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Source of groundwater salinity in coastline aquifers based on environmental isotopes (Portugal): Natural *vs.* human interference. A review and reinterpretation

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ABSTRACT

Environmental stable ($\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C$) and radioactive (^{3}H and ^{14}C) isotopes, together with geochemical data were used to identify the origin of salinization in different environments. Three case studies from sedimentary basins of continental Portugal are presented: (i) two at the Meso-Cenozoic Portuguese southern border (Algarve basin) and (ii) one at the Lower Tagus–Lower Sado basin (central Portugal), with a new data interpretation. Groundwater salinization occurs in all three cases, and may reach values of several grams of Total Dissolved Solids per liter; above accepted limits for drinking water. The source of this high mineralization could be: (a) seawater intrusion (ancient or modern); (b) dissolution from diapiric structures intruding on the aquifer systems; (c) brine dissolution at depth; and (d) evaporation of irrigation water. The results obtained have provided an effective label for seawater and freshwater, to enable seawater intrusion to be traced, as well as the identification of other processes that might be responsible for groundwater salinization, such as salt minerals dissolution and ion exchange.

1. Introduction

Steady increase in the salinity of most of the major aquifers being used for water supply in coastal regions, in particular in areas under arid and semi-arid conditions, provide evidences of water quality deterioration (e.g., Shi et al., 2001; Kim et al., 2003; Cartwright et al., 2004; Pulido-Leboeuf, 2004; Klein-BenDavid et al., 2005; Jalali, 2007; Bouchaou et al., 2008). This increase in mineralization of groundwater resources is often due to inflow of saline (dense) water, during heavy withdrawals of fresh water from coastal aquifers, and/or mobilization of saline formation waters by overexploitation of inland aquifer systems. Not only seawater mixing is responsible for water resource degradation. Water pollution due to extensive irrigation and the use of fertilizers and other pesticides is also growing all over the world. As a consequence of the different income sources for groundwater quality deterioration, it is necessary to identify and characterize the specific processes involved. Among the different approaches, isotope techniques are particularly effective for identifying the source of salinity and renewability of groundwater all over the world (e.g., Carreira, 1991; Cabral et al., 1992; Carreira et al., 1994, 2010; Gaye, 2001; Kim et al., 2003; Cartwright et al., 2006; Möller et al., 2007; Bouchaou et al., 2008; Carol et al., 2009; Koh et al., 2012).

The differences observed between the stable isotopic composition of groundwater and that of local precipitation composition can be due to: (i) different recharge episodes; (ii) to different recharge sources (for example surface waters and precipitation) or (iii) even to contamination inputs by mixing processes between different aquifer systems, which can lead to an isotopic deviation between groundwater and local precipitation.

On the Portuguese mainland, seawater intrusion has been described along the Atlantic coast from Aveiro, in the N of Portugal, to Algarve in the S, usually in relation with sedimentary basins. In these areas, the overexploitation of groundwater has resulted in salinization extending inland. This has worsened in recent decades, especially during the summer months when both the local population is boosted by significant numbers of tourists and demand for irrigation water peaks.

In this paper three case studies will be presented, where the main goals were to identify and understand the importance that different salt origins (ancient or modern seawater intrusion, dissolution of evaporitic minerals) could have on the groundwater quality deterioration for human uses and the characterization of the specific processes involved.

Environmental isotope studies were applied in order to assess the origin of salinization. These were complemented by geochemical investigations, which in some cases were not able to resolve the questions. Both regions (Algarve and Sado groundwater systems) are found near the coastline, within sedimentary basins where the presence of evaporitic minerals dispersed or

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concentrated in the geological layers is not unusual. Three case studies on coastal aquifers will be presented: (i) two at the Meso-Cenozoic Portuguese S border (Algarve basin), and (ii) a third one at the Lower Tagus–Sado sedimentary basin (central Portugal). In all these case studies groundwater salinization occurs, reaching values of several grams of Total Dissolved Solids (TDS)/L. Based on the geological features of each area the source of this high mineralization could be ascribed to: (a) seawater intrusion; (b) dissolution of diapiric structures, intruding the aquifers, or spreading saline minerals; (c) brine dissolution at depth or mixing with ancient seawater and (d) evaporation of irrigation water.

2. Analytical methodology

2.1. Background

A qualitative and quantitative characterization of groundwater recharge is essential to ensure the sustainable development and management of groundwater resources. A reliable estimate of recharge rate can be obtained on the basis of classical approaches, such as water level monitoring (Custódio and Llamas, 1983). However, examination of isotopic composition allows a differentiation of recharge and even precipitation sources, and hence of recharge mechanisms (Fig. 1a). Isotopic composition of groundwater ($\delta^{18}O$ and $\delta^{2}H$ values) is defined by the isotopic signatures of recharge. If most of the recharge is derived from direct infiltration of precipitation, the groundwater will reflect the isotopic composition of that precipitation (Craig, 1961; Dansgaard, 1964; Rozanski et al., 1992; Gourcy et al., 2005). However, if most of the recharge is derived from surface water (rivers or lakes) instead of precipitation, the groundwater will reflect the mean isotopic composition of the contributing river or lake waters. On the other hand, it should be noted that in some cases the isotopic composition of precipitation may be close to that of river waters (Fritz, 1981). However in large and sometimes in small basins rainfall isotopic composition can diverge, and the river will be a proportional mixing of all rainfall contributions (Mas-Pla et al., 2013). This deviation (surface waters–groundwaters) will be more perceptible when a topographic gradient is well defined.

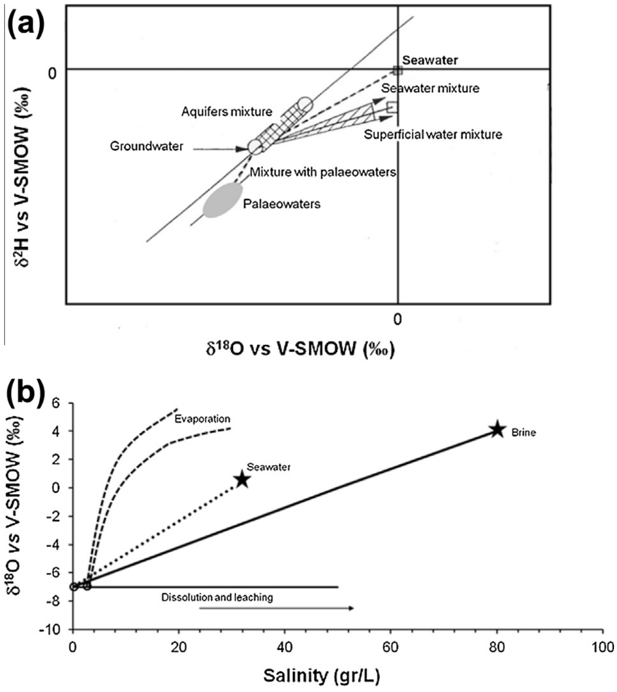

Fig. 1. (a) $\delta^{2}H$ *vs.* $\delta^{18}O$: change in isotopic composition of the groundwater associated with different processes (adapted from Gat, 1981). (b) $\delta^{18}O$ *vs.* salinity: change in isotopic composition of water, ascribed to different salinization processes (adapted from Gonfiantini and Araguás, 1988).

Stable isotopes provide an effective label for seawater and freshwater, to enable tracing of seawater intrusion, as well as identifying other processes that might be responsible for groundwater salinization. Evolution of stable isotope concentration of water during different processes related to water salinization is presented in Fig. 1b. In studies dealing with seawater intrusion and the identification of groundwater salinization processes, it is common to consider both isotopic and hydrochemical evolution. Such an approach enables the salinization process (or processes) to be clearly distinguished, for cases where freshwater salinity may be caused by direct seawater intrusion, leaching of salt formations, mineral dissolution, or salt accumulation due to evaporation (Aráguás-Aráguas and Gonfiantini, 1989; Edmunds and Droubi, 1998; Yurtsever, 1997). During salt formation or mineral dissolution processes, the stable isotope content of the water is not affected but water salinity increases (Fig. 1b). This is a unique feature that enables identification of such processes based on isotopic and geochemical data.

In hydrological settings in which groundwater is old (>10,000 years), regional climatic conditions at the time of recharge may have been different from those existing today, and this is reflected in the isotope composition of the groundwater. The present-day characteristic values in ^{18}O and in ^{2}H observed in precipitation may be used as sensitive indicators of change and complexity in past temperatures, precipitation patterns and air masses circulation. Past rainfall stored as palaeogroundwater, provide evidences of former climatic conditions. Climatic changes are expressed primarily as (i) isotopic depletion relative to modern groundwaters with reference to the meteoric water line; (ii) change in deuterium excess, signifying changes in humidity in the air mass as it detaches from its primary oceanic source moving over arid regions; and (iii) local condensation and evaporation effects within the colds or in falling rain (Rozanski et al., 1992; Edmunds, 2005).

Moreover, if the flow regime is simple and mixing is negligible, the aquifers can serve as archives of information about environmental conditions at the time of recharge (e.g., Rozanski, 1985; Rozanski et al., 1992; Darling et al., 1997; Edmunds and Droubi, 1998; Edmunds, 2005; Bouchaou et al., 2008). The stable isotopes of hydrogen and oxygen in palaeowaters (groundwater recharged under climate conditions different than today) reflect the air temperature at land surface and the air mass circulation (origin of moisture) at the time of precipitation and infiltration (e.g., Rozanski, 1985; Stute et al., 1995; Edmunds, 2005). Therefore, dating groundwater will help in the identification of the seawater intrusion mechanism, i.e., if we are dealing with modern or ancient salt water bodies such as seawater, brackish or brine waters.

Groundwater dating with ^{14}C is not an easy procedure, in particular in carbonate aquifers or even when carbonate layers are present within the geological strata, as occurs in the Lower Sado–Lower Tagus sedimentary basin. In a simple approach to carbon-14 dating of groundwater systems it is assumed that ^{14}C "travels" with the water molecules along the flow path, and that the main mechanism that is changing the ^{14}C content of the groundwater (Total Dissolved Inorganic Carbon – TDIC) is "pure" radioactive decay. However, the isotopic signature of the ^{14}C may be diluted, particularly by ^{14}C-free sources, leading to apparent groundwater ages higher than reality (Carreira et al., 2008).

A common and straightforward way to estimate the initial ^{14}C activity is by relating the $\delta^{13}C$ content of the DIC in the groundwater to the mixed carbon from carbonate rocks, using carbon from soil CO_2 and a fractionation factor between the different carbonate