Assessment of groundwater contamination in an agricultural peri-urban area (NW Portugal): an integrated approach

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Abstract The excessive use of pesticides and fertilisers in agriculture has generated a decrease in groundwater and surface water quality in many regions of the EU, consti- tuting a hazard for human health and the environment. Besides, on-site sewage disposal is an important source of groundwater contamination in urban and peri-urban areas. The assessment of groundwater vulnerability to contami- nation is an important tool to fulfil the demands of EU Directives. The purpose of this study is to assess the groundwater vulnerability to contamination related mainly to agricultural activities in a peri-urban area (Vila do Conde, NW Portugal). The hydrogeological framework is characterised mainly by fissured granitic basement and sedimentary cover. Water samples were collected and analysed for temperature, pH, electrical conductivity, chloride, phosphate, nitrate and nitrite. An evaluation of groundwater vulnerability to contamination was applied (*GOD-S*, *Pesticide DRASTIC-Fm*, *SINTACS* and *SI*) and the potential nitrate contamination risk was assessed, both on a hydrogeological GIS-based mapping. A principal component analysis was performed to characterised pat- terns of relationship among groundwater contamination, vulnerability, and the hydrogeological setting assessed. Levels of nitrate above legislation limits were detected in 75 % of the samples analysed. Alluvia units showed the highest nitrate concentrations and also the highest vulner- ability and risk. Nitrate contamination is a serious problem affecting groundwater, particularly shallow aquifers, especially due to agriculture activities, livestock and cesspools. GIS-based cartography provided an accurate way to improve knowledge on water circulation models and global functioning of local aquifer systems. Finally, this study highlights the adequacy of an integrated approach, combining hydrogeochemical data, vulnerability assessments and multivariate analysis, to understand groundwater processes in peri-urban areas.

Keywords Groundwater quality · Agricultural activity · Vulnerability · Urban hydrology · NW Portugal

Introduction

Groundwater quality and agriculture interactions occurring in hydrological systems are complex and manifold. Agri- cultural soils in peri-urban areas are important for food supply to the growing city population. However, ground- water contamination is increasing as a result of a significant intensification in agricultural production.

During the last 50 years there has been an enormous rise in food production in many countries through the increased use of irrigation. Much of this irrigation water has been drawn from groundwater as people realised the advantages to increased productivity of timely irrigation and security of application (Morris et al. 2003; Gleeson et al. 2010). Most agricultural land uses have provided major sources of diffuse groundwater contamination since the introduction of mechanisation and use of fertilisers (Capri et al. 2009). In particular, the past decades have led to an increasing use of fertilisers and pesticides, most of them with high con- centrations of nitrogen and phosphorus (e.g. Rodvang and Simpkins 2001; Eickhout et al. 2006; Candela et al. 2008), that can contribute in the long term to groundwater pollu- tion (Razowska-Jaworek and Sadurski 2005).

Nitrogen fertilisers are applied extensively in agriculture to increase crop production, but excess nitrogen supplies can cause air, soil, and water contamination. Groundwater and surface water quality degradation often depends on the use of nitrogen fertilisers. In recent years, the use of residues has increased, especially livestock residues (liquid and semi- liquid manure), leaching towards the subsoil through rainfall or irrigation. Direct discharges of nitrogen compounds from on-site sanitation and from sewer effluent also exacerbate the problem. Moreover, the contamination of drinking water supplies can pose immediate risks to human health (e.g., Morris et al. 2003; Corniello et al. 2007; Di Lorenzo et al. 2012; Wick et al. 2012; Esmaeili et al. 2014).

Nitrate (NO_3^-) is very soluble and readily leaches to groundwater or drainage tiles when fertiliser or manure application rates are greater than plant nutrient needs (e.g., Rodvang and Simpkins 2001; Jalali 2011; Cheong et al. 2012; Esmaeili et al. 2014). Phosphorus is the principal limiting nutrient in fresh waters and in excess it is responsible for anthropogenic eutrophication. Phosphorus surpluses tend to be greatest in areas with a high density of livestock operations (Rodvang and Simpkins 2001).

In the European Union (EU), the Nitrates Directive 91/676/EEC (OJEC [Official Journal of the European Communities] 1991) was drawn up with the specific purpose to reduce water contamination caused by nitrates from agricultural sources and to prevent this contamination. EU member states had, among other actions, to identify waters affected by nitrate contamination and to designate Nitrate Vulnerable Zones (NVZs) (Stigter et al. 2006, 2011). Within this context it is important to note that groundwater and surface water are a single and global resource (Winter et al. 1998; Sophocleous 2002). The fissured bedrock and soil media properties are significantly important to the hydraulic flow path dynamics. Also, the shallow aquifers are often connected to surface water becoming more exposed to contamination sources. Adding to this, the small-scale features between unsaturated and the saturated zones have a key influence on the behaviour of hydrological systems. Hence, groundwater vulnerability to contamination is an intrinsic relative, non-measurable, dimensionless property of a groundwater system that depends on its sensitivity to human and/or natural impacts (e.g., Foster 1990; Vrba and Zap- orozec 1994; Vrba and Lipponen 2007). Moreover, the assessment of groundwater vulnerability is an important basis to accomplish the demands of the EU Water Frame- work Directive 2000/60/EC (OJEU [Official Journal of the European Union] 2000) and EU Groundwater Directive 2006/118/EC (OJEU [Official Journal of the European Union] 2006).

The main objectives of this study were:

1. To detect and assess contamination of groundwater by nitrate and chloride in a peri-urban area (Vila do Conde, Porto metropolitan region, NW Portugal) embedded in a context of a Nitrate Vulnerable Zone;
2. To evaluate groundwater vulnerability to nitrate con- tamination in relation to the peri-urban hydrogeolog- ical setting, taking advantage of GIS-based mapping for management purposes;
3. To improve knowledge of groundwater processes in such areas and their importance to the design of the hydro- geological conceptual model and an integrated urban water management in complex hydrogeological systems.

Study area: hydrogeological setting

Vila do Conde peri-urban area is located in the Porto metropolitan region (NW of Portugal), to the South of Ave River and close to the Atlantic Ocean (Fig. 1). Vila do Conde is a municipality with a total area of 149.31 km^2 and 79,390 inhabitants (INE—Instituto Nacional de

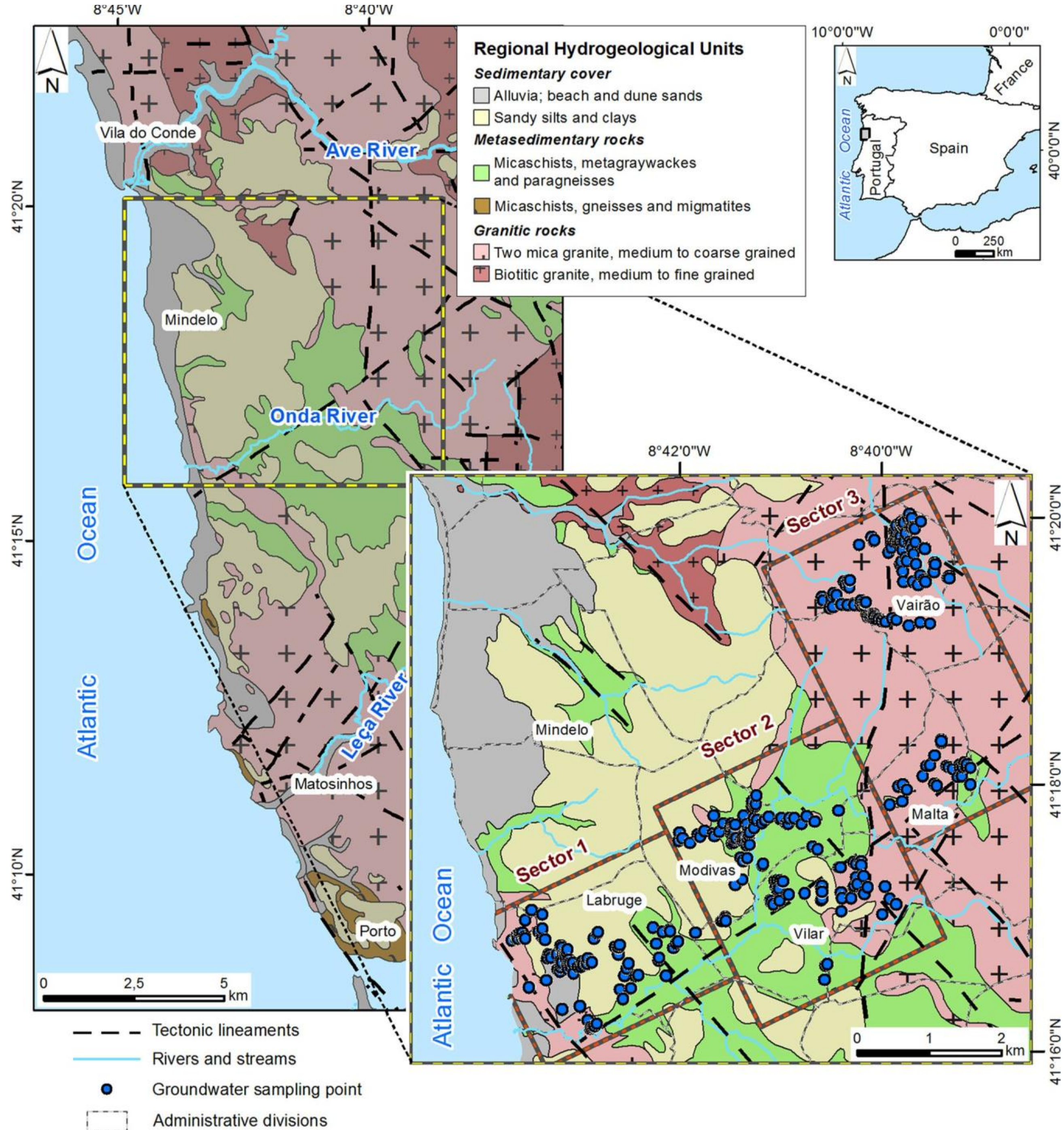


Fig. 1 Regional hydrogeological setting from Vila do Conde peri- urban area (cf. Table 1), Porto metropolitan region, NW Portugal (geological background updated from Carr´ıngton da Costa and Teixeira 1957; Teixeira and Medeiros 1965; Pereira et al. 1989; Chamine´ et al. 2003; hydrogeological framework adapted from Pedrosa 1999; Afonso et al. 2004; Carvalho 2006; Afonso 2011). Study sites (*Sectors 1, 2 and 3*) are shown in the lower right corner of the figure

Estat´ıstica 2011). This region has an Atlantic mild tem- perate climate, with a mean annual precipitation around 1,200 mm and a mean annual air temperature of 14 °C (Afonso et al. 2007; Afonso 2011). Groundwater is the fundamental source of fresh water supply, either for drinking, domestic use or agricultural practices within the region. Most of the population does not have public water supply and sanitation systems and depends on agricultural

Table 1 Regional hydrogeological units (cf. Fig. 1) and related features in the Vila do Conde area, Porto urban region (updated from Pedrosa 1999; Carvalho et al. 2005, 2007; Carvalho 2006; Afonso et al. 2007; Afonso 2011)

Hydrogeological groups	Sedimentary cover		Metasedimentary rocks		Granitic rocks	
Regional hydrogeological units	Alluvia; beach and dune sands (ABD)	Sandy silts and clays (SC)	Micaschists, metagraywackes and paragneisses (MR)	Micaschists, gneisses and migmatites (MRM)	Two-mica granite, medium to coarse grained (GR)	Biotitic granite, medium to fine grained (BGR)
Hydrogeological features						
Thickness (m)	\15	15–25	[50	[50	[100	[100
Weathering profile						
Low (m)	n.a.	n.a.	10–20	5–10		
High (m)	n.a.	n.a.			20–50	20–50
Silty and/or clayey	n.a.	n.a.	x			x
Sandy	n.a.	n.a.		x	x	x
Connectivity to the drainage system						
With	x	x				
Possible			x	x	x	x
Type of flow						
Porous media	x	x				
Fissured media			x	x	x	x
Transmissivity (T, m^2/d)	[20	\1	4–18	5–10	5–10	5–10
Groundwater confinement	Unconfined aquifer	Aquitard	Semi-confined to confined aquifer	Semi-confined to confined aquifer	Semi-confined to confined aquifer	Semi-confined to confined aquifer
More suitable exploitation structures						
Dug wells, galleries and springs	x	x		x	x	x
Boreholes			x			
Well discharge, Q (L/s)						
Very low (Q \1)		x	x	x	x	x
Low (1\\Q\2)	x					
Hydrochemical facies	Cl–Na to NO_3–Na	Cl–Na to NO_3–Na	Cl–Na–Ca to HCO_3–Na–Ca	Cl–Na–Ca to HCO_3–Na–Ca	Cl–Na	Cl–Na to HCO_3–Na

n.a. not applicable

production (namely potatoes, vegetables, fruits and maize) and farming and cattle raising (especially bovines). These products are one of the most important food supplies to the surrounding villages and cities. The period of fertilisation is mostly concentrated in early spring for summer crops like maize. The two main types of fertilisation are: organic, especially manure (ca. 700 kg/ha/year), yet sewage is also used, and inorganic (ca. 120 m^3/ha/year). The inorganic fertilisers are composed mainly by nitrogen, phosphorous and potassium, but nitrogen prevails among the other two (Pedrosa et al. 2002). Sprinkler is the dominant irrigation system. In this region, groundwater resources are mainly conditioned by the described climatological conditions, as well as by geologic and morphotectonical features. The regional geological framework comprises a crystalline fissured basement of highly deformed and overthrusted Late Proterozoic/Palaeozoic metasedimentary and granitic rocks. The post-Miocene sedimentary deposits often overlay the bedrock (Pereira et al. 1989; Chaminé et al. 2003, and references therein). The morphotectonic background comprises a littoral platform characterised by a quite regular planation surface dipping gently to the west, culminating around 100 m a.m.s.l (Araújo et al. 2003). Incised river valleys, namely Ave and Leça, intersect the flatness of this morphological surface, which evidence a regional tectonic control. The main features of the regional hydrogeologic units in this area are described in Table 1.

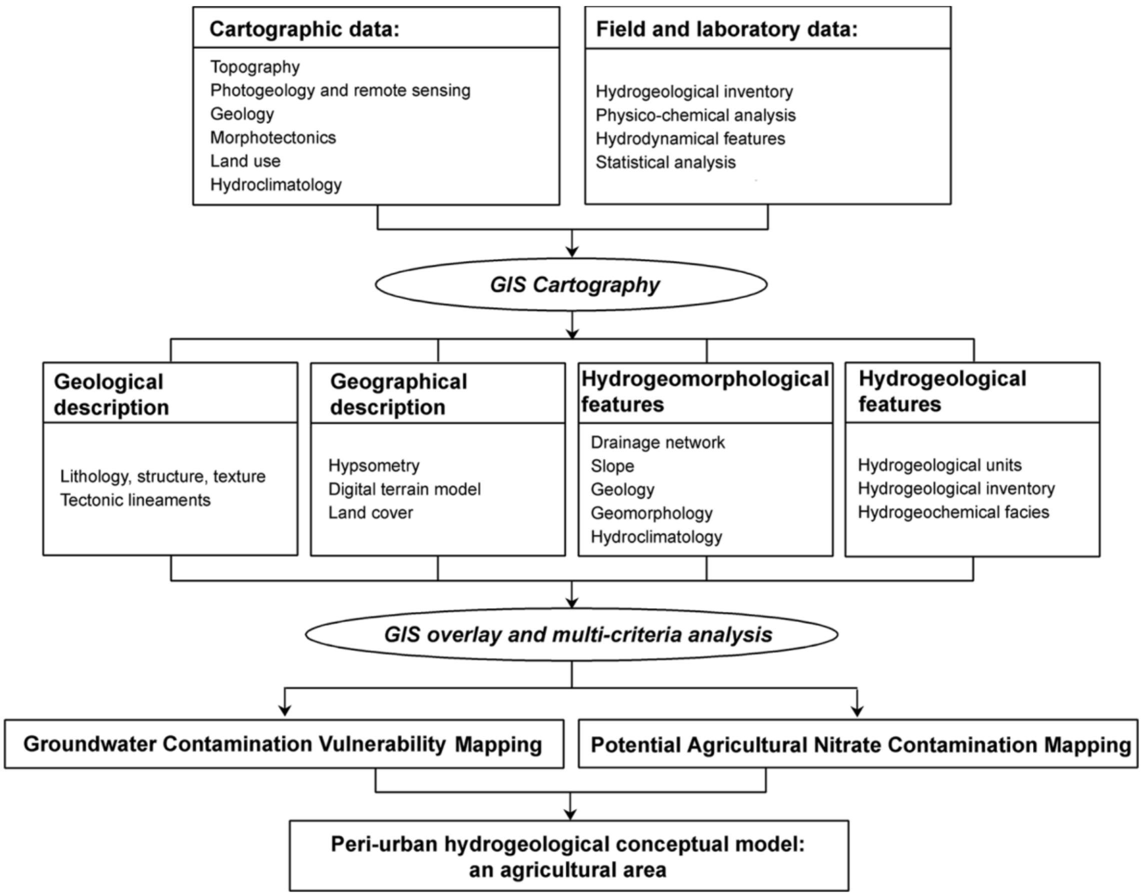


Fig. 2 Conceptual flowchart representing methodologies applied in this study

According to Monteiro (2005), the following pedologic units (nomenclature in agreement with the IUSS Working Group WRB 2007) occur in this area: the most represen- tative are dystric cambisols and humic cambisols, mostly associated with granitic rocks, their source material; haplic arenosols and dystric fluvisols also occur, the former in the littoral area, related with dune and beach sands, and the latter connected with alluvia.

The study area was divided into three key sectors (Fig. 1), each of them dominated by a hydrogeological group: sector 1, in the sedimentary cover, sector 2 in me- tasedimentary rocks and sector 3 in granitic rocks.

Materials and methods

This study followed a geo-environmental approach with the aim of understanding and assessing the nature and suitability for human consumption and agricultural prac- tices of these peri-urban groundwater systems (Fig. 2).

The area was studied using the following tools (e.g., Vrba and Zaporozec 1994; Struckmeier and Margat 1995; Assaad et al. 2004; Witkowski et al. 2007; Chaminé et al. 2013): geological and hydrogeological mapping, hydro- logical techniques and aquifer vulnerability evaluation. Geological fieldwork surveys were first carried out to identify major geologic features responsible for ground- water circulation paths and to assess litho-structural and textural heterogeneities.

A hydrogeological field inventory was developed, which included dug wells, boreholes and water galleries. Groundwater samples were collected in all three study sectors and used for the hydrochemical evaluation, and subsequent identification of areas at increased risk. In situ determinations included temperature, pH, and electrical conductivity using a multiparametric portable equipment (Hanna Instruments, HI 9828). Groundwater samples were collected in 1.5 L pre-cleaned bottles, for the analysis of major cations and anions, to evaluate the main regional hydrogeochemical facies. AquaChem 5.1 software was used for the hydrochemical interpretation. All the inventory and sampling sites were georeferenced with a high-accu- racy GPS (Trimble® GeoExplorer).

In total, 380 sampling sites were established in the three sectors (Fig. 1): Sector 1, dominated by a sedimentary cover, with 106 water points; Sector 2, mostly by metasedimentary rocks, with 126 water points; Sector 3, granitic rocks, with 148 water points. Because one main aim was to assess suitability and risk for human consumption, most of the sampling points (86 %) were located in the peri-urban fabric. The remaining sampling points were located in associated agricultural areas.

The hydrochemical analyses included the determination of chloride (Cl^-), phosphate (PO_4^{3-}), nitrate and nitrite (NO_2^-). Samples were conditioned and analysed according to standard field procedures. All reagents used were of pro analysis grade and obtained from Merck (Darmstadt, Ger- many). Ultrapure water (0.054 μS/cm) was produced by a Milli-Q system from Millipore (Milford, MA, USA). The content determination of the parameters was based on the procedure described in standard methods for the exami- nation of water and wastewater issued by the American Public Health Association (APHA 1995). To validate all the methodologies an inter-laboratory study was done.

Data pertaining to the hydrochemical parameters mea- sured were compared by one-way analysis of variance (one-way ANOVA) to investigate differences among the studied sectors, and the hydrogeological units, as well. For the purpose of data analysis values below the limits of detection were replaced by half of the respective limit value. Prior to the analysis data were checked for normality and variance homogeneity using the Kolmogorov–Smirnov and the Levene's tests, respectively.

Groundwater vulnerability to contamination was evalu- ated using several methods: *GOD-S* (Foster 1987; Foster and Hirata 1988; Foster et al. 2002), *Pesticide DRASTIC- Fm* (Aller et al. 1987; Denny et al. 2007), *SINTACS* (Civita 1994, 2010; Civita and De Maio 2000) and *SI* (Ribeiro 2000; Francés et al. 2001). For *DRASTIC-Fm*, two updates were done: (1) the assigned weights for *DRASTIC* were those proposed for *Pesticide DRASTIC*; (2) the *Fm* parameter was derived from the tectonic lineaments density map and grouped into five classes (km of lineaments/km^2): ≤4, 4–8, 8–12, 12–16 and ≥16, with ratings of 2, 4, 6, 8 and 10, respectively. Concerning *SINTACS*, the weights of Nitrates String were used (Civita 2010). Finally, for *SI*, the Land Use (*LU*) parameter was derived from land cover maps (CLC2006, Painho and Caetano 2006; COS2007, IGP—Instituto Geográfico Português 2010). Hydrogeo- logical background was on the basis of the computation for the vulnerability approach. Groundwater vulnerability was subdivided into several broad classes from "Negligible— Low" to "Extremely High". The national colour code for *DRASTIC* index ranges was applied. Finally, an integrated assessment between all the methods was made.

A principal component analysis (PCA) was then per- formed with hydrochemical variables and the data obtained through the assessment of groundwater vulnerability. PCA is an effective tool for the characterisation of anthropo- genic inputs (Lorenzo et al. 2007). It allows for a description of a multidimensional system by reducing the number of studied variables to a few significant summary components facilitating the interpretation of relationships among them and the identification of contamination pro- files for large data bodies. Here, the aims were to investi- gate the relationships between groundwater vulnerability and the hydrochemical data, compare the bedrock profile in terms of vulnerability and hydrochemical load, and search for patterns that could improve the design of the hydro- geological conceptual model in urban areas. For this, the vulnerability indexes obtained through the GIS-based analysis, the hydrochemical data and the depth of the sampled water wells were entered in the PCA as quanti- tative variables. The hydrogeological unit was entered as supplementary qualitative variable. Only principal com- ponents (PCs) with Eigen values ≥1 were retained for interpretation. PCA interpretation was based on the examination of the correlations between the variables and the PCs obtained. Confidence ellipses were drawn around the hydrogeological units (i.e., around the barycentre of the samples assessed on each unit) to enable visualising whe- ther or not the units differ significantly. PCA was carried out with FactoMineR.

Based on the PCA results, an assessment of potential nitrate contamination risk was made by correlating the agricultural nitrate hazard index—*IPNOA* (Padovani and Trevisan 2002; Corniello et al. 2007; Capri et al. 2009)— with the *SINTACS* index. For *IPNOA* only the nitrogen load from farming was taken into account and so only farmed areas, which are the leading sources of potential nitrate contamination, were considered.

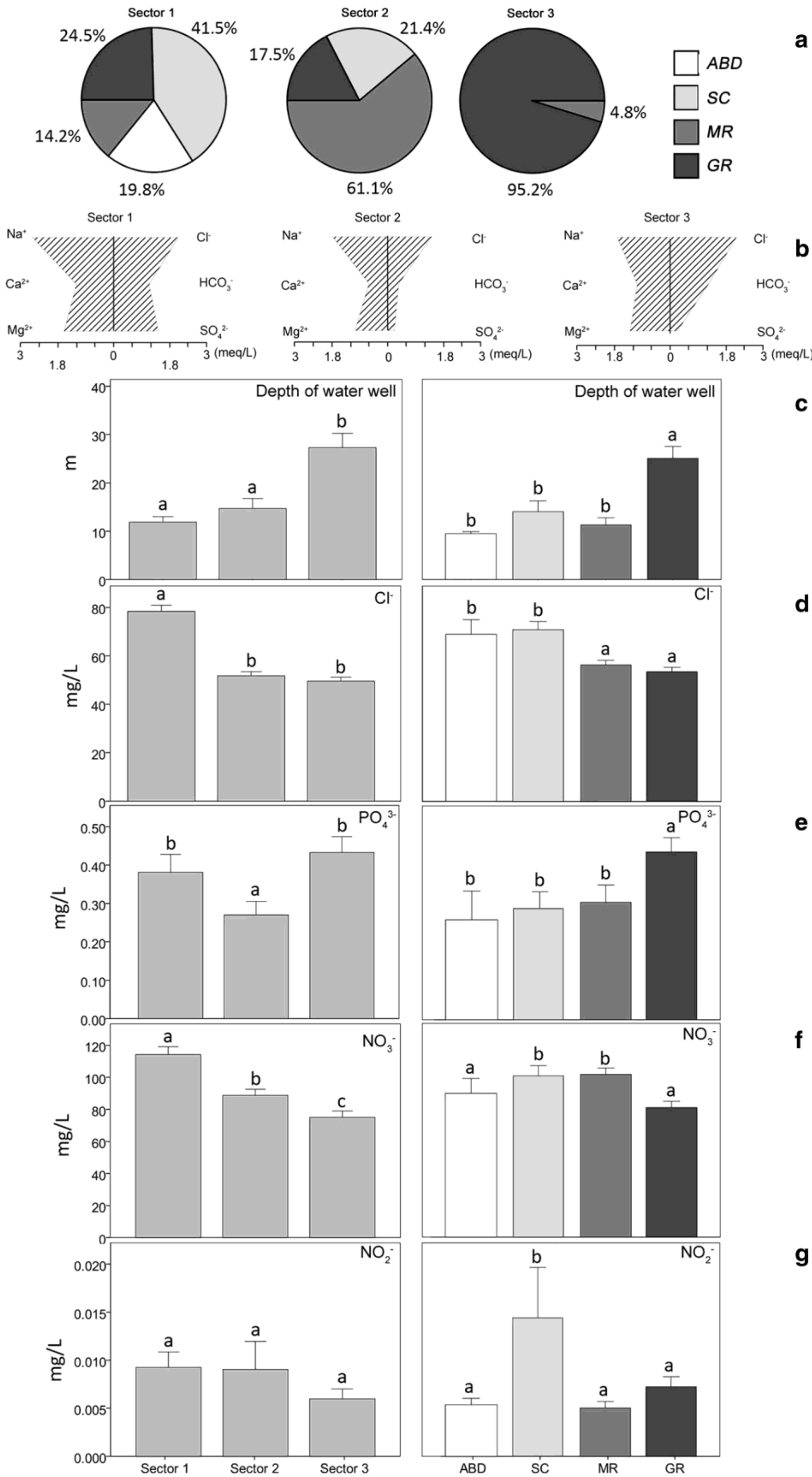
The hydrogeological and hydrogeochemical database generated in this study can be updated at any time if one of the parameters modifies its characteristics, and thus new maps can be easily generated. This integrative methodol- ogy is possible through the application in a GIS environ- ment (ArcGis 9.3 platform) followed by a multivariate analysis, which were in this study strongly helpful for the presentation and interpretation of the results.

Results and discussion

Hydrogeochemistry

The hydrogeological units that dominate in the selected key sectors are (Fig. 3a): sedimentary cover (ABD and SC), in Sector 1, particularly sandy silts and clays (SC); metasedimentary rocks (MR), micaschists, metagraywac- kes and paragneisses, in Sector 2; and, finally, in Sector 3, granitic rocks (GR), two-mica granite, medium to coarse grained.

Fig. 3 Hydrogeochemistry versus hydrogeological units and study sectors. a Distribution of hydrogeological units in the three study sectors; b stiffdiagrams for Sectors 1, 2 and 3 (adapted from Afonso 2011);
c depth of water wells; concentrations of chloride (d), phosphate, (e) nitrate, (f) and nitrite (g)



The groundwater analysed are slightly acidic with a mean pH value of 6.3. Minor differences between sectors were found: sectors 1 and 2 showed pH values around 6.2 and sector 3 about 7.1. Electrical conductivity measurements ranged from 354 to 688 IS/cm, which indicate the presence of medium mineralised waters. The median values for each sector were fairly diverse: 654 IS/cm for Sector 1, 392 IS/cm for Sector 2 and 425 IS/cm for Sector 3. The values are in good agreement with data reported previously for this area (Afonso et al. 2007; Afonso 2011). Moreover, they are consistent with the hy- drogeochemical signature determined for these groundwater, which are of Cl type, with minor differences among sectors (Fig. 3b): Sector 1, Cl–SO_4–Na type; Sector 2, Cl–Na type; and Sector 3, Cl–Na–Mg type (Afonso2011).

Concerning the water supply structures, most of them (91.4 %) are dug wells, boreholes constitute 7.8 % and water galleries represent only 0.8 %. The average depth of the water wells (Fig. 3c) is similar in Sectors 1 and 2, between 10 and 15 m, and significantly higher in Sector 3, around 30 m. This agrees with the fact that most of the boreholes, with higher depths, are located in Sector 3, where granitic rocks prevail.

Sector 1 showed significantly higher ([35 %) Cl^- concentrations respect with to Sectors 2 and 3 (Fig. 3d). Regarding variation of Cl^- values among hydrogeological units, significant differences were observed also for the sedimentary cover (ABD, SC), relative to the remaining units, with concentrations there exceeding 70 mg/L.

Concerning PO_4^{3-} (Fig. 3e), although the concentra- tions are low, Sector 2 presented significantly lower (by about 35 %) PO_4^{3-} values than Sectors 1 and 3. The same tendency was found for ABD, SC and MR hydrogeological units in relation with GR unit.

Significant differences among sectors were also found for the concentrations of NO_3^- which decreased from Sector 1 to Sector 3 (Figs. 3f, 4). SC and MR

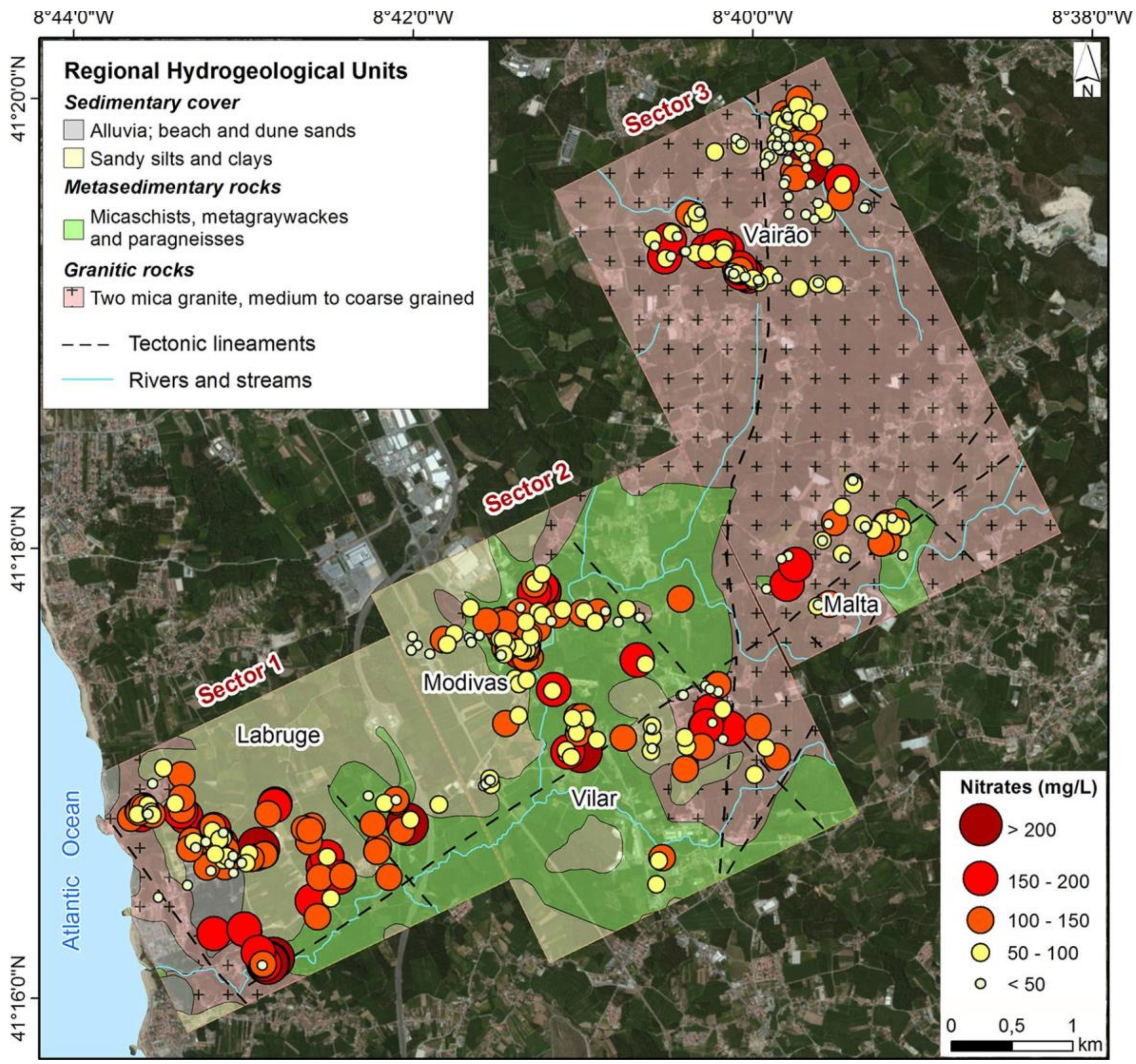


Fig. 4 Nitrate concentrations in groundwater samples from the three study sectors

hydrogeological units presented the highest average concentrations of NO_3^- detected and significantly higher than those measured in samples from ABD and GR units. The highest nitrate value (280 mg/L) was found in Sector 2, linked to the MR unit. It is also of note that all the sectors and the four hydrogeological units showed mean nitrate values above 50 mg/L.

Regarding NO_2^- (Fig. 3g), no significant differences were found among the three sectors, which presented concentrations lower than 0.01 mg/L. Nevertheless, SC hydrogeological unit showed significantly higher levels than the remaining units.

Taking into account the European guidelines for the use of groundwater for human consumption, these groundwater do not exceed the parametric values for chloride (250 mg/L) and for nitrite (0.5 mg/L). On the contrary, nitrate exceeds the parametric value (50 mg/L) in 75 % of the samples. Moreover, according to the Portuguese legislation for irrigation activities (MA—Ministe´rio do Ambiente 1998), 70 mg/L and 50 mg/L are the maximum allowed parametric values for chloride and nitrates, respectively.

Groundwater vulnerability and patterns of relationship to hydrogeochemistry

Figure 5 synthesises the groundwater vulnerability mapping obtained with the four employed methods and the principal component analysis (PCA) of hydrogeochemical and vulnerability data. The study area displayed a generally moderate to high vulnerability to contamination.

Globally, in the PCA, three components presented Eigen values higher than 1, expressing 72.47 % of the total variability observed in the data. The first component (PC1) summarises 40.53 % of the total inertia, expressing 2.36 times more variability than the second component. The second component (PC2) was of relative importance, summarising 18.92 % of the variability. The third component provided limited additional information, hence PCA interpretation was based on the first two PCs (expressing 59.45 % of the total variability). PC1 is mainly linked to the vulnerability of hydrogeological units. It groups all four vulnerability indexes, showing high positive correlations (≥ 0.90, $p < 0.001$) with the component, in a highly homogeneous group. The correlation between any two of these indexes is equal to or higher than 0.85.

Further, it expresses a gradient opposing units showing low vulnerability on average (MR and SC, $p < 0.001$) to units showing high vulnerability (ABD, $p < 0.001$). PC2 is highly associated to NO_3^- levels, which show a significant high positive correlation (0.82, $p < 0.001$) with this axis. Cl^- levels are also positively correlated to PC2, although to a lesser extent (0.68, $p < 0.001$), and negatively correlated to the depth of the water wells (−0.60, $p < 0.001$).

Correlations of NO_3^- or Cl^- with the depth of the water wells were −0.35 and −0.13, respectively. Also, contribution of individual samples to data structuring was not clearly related to the depth of the wells. Despite the variability observed, the gradient opposes GR unit which tends to show lower than average NO_3^- and Cl^- levels to ABD, which exhibits higher levels of these ions.

Overall, vulnerability of the hydrogeological units reflects the main structuring of the data. The fact that all four vulnerability indexes employed in the present study show high positive correlations among themselves and with the first PCA component suggests that they perform equally well in assessing the vulnerability of this type of hydrogeological framework. Different vulnerability and contamination profiles were exhibited by the four hydrogeological units. Vulnerability appears to be associated with NO_3^- and Cl^- in the ABD unit (West part of Sector 1) but not in the remaining units. Indeed, ABD is characterised by high to extremely high vulnerability and higher NO_3^- and Cl^- levels, consistent with its porous nature, sandy lithology and high permeability, which favours the leaching of nitrates and chlorides into underlying groundwater. Conversely, SC and MR (mostly located in Sectors 1 and 2) are characterised by very low to low vulnerability and exhibit a range of NO_3^- and Cl^- levels around average. This is dependable of the fact SC and MR have a low permeability, since SC is a porous media with a clayey nature and MR has a silty to clayey weathering profile. GR shows a moderate vulnerability and a tendency for lower NO_3^- and Cl^- levels. Although GR (mainly situated in Sector 3) is the unit with deeper depth of the sampled water wells, the correlation between NO_3^- or Cl^- and depth is rather low. This suggests that circulation paths through the, sometimes, high thickness weathering profile of the granitic bedrock may promote retention of NO_3^- and Cl^- ions, resulting from contamination events driven by superficial anthropic activities, such that low ion levels are found in samples collected at deeper depths.

Agricultural and non-agricultural origins for nitrates in groundwater are well documented in the literature (e.g., Barrett et al. 1999; Razowska-Jaworek and Sadurski 2005; Wakida and Lerner 2005; Schirmer et al. 2013). The high values of nitrates in the study area are most probably due to agriculture activities and livestock production located in the surroundings of the sampling sites. Contamination from household discharges connected to on-site sewage disposal (cesspools, septic tanks) and improper water wells protection may have a relevant contribution to this contamination, as well. The identification of sources of agricultural and anthropic contaminants should also be based in other hydrochemical and isotopic analyses. Therefore, sulphate data and the isotopic composition of nitrate and sulphate should be analysed in future investigations (e.g., Rock and

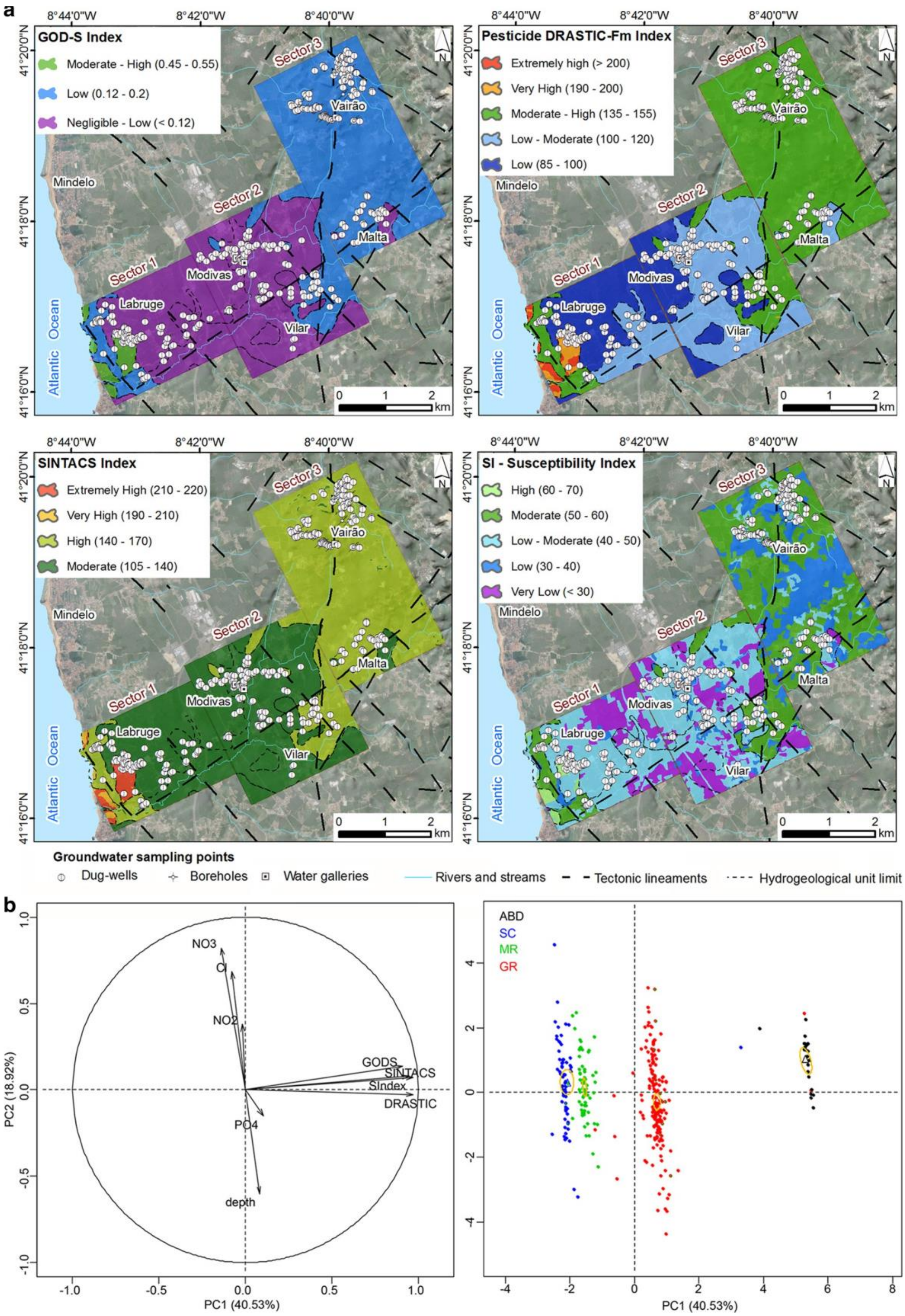


Fig. 5 Groundwater vulnerability indexes (a): *GOD-S* (*top left*), *Pesticide DRASTIC-Fm* (*top right*), *SINTACS* (*down left*) and *SI* (*down right*). Principal component analysis (PCA) of hydrogeochemical and vulnerability data (b); caption as in Fig. 3

Mayer 2002; Kaown et al. 2009; Cheong et al. 2012; Di Lorenzo et al. 2012).

Concerning chlorides, their origin should be meteoric, including sea spray, and by anthropic contamination, namely organic fertilisers and cesspools. These conclusions agree with those by Heitor (2000), Pedrosa et al. (2002), Gonc¸alves et al. (2006), Silva et al. (2006), Afonso et al. (2007), Correia et al. (2010) and Afonso (2011).

Groundwater risk to contamination

The *IPNOA* index was applied to farmed areas to produce the nitrate contamination hazard map (Fig. 6a). This map was then overlapped with a vulnerability index. Based on the PCA results, which indicated that all four indexes employed in the presence study were highly correlated among themselves (Fig. 5a), the *SINTACS* index was chosen for the overlapping. *SINTACS* takes into account several environmental factors such as topography, hydrol- ogy, geology, hydrogeology, and pedology. The overlap- ping of both maps allowed creating the map of potential risk to nitrate contamination (Fig. 6b).

The nitrate contamination hazard is generally high. Few areas are classified as moderate, although the hazard index (9.17) is close to the high class. Areas with a very low hazard correspond mainly to discontinuous peri-urban areas, associated with backyards. In these areas, fertilisers are mainly inorganic and in much less quantities and tillage is considered minimum.

The potential risk of nitrate contamination was generally high to moderate, owing to the aquifer vulnerability. Extremely high risk was associated to sandy lithologies, alluvia and beach and dune sands, consistent with the results of the vulnerability analysis and with the high levels of nitrates measured in groundwater.

Conceptual hydrogeological model

This integrative approach improved the peri-urban hydro- geological conceptual model for these groundwater sys- tems (Fig. 7). Three main aquifer systems coexist and interlock:

1. Alluvia and beach and dune sands (ABD): porous media, low thickness (\15 m), unconfined, hydraulically con- nected to the drainage system, shallow water table (\5 m), moderate to high permeability (\10 m/d), Cl–SO_4–Na water type, high to very high vulnerability to contamination, and a high to very high potential risk to nitrate contamination;
2. Complex of micaschists, metagraywackes and parag- neisses (MR): fissured media, semi-confined to con- fined, sometimes moderately weathered with thicknesses that may reach 15 m, shallow to moderate piezometric surface (\15 m), low to moderate perme- ability (\2 m/d), Cl–Na water type, low to moderate vulnerability to contamination, and a low to moderate potential risk to nitrate contamination;
3. *Granite* (*GR*) fissured media, semi-confined to con- fined, moderately to highly weathered with thicknesses in the range of 20–30 m, shallow to moderate piezo- metric surface (\10 m), low to moderate permeability (\1 m/d), Cl–Na–Mg water type, moderate to high vulnerability to contamination, and a moderate to high potential risk to nitrate contamination.

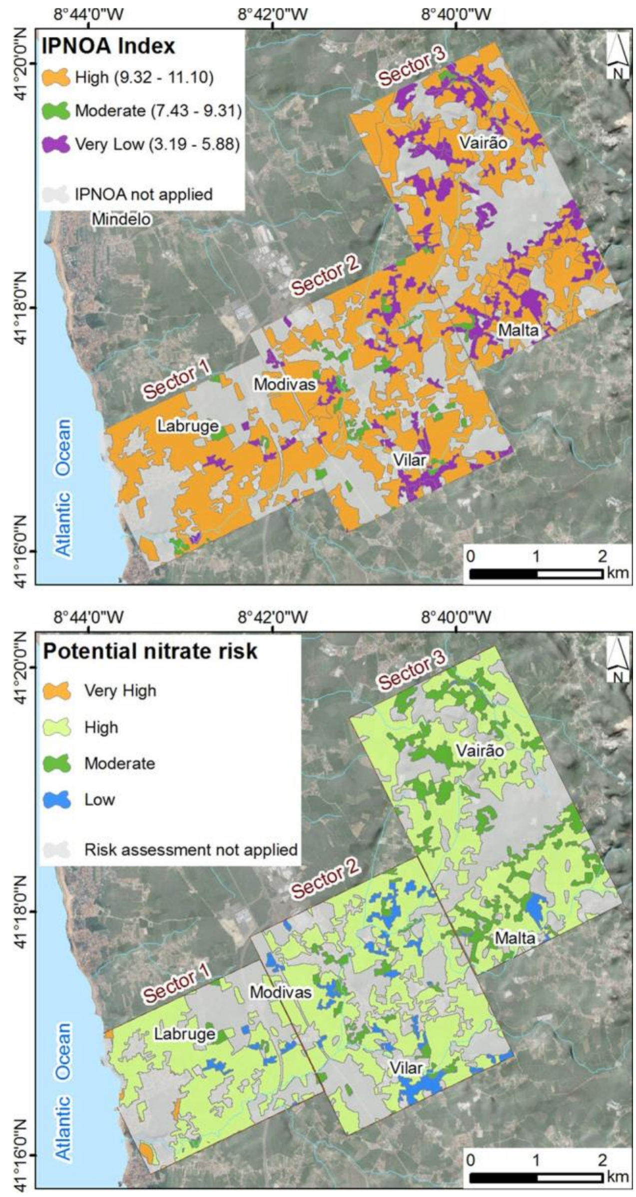


Fig. 6 Map of the IPNOA index of nitrate hazard and map of the potential nitrate contamination risk from agricultural sources in the study area

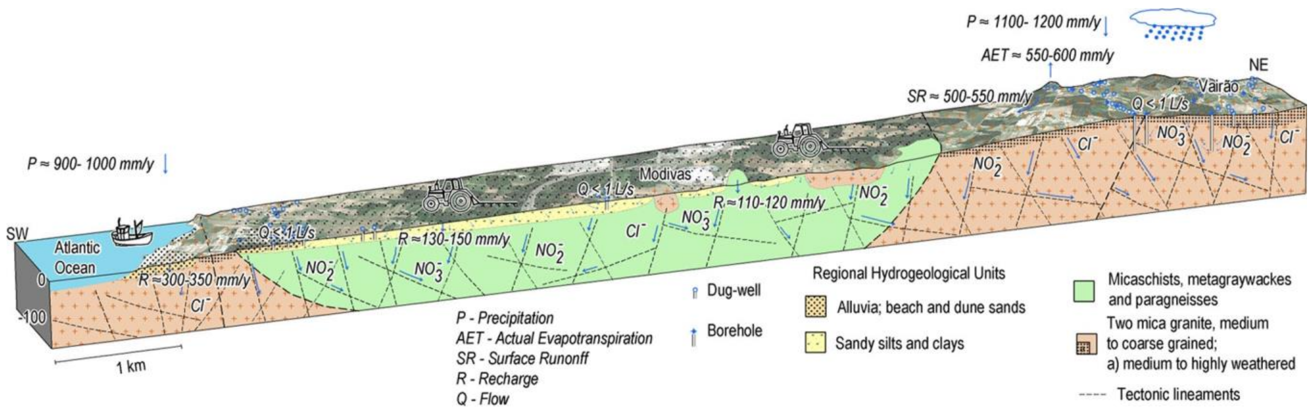


Fig. 7 Hydrogeological conceptual model as resulted from the integrated approach

Concluding remarks

The results of this study provided a comprehensive picture of the groundwater chemical status, with regard to chlorides, phosphates, nitrates and nitrites. It also confirmed the utility of intrinsic vulnerability indexes (*GOD-S, Pesticide DRASTIC- Fm, SINTACS* and *SI*) and specific vulnerability to nitrate contamination index (*IPNOA*) for evaluating the groundwater vulnerability in Northern Portugal on a regional scale.

Vila do Conde region may be classified as a vulnerable area because of the high nitrate concentrations that may be found either in groundwater, soil or even vegetables, as a consequence of intensive agricultural activity. The present results further support this, revealing levels above legisla- tion limits in the peri-urban area. Additionally, they sug- gest that organic and inorganic fertilisers and anthropic activities, which are driven to groundwater via irrigation and rainfall, seem to be the main factors causing the nitrate and chloride contents observed.

Vulnerability methods can be a useful groundwater management tool, at medium to small scales for designat- ing new Nitrate Vulnerable Zones and in agro-environ- mental policies, as defined in EU legislation. The use of groundwater would imply the review of the available nitrogen for fertilisation, following the Code of Good Agricultural Practices, which has become mandatory in consequence of the application of the Nitrates Directive.

The results presented herein raise special concerns since many of the sampling sites assessed are in use as source of drinking water. They warrant further research to assess the evolution of nitrate levels in this area, particularly in alluvia and beach and dune sands units, and the efficacy of measures to constrain nitrogen inputs into the environment. To better define the anthropogenic sources of the dissolved nitrates, an isotopic investigation of $d^{15}N$ and $d^{18}O$ in dissolved nitrates should be carried out. Moreover, sulphate data should be collected and $d^{34}S$ and $d^{18}O$ values of sulphates should be determined to evaluate the contami- nation by sewage of these groundwater.

Mapping of the vulnerability to groundwater contami- nation is indeed a powerful tool for communication between groundwater investigators and those working in water resources and land use planning and management. Nevertheless, one should never lose sight of two realities (Foster et al. 2013): primarily, all vulnerability assessments symbolise a 'best professional synthesis' of available information, and also, all vulnerability maps are a screen- ing tool to identify where priority protection measures are likely to be required to manage a potential groundwater contamination threat.

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