GEOCHEMICAL EVOLUTION AND TIMESCALE OF SEAWATER INTRUSION IN A CONFINED COASTAL AQUIFER: CASE OF THE RHONE DELTA

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Abstract

Since the last decades, coastal areas are subject to two main hazards: important anthropization and sea level rise; two points which have a strong impact on the groundwater resource and more particularly on its quality. Located between the two arms of the Rhône River, the Camargue delta provides a good example of such issues: the human pressure since the end of the nineteen century has led to a strong modification of the delta and its vicinity (huge industrial and harbour area on the other side of the Rhône River). Moreover, this low deltaic plain is particularly sensitive to the acceleration of the sea level rise estimated at 2mm/year since 1905 in this area.

Within the framework of the ORE RESYST (Environment Research Observatory: Response of a delta system to external forcing), an affiliated LOICZ programme (Liaison with Land-Ocean Interactions in the Coastal Zone), a hydrochemical and isotopic study of the saline confined aquifer of the Rhône delta has been carried out to better assess the consequence of these issues on the groundwater. Understanding the origin and mechanisms of the salinization process of the confined aquifer is an important point for preventing further deterioration of this groundwater resource.

Groundwater presents strong values of electric conductivity (up to 58 mS/cm) rising from the north of the delta to the Mediterranean Sea. Chemical and isotopic (^{18}O, ^{2}H, and ^{13}C) analyses performed on monthly samples from 8 boreholes revealed that seawater intrusion occurs in the aquifer. The seawater contribution varies in the groundwater from about 6% to 98%. However, the ideal two end-members mixing between freshwater and Mediterranean seawater is strongly modified by water/rock interactions. Two different zones have been identified within the aquifer: (i) in the less saline part of the aquifer (up to 20% of seawater), cation exchanges prevail whereas (ii) in the most saline part of the aquifer sulphates reduction processes and precipitation phenomena occur.

In order to date the seawater intrusion, new samples have been taken for ^{3}H and ^{14}C analyses in the confined aquifer and its potential recharge sources (Mediterranean Sea, unconfined Crau aquifer, Rhône River). Except for one sample, groundwaters contain no tritium suggesting that groundwaters have a mean residence time higher than 50 years ago and that the freshwater recharge from the Rhône River and the Crau aquifer is a slow process. The low ^{14}C activities measured in groundwater seem to confirm the non-recent origin of groundwater. However the high water/rock interactions have to be taken into account to correct the apparent groundwater ageing.

This paper discuss the geochemical reactions which have to be accounted to correct apparent ^{14}C water ages in a deltaic aquifer where the sedimentary organic matter has a strong influence on the water chemistry. The results will have important consequences in the hazard assessment of a sea level rise due to climatic changes.

Keywords: Rhône delta, confined aquifer, seawater intrusion, 14C, Tritium, organic matter oxidation

1. Introduction

The Camargue wetland (Rhône delta), located along the Mediterranean Sea, is a sedimentary fluvial formation of Pleistocene to recent age. Since the first works carried out in the 70's, the saline feature of the Pleistocene confined aquifer of this delta was pointed out (DDA des Bouches du Rhône, 1970). But, over thirty years, the situation has worsened and now, one point shows high salinity close to that of seawater. A previous work has demonstrated the marine origin of the salt but has also pointed out the possible old origin of the seawater. The saline water could correspond to unflushed

water from the last marine Holocene transgression when the Pleistocene sediments were encroached by seawater (Edmunds et al., 2001). New samples for Tritium and $^{14}C_{TDIC}$ analyses were taken to investigate this assumption.

Carbon-14 (^{14}C) and Tritium are the most commonly used environmental radioisotopes for dating groundwater. Tritium has a short half life (12.3 yrs) which allows to date young groundwater and to identify quick flows from surficial waters. The ^{14}C, has a longer half life (5730 yrs) and is a useful tool for dating groundwater up to 30000 years (Clark and Fritz, 1997). It is thus appropriated to evaluate the influences of the last Holocene marine transgression on groundwaters (Loosli et al., 2001).

The $^{14}C_{TDIC}$ activity (^{14}a) of dissolved inorganic carbon (DIC) decreases due to radioactive decay which depends on the time elapsed since groundwater was cut off from recharge. Due to the various water-rock interactions in the unsaturated and saturated zones, dilution by "dead carbon" lowers the initial ^{14}C activity (a_0) and consequently increases artificially the mean residence time of groundwater (Clark and Fritz, 1997; Geyh, 2000; Mook and Vries, 2000). The main difficulty of the ^{14}C dating is thus to identify the water-rock interactions occurring in the aquifer and to quantify their influence on the ^{14}C activity decrease (Clark and Fritz, 1997; Geyh, 2000).

In this study, the tritium and the ^{14}C are used to precise the recharge area and to specify the geochemical reactions occurring in the confined aquifer of Camargue. The well knowledge of the Carbon evolution in groundwater is indeed a basic statement for a further groundwater dating.

2. Methods

In the Rhone delta, few data are available on the Pleistocene confined aquifer since only a small number of boreholes have reached the Pleistocene unit. 8 piezometers mainly bored in the 60's and located between 8 km and 20 km from the coast (Fig. 1) have been used for this study.

A monthly chemical and isotopic monitoring of the 8 piezometers have been carried out during one year (May 2005 to May 2006)(de Montety et al., in Press) in order to constrain the geochemical system of the confined aquifer,. Major ions and stable isotopes of the water molecule (^{18}O, ^{2}H) and the Carbon (^{13}C) were analysed; temperature, electrical conductivity (EC), pH, redox potential (Eh) and alkalinity were measured in situ.

For the present study, 8 new samples have been taken in November 2006 for tritium analyses and 5 samples (S_1, S_2, S_5, S_7, F_{11}) in March 2007 for $^{14}C_{TDIC}$ analyses. Samples from surface waters (Rhône River, Mediterranean Sea) and surficial waters (Camargue unconfined aquifer and Crau aquifer) were also included.

3. Hydrogeological settings

The investigated area of the Camargue is a saline wetland of 750 km^2 located south-east of France along the Mediterranean coast (Fig. 1). The Camargue is delimited by the two branches of the Rhône River which divides 40 km upstream from the coastline and is bordered in its eastern part by the Crau plain. The Camargue represents the major part of the Rhône delta.

The Rhône delta formed mainly during the Quaternary. The very low Mediterranean sea level during the Last Glacial Maximum (~-120 m, 18000 yr BP; (Edmunds et al., 2001)), allowed the deposition of continental sediments (fluvial terraces and deltaic sedimentary bodies). The rapid rise of sea level during the Holocene (Flandrian transgression) and its progressive deceleration since 6000 yr BP favoured the formation of the Rhône delta *s.s.*, with the progradation of sedimentary bodies under the influence of riverine sediment fluxes (Boyer et al., 2005; Vella et al., 2005).
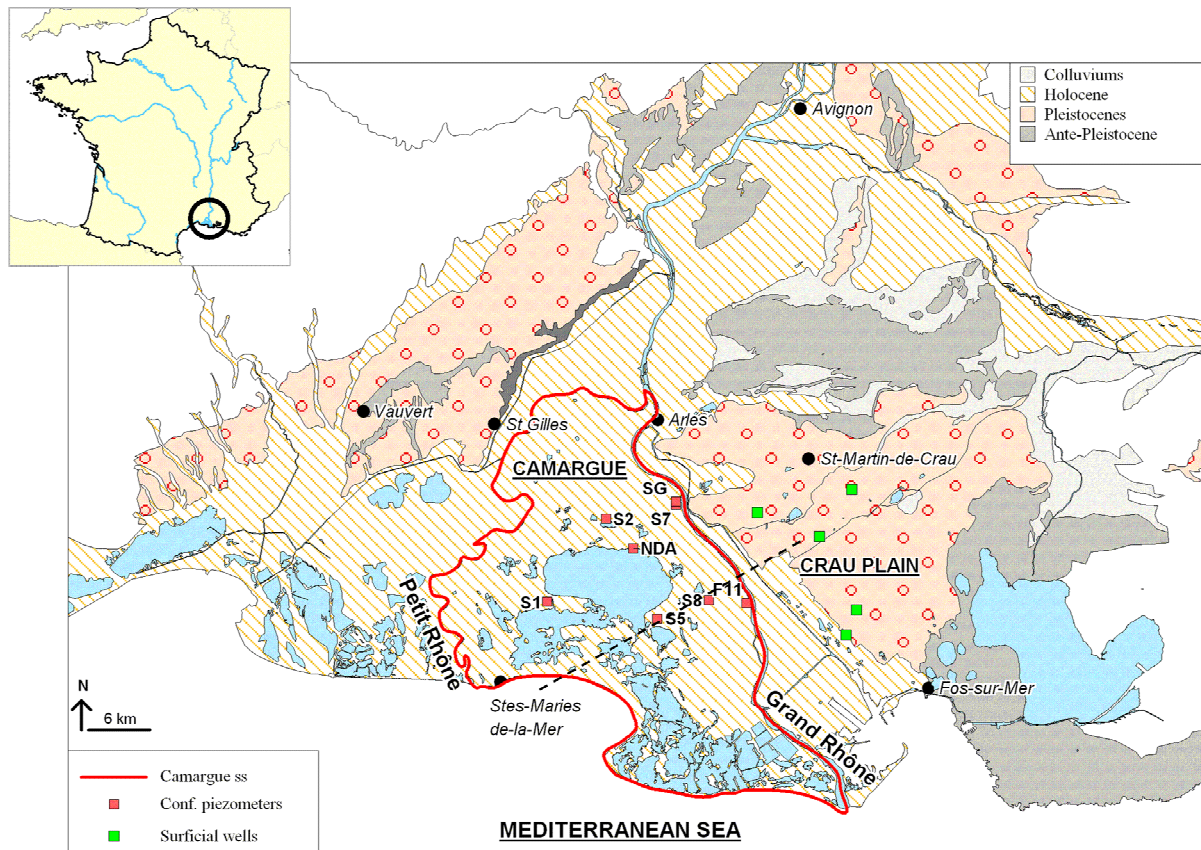
Fig. 1. Location of the investigated area and its monitoring network. The dashed line stands for the cross-section (Fig.2).

This geological context induced the formation of a three-unit structure overlying a thick marly marine substratum of Pliocene age. From bottom to top, the following units are observed:

(i) Pleistocene gravels which presently outcrop in the Crau plain, and dip gently southwestwards to 50 m below sea-level on the coastline; their thickness varies from 10 m to 70 m (Boyer et al., 2005; DDA des Bouches du Rhône, 1970; Marinos, 1969). The gravels are mainly made of limestone with some quartzite and granulose rocks in a sandy-clay matrix. This unit contains the investigated aquifer.

(ii) The former gravels are covered by 2 to 30 m thick marine clays and silts with sand interlayers (Boyer et al., 2005) deposited during the early stage of the transgression (18000 to 6000 yr BP). Numerous peat interlayers formed during the main stops or decelerations of the sea level rise are also identified. This low permeable unity behaves as an aquitard and corresponds to a confining layer for the previous deep aquifer.

(iii) The uppermost unit (up to 10 m thick) is made of Holocene to present-day clays with marine fauna, horizontally bedded sands and, at the uppermost part, modern continental deposits. It contains a low permeable, heterogeneous surficial aquifer with fresh to saline or hypersaline waters (up to 100 mS/cm) (DDA des Bouches du Rhône, 1970; Marinos, 1969).

This three-unit structure of the Rhône delta is similar to those observed for other Mediterranean deltas like Pô and Nile deltas or the Llobregat and Ebro deltas for the western Mediterranean (Boyer et al., 2005; Edmunds et al., 2001).

The investigated aquifer, located in the Pleistocene gravels, is found on both sides of the Rhône River but with different hydrodynamic features:

(i) East of the Rhône River, in the Crau plain where the gravels unit outcrops, it is a fresh unconfined aquifer (Fig. 2) highly exploited for drinking water and industries. It has two main sources of recharge: 2/3 from irrigation excess with water from the Durance River and 1/3 from rainfall. In

addition to its exploitation, this aquifer has a natural discharge which corresponds to a swampy area in the eastern border of the Rhône River, where the formation dips under the confining layer (Fig. 2).

(ii) West of the Rhône River, in Camargue, the aquifer is confined and artesian in places. The end of the aquifer under the sea could be located around the continental shelf edge (around 30 km from the shoreline; Boyer et al. (2005)). The groundwater electrical conductivity (EC) rises from north-east to south-west from 4 mS/cm up to 58 mS/cm.
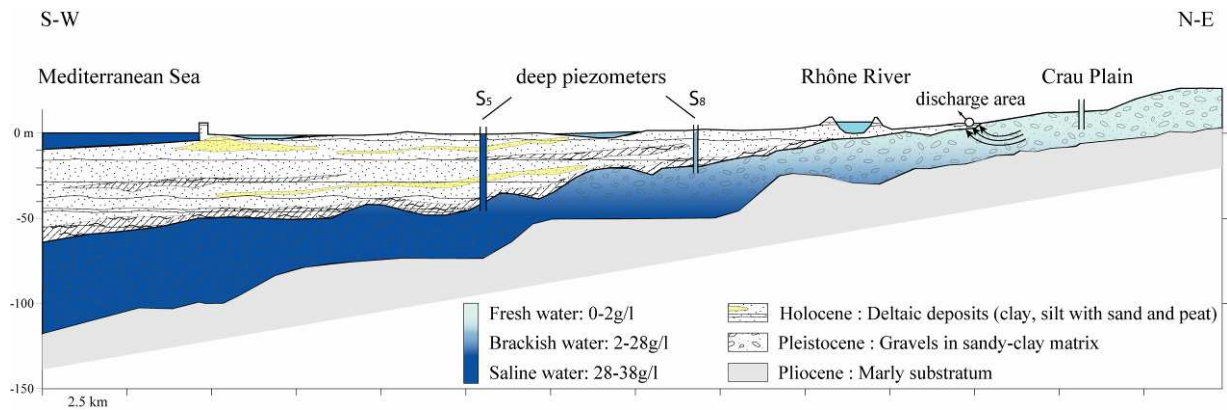

Fig. 2. Schematic cross-section of the investigated area.

4. Hydrochemistry of the confined aquifer

The piezometers are relatively far from the coast (8 km at least), but the water is strongly mineralized (from 4 mS/cm to 58mS/cm). All the groundwater samples are of Na-Cl type (Fig. 3). The Cl^- content of the groundwater increases towards the south-west direction, in relation to the proximity of the coastline, from 35 meq/l (S_7) to 600 meq/l (S_5), a value close to that of the Mediterranean seawater (~610 meq/l).

Typical ionic ratios of seawater (Na/Cl and Br/Cl) and the stable isotopes (^{18}O, ^{2}H) demonstrate that the groundwater chemistry results from a two end-member mixing between the Mediterranean seawater and a continental freshwater end-member (Crau aquifer, Rhône River) (de Montety et al., in Press). Using the Cl^- content of the groundwaters, the seawater contribution in the aquifer has been evaluated at 6% near the fresh recharge area (S_7) up to 98% at 8 km from the shoreline (S_5).

Significant deviations compared to an ideal two end-members mixing (Fig. 3) have been identified for non conservative elements and 3 main water-rock interactions have been highlighted according to the degree of seawater contribution (arrow a, b and c; Fig. 3) (de Montety et al., in Press):

(i) In the less saline part of the aquifer (S_7, S_g, S_2, NDA: seawater contribution < 20%), the intrusion mainly induces an increase of Na^+ in groundwater leading to Ca^{2+}/Na^+ exchange processes (arrow a; Fig. 3). Moreover, enriched $\delta^{13}C_{TDIC}$ value indicates that in the less saline sample (S_7), isotopic exchanges could occur with the carbonated matrix.
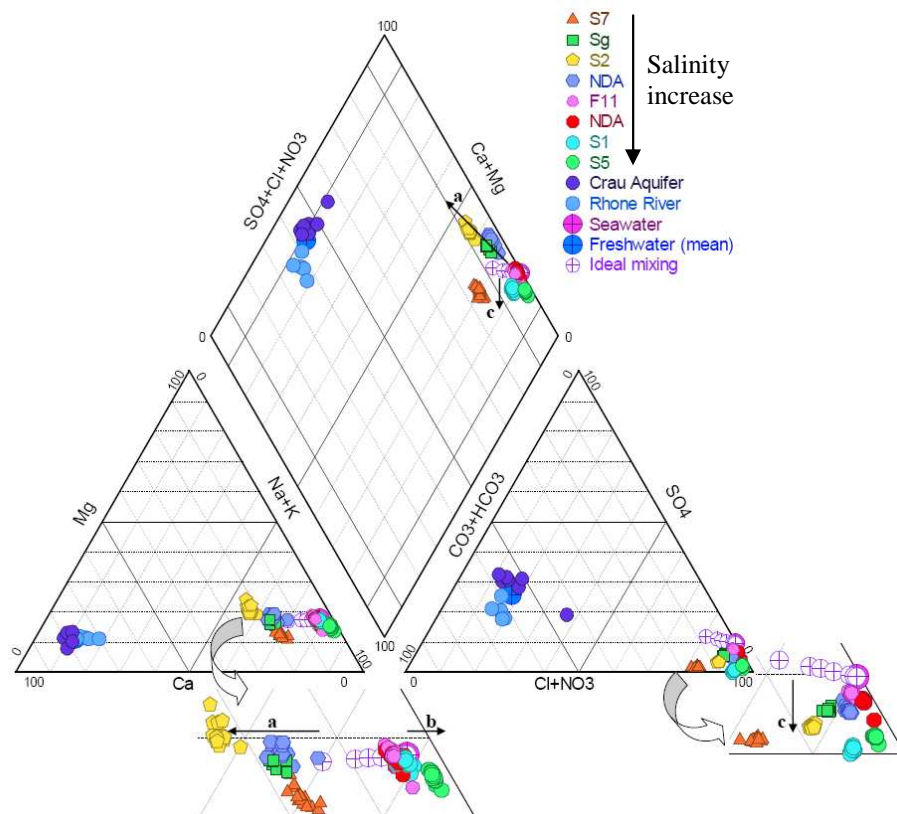
Fig. 3. General features of the confined aquifer groundwater. The main geochemical evolutions are shown by the arrows (a, b, c). See text for details.

(ii) In the saline part of the aquifer (F_{11}, S_8, S_1, S_5: seawater contribution > 20%), the intrusion mainly induces sulphate reduction (arrow c) due to the presence of fossil organic matter (OM) which is confirmed by highly depleted $\delta^{13}C_{TDIC}$ values (up to -19‰). The increasing content of HCO_3^- from the oxidation of OM shifts the carbonate equilibrium and leads to dolomite and/or magnesian calcite precipitation (arrow b).

Finally, the monthly chemical and isotopic analyses of the confined groundwater show very low temporal variations (de Montety et al., in Press) which underline the absence of quick flow within the aquifer and the low connexion of the aquifer with surficial waters.

5. Use of Tritium to assess the groundwater age

All the surface water and surficial groundwater (Crau aquifer, surficial Camargue aquifer) show measurable tritium activities. Rhône River sample has a high tritium activity (43 UT) due to the influence of nuclear plants settled upstream along the River. Surficial Camargue groundwaters have high tritium content due to the main contribution of irrigation from the Rhône River to the aquifer recharge whereas Crau aquifer samples have lower values close to that of the rainwater (~6 UT). Seawater sample shows low tritium activity (1.5 UT) similar to other measurements in Mediterranean sea (~2.3 UT in Spain (Araguas Araguas, 2003) ; 2.2 UT in Israël (Sivan et al., 2005)).

Thus high tritium value in the context of the Camargue is a good indicator of flow from the Rhône River.

In the confined aquifer, almost all the samples have tritium contents below detection limit (Fig. 4) which is particularly surprising for S_7 and S_g located at only 500 m from the River. One sample of the confined aquifer located close to the Rhône River (F_{11}) shows significant tritium activity (3.4 UT).
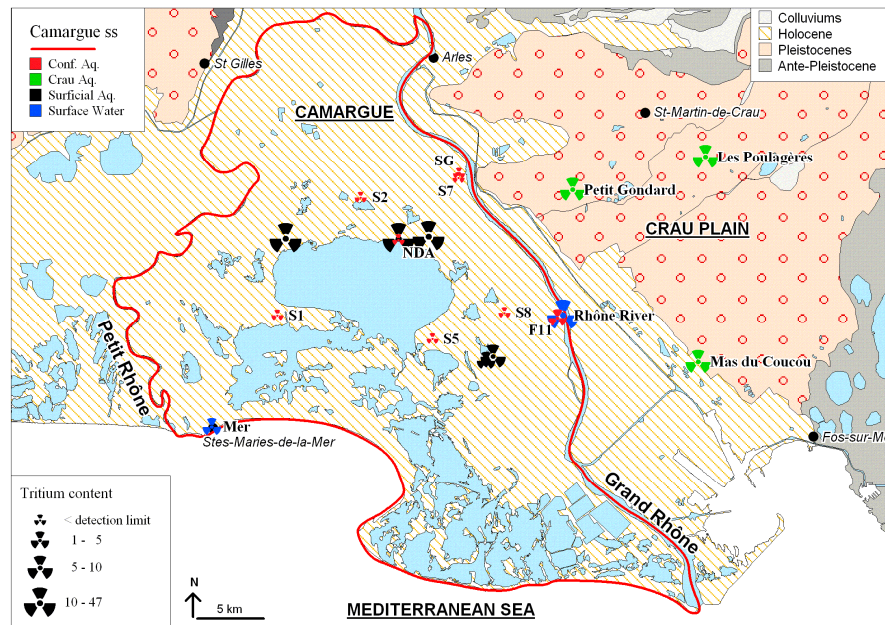
Fig. 4. Tritium distribution in the Rhône delta

The low tritium values in the confined aquifer indicate that except for one sample (F_{11}) no quick flows occur from the recharge area. This result is in agreement with tritium samplings carried out in 1969. At this time, the tritium activity in the recharge was much higher due to atmospheric testing of nuclear weapons and reached more than 300 UT in the Rhône River, but no measurable tritium activity was detected in the confined aquifer except in S_1 (Griolet, 1976; Marinos, 1969). For this latter piezometer, activity up to 286 UT was measured in 1969. Since there are very low flows in the confined aquifer (gradients close to zero), and according to the 12.3 yrs half life of the tritium, we should find now measurable tritium activities in this sample (up to 34 UT if no dilution occurred). Thus, the absence of tritium in this point suggests a pollution of the 1969 sample.

These results indicate that the water recharge of the confined aquifer was in contact to the atmosphere before the nuclear testing in the 60's. The mean residence time of groundwater is thus more than 50 years. The positive tritium value measured in the F_{11} sample could be explained by a total slow recharge from surficial water or by mixing between modern water and old water. Finally, due to low tritium activities of seawater, the absence of tritium in the two most saline samples (S_1 and S_5) does not evidence an old seawater intrusion. Thus, the tritium is not a determining element for dating the marine intrusion.

6. Use of ^{14}C activities to identify geochemical reactions

The Rhône River shows higher ^{14}C activity (149 pcm; Fig. 5) than the defining 100 percent of modern carbon (pcm) due to the influence of nuclear plants. This high value is in agreement with other measurements done in the vicinity of nuclear plants (Douville et al., 2004).

In the unconfined part of the aquifer (Crau), groundwater has ^{14}C activity of 100.5 pcm in accordance with a modern origin of unconfined groundwater evolving in open system conditions (Clark and Fritz, 1997; Geyh, 2000; Mook and Vries, 2000).

In the confined part of the aquifer, the ^{14}C activities of the dissolved inorganic carbon vary from 29 ± 0.3 pcm to 55.9± 0.7 pcm. The lowest ^{14}C activities are found in the two closest piezometers from the coastline. Nevertheless no clear correlation has been identified between the salinity increase in groundwater and the ^{14}a depletion although the seawater end-member has been identified as the possible old source (Fig. 5).
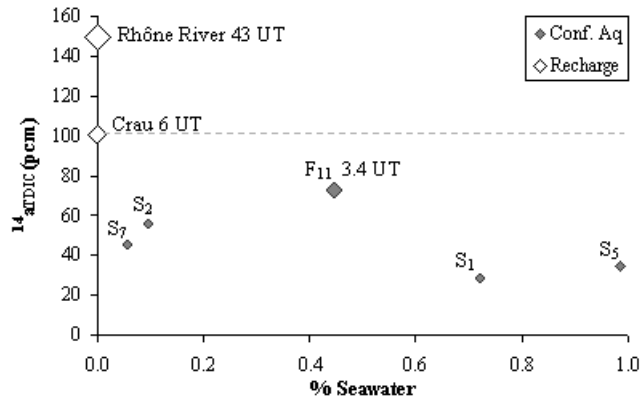
Fig. 5. ^{14}C activity in the groundwater and the freshwater recharges versus salinity expressed in contribution of seawater (cf. 4. Hydrochemistry of the confined aquifer)

F_{11} sample, which shows a positive tritium value, have a slightly higher ^{14}C activity than the other samples (around 73 pcm) but lower than the ^{14}C activity of a modern water (100 pcm). This value most likely reflects a mixing process between "old" groundwater and recharge water.

All the geochemical processes which increase, decrease or exchange carbon from the TDIC will affect the ^{14}C activity but also the stable carbon isotopic composition (δ^{13}C). As δ^{13}C has no radioactive decay, it can be used to identify the source of DIC and to quantify the part of the ^{14}C decrease due to a mixing and not to the radioactive decay.
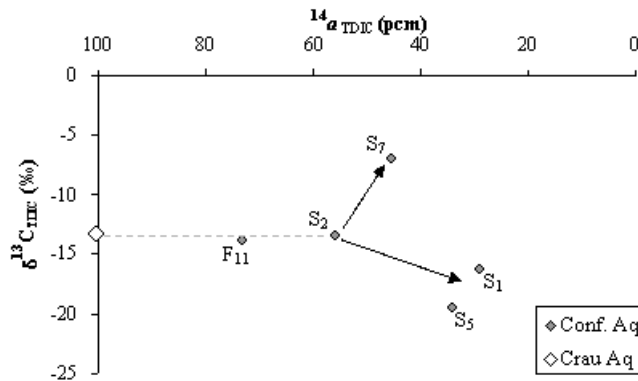

Fig. 6. Relationship between ^{14}a depletion and δ^{13}C evolution

There is no correlation between the ^{14}a depletion and the δ^{13}C evolution in the groundwater (Fig. 6). It suggests that the ^{14}a depletion is not due to a single process and different evolutions depending on the sample have to be considered. The depleted ^{14}a and δ^{13}C values in S_5 and S_1 suggest sulphate reduction processes, whereas ^{14}a depletion coupled with δ^{13}C enrichment in S_7 could be explained by isotope exchanges between dissolved inorganic carbon and the fossil δ^{13}C enriched carbonate matrix (δ^{13}C ~0‰ and ^{14}a ~ 0 pcm) (e.g. Clark and Fritz, 1997; Gonfiantini and Zuppi, 2003). Finally, S_2 sample shows a depleted ^{14}a value (~56 pcm) but a δ^{13}C value close to that of the recharge water of the Crau aquifer (-13.4‰). This depletion most likely reflects the evolution of a carbonated system in closed conditions which leads to ^{14}a between 50 and 80 pcm with δ^{13}C values between -12 and -14‰ (Clark and Fritz, 1997; Geyh, 2000).

The hydrochemical study has underlined the prominent role of the sedimentary Organic Matter oxidation on the carbon system, especially on HCO_3^- content and δ^{13}C depletion (de Montety et al., in Press). The correlation between ^{14}a depletion, the chemical indicators of organic matter oxidation (HCO_3^- content, Eh) and the Total Organic Carbon (TOC) has thus been studied (Fig. 7).
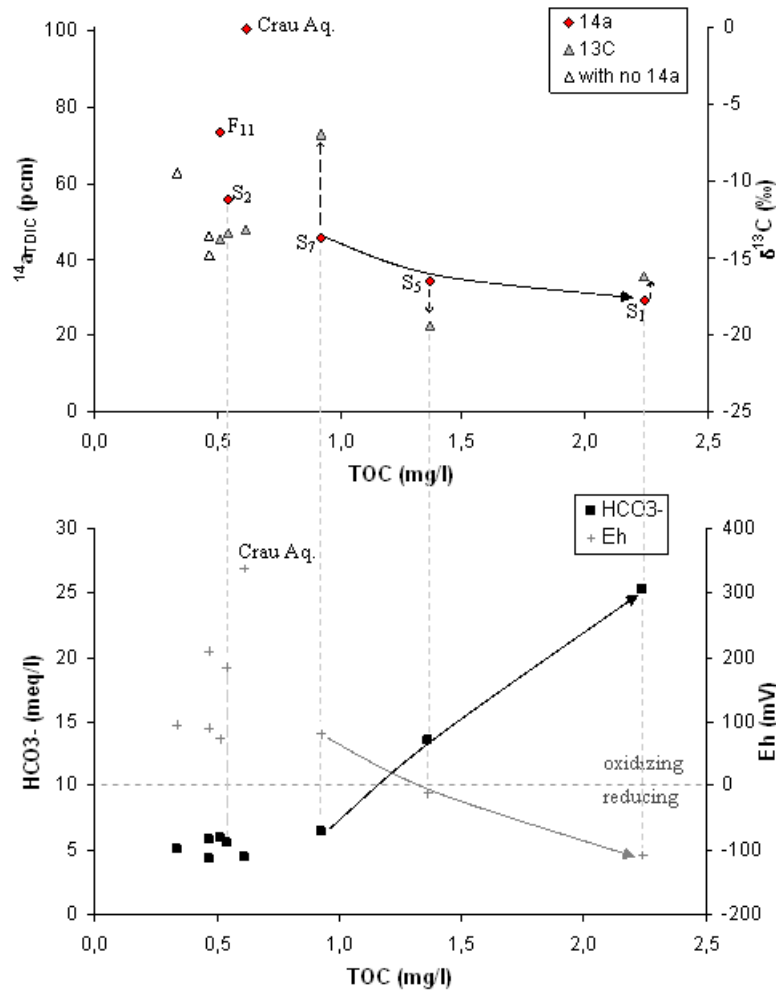
Fig. 7. Comparative evolution of the carbon isotopes (^{14}a, $\delta^{13}C$) and the chemical indicators of the organic matter oxidation (HCO_3^- content, Eh) versus the Total Organic Carbon (TOC) content of groundwater

Three samples (S_7, S_5, S_1) show measurable values of TOC (>0.6 mg/l) up to a mean of 2.3 mg/l for S_1 sample. For these three samples, Fig. 7 shows a good correlation between the ^{14}a depletion and the chemical indicators of the OM oxidation. This result suggests that the low ^{14}a value in S_7 do not correspond to isotopic exchange and is most likely due to organic matter oxidation. Thus, it highlights the prominent role of the organic matter on the ^{14}a depletion. According to the evolution way of $\delta^{13}C$ (dashed arrows; Fig. 7), two different OM oxidation pathways are distinguished:

(i) Sulphate reduction ($\delta^{13}C_{CO_2}$ ~-26‰±1) lowers the groundwater $\delta^{13}C_{TDIC}$ (S_5)

(ii) Methanogenesis ($\delta^{13}C_{CO_2}$ ~+10 ‰ from acetate fermentation pathway; (Clark and Fritz, 1997; Whiticar et al., 1986)) raises the groundwater $\delta^{13}C_{TDIC}$ (S_7).

An intermediate situation has to be considered in S_1 sample.

S_2 sample also shows low ^{14}a but has low TOC and HCO_3^- contents. Moreover, this sample shows a highly oxidizing feature (close to 200 mV). Consequently, this ^{14}a depletion can not be explained by the organic matter oxidation and confirm the evolution in closed system conditions. The widely used correction models of Pearson, Tamers and Fontes and Garnier (described in Clark and Fritz, 1997; Mook and Vries, 2000) have been applied to correct the initial ^{14}C activity of this sample. The corrected a_0 is found to be 59.6 ±0.2 pcm which correspond to an estimated age of 530 ± 131 years BP.

7. Conclusion

Tritium measurements in the low saline samples of the Camargue confined aquifer have shown that no quick flows occur from the recharge area and that the mean residence time of fresh groundwater is more than 50 years. But due to low tritium activity in the seawater, tritium is not a relevant element for dating the marine intrusion in the Camargue confined aquifer.

Groundwaters show low ^{14}C activity (<100 pcm). This ^{14}a depletion is neither correlated with the salinity increase nor with $\delta^{13}C_{TDIC}$. Furthermore the results highlight the prominent role of the organic matter oxidation on the ^{14}a depletion.

Moreover, this work shows the usefulness of the jointly use of ^{14}C and ^{13}C analyses to identify the geochemical processes which affect the dissolved inorganic carbon in OM-riche deltaic environment. The δ^{13}C enriched values in S_1 and especially S_7 samples show that in zones where methanogenesis processes occur, $\delta^{13}C_{TDIC}$ measurements alone are ambiguous.

The high OM content of deltaic aquifers highly affects the ^{14}C activities. In these complex systems, the conversion of the measured ^{14}C activity into time information is thus difficult. The usual correction models can not be used and an appropriate correction has to be done to take account of the dilution by the OM oxidation.

One sample is less influenced by OM and corresponds to the evolution of a carbonate system in closed conditions. An age of about 500 years has been estimated. Thus, groundwaters of the Camargue confined aquifer do not correspond to modern water and most likely reflect marine intrusion during the upper Holocene. The saline water would not have been totally flushed by fresh water due to low gradients in this area.

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