Groundwater vulnerability to pollution in karst aquifers, considering key challenges and considerations: application to the Ubrique springs in southern Spain

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Abstract

Groundwater vulnerability mapping is one of the tools most often applied to analyse the sensitivity of karst aquifers to pollution. These maps aim to support stakeholders in decision-making and to promote land-use management compatible with water protection. However, the validation of these maps is still a challenge in many cases, triggering high uncertainty. For karst media, due to the strong heterogeneity in recharge mechanisms and hydraulic characteristics, validation is a significant stage and it must be inherent within the groundwater vulnerability assessment process. This work aims to assess the implementation of tools used for protecting the quality of water discharging or extracted from the Ubrique karst system in southern Spain, which supplies drinking water that is threatened by periodical pollution/turbidity episodes. A groundwater vulnerability map, attained by application of the COP method and validated by multiple in-situ observations, shows an extremely vulnerable system due to the absence of protective overlayers and the significant development of exokarst landforms, including shallow holes. This map could constitute the basis for defining protection zones for the Ubrique springs. However, their comprehensive protection requires the implementation of monitoring tools and an effective management strategy, through an early warning system that assures stable

environmental and hydrogeological conditions and improves operational procedures associated with the drinking water service. This research establishes the strong relationship of the different methods applied to protect the source from contamination events, ranging from classical hydrodynamic and hydrochemical approaches to the implementation of protection zones and early warning groundwater quality monitoring networks.

Keywords: Karst, Vulnerability mapping, Groundwater protection, Early warning system, Spain.

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1 Introduction

The concept of the "contamination vulnerability" of an aquifer has been defined by many authors (Margat 1968; Foster 1987; Zaporozec 1994; among others) as the sensitivity to contamination of the groundwater resource, taking into account the geological, hydrologic and hydrogeological characteristics of the aquifer, independently from the nature and scenario of the contamination (Daly et al. 2002; Zwahlen 2004). This is the adopted definition for "intrinsic vulnerability", but if the pollutant properties are considered during the vulnerability evaluation, then it is redefined as the "specific vulnerability". Although the nature of the pollutant influences the contamination pattern throughout the aquifer, in most cases vulnerability mapping is based on the intrinsic concept, in order to simplify the vulnerability schemes and its transference as a tool for water protection and land-use planning. The principal objective of contamination vulnerability mapping is to identify and highlight the most vulnerable zones within catchment areas, as well as to provide unified criteria for protecting the groundwater resources. Vulnerability to pollution is not a characteristic that can be directly measured in the field, so indirect methodologies for vulnerability assessment are

required. In fact, the degree of groundwater vulnerability to pollution does not remain stable along time but varies according to the specific characteristics of each case.

The importance of karst aquifers as sources of good quality drinking water is well accepted worldwide. Roughly 20–25% of the world's population depends on water supplies from karst aquifers, directly or indirectly, and 10-15% of the world's land surface area has karst aquifers beneath it (Ford and Williams, 2007; Goldscheider et al. 2020). Karst groundwater is particularly sensitive to contamination, due to aquifer inner structure and hydrogeological behavior, which determine the rapid transfer of recharge waters and their fast distribution over large distances, achieving high flow velocities and short residence time. Consequently, the self-cleaning capacity of the karst groundwater is commonly low or very low (Doerfliger and Zwahlen 1998; Ford and Williams 2007). Therefore, karst aquifers require specific methodologies for vulnerability mapping which take into account their specific intrinsic properties (Zwahlen 2004).

A set of combined approaches, specifically adopted for karst environments, has been developed on the basis of the guidelines of the European COST Action 620, including –among others- the PI method (Goldscheider et al. 2000), the COP method (Vías et al. 2006), the Slovene Approach (Ravbar and Goldscheider 2007), and the PaPRIKa method (Kavouri et al. 2011). Spatial information and geographic information system (GIS)-based approaches are widely used for intrinsic vulnerability mapping of karst aquifers, although there are also relevant advances in geological and hydrogeological modeling (Butscher and Huggenberger 2008; Jeannin et al. 2013; Hartmann et al. 2013; Turk et al. 2014; Ghasemizadeh, et al. 2016).

In practice, the assessment of the aquifer vulnerability to pollution (at whatever scale) inevitably involves simplification of the naturally complex geological framework and related hydrological processes. Although this is a powerful tool, it incorporates a significant but variable level of uncertainty during mapping development and is not readily capable of independent calibration (Foster et al. 2013). In addition, the application of different methods on the same test site, using the same database, often leads to significant differences in mapping results (Vías et al. 2005; Neukum and Hötzl 2007; Ravbar and Goldscheider 2009; Marín et al. 2012). For these reasons, the validation of the vulnerability maps is a key element that has to be implemented as part of the vulnerability assessment, within a holistic perspective. Validation may involve a wide range of methods and techniques such as field tracing experiments, analysis of natural responses of karst springs, study of environmental tracers, numerical modelling, etc. (Marín et al.

2015). Despite the importance of mapping validation in the context of groundwater protection and management, this phase is still bypassed in many cases. However, since the final goal of the entire methodological process is to implement strategies for groundwater protection (i.e. protective zoning around abstraction points), as part of effective land-use planning, this needs to be inherent to the vulnerability assessment process in karst.

This paper aims to present the main advances related to vulnerability assessment of karst groundwater resources to pollution, highlighting the present challenges and new directions to perform this type of mapping under the complex scenario of karst aquifers. The test site, Ubrique aquifer (Cádiz province, southern Spain), needs a dynamic protection and management plan of karst groundwater resources due to the impact of high-turbidity peaks and associated bacterial contamination episodes threathening the drinking water supply. In Spain, the applied water legislation, i.e. the Royal Decree 140/2003 of 7 February, establishes the sanitary criteria and chemical thresholds for the quality of potable water for human consumption among which are the mentioned parameters that generate operational constraints in Ubrique drinking water supply. Consequently, this test site gathers conditions to implement an effective decision-support system (DSS) in order to improve operational procedures in drinking water services.

All the stages that should be conducted during the adoption of an effective system for protecting groundwater against contamination are illustrated in the present work. The procedure, which is not unidirectional, but rather feeds back from the interactions of the different stages, consists of: (1) hydrogeological characterization of the test site, gathering information on significant karst features; (2) implementation of a suitable holistic approach as a methodology for vulnerability mapping; (3) the validation method, with a particular focus on data requirements to implement this stage; (4) discussion of the potential role and applicability of the adopted methodology according to the understanding of the hydrogeological background and validation results; and finally (5) testing the implementation of the common and newly developed approaches for safeguarding groundwater resources by means of early warning systems (EWS).

2 Test site

The study area is the Ubrique karst aquifer, a hydrogeological system of area 26 km^2 located within a larger mountainous region known as Sierra de Grazalema, in Cadiz province, southern Spain (Fig. 1). The mountainous relief ranges from 400 to 1,500 m above sea level (a.s.l.), being the highest elevations associated with the NE-SW

alignments. The climate is humid Mediterranean, with a marked seasonal pattern in the annual variations of precipitation and air temperature. Rainfall occurs from autumn to spring times, associated with wet winds coming from the Atlantic Ocean. Climate conditions are also characterized by a dry season (very often of up to 3–4 months), practically without rain, in summer. The mean annual precipitation in this area, calculated from isohyets maps, was around 1,350 mm for the period of hydrological years 1965 - 2006, with a spatial distribution influenced by the elevation: it was below 1,000 mm in the lower parts (southwestern border) and up to 1,600 mm in the higher areas (Andreo et al. 2014). The air temperature records show mean annual values from 14 to 16 °C, depending on the elevation.

From a geological standpoint, the experimental field site and the other reliefs that make up the Sierra de Grazalema area are situated within the Betic Cordillera; this consists of (from the bottom to the top): Upper Triassic (Keuper) clays, dolomitic beds, sandstones and evaporite rocks (mainly gypsum), Jurassic dolostones (lower) and limestones (upper) -500 m thick-, and Cretaceous-Paleogene marly-limestones and marls (Martín-Algarra 1987). The geological structure is characterized by open anticline folds whose axes plunge towards the SW and tight synclines matching with depressions constituted by younger marly-limestones materials. Over the previous rocks and overthrusting them appear outcrops of Tertiary flysch-type clays and sandstones. The entire structure is affected by more recent strike-slip faults (NW-SE) and normal fractures (NNW-SSW and N-S) which configure the geological structure and orography of the area. The predominance of Jurassic oolitic limestones, densely fractured, jointly with bedding planes and the prevailing climate conditions, reinforce karstification phenomena and a noteworthy development of exokarst landforms over the bare carbonate outcrops. These include large karrenfields, dolines, uvalas and swallow holes (Delannoy 1987). The presence of low-permeability rocks (marls and clays) in syncline cores, sometimes affected by inverse faults, result in the establishment of endorreic areas, whose natural drainage occurs through swallow holes (Figs 1 and 2) hydrologically connected with shafts and other endokarst features.

In hydrogeological terms, the Ubrique aquifer is formed by fractured and karstified Jurassic carbonate rocks, limited by low-permeability materials at all their borders (flysch clays, Cretaceous-Tertiary marls, and Triassic clays). The exception is a 1-km-long open limit on the northeast edge, delineated after the interpretation of the results derived from the multitracer tests considered in the present work. The geometry of the aquifer is particularly determined by the anticlinorium folds that define respectively the Sierra de Ubrique and the Sierra del Caillo, and locally by a NE-SW inverse fault affecting the syncline structure located between previous ones. The Ubrique aquifer is a binary karst

system with the interpretation expressed by Bakalowicz (2005) and Mayaud et al. (2014) among others, since duality in recharge mechanisms was proved: more or less diffuse infiltration from rainfall through the carbonate outcrops (autogenic component), and the concentrated infiltration of water runoff from a small neighbour catchment formed by low-permeability materials (flysch clays and Cretaceous marls; Fig 1). Superficial allogenic input enters the system through the Villaluenga del Rosario shaft. This represents one of the most important hotspot in the aquifer from the protection of groundwater perspective. On the other hand, natural drainage occurs through the permanent and temporal (overflow) springs located at the SW border of the aquifer. The most significant ones are the Cornicabra (located at 349 m a.s.l.) and Algarrobal (317 m a.s.l.) perennial outlets, which have discharge rates of 10 to 2,460 l/s (mean 406 l/s) and 10 to 2,625 l/s (mean 157 l/s), respectively. Additionally, several overflow springs appear in this sector at increasingly higher elevations during high flow; the most relevant is Garciago spring (422 m a.s.l.) whose discharge rate is, on average, 311 l/s but ranges from 0 to 6,059 l/s (Sánchez et al. 2018). Cornicabra and Algarrobal supply drinking water for the neighbour village, Ubrique (18,000 inhabitants). These springs are peridocaly affected by high turbidity peaks linked to inorganic sediment particles during stormy periods but also to the runoff water infiltrated in the Villaluenga del Rosario shaft, that lixiviates the fecal remains of the livestock from the endorreic area and receives partially treated waste water from 500 inhabitants. These turbidity episodes generate operational constrains and hinder the exploitation of the available water resources from the aquifer.

Since the test site is a part of Sierra Grazalema Natural Park, and as a result of its valuable environmental, botanical and faunistical aspects, the conservation of natural conditions has been a priority for the different administrations. Consequently, livestock farming (primarily cattle), leather production and active tourism represent the only significant economic activities in this protected area. Vegetation is mostly Mediterranean shrub and pasture, except for the highest areas, where there is neither soil development nor vegetation. Two main soil types can be distinguished: the carbonate outcrops are covered by patchy leptosols and regosols, whereas less permeable soils with a thickness of 10–70 cm and a silty–clayey texture overlie Cretaceous marl outcrops.

3 Methodology

3.1 Hydrogeological characterization

The implementation of one of the already existing methods for vulnerability mapping presents, *a priori*, two key issues: a comprehensive understanding of the hydrogeological characteristics and behavior of the site where the methodology will be implemented, and sufficient technical knowledge of the GIS tools used. Regarding the GIS skills, in many cases, this is easily afforded by means of training and tutorials, being directly replicable for all the aquifers assessed. Nevertheless, the most crucial element in vulnerability mapping in karst is the consistent hydrogeological knowledge applied as expertise. Since karst aquifers are individually different in terms of distinctive behavior and characteristics (geological, climatological, hydrological, land uses, etc.), specific site knowledge is necessary.

The hydrogeological characterization encompasses jointly qualitative and quantitative analyses of the information derived from geological, geophysical and speleological methods, hydrological and hydraulic techniques, and the use of natural tracers, such as isotopes and hydrochemical parameters, as well as the application of dye tracer tests (Goldscheider and Drew 2007; Hartmann et al. 2014; Stevanovic 2015; Mudarra et al. 2019). This allows the implementation of the vulnerability mapping methodology and its later validation, enhancing the reliability and accuracy of the results from the mapping procedure.

The type of recharge (concentrated or diffuse *versus* allogenic or autogenic), the flow conditions within the system (conduit or diffuse flow) and the storage capacity of the aquifer are the major factors controlling the functioning of the aquifer (Goldscheider and Drew 2007). Since vulnerability mapping involves a spatially explicit model, the most basic information includes a definition of the limits and geometry of the aquifer and the consequent dimensions of its catchment area, which are used as a reference to implement the methodology. The vulnerability map must cover the recharge area extent, including the allogenic area if this contributes significantly to the aquifer recharge or spring behaviour. In this way, the analysis of natural and artificial (dye) tracer records has been increasingly used in karst hydrogeology to identify the flow paths, to delineate recharge areas, and to characterize solute transport processes (Batiot et al. 2003; Celle-Jeanton et al. 2001; Andreo et al. 2006; Perrin et al. 2007; Goldscheider et al. 2008; Barberá et al. 2018; among others).

In addition, the analysis of spatial variations of groundwater chemistry within aquifers, but also temporal evolution of selected hydrochemical parameters (chemographs), help to understand the groudwater's hydrogeological behavior, providing realistic information under different hydrological conditions (flood, recession, depletion, etc.). Some of the

185 characteristics that define the hydrogeological functioning of a karst system, such as the degree of functional
186 karstification (the active karst network that permits the flow path integration through the aquifer from the surface to
187 the spring, Mudarra and Andreo 2011) or water sources and mixing, can be inferred from the joint analysis of chemical
188 constituents integrating chemographs, including natural tracers of infiltration (such as intrinsic fluorescence), total
189 organic carbon (TOC), and NO_3^- (Hunkeler and Mudry 2007; Mudarra et al. 2014; Barberá and Andreo 2012). These
190 parameters must be clearly characterized and properly assessed in order to define correct protection strategies for the
191 karst groundwater.

192 Detailed hydrogeological investigations, including dye tracer tests, have been carried out in the Ubrique aquifer since
193 2012 (Sánchez et al. 2016; Martín-Rodríguez et al. 2016; Sánchez et al. 2017). These original investigations enabled
194 researchers to define the recharge area, to perform water budget computations, to infer the hydrological and
195 hydrodynamic behaviour, and to document most of the environmental characteristics of the test site, i.e. climate, soil
196 mapping, flow concentration within the epikarst, etc. Although most of the methods for groundwater vulnerability
197 mapping aims to be applied using geo-environmental data available in most countries, some fieldworks for adjusting
198 or tailoring the previous geodatabase to fit the vulnerability topic were done within the context of these research
199 projects (see section '*Results and discussion'*).

200

201 **3.2 Groundwater vulnerability mapping**

202 The objective of contamination vulnerability mapping is to identify the most vulnerable zones within catchment areas,
203 providing scientific reliable criteria for groundwater protection. The vulnerability to pollution of an aquifer is not
204 directly measurable in the field, so indirect methods for its assessement are required. These widely used approaches
205 are based on multiparametric analyses (on overlay and index techniques), with the assistance of GIS-based tools, relying
206 on the quantitative or semiquantitative compilation and interpretation of mapped data (Gogu and Dassargues 2000). GIS
207 allows for matching data on the characteristics of the study aquifer keeping the geographical framework as reference.
208 Each parameter represents the variables involved in groundwater vulnerability that are discretized using scored
209 intervals according to the relative degree of sensitivity to contamination.

210 As mentioned above, karst aquifers are particularly vulnerable to contamination due to flow concentration within the
211 epikarst layer and concentrated recharge via swallow holes. As a result, contaminants may easily reach the saturated

zone and then be rapidly transported through karst conduits over large distances (Goldscheider 2005). Many methods have been developed to assess groundwater vulnerability to contamination. These include methods that take account of the geological, hydrological, and hydrogeological characteristics of a karst system and climate variables, such as precipitation dynamics. Two types of vulnerability assessment can be differentiated (Daly et al. 2002): for the resource and for the source. According to the European guideline for vulnerability mapping (Zwahlen 2004), the assessment of resource vulnerability considers processes that control the flow of infiltrated water from the surface (all the modalities) to the main phreatic zone. An additional characterisation of groundwater flow through the saturated zone makes possible the mapping of the vulnerability of a water source.

In this work, the COP method has been selected for mapping the groundwater vulnerability of the experimental area. This method was primarily designed for resource vulnerability assessment (Vías et al. 2006), being later adapted for source vulnerability assessment, namely COP+K (Andreo et al. 2009). The COP method, worldwide applied (Vías et al. 2006; 2010; Yildirim and Topkaya 2007; Polemio et al. 2009; Katsanou and Lambrakis 2017; among other), has been succefully implemented in karst areas with similar climate and geological frameworks to Ubrique aquifer (Marín et al. 2012).

The COP method uses variables, parameters and factors in agreement with those proposed in the European Approach. Then, relevant factors deal with the permeability and thickness of the soil and rock composing the unsaturated zone (named O factor) and the concentration of runoff as influenced by topography, the karst features and the vegetation cover (C factor), and the distribution and intensity of precipitation (P factor). The COP vulnerability index value is obtained by multiplying the C, O and P scores.

The addition of the K factor, which considers the characteristics of water flow in the saturated zone, allow for mapping the source vulnerability. This map helps to define or redefine the protection zones of the karst aquifers that should support the decision makers when considering water supply protection and should promote sustainable development of the aquifer and surroundings (Marin et al. 2015).

3.3 Statistical assessment

The statistical assessment of the results derived from vulnerability tasks was done by the application of ordinary least squares (OLS) regression. Using the OLS tool-box (Arc-GIS® 10.7 ESRI Inc.), it is possible to evaluate relationships

between the explanatory variables (input variables used for vulnerability mapping by COP) and the dependent variable (COP value). The tool provides statistical information for each explanatory variable in the model, about the coefficient and the robust probability. The "coefficient" (hereafter as Coef.) represents the strength and type of relationship between each explanatory variable and the dependent variable while the "probability" (Prob.) determines the coefficient significance, based on the T test. In addition, the scatterplot depicts the relationship between an explanatory variable and the dependent variable. Strong relationships appear as diagonals and the direction of the slope indicates if the relationship is positive or negative.

Dependent and explanatory variables should have numerical fields containing a variety of values. For the application of the OLS tool, in addition, the variables must be discretized. The vulnerability map, which was produced in raster format at pixel size 5 x 5 m, has been resampled to 50 x 50 m, generating a database of 11,060 points within the Ubrique aquifer extent.

The input variables of COP were screened to select those that accomplish with the requirements: soil subfactor (OS, meaning soil characteristics), lithology subfactor (OL, related to the attenuation capacity of each layer within the unsaturated zone), lithology degree of fracturing (ly), thickness of unzaturated zone (zns), slope and vegetation characteristics (sv), surface karstic features, that include the distances to swallow hole whithin the scenario 1 (Karst_f), mean annual rainfall of a historical series of wet years (Pq) and intensity of precipitation (P_int).

3.4 Validation

Vulnerability maps can be validated by means of several methods (Zwahlen 2004), such as analysis of the hydrochemical responses of the karst springs, solute transport dynamics (natural or artificial) and/or by the use of hydrodynamic modeling approaches. Each of these procedures informs us about the single or a limited number of hydrological processes within the aquifer. To obtain a comprehensive understanding that leads to an accurate validation, it would be necessary to use a wide range of approaches to characterize both fast and slow flows within the system, recharge mechanisms, aquifer responses in both high and low water conditions, system dynamics at event-scale and, in general, the aquifer functioning. The hydrodynamic response of the spring water, especially during recharge periods, in conjunction with hydrogeochemical properties, has been largely used in a complementary way to characterize the hydrogeological functioning of karst aquifers (Shuster and White 1971; Mudry 1987; Genthon et al.

2005). In addition to the hydrodynamics, which constitutes the most elementary tool for validation, the temporal evolution of natural tracers of rapid infiltration (originating in the soil layer), and dye tracer tests specifically adapted to check the vulnerability to pollution, are the most powerful set of tools to validate the vulnerability maps in karst regions (Perrin et al. 2004; Marin et al. 2015). Yet because natural and dye tracers complement each other, their joint use can enhance our understanding of karst aquifer processes (infiltration, recharge and vulnerability), as noted by Marín and Andreo (2015).

In this work, the validation of the vulnerability map has been done using the time series of TOC and NO_3^- contents and turbidity values detected in the spring waters, coupled to hydrodynamic responses. In addition, the results of two previous tracer tests carried out in the framework of hydrogeological investigations have been used to characterize the concentrated recharge and to calculate flow velocities for inferring vulnerability classes.

4 Results and discussion

4.1 Hydrogeological characterization for implementing vulnerability mapping

Ubrique aquifer shows favorable features for vulnerability mapping applications given its confirmed duality in recharge mechanisms but also a well-defined geometry inferred by hydrogeological criteria, after several years of investigations (Sánchez et al. 2016; Martín-Rodriguez et al. 2016; Sánchez et al. 2017). The recharge area of the aquifer is well defined by tracer tests and water balance assessment (Fig. 1). According to the hydrodynamic information, the total discharge measured from all springs draining the Ubrique aquifer accounted for 35.1 hm^3/year during the period 2012 - 2015 (Martín-Rodriguez et al. 2016). On the other hand, mean annual values of diffuse recharge were indirectly assessed using the soil water balance method, after application of the Hargreaves and Samani (1985) approach for evaluation of the potential evapotranspiration (50 mm of useful reserve in the soil according to the edaphic properties of the experimental area). From these values, an effective rainfall value of 31.4 hm^3/year was calculated for the study area, equivalent to the diffuse recharge occurring over 26 km^2 of carbonate outcrops. In agreement with these results, the average total outputs exceed the input value by 3.7 hm^3/year. The difference mainly corresponds to the relative allogenic contribution of water runoff to the system recharge that enters through the Villaluenga del Rosario shaft, as well as slight contribution due to the measurement uncertainties.

To check the hydrogeological connection between direct/runoff infiltration points and the main outlets draining the Ubrique aquifer, two multi-tracer field experiments were performed in 2018, with the Villaluenga del Rosario shaft as the common injection point. The dye tests allowed for identification of the recharge dynamics that occur in the system (Fig. 2). Additionally, maximum flow velocities were estimated, being 184 m/h for Garciago spring, 129 m/h for Algarrobal spring and 178 m/h for Cornicabra spring. The tracer field experiments confirmed that the recharge of the test site partly occurs in a fast and concentrated way, through several swallow holes (Figs. 1 and 2). However, this recharge type has dual autogenic and allogenic contributions, with confirmed flow paths from the endorheic area drained by the Villaluenga del Rosario shaft (allogenic) and other minor endorheic areas located in the Sierra del Caillo (autogenic). The bare epikarst is extremely developed on most of the limestone outcrops (karrenfields), resulting in non-runoff and/or concentrated recharge due to the hierarchical network of the vertical flow system.

4.2 Vulnerability mapping by the COP method

Figure 3 shows the resulting maps from applying the COP method in the Ubrique aquifer. The O factor reflects the protective capacity of the overlying layers provided by soils (texture and thickness) and the lithology of the unsaturated zone (fracturing, the thickness of each layer, and the confining conditions). In the test site, the soil layer is scarcely developed and the carbonate rock is roughly homogenous and uncovered over most of the aquifer's extent. One of the main challenges for mapping of the variables involved in the O factor is related to the absence of boreholes (or any observation point) in the inner part of the aquifer. This issue is particulary common in mountainous karst aquifers and leads to use of interpolation tools to simulate the approximate thickness of the unsaturated zone, for which the uncertainty and reliability depend on the number of measurements and their spatial distribution across the study area.

Regarding the factor C, the individual map shows the two recharge scenarios provided by the COP method: concentrated recharge through the swallow holes (scenario 1) and the diffuse recharge (scenario 2). For the detection of exokarst features, aerial photos, digital terrain models, and satellite images can be used jointly with field surveys. A digital elevation model (DEM) with 0.5 x 0.5 m grids and 0.1 m of vertical resolution, derived from light detection and ranging data (LiDAR) captured in 2014, was obtained from public databases for this study (PNOA, 2016). The DEM in raster format was corrected for no data values prior to being run in this analysis. Data correction was performed by filling null data with average values from the surrounding grids by applying the moving window method.

In this research, ‘doline’ refers to any enclosed depression falling into defined morphometric attributes without consideration of their genetic features.

The spatial delineation of the recharge basins of the swallow holes and sinking streams (scenario 1) should be based not only on topography criteria but also on lithology, both concepts will highly condition their functionality regarding concentrated recharge towards the sinking point. This explains the fact that in karst aquifers it is quite common that carbonate outcrop areas, with well-developed epikarst, do not generate or develop effective run-off even for the topographic basins of swallow holes due to its high permeability. These areas would be excluded from scenario 1. Then, although GIS-based tools can readily calculate the drainage basins, the delimitation of the effective basin requires detailed field observations and *in-situ* monitoring, particularly during the transitory activation of swallow holes. In the test site, the functional recharge areas of the swallow holes were defined by *in-situ* obervations during heavy rain episodes because these points are activated under certain rainfall thresholds and during short time periods, of 1 or 2 weeks as maximum.

On the other hand, to create the P factor map, the precipitation data of wet years from 4 rainfall stations from 1984 - 2018 were used. For this historical period, the mean annual precipitation of wet years ranges from 1,292 to 2,314 mm and the average occurrence of rainy days is 88 per year.

The vulnerability is “High” and “Very High” in most of the recharge area (Fig. 3d). A large area is characterized as “Very High” vulnerability due to the low natural protection of the karst aquifer (very low values of O factor), resulting from the physical properties as well as the thickness of the layers above the saturated zone and the important role of exokarst features that, in fact, are highly developed in the test site. Only in areas where carbonates are overlaid by marls, and the surface flow is not drained towards swallow holes, the vulnerability class is “Low” or “Very Low”, but these are very small patches and account for only small areas.

The statistical assessment of the results associated with the explanatory variables, done by the application of the OLS regression, is shown in Table 1 and in Figure 4. In addition to the analysis of the complete database, the data were distributed between the points within the swallow hole recharge areas (886 points) and outside them (10,174), to determine whether there are differences in the relationship of the explanatory variables with the vulnerability index COP.

According to the statistical assessment, the COP values in the Ubrique aquifer are mainly related to the variable associated with exokarstic modeling forms (Karst-f) and, secondly, by the variable associated with lithology (OL). However, "ly" and "zns" present a weak relationship with COP as single variables. Then, as was expected, the combination of lithology and thickness of the unsaturated zone determines the effect and weight on the vulnerability of an aquifer. On the other hand, the variability of soil does not present a significant relationship with the vulnerability index in this test site. The role of soil in the natural attenuation processes and, as a consequence, in groundwater protection, is very relevant. However, in the Ubrique aquifer, this variable shows a very low degree of development in most of the area, since it is spatially homogeneous, and has a small effect on the spatial pattern of the vulnerability index. As an additional point, the statistical analysis suggests that the strong relationship between the variable OL and the dependent COP disappears, until there is no significance, when performing the analysis with data of the watersheds, as expected. In this area, variables associated with recharge (Karst_f and Sv) have the strongest and the most significant relationship.

Table 1 Summary of the OLS regression results with respect to explanatory variables

Variable	Whole catchment area			Scenario 2 (non- swallow hole recharge area)			Scenario 1 (swallow hole recharge area)		
	Coef.	StdError	Robust_ Pr	Coef.	StdError	Prob.	Coef.	StdError	Prob.
OS	-0.049	0.021	0.019	0.001	0.000	0.000*	0.136	0.045	0.002*
OL	0.366	0.010	0.000*	0.484	0.012	0.000*	0.048	0.029	0.103
ly	-0.001	0.000	0.000*	0.315	0.005	0.000*	0.000	0.000	0.936
zns	0.000	0.000	0.009*	0.000	0.000	0.967	0.001	0.000	0.000*
Karst_f	1.377	0.019	0.000*	1.299	0.010	0.000*	0.420	0.034	0.000*
Sv	0.018	0.060	0.771	0.658	0.025	0.000*	0.594	0.288	0.039
Slope	0.001	0.000	0.000*	0.000	0.000	0.004*	0.008	0.001	0.000*
P_int	0.117	0.010	0.000*	-0.035	0.004	0.000*	-0.460	0.043	0.000*
Pq	-0.002	0.000	0.000*	0.000	0.000	0.000*	0.003	0.001	0.000*

* indicates a statistically significant p-value ($p < 0.01$)

OS: soil characteristic
OL: lithology subfactor (related to the attenuation capacity of each layer within the unsaturated zone)
ly: lithology degree of fracturing
zns: thickness of unzaturated zone
Karst_f: surface karstic features, that include the distances to swallow hole within the scenario 1
Sv: slope and vegetation characteristics
Slope: slope in percentage
P_int: intensity of precipitation of wet years
Pq: annual rainfall of a historical series of wet years

4.3 Validation of the vulnerability map

In a similar framework to that used by previous research projects, discharge rates and selected hydrochemical parameters were monitored in the permanent springs as well as in the overflow points. Figure 5 displays the hydrodynamic behaviour of the two permanent outlets, plus Garciago overflow spring, in order to illustrate the functioning of the test site. Time series of spring discharge show a large variability, ranging in the case of Garciago spring from zero discharge to nearly 10 m^3/s discharge after 1 day from the main precipitation event. The magnitudes of the observed flood peaks in the springs are proportional to that of the recharge and they tend to recover pre-event values once the recharge effect is finished. In general, the studied outlets show a typical karst behaviour with sudden and rapid variations of hydrodynamic responses during rainfall events, as well as a low natural attenuation capacity against the rainfall. Therefore, the results obtained from the hydrodynamic analysis suggest a well-developed conduit network that enables a rapid groundwater flow within the aquifer. According to the latter hypothesis, rainwater infiltrates into the aquifer and rapidly moves through interconnected conduits and fractures, causing increases in hydraulic pressure transference and decreases in groundwater mineralization.

The groundwater resources, drained by the springs and used for human consumption, are threatened quantitatively and qualitatively. Concerning the quantity of pumped groundwater resources intended for human consumption, the discharge rates during recession periods are almost zero in Algarrobal and zero in Garciago springs (Fig. 5). On the other hand, during flood events the water quality is impacted by high turbidity levels in the majority of karst outlets and by the relationship between turbidity and potential pollutant load. Turbidity or particle dynamics (considered as natural tracer) highlight the arrival of water from the surface and/or from dry/flooded conduits (or saturated syphons) within the aquifer system. Turbidity evolution observed in karst springs during high-flow periods shows fast increases after an intense precipitation event, with narrow peaks detected 25 hours (on average) before the peak discharge (Fig. 6; Martín-Rodríguez et al. 2019). In a similar way, the TOC and NO_3^- contents show rapid increases after the precipitation events due to the arrival of recently infiltrated waters in the aquifer through vertical karstic dissolution

conduits or fractures, which rapidly reach the saturated zone (Fig. 5). The effects of rainfall on the water mineralization are noticeable after several hours. All these results denote an overall high vulnerability for the Ubrique aquifer.

Three dye tracers (pyranine, suforhodamine B and aminorhodamine G) injected into swallow holes in 2018 were detected in the main outlets of the Ubrique aquifer, shown in Figure 1. The results of tracer tests (carried out in high-water conditions), with a modal flow velocity ranging between 92.2 and 117.4 m/h, inferred an important degree of inner karstification. These data again provide evidence to support the hypothesis of high vulnerability of the system, especially when recharge water enters through the swallow holes.

In summary, the analyses of natural and artificial chemical constituents in the karst spring water confirm the extreme vulnerability to contamination of the pilot site, which is coherent with the vulnerability map resulting from the application of the COP method. However, some sectors of the aquifer surface where karrenfields are quite well developed, display very high vulnerability in the areas close to swallow holes. To get a complete validation of the vulnerability map, an additional dye tracer test designed specifically for validating the vulnerability related to diffuse infiltration is further needed. This additional field experiment, in which fluorescent substances should be injected into karrenfields and swallow holes, would allow one to confirm whether the high development of exokarst features leads to a significant contribution to the concentrated recharge at depth or, by contrast, whether the vertical permeability is quite limited. If the results of the proposed additional fieldwork are conclusive, it would permit a rethink and re-design of the current conceptual hydrogeological model of the pilot site. In karst media, transferring improvements from conceptual modeling to vulnerability assessment must be constantly conducted to enhance understanding of the hydrogeological systems and better manage the water resources.

4.4 Future perspectives: early warning systems (EWS)

Within the framework of water supply protection, delineating protection zones for groundwater sources intended for human consumption is a sanitary measure accepted and promoted in most water-related policies. In fact, as established

by the official guidance documents on the protection of groundwater used for drinking water (e.g. European Commission 2007), protection zones in karst aquifers may need to be defined using vulnerability maps as the preferred tools. However, groundwater protection requires not only static protection measures, but also the implementation of monitoring and security systems. These procedures are designed to ensure the stability of the environmental and hydrogeological conditions under which the protection perimeter was defined, in order to identify whether any changes might impact (1) the vulnerability pattern and (2) the water quality. In both cases, vulnerability maps would require revision to redefine perimeters and spatial criteria associated with planning. An early warning system (EWS) (Bartrand et al. 2017, Grimmeisen et al. 2018) is one of the most adequate tools to ensure this regular monitoring.

The concept of an EWS comprises a set of strategies designed to support operational tasks in water supply systems to optimize raw-water capture by predicting the arrival of low-quality karst groundwater. An EWS aims to identify and reliably detect contamination episodes, and therefore facilitates the adaptation of drinking-water operational procedures and water management strategies accordingly. The EWS and vulnerability assessment procedures share the same hydrogeological knowledge as a basis for groundwater management and protection, and consequently a stable feedback should be established between both approaches. Thus, vulnerability mapping is an essential step for designing and improving an EWS and its related groundwater monitoring network techniques. Also data on natural tracers recorded within the monitoring network of the EWS can help to validate the vulnerability maps.

In rural karst areas, such as the Ubrique test site, fecal bacteria and other pathogens often originate from farming and agricultural activities, such as cattle pasturing and the application of manure (Drew and Hötzl 1999; Boyer and Pasquarell 1999). These kinds of pollutants (and other inorganic substances), which pose a threat to drinking water catchments, can easily enter the aquifer through preferential flow paths. Prolonged periods of good water quality may thus be interrupted by short microbial contamination events. Identifying those is a major challenge in the protection of karst water sources (Pronk et al. 2007). The EWS quality monitoring strategies have been presented as a promising tool that can foresee and detect the effects of pollution on groundwater quality in karst aquifers intended to drinking water supply of both urban and rural populations. An EWS identifies easy-to-measure parameters or combinations of them that indirectly predict the possible arrival of microbial pathogens at supply points. Different approaches have been selected to achieve this objective in near real-time, and which have shown a good correlation with fecal contamination and microbial pathogens: turbidity (Nebbache et al. 1997; Ryan and Meiman, 1996; Massei et al. 2003), organic carbon content (Pronk et al. 2005, Frank et al. 2018), spring discharge (Auckenthaler et al. 2002), particle size

distribution (Pronk et al. 2007; Goldscheider et al. 2010), and other indirect methods, like the measurement of the enzymatic activity (Ryzinska-Paier et al. 2014; Ender et al. 2017), fluorescence-based techniques (Frank et al. 2018) or tryptophan-like fluorescence (Mudarra et al. 2011; Sorensen et al. 2015).

Water drained by Ubrique aquifer springs (Cornicabra, Algarrobal and Garciago) is used for drinking water purposes. The spring waters suffer frequent pollution episodes, in which high loads of inorganic sediment particles and bacteria arise during stormy rainfall events (Sánchez et al. 2017; Martín-Rodríguez et al. 2019). These events of high turbidity affect the exploitation of the available water resources, since during these conditions it is not possble to capture pristine groundwater and use it for water supply. Under these circumstances, the implementation of an EWS is an unique opportunity for safeguarding water quality.

The procedure for the implementation of the EWS at Ubrique test site consists of three phases for its full execution (Fig. 7): (1) continuous monitoring of the natural responses of the springs, including both easy-to-measure (discharge, electrical conductivity, water temperature and turbidity) and novel (DOM, TOC, tryptophan, *E. Coli* and particle size distribution) parameters; (2) analysis of short/long-term data series and application of properly adapted artificial neural network (ANN)-based algorithms (Zhang et al. 2018) to identify the presence of microbial pathogens for their indirect detection from easy-to-measure *in-situ* parameters and to forecast water quality based in meteorological predictions; (3) system launch with an operational perspective, and the assessment of selected operational key performance indicators (KPIs) for EWS optimal performance. These KPIs are statistical metrics used to gain insights into the efficiency and productivity of the measurement strategies carried out to optimize user-defined operational protocols. Phase 1 allows one to acquire records of physico-chemical water parameters, together with dye test performance data, to get a full picture of the system dynamics. By the application of algorithms based on ANN, using as inputs the database acquired in phase 1, the combination of parameters that most accurately indicates the presence of microbial pathogens will be identified. The ANN approach for better predictions of microbiological contamination events based on near real-time multi-parameter monitoring has been successfully used for EWS of water quality (e.g. Zhang et al. 2018).

Finally, in the operational phase, the information provided by the easy-to-measure recording probes for real-time monitoring and meteorological predictions will be transferred online to a web database. Based on the hydrological and hydrochemical monitoring data, the algorithm continuously assesses the potential risk of a contamination event

occurring and automatically validates its forecasting in near real time (hourly resolution), to give a warning about the risk of contamination for spring water quality (Grimmeisen et al. 2018, Zhang et al. 2019). Consequently, the water company operator could be assisted by the system in terms of operational works. The system alerts the drinking water suppliers when the performance algorithm reaches a critical threshold. The optimization process will be continuous, as the system gets a feedback from the analysis of data acquired on each contamination event, which will permit a continuous optimization in system performance from the analysis of selected KPIs.

5 Challenges in karst groundwater vulnerability mapping

Methods of groundwater vulnerability mapping in karst aquifers have progressed in the last 20 years, being solid, useful and effective tools in the protection of water resources. Groundwater vulnerability assessment methods have been developed as the necessary basis for implementing groundwater protection measures, with the delimitation of protection zones being one of the most relevant tools. However, as mentioned in previous sections, given that the vulnerability to contamination is not empirically quantified, but rather requires a modeling and simplification of hydrogeological characteristics, vulnerability mapping and assessment are not exempt from uncertainties, and integral water supply protection is still a challenging issue. Among the most relevant challenges that researchers will have to deal with in the near future are:

1. The development of protocols and tools that strengthen the decision tree during the implementation of the methodologies, as well as the validation of the results. Vulnerability mapping has become a routine procedure to support land-use planning as a measure to protect groundwater quality; the validation of vulnerability maps and protection zoning is essential for proper land-use planning and for understanding what is really meant by the vulnerability degree shown on the map. Validation may be undertaken by analysis of the hydrodynamic and hydrochemical responses of the main springs, combined with analysis of the temporal evolution of natural tracers of infiltration and complementary dye tracer tests that must be specifically designed to check the vulnerability to pollution (Marin et al. 2015). A good knowledge of hydrogeological functioning and karst behavior constitutes a complementary procedure that feeds back into the vulnerability mapping exercise (Marin et al. 2015, Kazakis et al. 2018). Thus, the hydrogeological characterization should not be the end in

itself, but a way to assess the vulnerability of groundwater to contamination, and the validation of vulnerability can contribute to extending knowledge about the karst aquifer. This symbiotic relationship also occurs between the EWS and vulnerability mapping, where the results of the latter help to design the EWS monitoring network, at the same time that chemographs will allow a better interpretation of the system functioning and, therefore, a readjustment, in a feedback manner, of those parameters that should be involved in the assessment.

2. Groundwater exploitation and contamination have become of global concern (Gregory et al. 2013; Zheng and Liu 2013). A suitable groundwater protection strategy requires the conceptualization of the hydrogeological functioning for system characterization. The proper protection of karst groundwater becomes a difficult talk in developing countries where important gaps in hydrogeological knowledge exist for vast regions (Taheri et al 2015). Therefore, the availability of consistent water-related databases and approaches, and their validation and interpretation, are of utmost importance for complex hydrogeological systems such as karst aquifers. This situation stimulates a demand for establishing flexible and simplified methods that could be applied with the least available data and still lead to acceptable interpretations. However, this simplification needs to be addressed carefully since vulnerability mapping in karst can result in a considerably large degree of uncertainty. As mentioned previously, this uncertainty could be unmanageable, resulting in a poor assessment and incorrect evaluation. For relevant countries, since the Sustainable Development Goal 6 (SDG6) of the United Nations (UN-Water 2018) aims to ensure availability and sustainable management of water and sanitation for all, a strong commitment of local and international organizations with experience in the research and protection of groundwater are necessary, as a long-term prospect.

3. In the climate change context, the predicted changes, such as an increase in the frequency of extreme drought in the Mediterranean domain or increase of extreme precipitation events in the Atlantic and Boreal biogeographical regions (EEA 2017), will affect the current hydrogeological balance and the trade-off of water supplies for different end-users. Some research has shown that the flood pulses caused by precipitation events after a long dry period cause a significant deterioration in water quality, with a significant increase of turbidity, as occurs in Ubrique springs, and even in the amount of coliform bacteria in the water (Ravbar et al. 2018). Therefore, the proper identification of the vulnerable zones of recharge areas becomes even more

relevant, at the same time that the implementation of EWS will be an increasingly necessary management and control tool for continuous monitoring of the karst water quality to ensure safe quality. Further work needs to be done to simulate site-specific hydraulic responses to different climate scenarios, and there needs to be further thought on how to adapt water management and protection plans towards an increase in the resilience of water supply that supports the local population.

6 Conclusions

Karst aquifers are highly sensitive to the effects of contamination, and priority must be given to contamination prevention for the sustainability of groundwater resources. This work, which has a groundwater vulnerability perspective and a purely hydrogeological focus, provides evidence (supporting previous work) that karst aquifers require the development of common groundwater protection strategies, resulting in integrated management plans based on the continuous processes of feedback and re-evaluation of the system function and protection criteria (Kazakis et al. 2018). In the case of the test site, the characterized karst behavior and conduit flow system, and the significant contribution of the allogenic component to the total recharge of the aquifer, permit the mobilization of contaminants originating from livestock in the surrounding areas and from partially treated waste water, as well as inorganic sediment particles when stormy rainfall events occur. Consequently, the protection of groundwater and the preventive principles must be considered as the appropriate strategies to minimize the water pollution risk and the potentially negative effects on human health.

The work presented here is part of a broader project that includes the implementation of an EWS, addressing an integrated protection and management strategy for the Ubrique aquifer. Considerable progress has been made, but advances are still necessary due to the hydrological complexity of the karst aquifers here. Ongoing investigations, whose initial phases are presented in this work, should trigger the implementation of tools for comprehensive and safe management of the karst groundwater resources. Despite its humid climate, having precipitation much higher than that of the rest of the Andalusia region of Spain, and even at country level, the rainfall regime at the study area is also threatened in the future projections associated with climate change. The delineation of the protection zones of the karst springs (Cornicabra and Algarrobal) used for water supply, based on vulnerability mapping and land-use management policies, and the operational implementation of an EWS in the captured points for potable use, will mean advances in

549 the management of the water supply, including enhanced safety and resilience for the water supply to the nearby rural
550 municipalities.

551 This research links different methods applied to the protection of the source from contamination events. The methods
552 range from classical hydrodynamic and hydrochemical approaches, to the implementation of protection zones and
553 early warning groundwater quality monitoring networks. Such a combined application allows a deeper understanding
554 of contaminant transport in karst aquifers, natural attenuation processes, transit times, and the influence of these factors
555 on other water parameters. For the development and implementation of an EWS for karst springs, it is necessary to
556 have a solid understanding of the hydrogeological functioning of the whole aquifer, particularly with regard to
557 groundwater vulnerability to pollution. EWSs have become a promising integrated monitoring tool for practical
558 application of vulnerability maps, focusing on the source protection. A double-sense feedback is established between
559 both tools: on one hand, vulnerability mapping is an essential step for an optimal design of the EWS and its related
560 groundwater monitoring network techniques (providing continuous feedback from data gathering), as well as
561 identifying potentially hazardous human activities which could rapidly change the chemical and microbial quality of
562 the groundwater. On the other hand, continuous validation of vulnerability maps can be achieved through the data
563 analysis of natural and/or anthropogenic-induced tracers recorded by the spring monitoring network. The acquired
564 knowledge of solute transport in the groundwater, and its reactiveness, also allows for testing the accuracy of the
565 selected vulnerability mapping approach. The use of dye tracers specifically planned to validate vulnerability mapping
566 are highly recommended to assess the accuracy of the selected vulnerability mapping approach as well as be also
567 useful for EWS delineation.

568

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817

FIGURE CAPTIONS:

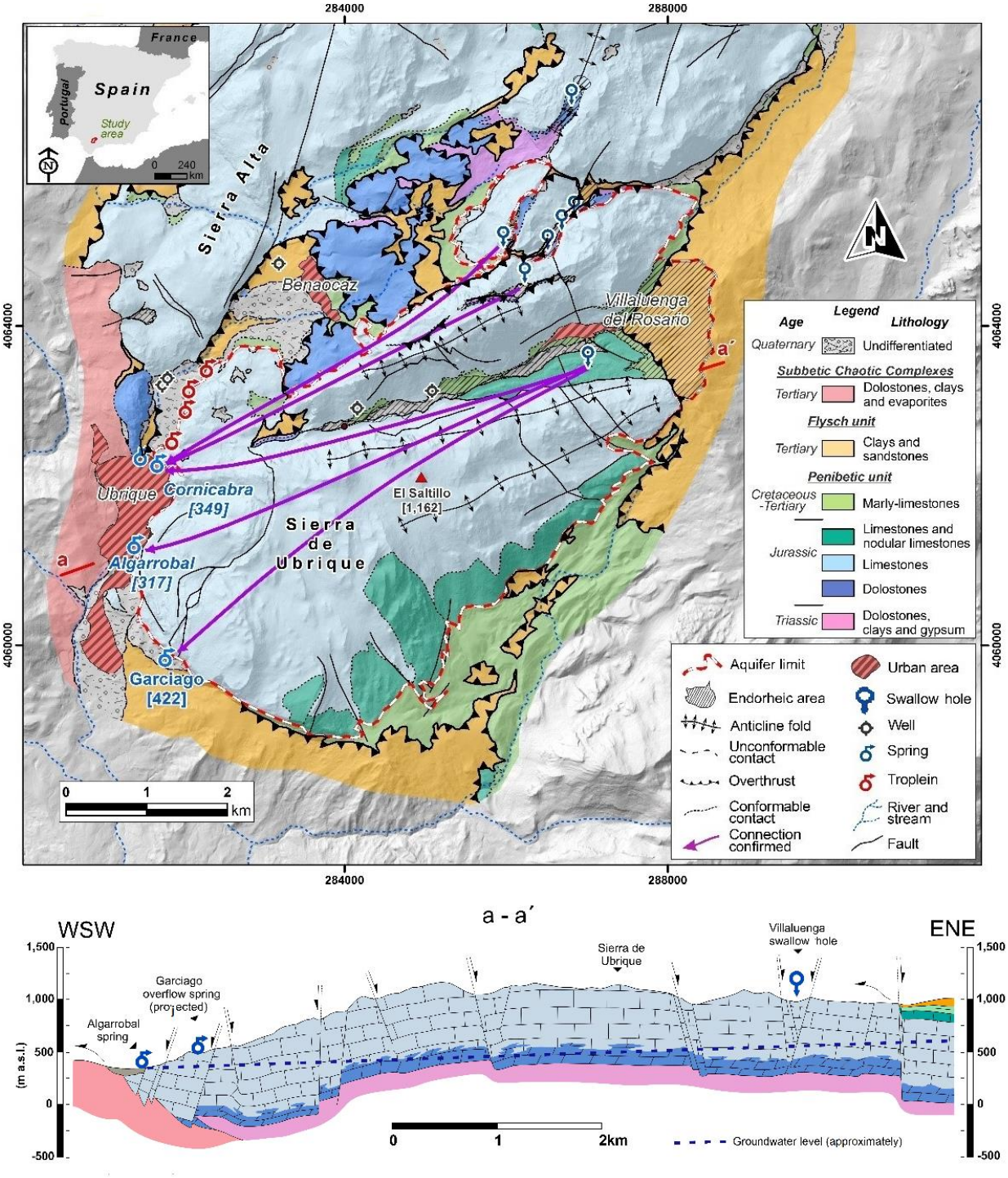


Fig. 1 Location, geological map and SE-NW oriented hydrogeological cross-section of Ubrique aquifer. Additionally, confirmed karst connections from the tracer test performed in 2018 are displayed

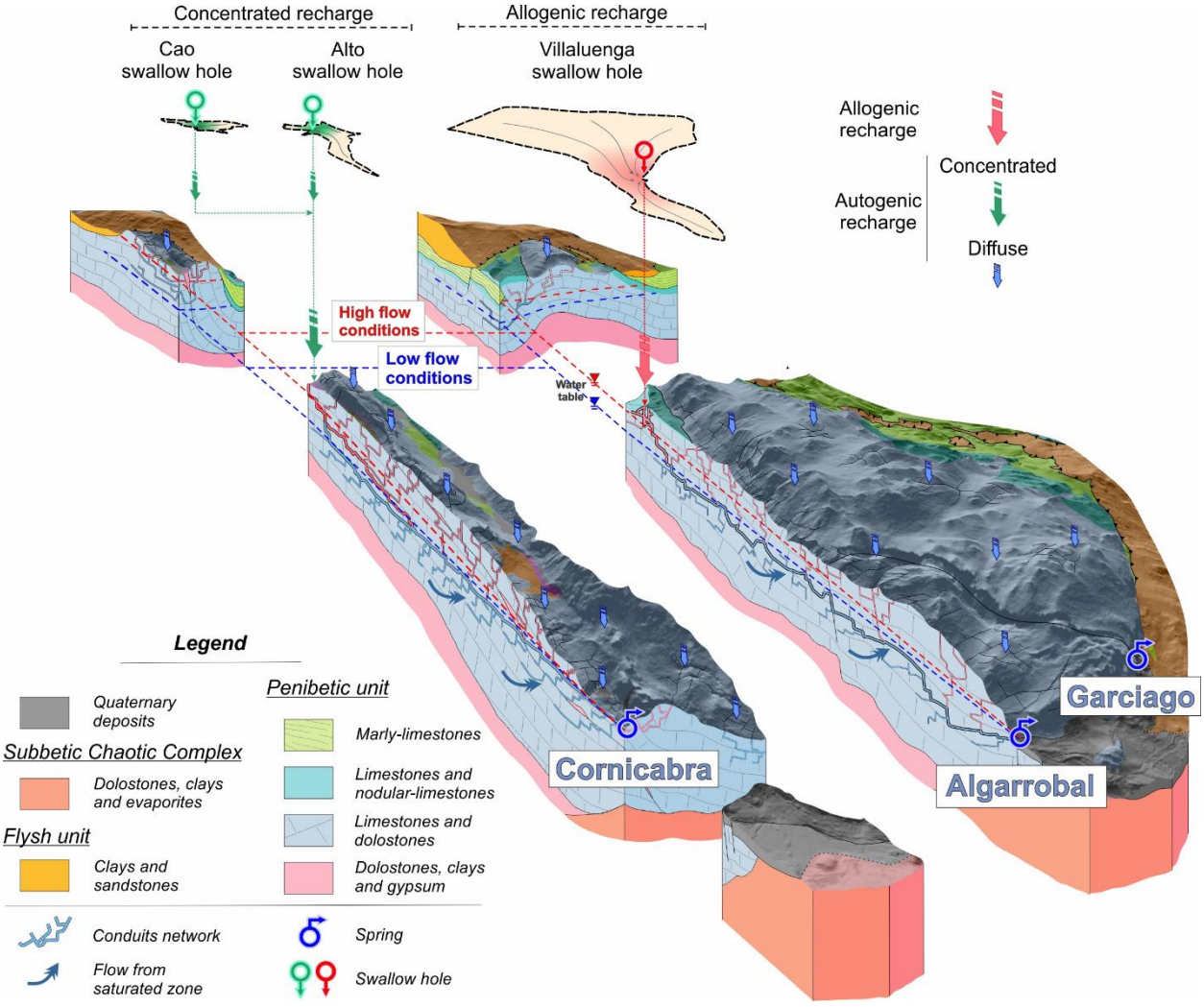
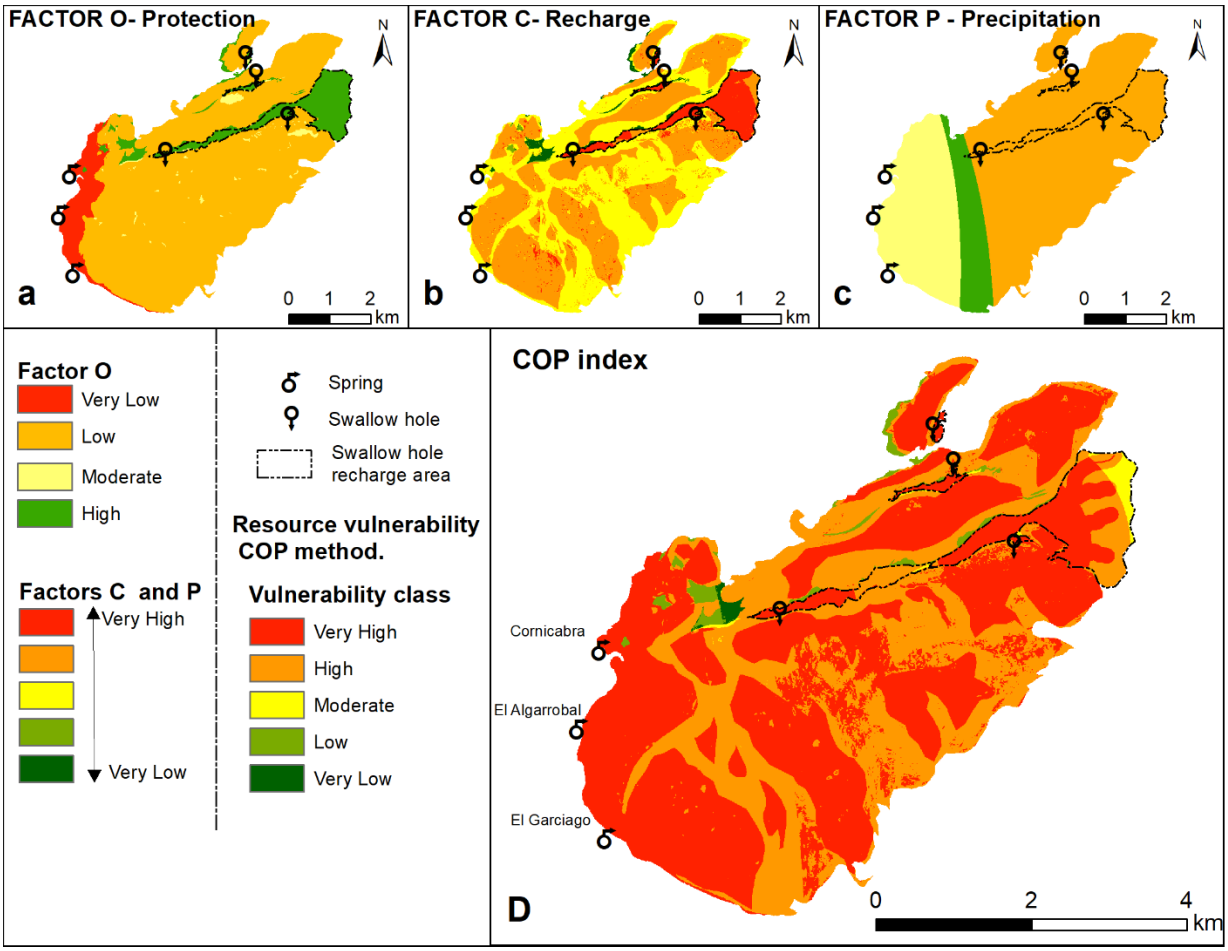


Fig. 2. Hydrogeological conceptual model showing recharge modalities (allogenic *versus* autogenic infiltration), sinking points, karst springs, and traced karst flow paths in selected cross-sections (NE-SW oriented) of the Ubrique aquifer



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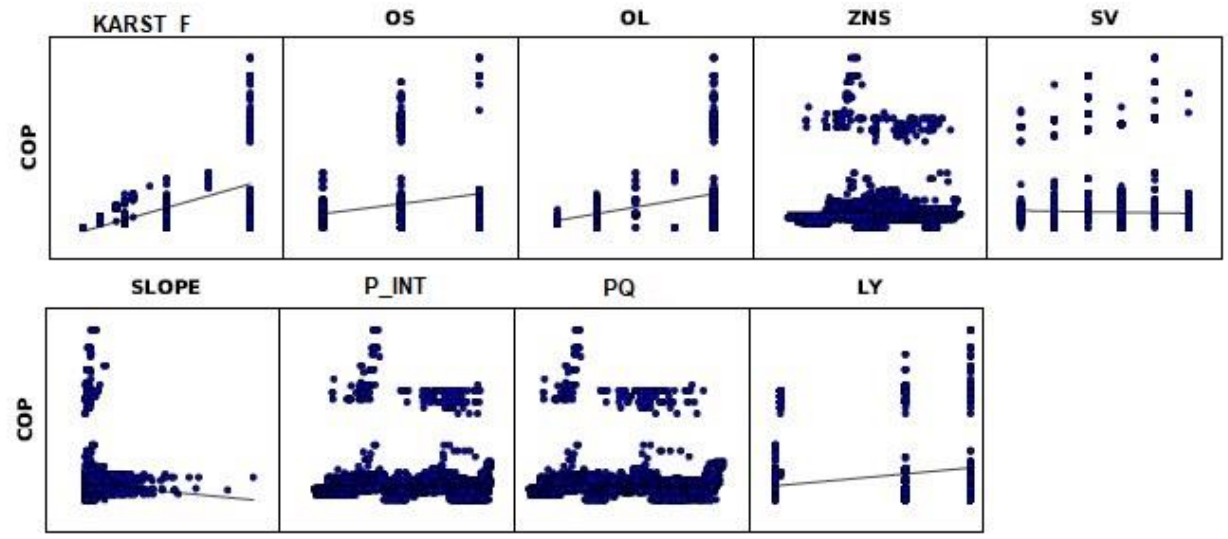
827 **Fig.** 3 Maps of resource vulnerability to contamination in the Ubrique aquifer. **a**: factor O, protective capacity of the
828 overlying layers; **b**: factor C, concentration flow; **c**: factor P, precipitation condition; **d**: COP method, resource
829 vulnerability classes. Green colours mean favorable conditions (lower degree of vulnerability) and red colours mean
830 unfavorable conditions (higher degree of vulnerability) for the protection of the groundwater



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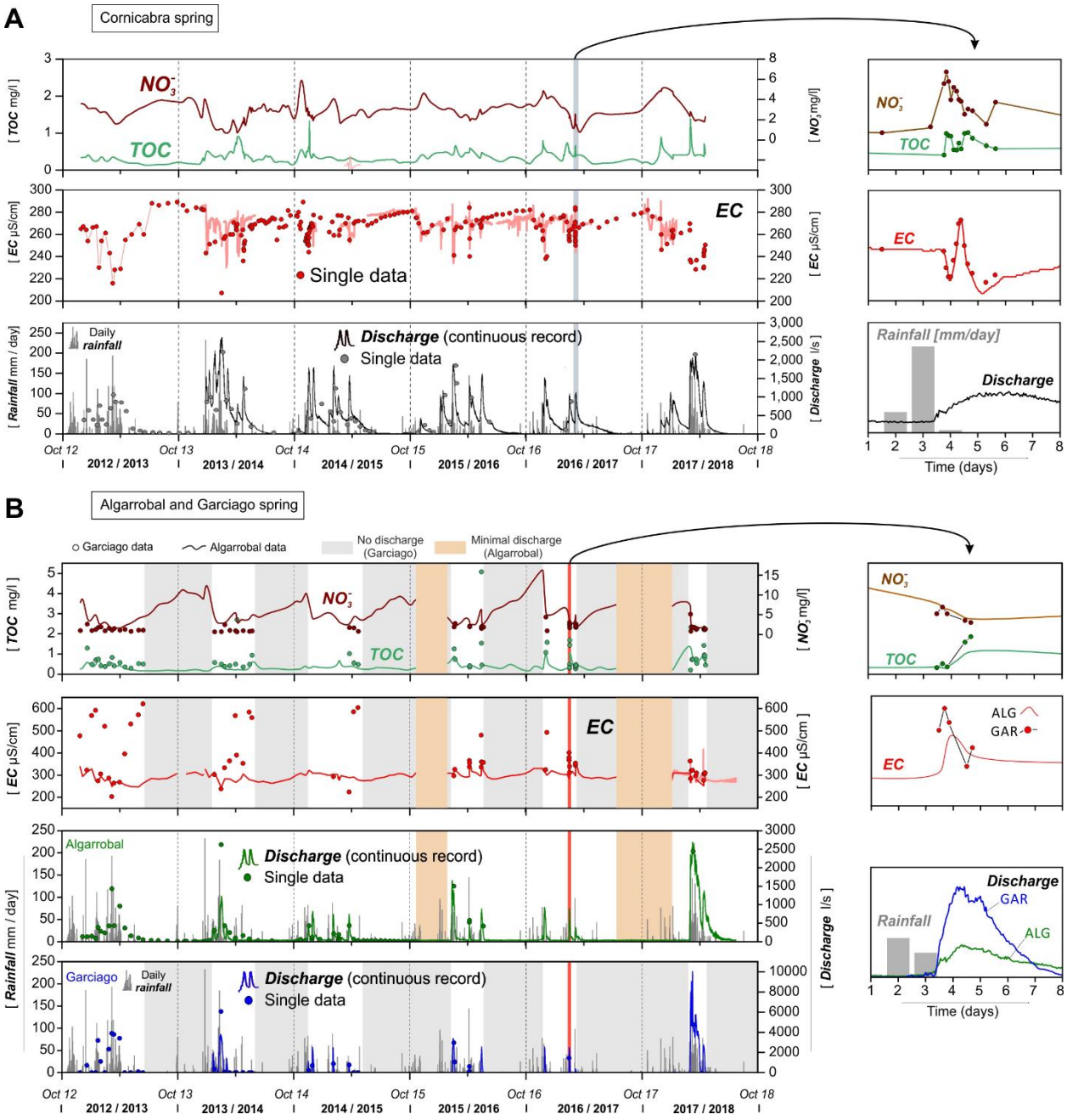
832 **Fig. 4.** Scatterplots for each explanatory variable and the dependent variable. Stronger relationships are depicted as

833 black lines and the slope indicates if the statistical correlation is direct or reverse



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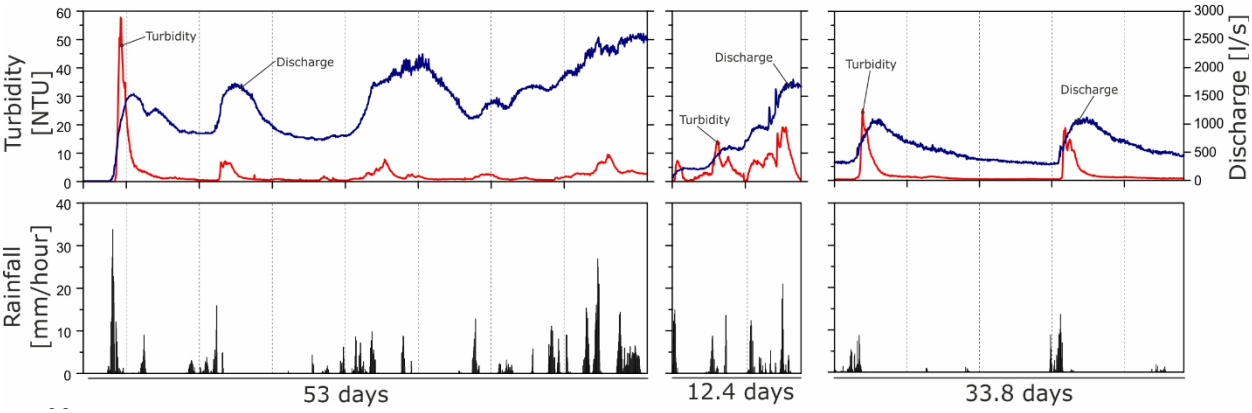
835 **Fig. 5** Seasonal (main panels) and single event-based (individual right panels) time evolutions of electrical

836 conductivity (EC), TOC, and NO_3^- concentrations measured in **(a)** Cornicabra and **(b)** Algarrobal and Garciago springs



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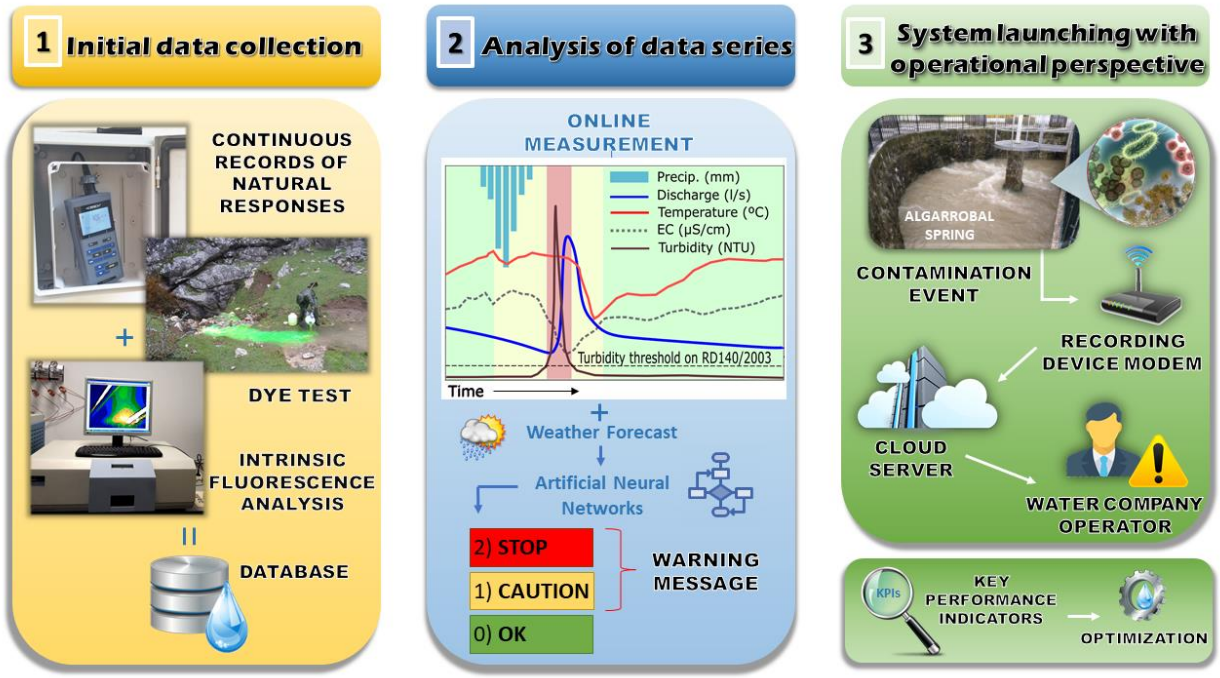
838 **Fig. 6.** Time series of discharge and turbidity in Algarrobal spring after several rainfall episodes during an

839 approximately 2-month time window



840

841 **Fig. 7.** Set-up and implementation steps of the early warning system (EWS) that will be developed in the karst springs

842 draining Ubrique aquifer (adapted from Grimmeisen et al. 2018)

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