The use of natural tracers to highlight seawater intrusion in the confined coastal aquifer of the Rhône Delta

Veronique de Montety, Olivier Radakovitch, Christine Vallet-Coulomb, Bernard Blavoux, Daniel Hermitte

Abstract **This work shows the usefulness of water chemistry as an indicator of seawater intrusion The study deals with the deep alluvial aquifer of the Camargue delta (750 km^2), South of France. This confined aquifer lies on a marly substratum and dips from 10m at the North East to 55m at the South West with a variable thickness (between 20m and 70m). The groundwater presents strong values of electric conductivity (from 4 to 58mS/cm) rising from the North of the delta to the Mediterranean Sea. This work aims at identifying the origin of the water chemistry in order to better understand the recharge/discharge processes and the influence of the sea. A natural tracing approach is proposed including monthly sampling in 7 boreholes for chemical and isotopic analyses (^{18}O, ^{2}H, ^{13}C).**

The jointly use of Cl$^-$ and ^{18}O analyses demonstrate that strong salinities are not due to seawater evaporation but to a mixing between Mediterranean seawater and some freshwater which could originates from the Rhône or the Durance Rivers. The seawater intrusion induces a particular water chemistry of the aquifer. Due to the presence of fossil organic matter, reduction processes could exist like sulphates reduction. The importance of the organic matter reduction is confirmed by ^{13}C analyses on total dissolved inorganic carbone. Moreover, Calcium values show that exchange processes take place within the aquifer. In the area mostly influenced by seawater intrusion, the carbonates equilibria strongly constrain the system.

Index Terms **delta, Camargue, hydrogeology, natural tracers, seawater intrusion**

I. INTRODUCTION

GROUNDWATER salinization in coastal areas occurs in many aquifers around the world. Understanding the origin and mechanisms of this process is an important point for preventing further deterioration of groundwater resources.

Many investigations have dealt with the origin of saltwater in coastal aquifer [1], [2] and several sources have been principally identified: evaporites dissolution [3], [4], downward leakage from superficial salty water through failed or improperly plugged or constructed wells, deep brines [5], fossil seawater [6] or present seawater intrusion often due to excessive pumpings [7]. In all theses studies, hydrochemistry and the use of natural tracers (stable isotopes, ionic ratios) has proved to be a relevant method to conclude on the origin of the salt and to understand the different processes leading to the mineralization of the aquifer.

Seawater intrusion is more frequently observed in the case of unconfined aquifer connected to the sea where a strong demand in water resources induced a decrease of piezometric level. In the case of a confined aquifer, like the deep aquifer of Camargue, the process should be more complex. Indeed, this aquifer is confined and separated from seawater in its main part by a layer of marly sediments. Moreover, the Camargue delta is a low density population area where the Rhône River is the main water resource. However, in spite of low pumpings, the deep confined aquifer presents particularly high salinity values, from 2g/l to 38g/l. Such salinities as well as the presence of a salted to over-salted superficial aquifer rise the question of the origin of this salinity and the possibility of a seawater intrusion.

In this study, chemical and isotopic compositions of groundwater are used to determine the origin of salinity. Then, water chemical compositions are compared to an ideal seawater/freshwater mixing to highlight processes in charge of the water mineralization.

II. HYDROGEOLOGICAL SETTINGS

The investigated area is located in the South-East of France along the Mediterranean coast (Fig. 1). Downstream from Arles, the Rhône River divides into two arms (Grand Rhône and Petit Rhône) delimiting a swampy area of about 750km^2 called "Camargue". The main pond of "Vaccarès" (75km^2, 2m deep) stands in the centre of the delta. The Camargue delta is bordered in its Eastern part by the Crau plain and to the South by the Mediterranean sea. It is a low alluvial plain with a mean

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slope of 0,17‰. from Arles (Northern border) to the sea. Like many deltas, the Camargue has been subjected to a strong human influence: the dyking of the Rhône and the built of a seawall at the end of the 19th century has cut off the Camargue from a part of its natural water supply. Thus, the Camargue is protected from marine invasions but is also deprived of fresh flush flood by the Rhône. The superficial hydrology is also highly controlled: an significant canals network brings Rhône water to the cultures (mainly rice) then returns the waste water to the Rhône or the Vaccarès pond.
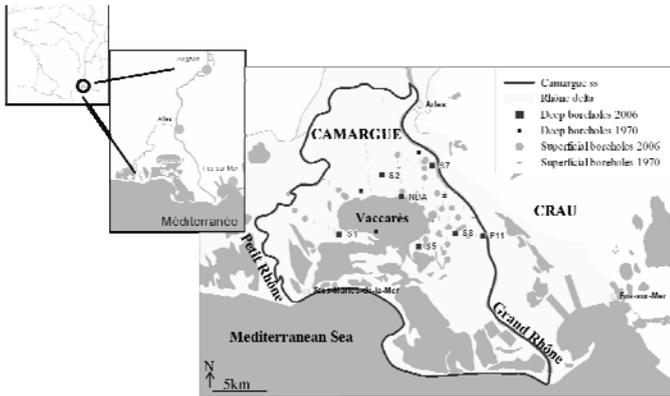

Figure 1. Geographic situation of the investigated area and its monitoring network

Regarding geology, the delta is filled with quaternary deposits lying on a thick marly substratum of Pliocene age. Pleistocene fluvial sediments of limestone gravels and sands (Villafranchian and Astian) were first deposited during a low sea level period. Then the rise of the sea level during the Holocene has induced the deposit of a transgressive prism. According to Boyer [8] its lower part consists mainly of clay and silt with boggy levels whereas the upper part is made up of sandy to silty deposits from marine to continental origin (fluvial, paludal, lagunal, eolian or littoral sediments). Two aquifers were identified within the quaternary deposits. The superficial aquifer extends in the upper part of the Holocene deposits, while the deep aquifer corresponds to the fluvial deposits. The first one is unconfined, heterogeneous and shows low permeabilities. These characteristics infer a preferential vertical flow path within the aquifer. Important salinity variation is found in superficial groundwaters, from freshwater to saline or hypersaline waters (up to 100mS/cm). Water table and salinity maps showed the predominant role of superficial hydrology and more particularly of irrigation in the aquifer recharge [9], [10]. The deep aquifer is constituted by the Pleistocene gravels which outcrop in the Crau plain and dips from North-East to South-West (from -10m in the South of Arles to -50m on the coastline). Its thickness varies from 10m to 70m [8]. Previous studies found permeability values for the gravels between 10^{-5}m/sec and 10^{-2}m/sec. This deep aquifer is confined and artesian in places. The electric conductivity (EC) is rising from North-East to South-West from 4mS/cm up to 58mS/cm. The most Southern borehole is particularly salted (38g/l) although located 8km far from the sea.

III. METHODS

This work uses a monitoring network set up in the 1960s by the Departmental Direction of the Agriculture [9], [11]. Ten boreholes (polyethylene pipes) were drilled into the deep aquifer, but none of them entirely crossed the aquifer because of the gravels hardness and only few meters have been drilled in it. They are located between 8km to 20km of the coast (Fig. 1). In the same time 60 boreholes have been set in the superficial aquifer. Now, only 5 deep boreholes and 20 superficial are still operational. Two new private boreholes have been also used to study the deep aquifer.

Monthly sampling has been carried out in deep boreholes between February 2005 and May 2006 and a water level monitoring, currently in progress, has been set. Sampling from the Rhône and the Mediterranean Sea was carried out. In addition, isotopic data obtained from sampling in five wells (S1, S2, S5, S7, S8) between April 2003 and March 2004 are also used. Samples were collected with a low flow rate (less than 6 l/min) after a pumping period corresponding to the sewage of the borehole. Direct measurements of water temperature, electrical conductivity (EC), pH and redox potential (Eh) were performed in a flow cell. Bicarbonates were determined on field by colorimetric method with a 1N HCl acid. Two water samples were filtered through a 0.45μm acetate cellulose membrane and collected in polyethylene bottles for cations and anions analysis. Six drops of HNO_3 were added in the cations set to prevent precipitation. Three water samples were collected without filtration for the analysis of stable isotopes (^{18}O, ^2H), Total Organic Carbon (TOC) and ^{13}C. Three drops of mercuric chloride were added to the ^{13}C and TOC samples to prevent degradation of organic carbon. The samples were kept refrigerated until their determination in the Hydrogeology laboratory of the University of Avignon. Analyses of cations (Ca^{2+}, Mg^{2+}, Na^+, K^+, Fe^{2+}, Sr^{2+}) were carried out with atomic absorption spectrometry. The anions (Cl^-, SO_4^{2-}, Br^-, NO_3^-) were analysed by liquid phase ionic chromatography. The total relative uncertainty including the device accuracy and the repeatability error is less than 5% whatever the compound. Nevertheless, except for the Rhône water, the high-mineralized waters had to be diluted up to a factor 125. The mean total uncertainty including the dilution procedure can then be estimated at 10% to 15% for the dominant species (Cl^-, Na^+, SO_4^{2-}, Mg^{2+}) and less than 10% for the other compounds. The errors in the charge balances were less than 5% for most of samples since July 2005. ^{13}C analyses were performed by mass spectrometry with an accuracy of 0,2‰. The data accuracies for ^{18}O and ^2H are 0,1‰ and 1‰ respectively. For samples from February to June 2005, the use of a too small column for anions determination induced a bad separation of picks and led to overestimate the chloride contents and to underestimate the bromide contents.

TABLE 1. AVERAGE AND STANDARD DEVIATION (Σ) OF GROUNDWATER HYDROCHEMICAL PARAMETERS (6 OR 7 SAMPLES PER POINT), AND RHÔNE AND MEDITERRANEAN SAMPLES (CONCENTRATIONS IN MG/L

Sample	pH	EC µS/cm	HCO_3^-	Cl^-	Br^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na^+	K^+	Br^-/Cl^-
S1 mean	6.82	44517	1527	15884	61	123	360	887	7780	218	0.0017
σ	0.02	392	61	893	1	66	20	59	219	7	0.0001
S2 mean	6.97	7033	337	2140	8	115	293	164	827	22	0.0016
σ	0.07	181	15	67	1	8	5	14	10	1	0.0001
S5 mean	7.19	57957	834	22055	80	653	244	1104	11466	347	0.0016
σ	0.03	746	20	817	3	17	11	76	312	12	0.0001
S7 mean	7.04	4567	401	1274	5	34	140	62	611	13	0.0016
σ	0.03	50	18	61	0	2	2	6	15	1	0.0001
S8 mean	7.04	44614	366	16211	61	1558	478	948	7858	255	0.0017
σ	0.04	505	19	913	2	25	25	69	187	8	0.0001
F11 mean	7.13	27986	377	9497	35	1062	277	564	4881	165	0.0016
σ	0.04	679	19	331	2	44	14	57	61	6	0.0001
NDA mean	7.06	18201	260	4270	15	340	417	269	1792	55	0.0016
σ	0.03	12591	9	148	1	7	11	19	43	2	0.0001
Rhône	8	0.417	117.1	21.7	n.d.	56.9	69.6	6.8	12.0	1.8	-
Mediterranean	-	55800	165.9	21983	83.4	3050	449	1446	11676	433	0.0017

These analyses are not included in this paper. Analyses from February to May 2006 are still in treatment and have also not been included.

IV. RESULTS AND DISCUSSION

A. General features of the deep aquifer water

Average data from monthly sampling (July to January 2006) are given in Table 1.)Although the boreholes are relatively far away from the coast (8km at least), the water is strongly mineralized (> 4mS/cm). Electric conductivity (EC) shows a large scale of variation in space (4mS/cm to 58mS/cm) but a relative temporal stability. EC spatially increases in the North-East/South-West direction, in relation with the proximity of the sea. Chloride and sodium are the main chemical species and totally control the EC in the aquifer. Chloride concentrations increase from North to South together with a global evolution from a calcium bicarbonate water type to a magnesium sulphate type.

B. Interpretation

Diagrams of major ions plotted versus chlorides are presented in Figure 2. Na^+, K^+, Mg^{2+} and Br^- are well correlated with Cl^- indicating that they derive from a same source of saline water. Moreover for these ions, samples plot along a mixing line between the Rhone and seawater. The contribution of the Mediterranean Sea to the groundwater salinization of the deep aquifer is confirmed by the values of Br^-/Cl^- ratio (around 0,0016), which is a good indicator of the origin of salinity [2]. This ratio proves that there is no contribution of evaporates dissolution which would have lead

to a lower Br^-/Cl^- ratio (0.0005 for evaporites against 0.0017 for seawater).

In contrast to these ions, Ca^{2+}, HCO_3^- and SO_4^{2-} present a bad correlation with Cl^- indicating that other mechanisms occur with the seawater intrusion.

Analyses of the stable isotopes of the water molecule (^{18}O, ^2H) performed during previous works [12], [13] shown that the samples from the deep aquifer plot along a line located under the global meteoric water line (GMWL) (Fig. 3). Moreover, they are located between an isotopically depleted water (represented by the Rhône and the Durance Rivers) and the Mediterranean Sea.

This position under the GMWL can be attributed either to evaporation or to mixing with seawater. However, the $Cl^-/^{18}O$ relationship (Fig. 4) proved that samples result from seawater/freshwater mixing and not from evaporation or evaporitic phenomena (in particular by leakage from the superficial aquifer).

Thus the deep aquifer of the Camargue is subject to a significant marine intrusion.

In contrast to the previous elements, Ca^{2+}, HCO_3^- and SO_4^{2-} contents show notable variations from a single binary mixing, implying other chemical processes. In order to better understand the consequences of such intrusion on the water chemistry, we applied the method described by Appelo and Postma [14] and used by numerous authors [6], [15], [16] to the groundwater samples of the deep aquifer. Assuming conservative behaviour of chlorides, and considering a simple binary mixing between freshwater (i.e. Rhône River) and seawater (i.e. Mediterranean Sea), the seawater fraction of each sample has been determined using the following relation:

$$(1) \quad f_{sea} = \frac{m_{Cl^-,sample} - m_{Cl^-,fresh}}{m_{Cl^-,sea} - m_{Cl^-,fresh}}$$

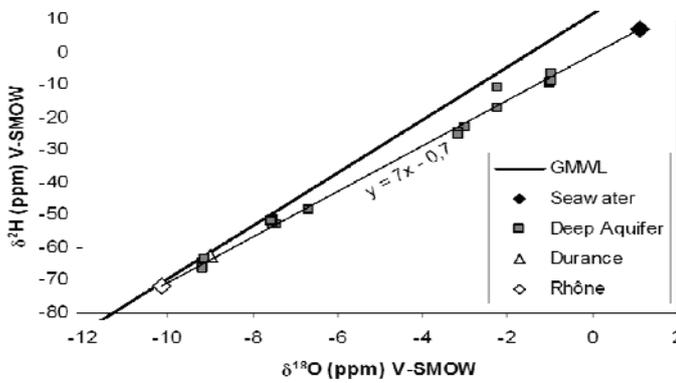Fig. 2. Plots of chemical constituents in groundwater versus chloride
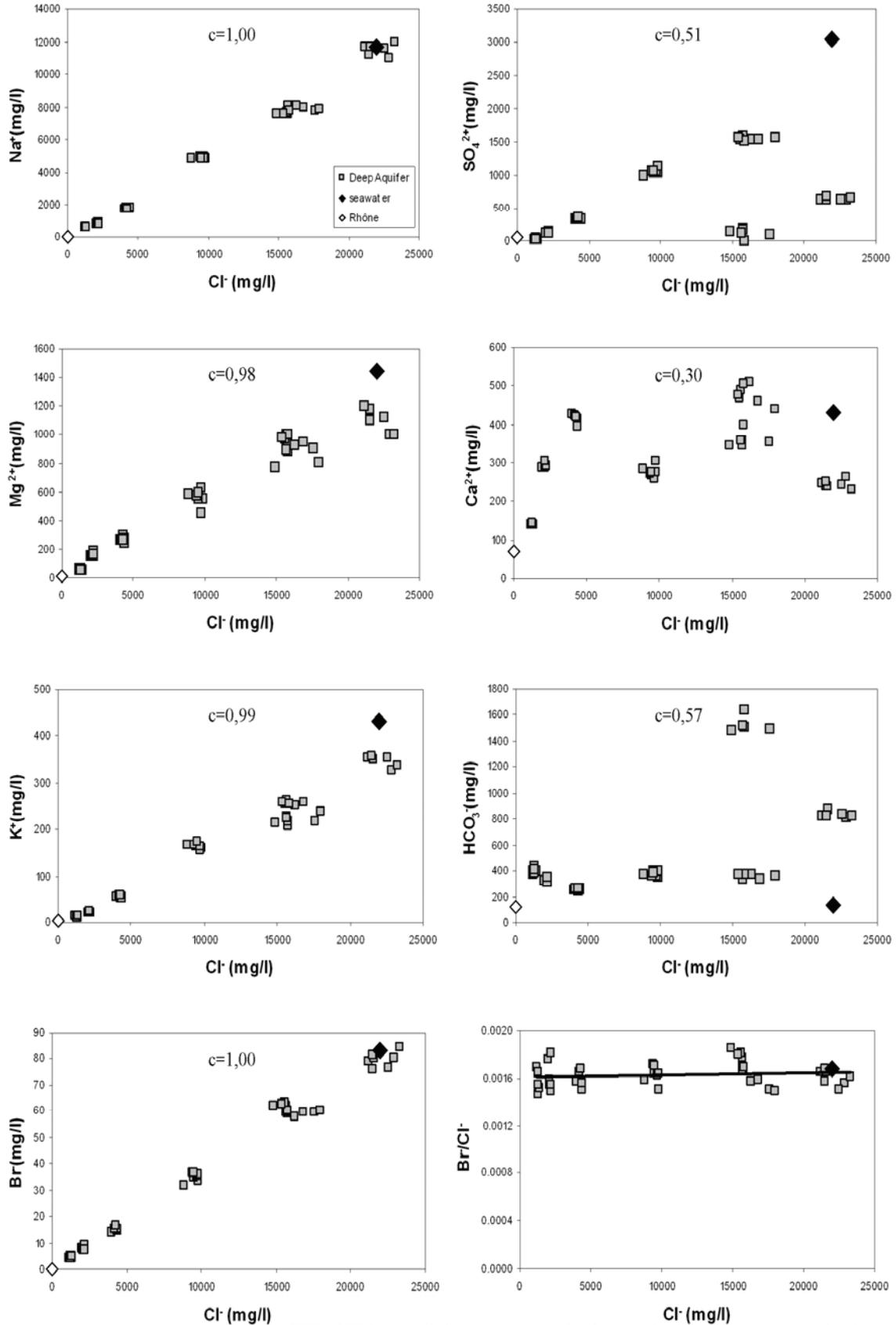
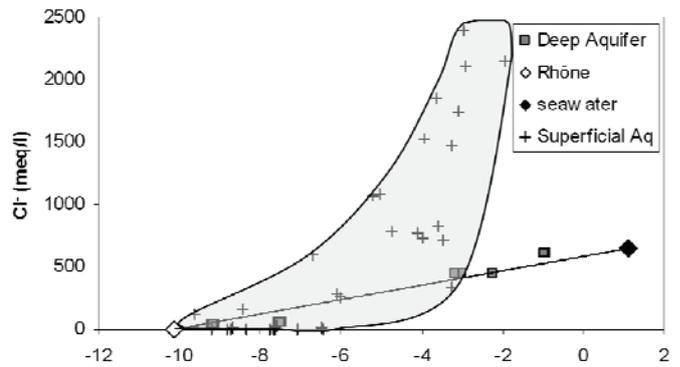Fig. 3. Relationship between δ2H and δ18O
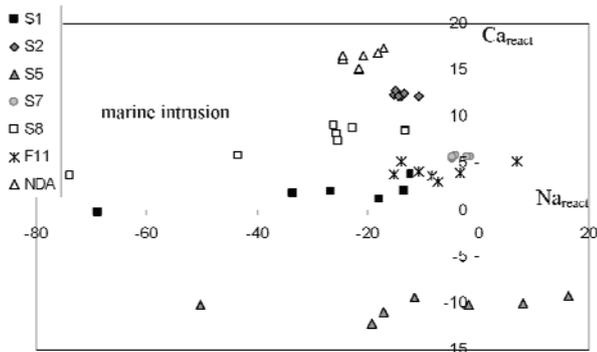

Fig.4. Plot of Cl vs. δ18O.

Fig.5. The enrichment of Ca2+ (Careact) in meq/l is plotted versus the depletion of Na+ (Nareact) for each samples.
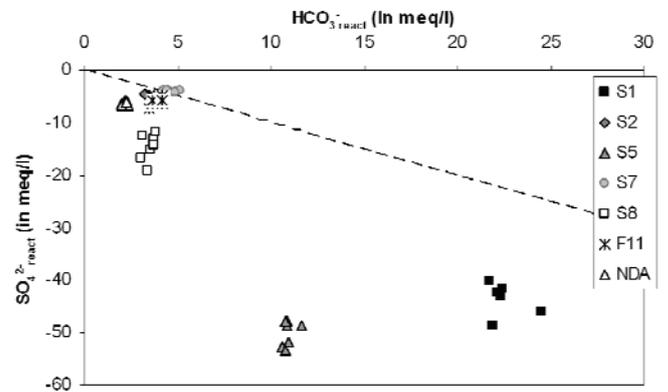

Fig.6. The enrichment of HCO3- (HCO3react) in meq/l is plotted versus the depletion of SO42- (SO4react) for each samples.

TABLE 2. AVERAGE (IN MEQ/L) AND STANDARD DEVIATION (Σ) OF RECALCULATED WATER ANALYSES

Sample	SW$_{fraction}$	Na$^+_{mix}$	Na$^+_{react}$	Ca$^{2+}_{mix}$	Ca$^{2+}_{react}$	Mg$^{2+}_{mix}$	Mg$^{2+}_{react}$	K$^+_{mix}$	K$^+_{react}$	HCO$_3^-_{mix}$	HCO$_3^-_{react}$	SO$_4^{2-}_{mix}$	SO$_4^{2-}_{react}$
S1 mean	0.72	367.1	-28.7	8.1	1.8	43.0	-13.0	8.0	-2.4	2.5	22.5	23.1	-43.7
σ	0.04	20.6	21.3	0.5	1.3	2.4	5.0	0.4	0.5	0.03	1.0	1.3	3.1
S2 mean	0.10	49.9	-14.0	1.1	12.4	5.8	1.9	1.1	-0.5	2.0	3.5	3.6	-4.9
σ	0.003	1.6	1.6	0.0	0.2	0.2	1.0	0.03	0.04	0.002	0.2	0.1	0.2
S5 mean	1.00	509.6	-10.8	11.2	-10.3	59.7	-28.5	11.1	-2.2	2.7	10.9	31.9	-50.1
σ	0.04	18.8	21.8	0.4	1.0	2.2	10.3	0.41	0.66	0.030	0.3	1.2	2.4
S7 mean	0.06	29.9	-3.4	0.6	5.7	3.4	-1.8	0.6	-0.3	2.0	4.6	2.4	-4.1
σ	0.003	1.4	1.6	0.0	0.1	0.2	0.7	0.03	0.04	0.002	0.3	0.1	0.2
S8 mean	0.74	374.7	-32.9	8.3	7.3	43.9	-9.7	8.2	-1.7	2.5	3.5	23.6	-14.7
σ	0.04	21.1	20.1	0.5	2.0	2.5	10.4	0.46	0.63	0.033	0.3	1.3	2.6
F11 mean	0.43	219.7	-7.4	4.8	4.1	25.7	-5.0	4.8	-0.6	2.3	3.9	14.1	-6.0
σ	0.02	7.6	7.5	0.2	0.8	0.9	5.4	0.17	0.28	0.012	0.3	0.5	0.8
NDA mean	0.19	99.1	-21.1	2.2	16.4	11.6	-1.0	2.2	-0.7	2.1	2.2	6.6	-6.2
σ	0.01	3.4	3.1	0.1	0.7	0.4	1.8	0.1	0.1	0.01	0.2	0.2	0.4

Considering the low chloride content in the Rhône (around 0,6mmol/l) in comparison to that of the Mediterranean (around 620mmol/l), the chloride content has been approximated to zero to simplify the equation 1. Results (Table 2) demonstrate a very large range of seawater contribution to the mineralization of the aquifer.

In the Southern area (S5), the aquifer contains almost entirely seawater (98%-100%) whereas its contribution is only 5% in the northern part. Using this calculated seawater fraction, the composition of theoretical samples can be calculated from:

$$(2) \quad m_{i,mix} = f_{sea} \times m_{i,sea} + (1 - f_{sea}) \times m_{i,fresh}$$

Depletion (negative values) or enrichment (positive values) of each specific ion is obtained by the difference between the ion content in the sample and that in the previously calculated mixing sample:

$$(3) \quad \Delta m_{i,mix} = m_{i,sample} - m_{i,mix}$$

It appears that almost all the samples display Na^+ deficiencies ($Na_{react} < 0$) compared to a pure mixing model until to a maximum depletion of 73meq/l for S8 sample. This depletion is a little bit less significant for S7 (1 to 5meq/l) and highly variable for S5 (1 to 50meq/l) which even shows Na^+ enrichment for two of its samples. In most of the cases, Na^+ depletion goes with a minor K^+ depletion, a Mg^{2+} depletion and a large range of Ca^{2+} enrichment (1meq/l to 17meq/l). The relative increase of Ca^{2+} opposed to the relative decrease of Na^+ (Fig. 5) characterises the $CaCl_2$ water type as defined by Appelo and Postma [14]. It reflects cation exchange processes occurring during seawater intrusion (sodium is taken up by the exchanger and calcium is released).

At the opposite, S5 samples do not show calcium enrichment but a low depletion and two samples are depleted for Na^+. A depletion of Ca^{2+} as well as Na^+ enrichment reflects an inverse exchange of cation where calcium is taken up from water in return for sodium [14].

Regarding the anions, all the samples are depleted in SO_4^{2-} (between 3meq/l for S7 and 53meq/l for S5) and enriched in HCO_3^- (until 26meq/l for S1; Fig. 6).
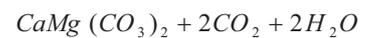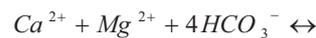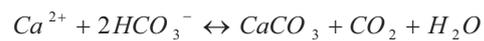
Sulphate depletion is commonly observed in aquifers affected by seawater intrusion [6], [16], [17]. Sulphate reduction processes must occur in the deep aquifer of Camargue following:

$$SO_4^{2-} + 2CH_2O \rightarrow H_2S + 2HCO_3^-$$
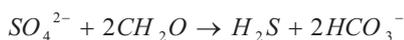
where CH_2O represents organic matter [14]. This reaction due to biological activity leads to the degradation of organic matter and to the production of H_2S. This result agrees with the strong and typical smell of H_2S noted on the field in S1 and S5, and it is confirmed by the first analyses of ^{13}C of the dissolved inorganic carbon (DIC). Indeed $\delta^{13}C$ content of the

samples are highly impoverished for S8, S1 and S5 (-14‰, -15‰ and -19‰ respectively) compared to the seawater ($\delta^{13}C$ close to zero). This impoverishment traduces the influence of an organic source ($\delta^{13}C \pm -25$‰) of DIC by microbial respiration [17]. Sulphate reduction requires a supply of reactive organic carbon presumably derived from the lower boggy part of the superficial aquifer. It also depends on the presence of sulphates which are in low content in the freshwater. Here the sulphates source is the seawater intrusion. Thus sulphates reduction in this context is a good marker of the head of the saline tongue. Because bacterial activity needs time to occur, sulphates reduction is also an indicator of long time residence of the water in the aquifer.

The SO_4^{2-} depletion does not present a linear correlation with the HCO_3^- enrichment for the high mineralized samples. The HCO_3^- enrichment seems to be limited in particular for S5. The increasing amount of bicarbonate produced by sulphate reduction as well as the supplementary calcium contribution from the cationic exchange reaction should displace calcite equilibriums and should cause supersaturation of calcite and dolomite according to:

$$Ca^{2+} + 2HCO_3^- \leftrightarrow CaCO_3 + CO_2 + H_2O$$
$$Ca^{2+} + Mg^{2+} + 4HCO_3^- \leftrightarrow$$
$$CaMg(CO_3)_2 + 2CO_2 + 2H_2O$$

To investigate this assumption, the average saturation index (SI = log(IAP/K), where IAP is the ion activity product) for carbonated minerals have been calculated using the geochemical code PHREEQC [18]. The results confirm the supersaturation of calcite and dolomite (Table 3) for S5 but also for S1.

TABLE 3. AVERAGE SATURATION INDEX FOR CARBONATED MINERALS.

Sample	Calcite	Dolomite
S1	0.37	1.41
S2	0.06	0.10
S5	0.27	1.48
S7	-0.01	-0.14
S8	0.07	0.70
F11	0.00	0.56
NDA	0.11	0.29

Calcite precipitation must occur in S5. Thus the constant depletion in calcium could be explained by its consumption during precipitation. Nevertheless, the supersaturation of water towards carbonates could also induce an inversion of the way of the cation exchanges which could explain the enrichment in sodium for two of the samples. These results highlight that the system is highly constrained by carbonates equilibria.

V. CONCLUSION

This hydrochemical and isotopic investigation of the deep aquifer of Camargue revealed that the strong salinities observed are not due to evaporates dissolution or downward leakage from the evaporated superficial aquifer. There is a mixing between the Mediterranean Sea and some freshwater which could be the water from the Rhône River (or the Crau aquifer, this assumptions is studied now). Such seawater intrusion induces modifications of the water chemistry by exchange processes (calcium enrichment) or sulphate reduction due to the presence of fossil organic matter in the aquifer. These reactions increase Ca^{2+} and HCO_3^- contents in the water. Thus the system is strongly constrained by the carbonated minerals equilibria which probably lead to calcite and dolomite precipitation as well as reverse way of the cation exchanges in S5.

These results show that the water chemistry is a good indicator of seawater intrusion. Since sulphate reduction processes are slow, their existence implies a relative low flow rate within the aquifer.

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