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title: **Contamination of a regional confined aquifer by leaky boreholes. Campo de Cartagena case study (SE Spain)**

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ABSTRACT

The present work provides a methodological approach to evaluate the impact of poorly constructed (leaky or without a gravel pack) and abandoned wells for facilitating the transfer of contaminants between aquifers at different depths. The approach was based on the use of nitrate as a tracer and the MIX_PROGRAM code for mixing calculations. Proposed methodology was applied to the Campo de Cartagena (SE Spain), where intensive irrigated agriculture takes place. The hydrogeologic unit consists of a multi-layer system constituted by an upper unconfined aquifer and a deep confined aquifer with a high density of wells exploitation (1.18 wells/km^2). Results show the increase of the unconfined aquifer impact on the confined aquifer along the groundwater flow direction toward the coast, although this general pattern is controlled by local factors (pumping, intensity of agricultural practices, density of wells and groundwater residence time).

INTRODUCTION

Abandoned, leaky and poorly constructed wells (leaky or without a gravel pack) may act as conduits transferring contaminants to underlying aquifers and are common features at many polluted groundwater sites. In a multi-layer aquifer, abandoned or poorly constructed wells penetrate through geological strata otherwise considered impermeable (aquitard) that supposes open conduits for pollutant migration. Aquifer interconnection may also occur via flow through aquitards in areas of reduced aquitard thickness which could be enhanced by water pumping in the underlying confined aquifer.

The present study was carried out in the Campo de Cartagena (SE Spain) (Fig. 1a), where the land is intensively irrigated for agriculture and groundwater pollution exists. The agricultural activities are practised over the unconfined aquifer, with an intensive mineral fertiliser application (0.9-1.6 t ha^{-1} yr^{-1}) which constitutes a source of contamination and is separated from the lower confined aquifer by a thick aquitard (Fig. 1b). The objective of the research is to evaluate the significance that abandoned and poorly constructed wells have on cross-formational groundwater flow and contaminant transport between the shallow unconfined and deep confined aquifers. The work provides a methodological approach based on the geochemical tools application and water mixing calculations from a numerical model. The state of saturation of groundwater samples for relevant minerals, and ionic speciation were calculated using the PHREEQC code (Parkhurst, Appelo, 1999). Water mixing calculations were carried out using the MIX_PROGRAM numerical code (Carrera et al., 2004), which provides theoretical estimates of the end-member concentrations, thereby reducing the uncertainty due to spatio-temporal variability and thus improving the reliability of the output mixing calculations.

METHODOLOGY

The regional groundwater flow direction for both aquifers is toward the coastal, from northwest to southeast. The aquitard between the two aquifers is composed of marls in regions 2 and 3, and mainly of evaporites in region 1 (Fig. 1b). Groundwater records for the 1974–2008 monitoring surveys were provided by the Quality Network of Water Authority (CHS-IGME). The chemical data set includes physico-chemical parameters (pH, temperature and electrical conductivity); major ion content (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, HCO_3^-, SO_4^{2-}, and NO_3^-); and CO_3^{2-}, NO_2^-, NH_4^+, and SiO_2. Some specific surveys in situ analysed dissolved oxygen (DO) and heavy metals.

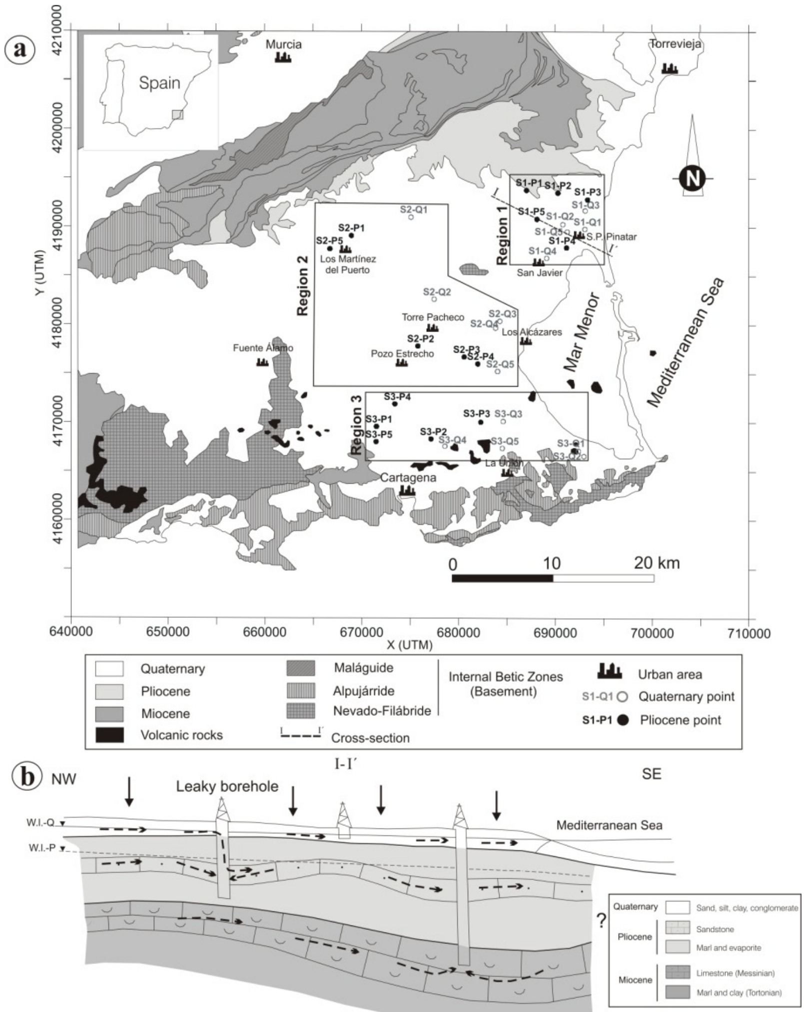

Figure 1. a) Study area and geological sketch. Location of the defined regions and sample points (S1 to S3 region; P: Pliocene aquifer; Q: Quaternary aquifer; 1 to n sample point). b) Geological cross section and conceptual model.

Due to the broad extension of the study area, three regions were defined based on land use and regional geology (Fig. 1a). A subset of five water sample points within the surveyed period for each aquifer and defined region was selected. Selection was based on the geographic location, aquifer sampled and length of available records.

Nitrate as an indicator of interconnected aquifers

In regional groundwater flow systems, which are shaped by the geology, the attenuation processes regulate nitrate transport and control its distribution in aquifers. Nitrate attenuation may occur by dilution, through mixing of groundwater in the aquifer (Altman, Parizek, 1995), or by denitrification. In reducing environments it is the only geochemical process that permanently removes nitrate from aquifers. Nitrate reduction can be mediated by oxidation of organic matter, pyrite and iron under anaerobic conditions (Korom, 1992).

For the three defined regions, nitrate constitutes a good indicator for assessing the Quaternary and Pliocene interconnection. Homogeneity in the spatial distribution of land covered by crops (source of nitrate), along with the long term records of nitrate concentration and dissolved oxygen values (oxidation-reduction potential), support this assumption.

Geochemical and mixing models

To calculate ionic speciation and state of saturation (saturation-index) for relevant minerals, PHREEQC was applied. This preliminary step is necessary to evaluate the potential geochemical reactions occurring in the aquifer, since deviations from mixing lines could be attributed to chemical reactions.

Concentrations of mixed samples, mainly affected by analytical errors, are likely to be more accurate than end-members, commonly with high spatial and temporal variability. This fact can be used to impose constraints on valid end-member concentration since taking mixing constraints into account may significantly reduce uncertainty in end-member concentration by imposing consistency. Consistency is dealt with in two ways: first, end-members should fall on the mixing line and second, mixed waters should fall within the interval defined by end-members. The MIX_PROGRAM code permits the mixing ratios in mixed samples to be derived, allows for redefinition of mixing lines.

The Cl/Br ratio (R), used as an indicator of seawater intrusion (R = 655±4) or evaporite dissolution (R = 1200–5400), was calculated in all available water samples in order to assess the importance of a third member for mixing calculations (Custodio, Herrera, 2000).

RESULTS AND DISCUSSION

Hydraulic conductivity of the aquitard ranges over several orders of magnitude, marls (10^{-5}–10^{-6} m d^{-1}) and evaporites (10^{-10} m d^{-1}). Considering the highest hydraulic conductivity value and vertical head difference through the aquitard, flow rate q ranges between 0–10^{-5} m d^{-1}. Flow through the aquitard was excluded as a major contribution to the pollution process.

Nitrate as an indicator

Average concentration in wells located toward the coast show a generally increasing trend (Fig. 2a), except for region 3, where nitrate average concentration is approximately constant, being controlled by the low hydraulic gradient of the Pliocene aquifer in this region. Nitrate presence in the unconfined aquifer clearly originates from the intensive agricultural practices; however, with regard to the confined aquifer much lower concentrations, even nil, should be expected since no agricultural development or anthropogenic activities take place in the recharge area (NW part of the basin, Fig. 1a and b). Moreover, the thick aquitard separating both aquifers should act as an impervious barrier, contributing to the attenuation of nitrate (Roberston et al., 1996) and related species (NO_2^- and NH_4^+) concentration if cross-formational flow occurs. DO content in both aquifers ranges between 1 and 9.8 mg l^{-1}; therefore, nitrate attenuation in both aquifers mediated by denitrification processes is unlikely.

The high variability of nitrate content observed in the lower confined aquifer (Pliocene) reflects the presence of pumping wells in the vicinity of a sampled point. Groundwater stratification due to water chemical composition (Guimerà, 1998) may also exist.

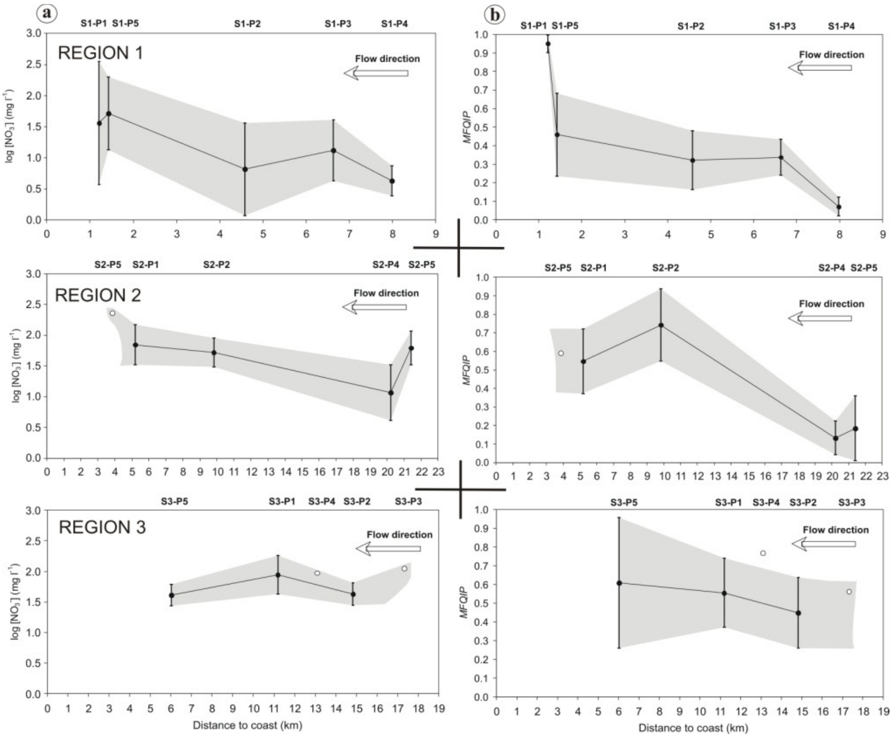

Figure 2. a) Average nitrate concentration of Pliocene aquifer for selected sample points versus distance to coast for each region. b) Quaternary aquifer water mass fraction (computed mixing ratios-MFQIP) introduced into the Pliocene aquifer versus distance to coast. Solid dots: average computed mixing ratios. Vertical bars: standard deviation. Empty circles: only one data available. Arrows: groundwater flow direction.

MIXING MODELS

The two end-members are the Quaternary (from 1980 to the present time) and Pliocene (natural background concentration 1970's, data set non-affected by agricultural pollution) aquifer water samples, and the two chemical species selected were chloride (Cl^-) and sulphate (SO_4^{2-}) (Table 1). Cl^- is a conservative compound but SO_4^{2-} can be affected by several processes. Sulphate reduction, pyrite oxidation and nitrate, instead of oxygen as the electron acceptor, control the SO_4^{2-} concentration in groundwater (Massmann et al., 2003). The decision for SO_4^{2-} selection was due to several reasons: (i) presence of oxic conditions, similar HCO_3^- concentration and non-existent H_2S in both aquifers; (ii) lack of pyrite in this geologic context (very low concentration of iron in groundwater); and (iii) higher NO_3^- concentrations in the unconfined aquifer than in the confined aquifer, indicating that NO_3^- as electron acceptor is not possible in the confined aquifer. Obtained values of the R = rCl/rBr ratio for both aquifers indicating the absence of saline intrusion and dilution of the middle aquitard evaporitic rocks (gypsum and halite). End-member data computed using the MIX_PROGRAM code for each of the regions are shown in

Tab. 1. The model runs not only allowed for obtaining more reliable mixing lines than those obtained through measured end- members, it also allowed for assessment of important existing differences between measured and computed end-members, mainly for the Quaternary aquifer and for the three regions.

Table 1. Measured end-member concentrations for the three defined regions (*m*: mean; *σ*: standard deviation). Computed end-member (e-m) concentrations from the MIX_PROGRAM (Carrera et al., 2004) are also shown.

Aquifer	Species	Region 1				Region 2				Region 3			
		Number samples (period)	*m* (mg l^{-1})	*σ* (mg l^{-1})	Computed e-m	Number samples (period)	*m* (mg l^{-1})	*σ* (mg l^{-1})	Computed e-m	Number samples (period)	*m* (mg l^{-1})	*σ* (mg l^{-1})	Computed e-m
Quaternary	Cl^-	129 (1980-2008)	1372.4	374.8	1214.7	91 (1980-2008)	1794.2	651.3	2559.2	37 (1980-2008)	1305.3	395.5	1418.4
	SO_4^{-2}		624.9	201.7	1082.2		1270.4	437.1	1871.3		766.2	430.4	1122.6
Pliocene	Cl^-	3 (1970´s)	493.7	17.6	457.4	4 (1970´s)	1121.3	141.9	974.9	3 (70´s)	1053.0	20.8	1041.1
	SO_4^{-2}		238.7	143.6	62.4		949.8	225.5	946.3		679.0	84.9	273.1

If the computed water mixing ratio Quaternary/Pliocene aquifers (mass fraction-*MFQIP*) is plotted versus distance to coast and flow direction (Fig. 2b), an increasing trend of the *MFQIP* average value and its variability toward the coast is observed, although local factors surrounding each sample point can disturb it. This result agrees with the important number of wells reaching the Pliocene aquifer according to the groundwater flow direction. For region 1, which presents the greatest density of wells, computed *MFQIP* values are the lowest (between 0.07 and 0.46) due to the short travel distance between recharge (upland) and discharge area (toward the coast). In region 2, high *MFQIP* values reaching 0.74 are observed due to high concentrations of Cl^- and SO_4^{2-} species in the Quaternary end-member along with the longer groundwater travel distance across the Pliocene aquifer. Finally, for region 3, sample points present similar average values of *MFQIP* (~0.53), although agricultural activity and the density of wells is lower than the other regions; this pattern appears to be controlled by the low hydraulic gradient of the Pliocene aquifer in this region.

CONCLUSIONS

Results proved the validity of the applied methodology to assess aquifer interconnection, primarily based on the presence of nitrate in groundwater and numerical mixing calculations, in areas highly impacted by agricultural activities as the Campo de Cartagena area.

The study shows that the upper unconfined aquifer (Quaternary), which is polluted by nitrate due to intensive agricultural activities, also constitutes the source of pollution of the lower confined aquifer (Pliocene). Contamination was caused by leaky wells in areas with high density of production wells and the induced leakage allowed for the downward flow of contaminated water from the upper aquifer into the unpolluted lower confined aquifer.

Water mixing fractions were estimated using the numerical code, which provides more accurate estimates of not only the end-member concentrations but also of the output mixing ratios. The mixing ratios approach showed that the Quaternary aquifer average mass fraction leaking into the Pliocene aquifer ranges between 0.07 and 0.74 and tends to increase toward the coast following the increase of well density.

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