Effects on the shallow aquifers by CO_2 leakages in a tertiary basin (province of Murcia, Spain)

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Abstract

Geological storage of CO_2 is nowadays internationally considered as the most effective method for greenhouse gas emission mitigation, in order to minimize its effects on the global climatology. One of the main options is to store CO_2 in deep saline aquifers at more than 800m depth, because it reaches its supercritical state. Study of the CO_2 natural accumulations as natural analogues of an artificial CO_2 storage is very useful in order to understand the CO_2 long term behaviour and thus to predict its possible impact on the surficial environment and life. Therefore the main objective of this work is to detect the affection of the CO_2 leakages from a deep saline aquifer on the shallow aquifers, all of them located in the Gañuelas-Mazarrón Tertiary basin (Province of Murcia, Spain). This CO_2 storage and leakage natural system can be analogous to an artificial CO_2 storage with leakage phenomena.

In order to reach these objectives, groundwaters from different aquifers in the site have been sampled and analysed for major elements, free and dissolved gases and stable isotopes, particularly $\partial^{13}C$ and $^3He/^4He$.

The results obtained allow to conclude that this natural system is an interesting example of natural analogue for an artificial CO_2 storage affected by leakage processes because the shallow fresh aquifers in the site are polluted by CO_2 from the deep saline aquifer as a consequence of an intensive over-exploitation of these freshwater aquifers.

Keywords: Carbon Storage; CO_2 Leakage; Tertiary Basin.

Introduction

The scientific community has general accepted that long-term extrapolation in terms of safety of a deep geological storage of toxic industrial wastes, such as high activity radioactive wastes, industrial and mining wastes and even greenhouse gases, can not be satisfactorily done on the basis of short term researches in the laboratory (Petit, 1992). Therefore, the countries affected by these problems have developed methods of investigation which include short-term tests in the laboratory, where the variables are controlled, as well as the study of natural analogues, either as a whole system or only considering a particular natural analogue process.

Although the studies about CO_2 natural accumulations are not yet sufficiently developed, some authors (Czernichowski-Lauriol et al, 1996; Pearce et al, 1996) have included in their works the existing CO_2 reservoirs in the world and the experimental reactions between CO_2 and the storage formations (Pearce and Rochelle, 1999). Moreover, in the last decade there are many works focused on the evaluation of the safety of a CO_2 geological storage by means of the study of CO_2 leakage natural analogue processes (Beaubien et al., 2005; Czernichowski-Lauriol et al., 2003; Hawkins , 2004; Lewicki et al., 2007; Nordbotten et al., 2005; Oldenburg and Lewicki, 2006; Riding, 2006)

Regarding Spain, there's one current important project cofunded by the Ministry of Science and Innovation and FEDER European Funds, whose main objective is the global study of the several CO_2 natural analogues in all over the country. Among them, it has to be noted the natural analogue of storage, and natural and artificial leakage of CO_2 located in the Mazarrón-Gañuelas Tertiary basin (Province of Murcia)

In this international and national framework, this sedimentary basin, which contains a deep CO_2 reservoir discovered through geothermal exploratory wells carried out in the eighties of the last century (ITGE, 1985), is being studied. Two of these geothermal exploratory wells, named El Reventón and El Saladillo, with 710 and 535m depth respectively, are indeed still discharging saline waters accompanied by very important CO_2 degassing. This phenomenon has also been detected, but in a less extent, in many abandoned and active hydrogeological wells existing in the region (Cerón and Pulido, 1996; Cerón et al., 1998; 2000), just as it has been demonstrated by the high salinity and dissolved CO_2 concentrations detected in their highly polluted waters As a consequence, the aim of this work is to provide a geochemical characterization of water and gas phases collected from the contaminated hydrogeological wells along the region (Fig. 1). Thus, the water and gas geochemical data, including the isotopic features, obtained in the September 2009 and March 2010 field campaigns are discussed on the basis of the geochemical and isotopic data obtained from water and gases collected in the El Reventón and El Saladillo wells.

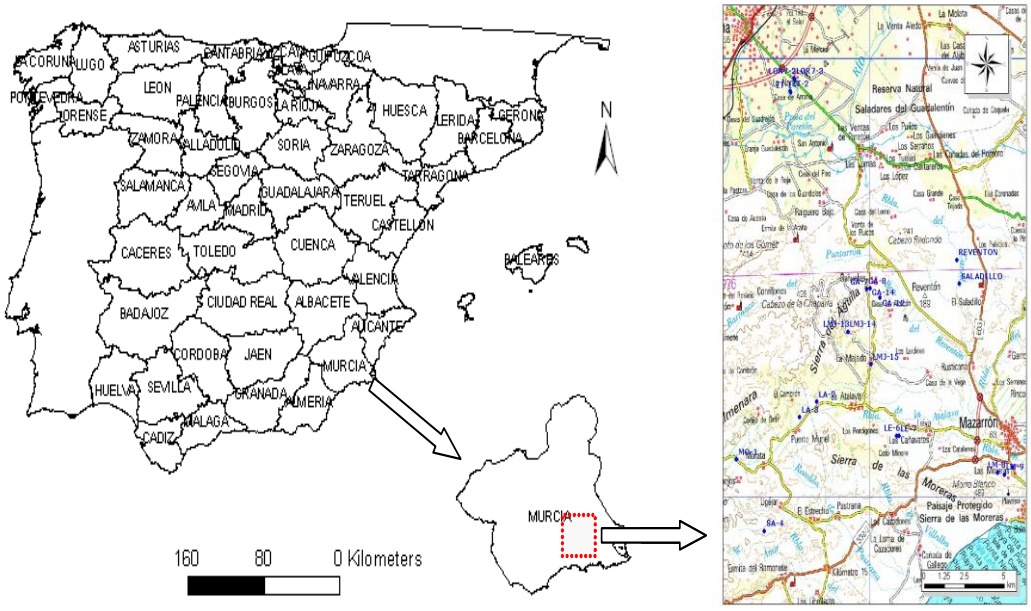

Fig. 1. Geographical location of the studied area (red square), with the local situation of the sampled water wells

Experimental

This section deals with the chemical composition of the well waters collected and during the sampling campaigns of September 2009 and March 2010 in the area, as well as with the chemical composition and isotopic signatures of free and dissolved gases, mainly CO_2. Water in the sampled wells is at different depths, from surface (upwelling wells) to 300m, approximately. They were collected by means of a bailer device as described in Nisi et al. (2010) or by pumping the water directly from the wells.

Temperature (°C), pH and electrical conductivity (mS/cm) were measured *in situ* in all the samples. The analysis of the water samples comprises main and minor cations and anions, as well as Total Dissolved Solids (TDS), both expressed in mg/L. For each sample, the sum of the cations and anions, expressed in in meq/L, is reported with the relative calculated electroneutrality parameters (Err. %) that is considered as a sort of analytical test, being the error <5% acceptable for these waters.

The geochemical characterization of the well waters for both campaigns is performed by using the Piper-Hill and Langelier & Ludwig's diagrams. In order to assess the possible sources of the different solutes and ascertain the presence of "pure" water (initial solution) with probable mixing processes, it has been represented some selected binary diagrams correlating different cations with the possible anions, both expressed in meq/L, deriving by congruent dissolution processes.

Chemical composition and isotopic signature of the free and dissolved gases, particularly CO_2, are expressed in both mmol/L and % by volume, and $\delta^{13}C$ units in ‰ *versus* PDB, respectively. The results have been obtained from the gases sampled at a depth of 75m, and also from soil gases. The $\delta^{13}C$-CO_2 values have been calculated from the empirical study of Luchetti (2006), so they had to be corrected by a factor of +0.83 ‰. The reason of this adjustment is because of the preferential enrichment of light isotope (^{12}C) when the gas is introduced into the vial, because the chemical bounds created by the CO_2 molecule with H_2O are weaker when ^{12}C is present (Nisi et al., 2010).

Results and discussion

Summarizing, the temperatures of the well-water samples range between 21.4 and 36.4°C in September 2009 and, setting aside El Reventón (45.7 °C) and El Saladillo (45.3 °C) thermal wells, between 21.6 and 36.1°C in March 2010. Therefore, they substantially do not show significant variations between the two seasonal samplings. The latter consideration can be also done for the pH values that range between 6.25 and 8.99, while waters from El Reventón and El Saladillo wells have pH values of 6.53 and 6.86, respectively.

A positive correlation between the electrical conductivity and the temperature is displayed for most of the samples, which lie in a theoretical line that connects the "pure" water (initial solution) with waters from the thermal wells of El Reventón and El Saladillo (final solution). It is worthwhile to mention that, in general, the electrical conductivity is very high, reaching values up to 12800 μS/cm.

In terms of geochemical facies, a large variability is clearly recognized. The waters are indeed ranging from the dominant Na(K)-SO_4(HCO_3) Cl-rich composition, to secondary Na(K)-Cl, Ca-SO_4, Mg-HCO_3 and Na-HCO_3 facies. All the waters tend to maintain the same

compositions in both samplings, although some slight modifications are resulting for those waters characterized by intermediate facies.

From the binary diagrams, we can suggest that well waters can be related to complex geochemical processes that involve Ca(Mg)-HCO_3 waters, typical of surficial or shallow aquifers, at which the dissolution of different evaporitic minerals has to be added.

Regarding the geochemical and isotopic characterization of the gases, it has to be pointed out that the higher the content of dissolved gases, the higher the amount of CO_2 and also that the most saline water samples are often accompanied by the highest CO_2 concentrations. Furthermore, it can be asserted that the isotopic signature of CO_2 in the Gañuelas-Mazarrón Tertiary basin is the result of five distinct processes that participate at different degrees: i) a deep-seated source of likely mantle origin (as also suggested by the helium isotopic values, Vaselli et al., 2009); ii) a surficial (biogenic) origin that is likely responsible of the most negative values, the typical isotopic imprinting of biogenic CO_2 being -21 ‰ (e.g. Rollinson, 1993); iii) a fractionation process that affects the carbon isotopes, such as the CO_2-rich gas that rises up and interacts with the deep and surficial-seated aquifers; iv) a reductive process able to positivize the residual carbon in CO_2; and v) with a higher uncertainty and at a very minor extent, a contribution related to thermometamorphic processes whose carbon isotopic values are between -2 to +2 ‰, that is apparently affecting the two thermal wells of El Reventón and El Saladillo.

Conclusions

On the basis of the geochemical investigation on the well waters from Gañuelas-Mazarrón Tertiary basin carried out in September 2009 and March 2010, the general picture emerging from this study is that the site is characterized by a complex geological and hydrogeological context. The latter is also likely related to the strong over-exploitation of the fresh water resources mainly used for irrigation purposes (e.g. Pérez del Villar et al., 2008; 2009; Nisi et al., 2010). This has possibly lowered the water table favoring the uprising of relatively salty and CO_2-rich waters with different chemical composition due to the presence of evaporitic sequences likely related to the Triassic materials from the Alpujárride Complex and/or to Cenozoic sediments of the Tertiary basin (Pérez del Villar et al., 2008; 2009 and references therein). The possible deep final solution can be represented by the CO_2-rich reservoir present at the depth of at least 800 m and related to El Reventón and El Saladillo deep thermal wells. Mixing processes with shallower aquifer(s) at different degrees and dissolution processes of the evaporitic sequences are thus responsible of the relatively large variety of geochemical hydrofacies recognized in the two sampling campaigns carried out in September 2009 and March 2010.

In terms of chemical and isotopic composition of the dissolved gases, results have shown that in most of the analyzed wells, CO_2 is the dominating gas phase with an isotopic composition that is generally similar or more positive with respect to the deep wells of El Reventón and El Saladillo. This indicates different contributions from a deep-seated site (mantle) and a biogenic source, in which fractionaction processes have taken place.

Therefore, from all the results, it can be concluded that the fresh waters from surficial aquifers are affected by CO_2-rich fluids from the deep saline aquifer, and this pollution has been increasing with the water over-exploitation of the region. The study of this natural system is interesting in the sense that it can provide the clues of the behaviour of the CO_2 leakages from

an artificial CO_2 storage, as well as its possible impacts on the extremely important water resources.

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