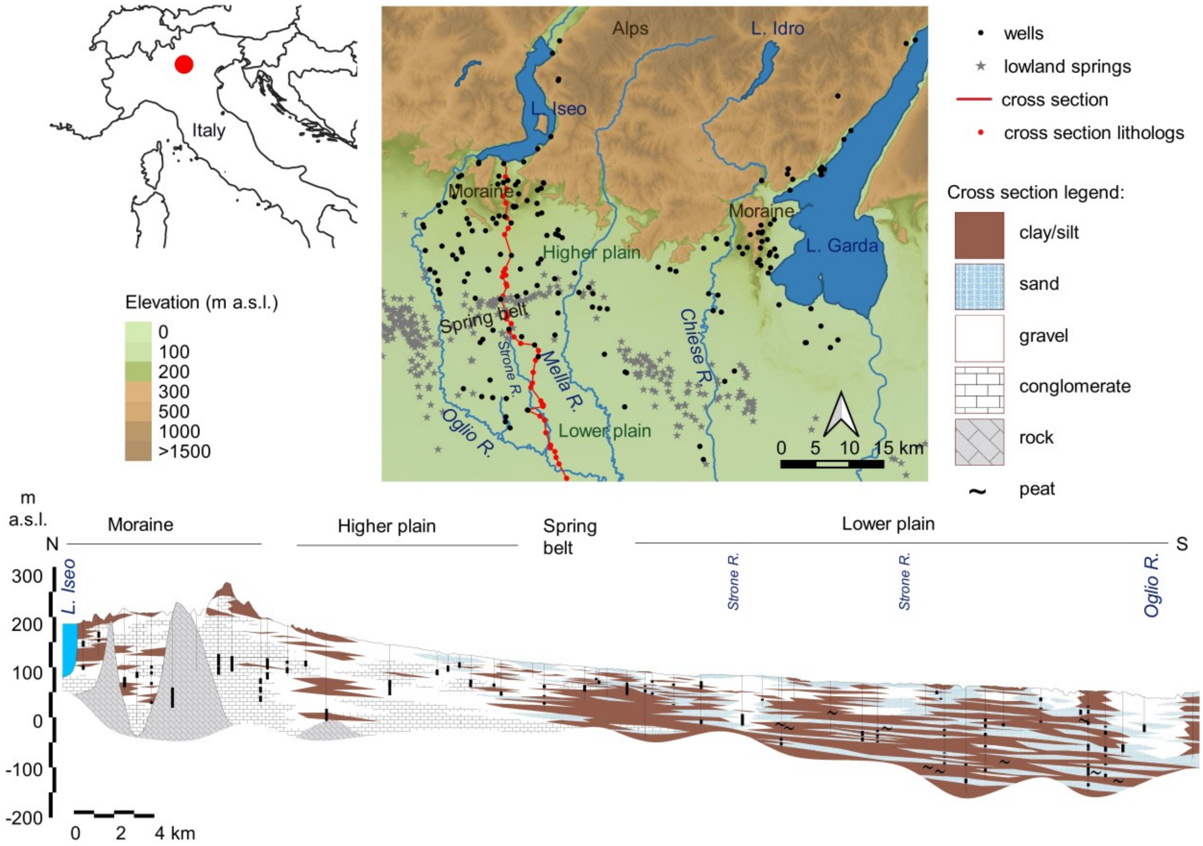


*Figure 1 – Study area and schematic cross-section.*

The Alpine area hosts unconsolidated aquifers within the valleys along main rivers and the alluvial fans, generally unconfined, and fractured aquifers within bedrocks, frequently discharging through springs.

In the morainic hills, moraine and fluvio-glacial/-lacustrine deposits overlap, determining a complex hydrogeological system composed of local superimposed aquifers alternating with silty/clayey aquitards of limited lateral extent (Cita et al., 2006).

The Po Plain area can be divided into a northern higher plain and a lower southern plain. Numerous (semi)natural lowland springs mark the transition zone between the higher and lower plain, the so-called "springs belt". The higher plain hosts a monolayer aquifer (at least in its first 100-150 m of thickness), mainly composed of gravel and sand. In the lower plain, the sediments become finer and the alternation of sand and silt/clay layers generates multilayer aquifer systems (Rotiroti et al., 2019). The regional groundwater flow direction is north to south in the higher plain and NW to SE in the lower plain

(Regione Lombardia, 2016). Aquifer recharge in the higher plain is mainly from local precipitation, irrigation, and losing rivers. In the lower plain, recharge is only from lateral groundwater inflow from the higher plain aquifer since surficial clay/silt layers prevent (or reduce) the infiltration of local precipitation or surface waters (Rotiroti et al., 2019). Concerning the main hydrochemical features, the higher plain aquifer hosts oxic groundwater mainly affected by diffuse nitrate pollution (Delconte et al., 2014; Martinelli et al., 2018). In contrast, lower plain groundwaters are anoxic and affected by natural arsenic pollution, together with the presence of iron, manganese and ammonium (Rotiroti et al., 2021).

## 2.2 Available data

Data for 181 drinking water supply wells were made available by the local water supplier, Acque Bresciane Srl.

For each well the water supplier provided technical information (geographical coordinates, depth, number of borings and screens, screen depth), lithostratigraphic data, hydrodynamic data in terms of static and dynamic groundwater levels (from 1996 to 2019) and hydrochemical data, such as pH, water temperature (Temp), electrical conductivity (EC), hardness, Cl, Na, $SO_4$, $NH_4$, $NO_3$, $NO_2$, As, Fe, Mn, Alkalinity, Al, Ca, Ni, Pb, K, Cr, Dissolved Oxygen (DO) as well as synthetic compounds (pesticides and their breakdown products, VOCs and halogenated organic compounds, BTEX) corresponding to untreated abstracted groundwater from 2009 to 2019.

Among the main physico-chemical parameters, only 13 were available for the whole set of wells (Temp, EC, Hardness, Cl, Na, $SO_4$, $NH_4$, $NO_3$, $NO_2$, As, Fe, Mn) which were used for the multivariate analysis. Note that the DO, a relevant parameter for the well vulnerability assessment, has no regulatory limit in the Italian and EU normative framework; therefore, it is not a routinely monitored parameter. Consequently, it was not available for a subset of wells under study.

To perform a thorough hydrochemical characterization, groundwater quality data on the 181 water supply wells were accompanied by chemical analysis (of the same parameters listed above) of water samples collected from 2009 to 2019 from 98 Alpine spring, 57 watercourse stations (rivers, streams and irrigation channels) and 10 lakes stations on Lakes Garda, Iseo and Idro. These data were provided by Acque Bresciane Srl and the Regional Agency for Environmental Protection of Lombardy (ARPA Lombardia).

Chemical data below the Limit of Detection (LOD) were substituted with LOD/2. The wide time frame of the data determined the presence of different LOD for a single chemical variable, which is an eventuality to be managed during the LOD/2 substitution to avoid the generation of a fictitious variability. Here, <LOD data were replaced using the minimum LOD/2 for each variable that presented more than one LOD.

## 2.3 Well vulnerability assessment

This work aims at assessing well vulnerability to both natural and anthropogenic pollution, considered as the two main classes of hazardous events potentially threatening groundwater quality. Vulnerability to natural pollution means, in the study area, vulnerability to the reduced species As, Fe, Mn and $NH_4$ released to groundwater by natural hydrogeochemical processes (Zanotti et al., 2021).

The approach to tackle the well vulnerability assessments (Fig. 2) consists in four main steps: 1) the development of a conceptual model through data-driven techniques, 2) the identification of the parameters influencing well vulnerability, 3) the categorization of these parameters into classes that could be representative of the heterogeneity of the area, in order to reach a diversification of the wells and 4) the well-specific classification and vulnerability assessment.

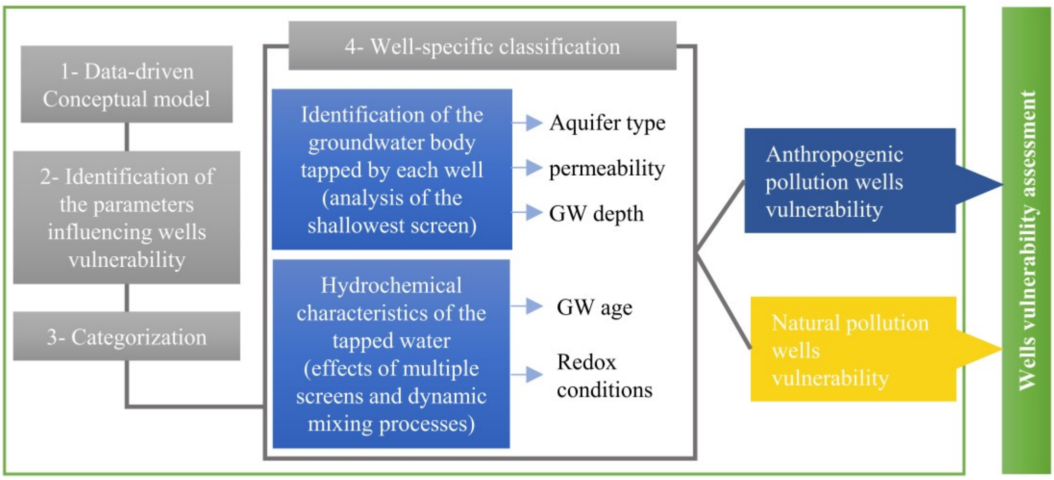


*Figure 2 – Graphical representation of the adopted workflow*

Therefore, as the indexes are meant to be a management tool for a specific well-field, they can be considered system-specific, while the process that led to their parametrization is intended to be replicable even in different regions.

Each drinking water supply well was classified according to these indexes and the obtained vulnerability classifications were then compared with actual natural and anthropogenic pollution data, with the aim of validating the method under study.

### 2.3.1 Multivariate statistical analysis

A Hierarchical Cluster Analysis (HCA) was performed on the 13 relevant physico-chemical parameters, available for the whole set of wells (see 2.2): Temp, pH, EC, Hardness, Cl, Na, $SO_4$, $NH_4$, $NO_3$, $NO_2$, As, Fe, Mn.

To use the mean parameter as a representative value of each abstraction in the multivariate analysis, an outlier analysis was performed to avoid the mean value being subject to unreliable anomalies' influence.

The outlier analysis was carried on the time series of each abstraction for each variable, using the non-parametric interquartile range approach (Tukey, 1972; Wang et al., 2018). The resulting outliers were then validated by the water supplier and all the data subject to non-standard purging, sampling and analysis methods or erroneous data storage were excluded. Subsequently, HCA was carried out on the mean values dataset, as the mean is more representative of the whole time series, including extreme data, compared to the median. HCA was performed using the Ward method (Ward Jr, 1963), based on the Euclidean distance (Cloutier et al., 2008). Data were standardized as z-score (i.e. mean=0 and standard deviation=1).

### 2.3.2 Well vulnerability indexes

The WSP approach for the risk assessment of the whole drinking water supply chain is based on a semi-quantitative approach (Bartram, 2009; Hoshyari et al., 2019; WHO, 2009), which consists in categorizing two parameters (likelihood and severity) and combine them in a risk matrix. As regards groundwater abstractions vulnerability assessment, Schmoll (2006) suggests that the semi-quantitative assessment for pollution in groundwater to occur is, for many settings, the best way to deal with data uncertainty especially in the scope of point sources of pollution.

Therefore, to fit within the semi-quantitative WSP framework, it is here proposed a semi-quantitative approach to tackle well vulnerability, based on the relative categorization of several factors and their successive combination into two vulnerability indexes.

The hydrogeological features and processes that inform the specific well vulnerability index for the studied system were identified based on the resulted hydrogeochemical conceptual model described in Sect. 3.1. Five parameters were identified to be key in determining well vulnerability to natural or anthropogenic pollution: 1) type of aquifer tapped by the shallowest screen of the well (A), 2) water table depth (D), 3) vadose zone permeability (P), 4) natural redox condition (NRC) of the tapped water and 5) groundwater age (GWA) of the tapped water. The A, D and P parameters are hydrogeological features describing the groundwater body tapped by each well, based on the screen depth in relation to the hydrogeological characteristics of the area. The NRC and GWA instead, are based on the hydrochemical characteristics of the tapped water (over a ten-years time span) providing information on the dynamic behavior of each well, including mixing processes associated to multiple screen, pumping effects and gravel pack structure .

Two vulnerability indexes were elaborated as follows:

$$V_{ant} = A + D + P + GWA$$

$$V_{nat} = A + GWA + NRC$$

Where $V_{ant}$ is the vulnerability index to anthropogenic pollution and $V_{nat}$ is the vulnerability index to natural pollution.

To develop semiquantitative indexes, each parameter was categorized, based on the hydrogeological variability of the area, and a numerical scoring was applied, ranging from 1 to 5, where 5 indicates the maximum vulnerability. Table 1 reports categories and associated scores for each of the five parameters composing the well vulnerability indexes.

The scores represent the role of each characteristic in relation to the vulnerability to natural or anthropogenic contaminations. This means that their numerical values take on different values, for natural or anthropogenic pollution, as explained in the next paragraphs.

To compare the risk associated with each well and perform a complete and integrated well vulnerability assessment, values of $V_{ant}$ and $V_{nat}$ have been scaled, so that they both range over a 0-100 interval. Finally, data were categorized into five vulnerability classes: negligible (0-20), low (20-40), moderate (40-60), high (60-80) and extreme (80-100).

*Table 1 - Categories and associated scores for each parameter composing the well vulnerability index. (n.i. = not included; bgs = below ground surface; $Red_{in}$ = initial reducing; $Red_{adv}$ = advanced reducing)*

| | | Vulnerability to anthropogenic pollution | Vulnerability to natural pollution |
|---|---|---|---|
| Aquifer type | unconfined | 5 | 1 |
| | semiconfined | 3 | 3 |
| | confined | 1 | 5 |
| Water table depth | 0-20 m bgs | 5 | n.i. |
| | 20-40 m bgs | 3 | n.i. |
| | >40 m bgs | 1 | n.i. |
| | Not applicable (confined aquifer) | 0 | n.i. |
| Vadose zone permeability | high | 5 | n.i. |
| | medium | 3 | n.i. |
| | low | 1 | n.i. |
| | Not applicable (confined aquifer) | 0 | n.i. |
| Groundwater age | young | 5 | 1 |
| | middle | 3 | 3 |
| | old | 1 | 5 |
| Natural redox conditions | Ox | n.i. | 1 |
| | $Red_{in}$ | n.i. | 2 |
| | Mixed | n.i. | 4 |
| | $Red_{adv}$ | n.i. | 5 |

The type of aquifer tapped by the well is closely related to the aquifer vulnerability and, consequently, to the well vulnerability. For each well, the depth and extension of the first screen were evaluated with respect to the lithostratigraphic data, the geological information of the area, detailed cross-sections and groundwater depth data to identify and classify the tapped groundwater body. Three main aquifer types were considered, as representative of this type of hydrogeological setting: unconfined, semiconfined and confined. Confined aquifers are less vulnerable to anthropogenic pollution (Foster, 1987; Taufiq et al., 2019) but, at the same time, they can be more vulnerable to the natural release of undesirable reduced species, associated with reducing conditions. Consequently, this parameter enters both the natural and anthropogenic vulnerability indexes to natural and anthropogenic pollution (Table 1), but with reverse scoring.

Water table depth is usually associated with vulnerability to anthropogenic pollution. Thicker vadose zone delays the infiltration of pollutants to the saturated zone, increasing the self-purifying capacity of the unsaturated zone (Juntakut et al., 2019; Panda and S, 2019; Truex et al., 2015). For each well, the water table depth expressed in meters below ground surface (bgs), was calculated as the maximum groundwater level (m a.s.l.) from the available piezometric time series, and then associated with one of the three classes: 0-20 m bgs, 20-40 m bgs and >40 m bgs, representative of the study area variability. Water table depth was incorporated only in the vulnerability index to anthropogenic pollution (Table 1). Furthermore, it was considered relevant only within unconfined and semiconfined aquifers.

The average permeability of the vadose zone can influence the vulnerability to anthropogenic pollution. Together with vadose zone thickness, as discussed above, vadose zone permeability determines the vertical infiltration rate of pollutants from the surface (Martin and Koerner, 1984; Rao et al., 2013; Stempvoort et al., 1993). Vadose zone permeability was incorporated only in the vulnerability index to anthropogenic pollution and for unconfined or semiconfined aquifers (Table 1). More specifically, the P was equated with the thickness corresponding to the actual vadose zone for the wells tapping unconfined aquifers, whereas for wells tapping semiconfined aquifers, it was estimated considering the depth from the land surface to the first well screen elevation. Vadose zone permeability was categorized into three classes: high, medium, and low.

The permeability classification of each well, depends on the stratigraphy of the vadose zone. Lithologs were analyzed evaluating the presence and thickness of well-sorted clay layers within the above-mentioned subsurface thickness. Based on the variability in this kind of hydrogeological setting, the high permeability was assigned when no well-sorted clay layers were present; medium permeability was attributed in the presence of well-sorted clay layers with a cumulative thickness smaller than 10 m or poorly-sorted clay layers with variable thickness; low permeability was assigned in the presence of well-sorted clay layers with a cumulative thickness greater than 10 m.

The kind of aquifer, water table depth and vadose zone permeability are considered as essential features in aquifer intrinsic vulnerability to manmade pollution (Wachniew et al., 2016). Particularly, these three parameters correspond to groundwater confinement, overlying strata and depth to groundwater which are the three parameters composing the GOD vulnerability method (Foster, 1987). Furthermore, vadose zone thickness and characteristics are the most relevant parameters in DRASTIC and SINTACS (Dassargues, 2000).

As discussed in 3.2, their role is key also to the well vulnerability assessment, but when it comes to assessing well vulnerability rather than aquifer vulnerability, other features need to be considered, especially when performing a complete risk assessment, including also natural pollution vulnerability. Indeed, in the aquifer vulnerability index-based or statistical methods, the eventuality of mixing between different aquifers or aquitard, or the induced recharge from surface water bodies are not represented, although these are very frequent conditions in well fields, largely affecting the tapped water quality. Insights on the recharge of the tapped water and evidence of mixing processes can be reached through the chemical analyses of the tapped water and their interpretation. An analysis of the chemical composition of the tapped groundwater indeed, can give detailed insight of the dynamic processes related to the design and the status of each specific well.

Here, the chemical information of the tapped water was declined into two parameters, contributing to well vulnerability to natural and anthropogenic vulnerability: natural redox conditions and groundwater age. The adopted parameters are DO, which is easily measurable on the field, and chemical parameters

($NO_3$ and Fe) which are among the chemical parameters with a potability threshold value set by most of the countries worldwide (WHO, 2021).

Natural redox conditions are strictly related to natural pollution by reduced species. Usually, redox conditions in groundwater are classified using threshold concentrations of redox-sensitive species (McMahon and Chapelle, 2008; Parrone et al., 2021; Voutchkova et al., 2021). Natural redox conditions were categorized into four classes: a) oxic (Ox), with DO >2 mg/L; b) initial reducing ($Red_{in}$), where the leading process is denitrification, with DO <2 mg/L, $NO_3$ >1 mg/L and Fe <100 µg/L; c) advanced reducing ($Red_{adv}$), ranging from Mn-/Fe-reducing to methanogenesis, with DO <2 mg/L, $NO_3$ <1 mg /L and Fe >100 µg/L; and d) mixed (Mix) between Ox/$Red_{in}$ and $Red_{adv}$, with $NO_3$ >1 mg/L and Fe >100 µg/L. In the mixed condition, Ox and $Red_{in}$ were not distinguished since they have typically low concentrations of undesirable reduced species (Mn, Fe, As, etc.).

Natural redox conditions entered only into the natural pollution vulnerability index with an increasing scoring from Ox to $Red_{adv}$ (Table 1). However, as explained below, natural redox conditions were also indirectly incorporated into the anthropogenic vulnerability index through the groundwater age.

Groundwater age is directly related to vulnerability (Clark, 2015; Hinsby et al., 2008). Large fractions of young groundwater can be associated with greater vulnerability to anthropogenic pollution than smaller fractions (Kingsbury et al., 2017; Lapworth et al., 2018; Wachniew et al., 2016). On the other hand, older groundwater circulating in confined aquifers is more prone to reducing conditions, thus being more vulnerable to the natural release of undesirable reduced species (Degnan et al., 2020).

The age of the tapped water provides a detailed picture of the dynamic behavior of each well, by representing the characteristics of the tapped aquifer but also all the mixing processes with different recharge components associated with the pumping. Therefore, it can be considered as a comprehensive indicator of all the phenomena associated with the presence of several screens, or with connections among different aquifers or surface water bodies. Groundwater age is usually assessed with isotopic analyses, through specific field campaign and expensive analyses, which make them rarely available to researcher and water suppliers in most of the countries. Therefore, it was here adopted a relative classification of the groundwater age, based on the hydrogeological features and on chemical analyses broadly investigated by water suppliers.

Groundwater age was categorized into 3 qualitative classes (young, middle and old) and the association of each well to a class was based on a combination of hydrogeochemical features considered as proxies of groundwater age: a) aquifer type, b) natural redox conditions and c) mixing processes. Generally, unconfined aquifers have younger groundwater due to their proximity to the land surface (Clark, 2015; Kingsbury et al., 2017). Therefore, wells tapping an unconfined aquifer were classified as young for GWA, whereas wells tapping a confined or semiconfined aquifers were classified from young to old depending on natural redox conditions and mixing processes.

Natural redox conditions of the abstracted groundwater were here considered as a proxy of groundwater age since the ecological succession of terminal electron accepting processes (TEAPs) proceed over time with a hierarchical order (Lovley and Chapelle, 1995), thus, in many hydrogeological settings, younger groundwaters are likely oxic whereas older groundwaters are likely highly reducing (McMahon et al., 2011, 2004; Puckett and Cowdery, 2002). Furthermore, groundwater at the most advanced reduced conditions have been proven to be less affected by anthropogenic pollution, compared to oxic water which is mostly found in more permeable and shallower aquifers (Feng et al., 2022).

Mixing processes during groundwater abstraction can affect the average age of abstracted groundwater. Aside from those mixing processes that generate mixed redox conditions, already incorporated within the redox classification as shown above, some mixing processes can operate with no changes of the redox classes considered in our "simplified" classification. An example of a mixing process without redox state change could be the mixing of younger groundwater under Mn-reducing conditions with an older groundwater fraction under methanogenesis, since both redox states fall under our class "$Red_{adv}$". Another example could be the mixing of younger oxic groundwater recharged from surface water bodies (lakes, rivers, etc.) as the result of pumping, with relatively older groundwater resident in the aquifer under oxic conditions. The presence of mixing processes with no redox class changes was categorized into two classes (yes/no). In general, the attribution of the class was made based on a specific conceptual model for each well. Some practical criteria used for the attribution of class "yes" were: a) identification of a Na-excess likely indicating lake induced recharge in oxic aquifers (see Sect. 3.1), b) Cl >5 mg/L in confined reduced aquifers indicating a likely infiltration of modern (human-impacted) recharge.

Table 2 reports all the possible combinations of aquifer type, natural redox conditions and mixing with no redox class change determining the class of groundwater age. Unconfined aquifers are considered as young, while in semiconfined and confined aquifers the groundwater age class increases together with the TEAP evolution, whereas the mixing phenomena with younger water determine the association of a lower age class.

*Table 2 – Procedural scheme for the attribution of the groundwater qualitative age classes.*

| Parameters combinations | | | Resulting groundwater age class |
|---|---|---|---|
| Aquifer type | Natural redox conditions | Mixing with no redox class change | |
| Unconfined | All classes | All classes | young |
| Semiconfined | Ox | no/yes | young |
| Semiconfined | $Red_{in}$ | no | middle |
| Semiconfined | $Red_{in}$ | yes | young |
| Semiconfined | Mix | - | young |
| Semiconfined | $Red_{adv}$ | no | middle |
| Semiconfined | $Red_{adv}$ | yes | young |
| Confined | Ox | no/yes | young |
| Confined | $Red_{in}$ | no | middle |
| Confined | $Red_{in}$ | yes | young |
| Confined | Mix | - | young |
| Confined | $Red_{adv}$ | no | old |
| Confined | $Red_{adv}$ | yes | middle |

Groundwater age composes both vulnerability indexes to natural and anthropogenic pollution with reverse scoring (Table 1).

### 2.3.3 Well vulnerability validation

The vulnerability classification of each well, obtained through the indexes described above, was tested using groundwater quality monitoring data. This analysis aimed to determine if the actually polluted wells would fall, as expected, within the most vulnerable classes. With regards to the vulnerability to anthropogenic pollution, two binary variables were created. The first variable indicated whether the well had at least one sample exceeding the regulatory limit for one of the synthetic compounds monitored (pesticides and their breakdown products, VOCs and halogenated organic compounds, BTEX.). The second variable indicated whether the well had at least two samples with a synthetic compound ≥LOD.

As for the vulnerability to natural pollution, the presence of reducing conditions in deep older groundwater leads to high concentrations of undesired species such as As, Mn and $NH_4$. Therefore, in order to verify the occurrence of natural pollution in the tapped groundwater, three binary variables were created indicating, respectively, the exceedance of regulatory limits for As, Mn and $NH_4$, in terms of mean concentration over the available time series. Fe was excluded since it was used as an indicator species in the redox classification for vulnerability calculations.

To verify whether the distribution of the polluted wells was actually associated with the vulnerability classes, chi-square and Fisher tests were performed, through SPSS statistics (Kim, 2017).

# 3 Results and discussion

## 3.1 Hydrogeochemical conceptual model

The HCA resulted in the identification of 17 clusters. The dendrogram is shown in Fig. 3, together with the clusters' maps, categorized by the type of abstraction. In Table S1 mean concentrations and standard deviation of each cluster are reported.

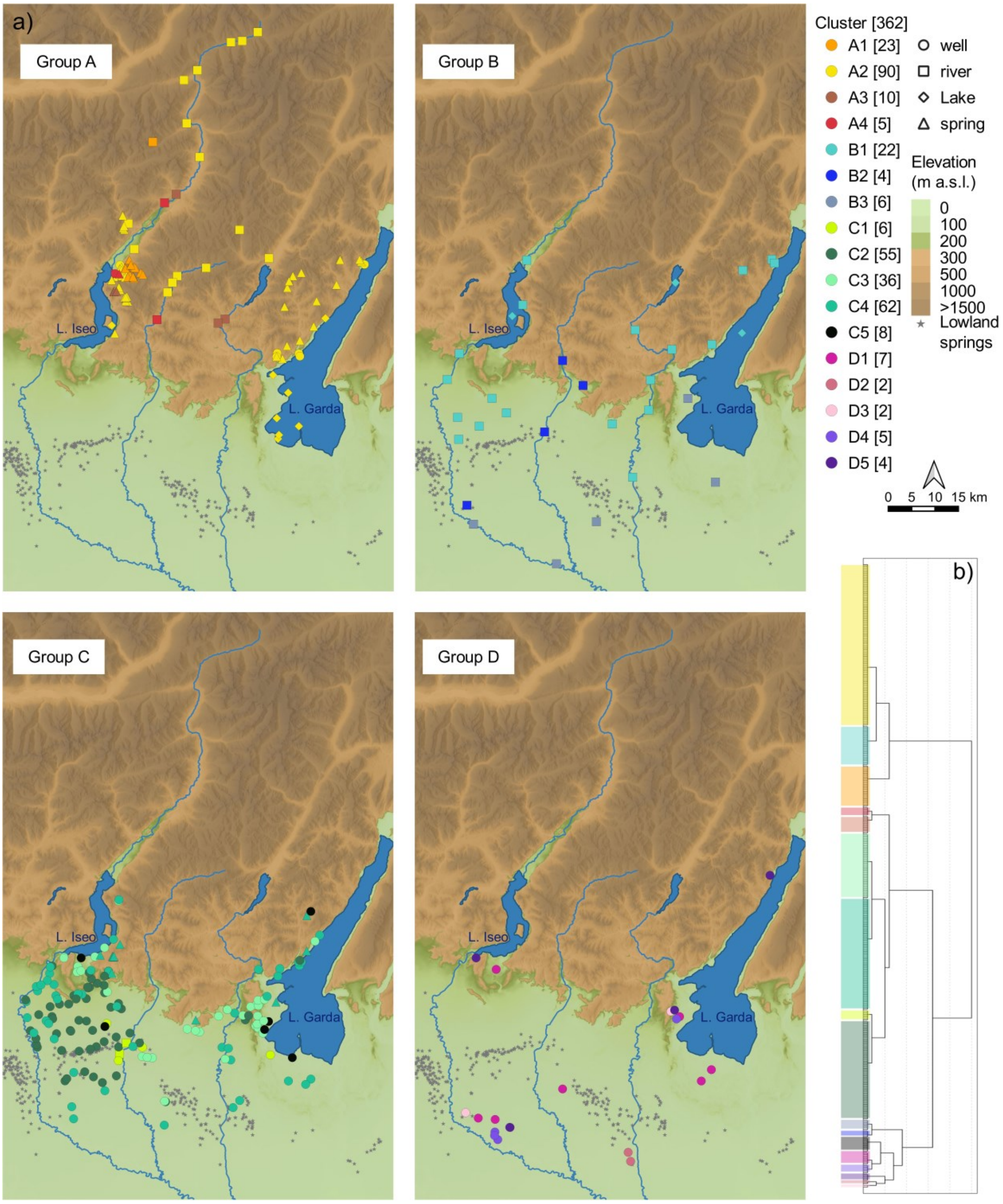


*Figure 3 – Hierarchical cluster analysis results: a) spatial distribution of the clusters (number of abstraction per cluster in sqare brackets), in the four-group classification and b) dendrogram.*

From the chemical and spatial interpretation of the clusters, with respect to the type of abstraction, the 17 identified clusters were grouped into four macro groups. The concentration box plots of the considered chemical variables are shown in Fig. 4 for each cluster; the clusters were grouped according to the four-group categorization. The mean concentrations and standard deviations for the four groups are reported in Table S2.

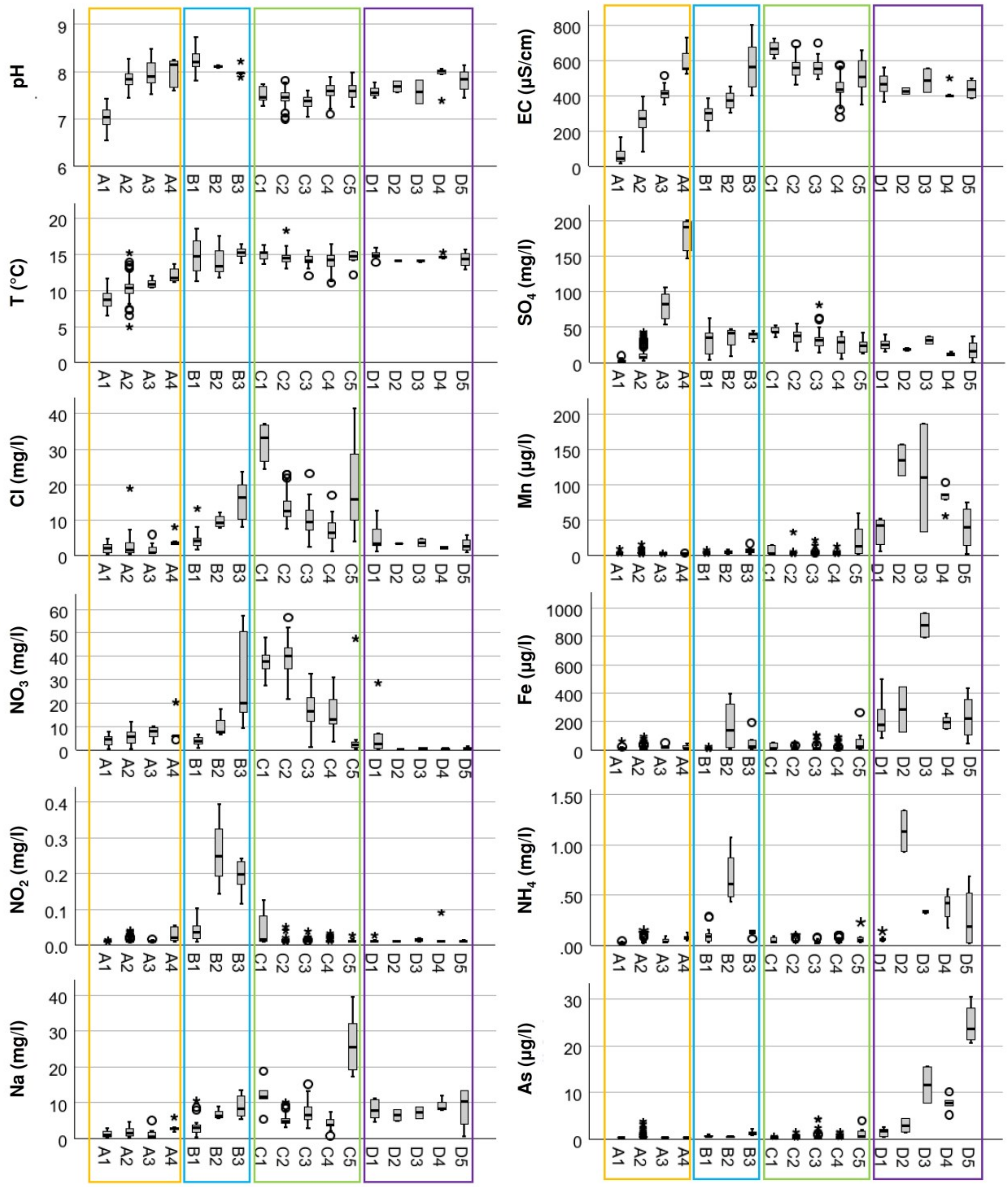


*Figure 4 – Concentration boxplots for each cluster, according to the 4-groups interpretation.*

Group A (four clusters, A1-4, yellow box in Fig. 4, map in Fig.2) represents Alpine waters, including groundwater, springs, rivers, and deep lake waters. These are generally colder waters (average Temp of 10.2 °C), with faster circulation and shorter residence times in the subsurface, evident from lower salinity (average EC of 249 µS/cm) and pH (average of 7.7). Anthropogenic impacts are weak (average Cl and $NO_3$ are 2.5 and 5.5 mg/L, respectively). Clusters A3 and A4 highlight a peculiar situation, grouping wells and springs with higher $SO_4$ (up to 200 mg/L) attributable to hydrogeochemical processes, such as the oxidation of pyrites or dissolution of gypsum or anhydrites.

Group B (three clusters, B1-3, blue box in Fig. 4, map in Fig.2) represents surface waters in the Po Plain area: river, stream, irrigation channel and shallow lake waters. Group B represents warmer waters (average Temp of 14.7 °C) with a higher pH (average of 8.2) with respect to Group A. Along their course, these streams suffer from anthropogenic impacts: B2 and B3 show increasingly higher values of Cl, $NO_3$ and EC (up to 23.6 mg/L, 57.4 mg/L, and 806 µS/cm, respectively) compared to the upstream clusters A2 and B1. These higher pollution levels in B2 and B3 can originate from point sources, surface runoff over impacted soils and/or gaining of impacted groundwaters.

The higher nitrite in B2 and B3 (average of 0.2 mg/L) indicates the operation of nitrification, triggered by inputs of ammonium of both anthropogenic and natural origin (gaining of naturally high ammonium groundwaters in the lower plain).

Group C (five clusters, C1-5, green box in Fig. 4, map in Fig.2) represents oxic/$NO_3$-reducing waters mainly in the higher Po Plain. This group includes plain and moraine groundwater and piedmont spring water with longer circulation paths than Group A springs. C1 and C2 represent the well-known diffuse nitrate pollution affecting groundwater in the higher Po plain (average $NO_3$ of 38.8 mg/L), with peaks in Cl (up to 31.8 mg/L) in C1.

C3 and C4 show lower $NO_3$ (average of 16.1 mg/L) but EC and Cl are still higher than group A and B (with peaks up to 23 mg/L), which is symptomatic of stronger human impacts. For higher plain groundwater falling in C3 and C4, the lower $NO_3$ can be due to a dilution effect generated by the low-$NO_3$ water used for irrigation and quickly recharging the aquifer (Rotiroti et al., 2019).

In broader terms, these results show, as expected, that wells tapping the highly permeable and unconfined aquifer of the higher plain are more vulnerable to anthropogenic pollution. A less obvious outcome is the finding of oxic or polluted groundwaters (C2, C3, C4) abstracted from semiconfined or confined aquifers in the lower plain. This finding reveals that a considerable fraction of younger and oxic water, thus more vulnerable to anthropogenic pollution, can recharge the wells even if they tap confined or semiconfined aquifers. It pinpoints that the mere analysis of the hydrogeological settings surrounding the well is not sufficient for assessing abstracted groundwater quality and its vulnerability. In addition, an estimate of the abstracted groundwater age is necessary for a reliable categorization.

C5 is characterized by high Na concentrations (up to 39.5 mg/L). In terms of Cl and $NO_3$, data appear scattered, ranging from 3.1 to 41.6 and from <LOD to 47.5 mg/L, respectively. Different cases can explain these results and are discussed below. The first case involves wells tapping oxic groundwaters in the higher plain and moraines in which indicators of anthropogenic impacts are found, such as Cl and $NO_3$, suggesting that the higher Na can be related to the same anthropogenic source (e.g., road de-icing salts, septic effluents, etc.). The second case involves higher plain wells, tapping reduced, and likely older, groundwater from deep confined aquifers. Here, Na is not accompanied by other indicators of anthropogenic impact. Therefore, the hypothesis of a natural release becomes plausible through the process of natural groundwater softening: a recharge of Ca-$HCO_3$ groundwater into the deeper part of the aquifer hosting Na-clays can lead to the release of Na through cation exchange (Boyle and Chagnon, 1995). The third case involves wells close to the Subalpine lakes, with low Cl concentrations (i.e., a Na-excess). Here, a component of ammonium-rich recharge induced by the pumping from deep lake water/sediments, which are likely anoxic, determines a release of Na from clays due to the greater affinity of ammonium with the cation exchanger compared to Na (Clark, 2015). This fraction of induced recharge from lake water constitutes a younger and more vulnerable recharge component to these wells.

Group D (five clusters, D1-5, purple box in Fig. 4, map in Fig.2) represents reduced groundwater: lower plain and moraine wells tapping confined aquifers with older groundwater at lower redox states.

In cluster D1, Fe and Mn are higher than groups A, B and C (up to 499 and 51.7 µg/L, exceeding the regulatory limit of 200 and 50 µg/L, respectively), but $NO_3$ is scattered, ranging between <LOD and

28.6 mg/L. The combination of high Fe/Mn and $NO_3$ indicates that some well tap a mixture of lower redox state groundwaters and higher redox state groundwater, implying a mixing of older and younger fractions of groundwater.

Recent studies highlighted that wells tapping fossil (thousands of years aged) groundwater often contain significant amounts of younger water, with a fraction of their age distributions younger than ∼100 years old (Jasechko et al., 2017; Kirchner and Jasechko, 2016) mostly induced by the pumping itself (Zinn and Konikow, 2007).

The presence of mixing results in peculiar conditions in relation to vulnerability assessment, since the younger fraction is more vulnerable to potential anthropogenic impacts while the older water is prone to natural reduced polluion. On the other hand, the dilution of the older reduced water with younger oxic water can lower the concentrations of reduced species.

Several well settings were identified to determine the mixing of groundwaters with different predominant TEAP, which are discussed below. The first setting is a multi-screen (or multi-column) well tapping different aquifers having different redox states. The second setting is a mono-screen well tapping both an oxic aquifer layer and an aquitard layer with reducing conditions. A third setting is a well with inadequate/damaged bentonite/concreate sealings connecting different aquifers with different redox states.

Cluster D2 shows generally high concentrations of Fe and Mn (average of 284.7 and 134.9 µg/L), indicating the operation of Mn and Fe oxides reduction, but relatively low As (average of 3 µg/L). Conversely, $NH_4$ is at especially high levels (up to 1.3 mg/L). Decoupled As and $NH_4$, an uncommon feature for the lower Po Plain aquifers (Rotiroti et al., 2021), may indicates that $NH_4$ has an anthropogenic input for this cluster. According to this explanation, it follows that a younger and human-impacted fraction of recharge mixed in the well with older groundwater.

D3 has the highest Fe concentrations (average of 878.3 µg/L) and higher As (average of 11.7 µg/L) with respect to D2. D4 has lower Fe, $SO_4$ and As than D3 (average of 195 µg/L, 12.22 mg/l, and 7.7 µg/L respectively), likely indicating the operation of sulfate reduction, which may imply the precipitation of iron sulfides, leading to lower Fe, $SO_4$ and As (Rotiroti et al., 2021). D5 has the highest As (up to 30.5 μg/L).

## 3.2 Drinking water supply well vulnerability

The spatial distribution of the different classes of each parameter composing the vulnerability indexes are represented in Fig. 5. Out of the 181 wells, 30 wells have missing stratigraphic or groundwater head data, which prevented their classification. Therefore, the vulnerability indexes were calculated for only 151 wells.

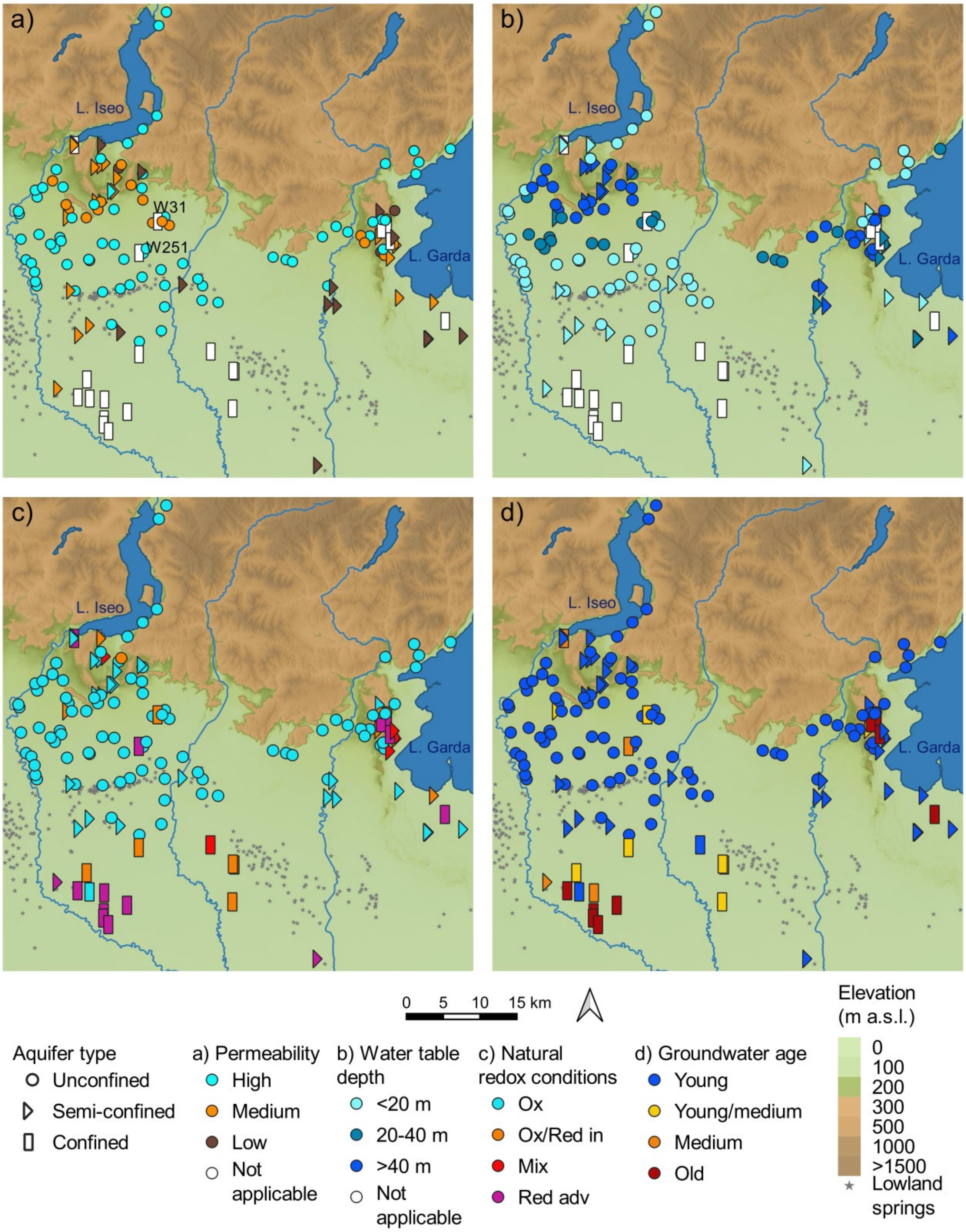


*Figure 5 – Representation of the features considered for the calculation of the vulnerability indexes. Shape indicates the kind aquifer type, color-codes indicate: a) permeability of the vadose zone, b) water table depth, c) natural redox conditions and d) groundwater age.*

For the wells having missing DO data, the distinction between Ox and $Red_{in}$ was based on the conceptual model of the area and on the concentration of the other redox sensitive species, which are available for the whole dataset. In a few cases, it was impossible to discriminate between Ox and $Red_{in}$ based on these characteristics: those cases were reported as Ox/$Red_{in}$. In the successive step of $V_{ant}$ and $V_{nat}$ calculation, they were treated as Ox, the most vulnerable class and therefore the most conservative option for the anthropogenic pollution, which involves a larger amount of compunds. The spatial distribution of the type of tapped aquifer (Fig. 5) and vadose zone permeability (Fig. 5a) highlight: a) the hydrogeological variability within the morainic hills, reflecting the greater complexity and heterogeneity of these areas, and b) a greater homogeneity in the Po Plain aquifer, showing a gradual change from the unconfined aquifer with higher permeability in the higher plain to confined aquifers with lower permeabilities in the lower plain. Two anomalies are evident in the higher plain, where two deep wells tap an underlying confined aquifer (W31 and W251, Fig. 5a). This classification is also supported by the natural redox conditions that differ from the other higher plain wells (Fig. 5c).

As regards water table depth (Fig. 5b), it appears that a more homogeneous situation exists in the morainic hills surrounding Lake Iseo, where there are the thickest vadose zones, except for the wells closest to the lake, while in the plain there is a gradual decrease from the north to south.

Regarding the natural redox conditions (Fig. 5c), most of the wells show oxic conditions, especially in the moraines and in the higher/middle plain. A few semi-confined and confined wells in these areas fall in the Mix or $Red_{adv}$ classes. In the lower plain instead, $Red_{adv}$ class is predominant. A few wells in the moraine and one well in the plain show the Mix conditions.

Groundwater age has a similar trend to the redox condition, being directly linked to it, with a general prevalence of the young class, and a predominance of older water in the lower plain, with sporadic cases in the morainic hills areas. This configuration agrees with the general north to south groundwater flow direction.

To highlight the variability of possibilities related to hydrogeological and wells' structures, Fig. S1 shows the variability of each parameter for each well over a schematic cross-section: the first screen of each well is color-coded based on the type of the tapped aquifer, and the other indicators show the classification of the parameters contributing to natural or anthropogenic vulnerability. It emerges that the variability of conditions could not be described by a single aquifer vulnerability. Indeed, different wells tap different aquifers, often more than one, and the extension of the aquiclude separating the aquifers can vary locally, especially if considering also the W-E variability . Furthermore, it emerges from Fig. S1 how even in wells tapping confined and deep aquifers, the chemical data can highlight the presence of oxic and young water, plausibly associable to the absence of sealings and the consequent connection with the shallower aquifer determined by the well itself. This condition can prevent the advancing of the redox processes to the undesirable stages but at the same time make the well more vulnerable to anthropogenic pollution from shallower aquifers.

Well vulnerability to anthropogenic pollution (Fig.6a) is highest in the northern area, due to highly permeable unconfined aquifers, hosting young water. Lower classes are also well represented in the moraines and in the middle plain due to thicker and/or less permeable vadose zones. Vulnerability varies between low and negligible classes among the confined wells, the latter determined by tapping older groundwater. The classification of well vulnerability to natural pollution (Fig.6b) shows an opposite trend, with the highest classes primarily grouped in the lower plain. The variability among moderate, high, and extreme values in relation to confined wells reflects the groundwater age and redox classification distributions, with a southernmost group in the highest vulnerability class and several local cases of wells tapping deep aquifers in the higher plain and moraines.

In Fig.6c and 6d a subset of wells, color-coded by their resulting vulnerability is shown over a schematic cross-section of the area.

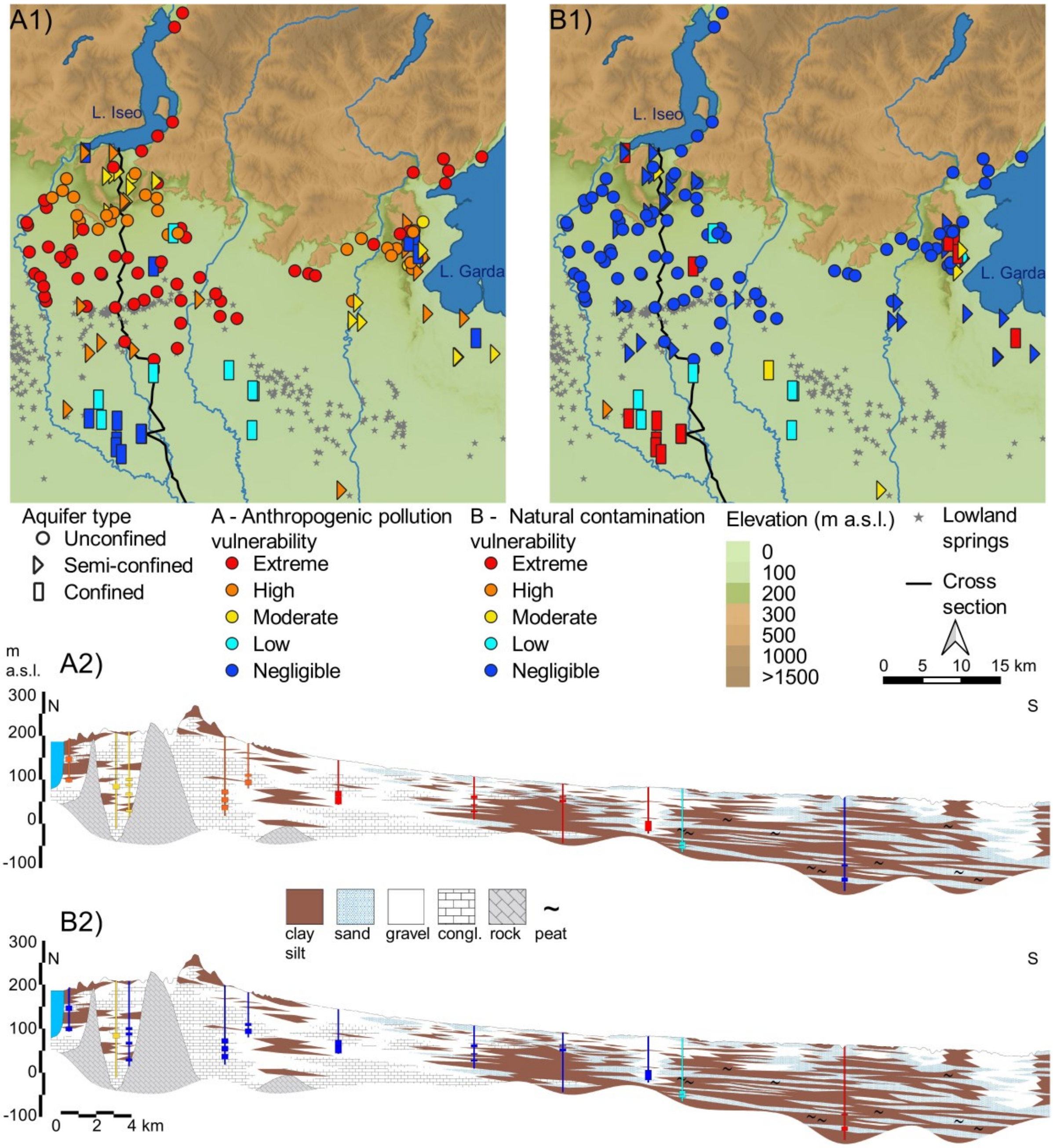


*Figure 6 – Spatial distribution of resulting vulnerability classes: a1) anthropogenic pollution vulnerability and b1) natural pollution vulnerability. Well vulnerability to anthropogenic pollution (a2) and natural pollution (b2) over a schematic cross-section.*

Results of the testing of the well vulnerability classification against pollution levels are shown in Fig.7 through histograms.

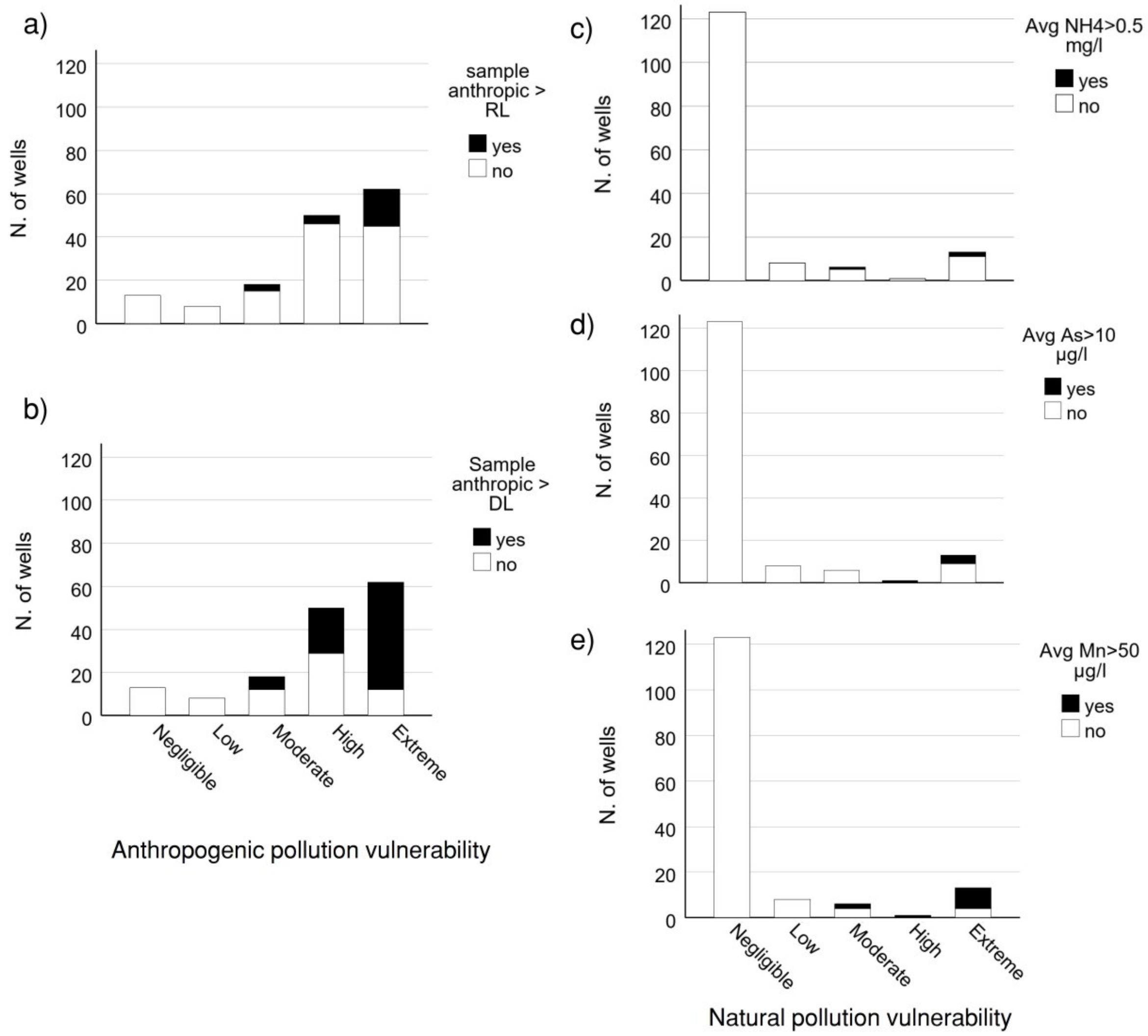


*Figure 7 – Validation of vulnerability indexes: anthropogenic pollution vulnerability compared to a) the presence of n>0 samples exceeding regulatory limit for anthropogenic compounds and b) the presence of n>1 samples with detected anthropogenic compounds; natural pollution vulnerability indexes histogram compared to the wells average exceedance of regulatory limit for c) $NH_4$, d) As and e) Mn.*

As for the well vulnerability to anthropogenic pollution, Fig. 7a shows wells having at least one sample exceeding the regulatory limit for synthetic compounds in their ten years' time series. Most contaminated wells fall in the extreme class, while 4 and 3 wells in the high and moderate classes. Similarly, Fig. 7b shows the vulnerability classification of the wells having at least two samples in which a synthetic compound was detected in their time series. Also in this case, most wells fall in the class extreme, and lower percentages in the high and moderate class, whereas no cases fall in the two lowest classes.

Regarding the well vulnerability to natural pollution, Fig. 7c-e highlight those wells exceeding the regulatory limit for the reduced species $NH_4$, As, and Mn. Also in this case, no wells fall in the lower classes, and most of the cases fall in the classes from moderate to extreme.

To validate the hypothesis that the polluted wells were not randomly distributed among the vulnerability classes, chi-square tests were performed. In each case, the test resulted significant at a 0.05 significance level. This means that the distribution of the polluted wells between the different vulnerability classes is not random but associated with the vulnerability classes. Chi-square results and the cross tables between vulnerabilities and pollution variable are reported in Table S3 – S11, with counts and expected counts (i.e., the count that would result if the variables were not associated). These results indicate that the proposed methodological approach led to a vulnerability classification that is echoed in the actual situation of natural and anthropogenic pollution affecting the study area.

## 3.3 Methodological approach pros and cons

The findings presented here demonstrate the robustness of the proposed approach for classification of well vulnerability to both, natural and anthropogenic pollution.

The integrated assessment of vulnerability to natural and anthropogenic pollution represents the main strength of this approach. In the scope of WSP, to guarantee safe water, both aspects are relevant, and it becomes essential to evaluate them both, on a comparable scale which can allow performing a complete chemical risk assessment of the well field.

Results pinpoint that the type of aquifer, together with water table depth and vadose zone permeability, are not sufficient alone to assess well vulnerability, since the specific wells structures and the dynamic conditions determined by the pumping introduce more variability. Therefore, there is a need to consider the specificity of the water tapped by each well through a classification of its age, which gives direct insight into vulnerability. Vulnerability is sometimes related to the specific structural condition of the well and to the pumping effects, factors that can dominate the water quality. The most appropriate way to determine groundwater age, or the presence of a young water fraction, would be through isotopic analysis. Since isotopic analysis is not part of water suppliers' routine water quality monitoring, they are rarely available. The well-known relation between the TEAPs progression and groundwater age were here exploited in this approach.

This work does not aim at proposing the best and most accurate possible way to assess well vulnerability, which would most likely require isotopic studies and in-depth knowledge of the recharge components of the water tapped by every single well. This work aims instead at developing a methodological approach to tackle the well vulnerability assessment over large wells fields, based on the data that are typically available to water suppliers and researchers worldwide, being regulated in most of the drinking water regulations (WHO, 2021), in order to favour and facilitate the spreading of the risk assessment approach (e.g. WSP) to guarantee safe water quality.

The proposed approach is based on water quality data, widely monitored by water suppliers. The use of widely available data is an advantage in terms of costs and time consumption, but it can constitute a possible limitation. This approach indeed, relies on the dataset quality which itself is susceptible to sampling, analytical and archiving errors more common in datasets not meant for research purposes. Furthermore, threshold concentrations of reduced species were used to assess the natural redox conditions, but errors can arise when anthropogenic pressure alters the redox condition. In these cases, the natural redox state should be deduced from the conceptual model rather than calculated from the available data.

Being based on a relative categorization of hydrogeochemical variables, the vulnerability indexes were tailored to the settings of the considered region (e.g. classes of the vadose zone permeability or water table depth) which makes it directly applicable to similar regions but, more generally, it would need to be adapted for different geological settings in different parts of the world. The replicability of this work lies mainly in the workflow (Fig. 2): from the conceptual model, to the identification of the main pollution sources, and the identification and categorization of the relevant processes influencing the vulnerabilities to the different pollution sources.

The need to categorize continuous variables into classes by ranges, introduces a certain degree of subjectiveness, which is a limitation of this approach. On the other hand, subjectiveness in this case can become an advantage when it comes to adapting the approach to the scientifically developed conceptual model of different hydrogeological regions. Designing the classes based on the hydrologic settings of the considered territory, allows for a more effective representation of the wells' variability. Indeed, using a single, valid worldwide, classification (e.g. for the permeability classification or water table depth) could result in the entire well field falling into a single class, or the presence of empty classes, preventing an effective ranking of the wells, which is the aim of the risk assessment for water suppliers.

Furthermore, in this study natural pollution was associated only with reduced species arising from the degradation of natural organic matter, which is the only relevant known source of natural water-quality degradation in the study area. Therefore, to perform a risk assessment in different areas, it may also be necessary to consider additional hazardous events related to different geologic sources of pollution (e.g. natural fluoride release in alkaline waters).

Opposed to a general aquifer vulnerability approach, the well vulnerability study with the proposed approach allows vulnerability to be analysed systematically, for wells tapping different aquifer types.

Mendizabal and Stuyfzand (2011) emphasize that a well (field) requires a dynamic vulnerability index, covering both aquifer and well properties in order to be able to evolve with well field adaptation measures, associating the last to the fraction of young water in the tapped groundwater. In the proposed method, this principle is respected by integrating hydrogeological aspects with chemical information linked to groundwater age.

## 3.4 Well vulnerability in the context of Water Safety Plan

To better contextualize the proposed well vulnerability index, it is necessary to describe the evaluation of risk for drinking water supplies under the WSP framework and the method that is going to be applied by the water supplier (out of the scope of this work).

According to the WSP guidelines (Bartram, 2009) the risk associated with each hazardous event is given as the multiplication of likelihood by severity. Severity (S) will be categorized through a numerical scoring ranging from 1 to 5, that ranks each pollutant by its potential adverse effects on human health (e.g., the score 5 attributed to microbiological pollutants, such as *Escherichia coli*, the score 4 to chemical hazards such as heavy metals, pesticides, etc., the score 3 to species such as Fe, $SO_4$, etc., and so on). For groundwater abstractions, the likelihood is associated with the pollution potential (Schmoll et al., 2006), given as the multiplication of vulnerability by pollution load. Pollution load (L) of each pollutant will be assessed categorizing the 95$^{th}$ percentile of measured concentrations/values on a 5 years' time span into 5 classes, from below the LOD (score 1) to above the regulatory limit (score 5). Furthermore, for the assessment of the risk to anthropogenic pollution, the calculation of pollution potential will be implemented adding a parameter related to type of land-use and human impact in the wellhead protection zone (WPZ). The WPZ will be categorized on the basis of: a) the criterion used for calculating the wellhead protection zone, b) the land-use within the wellhead protection zones, c) potentially impacting human activities within the wellhead protection zone, and d) wellhead sealing. In summary, the risk for groundwater abstraction will be assessed as follows:

$$R_{ant} = S \times V_{ant} \times L \times WPZ$$

$$R_{nat} = S \times V_{nat} \times L$$

Where $R_{ant}$ is the risk of hazardous events related to anthropogenic pollution, $R_{nat}$ is the risk of hazardous events related to natural pollution.

# 4 Conclusions

This work proposes a methodological approach for well vulnerability assessment in the scope of natural and anthropogenic pollution, using an index-based method.

This method consists in 1) elaborate a conceptual model of the area, 2) identify and 3) categorize the main processes influencing the vulnerability of the wells to a pollution and 4) perform a well-specific analysis to classify each well according to the identified parameters.

While the specific indexes elaborated in this work have a more regional relevance and can therefore be directly applied in northern Italy or different areas with similar structures, the proposed general approach and workflow can be applied worldwide to perform a well-specific vulnerability analysis in different regions.

The findings demonstrate that a reliable vulnerability assessment can be performed, even in cases where groundwater dating by isotopic analysis, and detailed information on wellhead protection zones are not available.

Well construction, lithostratigraphic and hydrodynamic data were used to identify the groundwater aquifer tapped by each well and assess its hydrogeological properties. Data from routine quality monitoring were exploited to assess the natural redox conditions and identify the presence of mixing phenomena associated to multiple screens or pumping-induced processes. These data are usually widely available to water suppliers in the scope of routine monitoring, often not exploited, which makes this work widely reproducible and cost-effective, as it does not require specific field campaigns or analysis, thus improving the knowledge of the system and water quality managing for human consumption.

Results highlight the importance of shifting the attention from aquifer vulnerability to well vulnerability, since the quality of the tapped groundwater is subjected to factors that go beyond the hydrogeology of the supplying aquifer. Indeed, the wells' dynamic conditions and structural characteristics determine the presence of fractions of water recharge in the wells with different ages and, therefore, different vulnerabilities, which can only be revealed by the chemical characteristics of the tapped water.

Furthermore, this integrated approach allows for a comparative analysis of natural and anthropogenic vulnerabilities, lending helpful support to the monitoring and management of water supply systems.

# Appendix A: Supporting Information

Supporting information to this article can be found online at ...

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## Authors Contributions

**Chiara Zanotti**: Conceptualization, Methodology, Data Curation, Formal analysis, Visualization, Writing - Original Draft, Project administration. **Marco Rotiroti**: Conceptualization, Methodology, Formal analysis, Writing - Original Draft, supervision, Funding acquisition. **Mariachiara Caschetto:** Conceptualization, Formal analysis, Writing - Review & Editing. **Agnese Redaelli:** Formal analysis, visualization. **Sonia Bozza:** Investigation, Resources**. Michela Biasibetti:** Investigation, Resources. **Laura Mostarda:** Investigation, Resources. **Letizia Fumagalli**: Methodology, Formal analysis, Visualization, Writing - Review & Editing, Supervision. **Tullia Bonomi**: Conceptualization, Resources, Writing - Review & Editing, Supervision, Funding acquisition, Project administration.

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