

## **DARCY 01**

### **Alluvial Aquifers in North China Plain**

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#### **Abstract**

The alluvial plain located in North China is one of the most important aquifers in East Asia which area is 140000km<sup>2</sup>. The recharges of shallow groundwater system are mainly rainfall. There are also recharges from surface water in riverside and irrigated area. Groundwater flow is from the front of mountains to coastal plain. The Isotopic data of deep aquifers show that the water flow from the front of mountains to the middle and coastal plain need about several thousands to more than 10 thousands years. Long term groundwater overexploited especially in deep aquifers not only cause many bore to go dry but also cause many eco-environmental problems. The detail investigation on the aquifers has been taken. Sustainable of Groundwater Usage for the social – economical developement are advanced.

#### **Geography and Hydrology**

North China Plain is one of the focus regions of China. Beijing, the capital of China, Tianjin city, most part of Hebei province and part of Shandong and Henan province are situated in this plain. The alluvial plain located in North China is one of the most important aquifers in East Asia. From Taihang Mountains in the west to Bohai Sea in the east, from Yan Mountain in the north to the Yellow river in the south, the area of north China plain is 140000 km<sup>2</sup>. The altitude is lower than 100m. According the formation and physiognomy, it could be divided to alluvial plain in front of mountain, the middle plain, and the coastal plain. There are some lakes and billabongs, especially in the middle and east part. The plain belong to semi-arid and semi-humid climate regions. The average annual precipitation is 500-600mm. The rainfall and evaporation are asymmetrical. 80% of the precipitation are fasten on Jun to September. The plain is a part of Yellow river, Hai River and Luan river catchments. Because of the upper reservoirs holding back, these rivers are almost dry up in most periods.

#### **Quaternary Aquifers**

The plain is large sediment basin of Cenozoic. It is the most significant; consist of alluvial sediments of up to 1000-3000m. In which, the Quaternary thickness is more than 600m in depression area and 200m in apophysis area. Groundwater exists in the Quaternary and tertiary pore aquifers. The aquifers system is 350-500m in thickness. The quaternary aquifers could be divided into four groups in the middle plain, and the coastal plain. The upper two groups are shallow aquifers. The lower two groups are deep confined aquifers. The bottoms of shallow aquifers are generally in depth of 40-60m. In alluvial plain in front of mountain, for mixed extractive, the shallow groundwater systems extend to 120-150 m depth. The bottoms of deep confined aquifers are 350-550 m depth. In the middle and coastal plain, there are the salt aquifers between shallow and deep fresh aquifers.

According to water circular and system character, there are three Groundwater systems in North China plain: Luanhe River system, Hai River system and ancient Yellow River system. They could be subdivided into 7 second grade subsystems, 17 third grade subsystems and

28 forth grade subsystems. They are the basis for groundwater system analysis and assessment. See Fig.1 and Table 2. The quaternary aquifers of Luan river system are composing with coarse sands. They are rechargeable with rain water and surface water. Those aquifers of Hai river system are complex. They are various from foreland to coastal area. The section of Fig. 2 shows the structure for the quaternary stratum. The shallow aquifers of ancient Yellow river system are recharged sufficiency. But the deep one is interbedded with clay.



Figure 1: Groundwater systems of North China plain

### Water Circular and Characters

The recharges of shallow groundwater system are mainly rainfall. There are also recharges from surface water in riverside and irrigated area. Groundwater flow is from the front of mountains to coastal plain. The coefficients of Transmissivity are 500-1000 m<sup>2</sup>/d in the front of mountains, 100-500 m<sup>2</sup>/d in the middle plain, and generally less than 50m<sup>2</sup>/d in coastal plain. The discharges of shallow groundwater system are exploitation and evaporation. A mass of shallow groundwater exploitation decreased the evaporation and increased the recharge in recent years. The TDS of shallow groundwater are in orderliness. The fresh water is distributed in the front of mountains. There is the salt water in coastal area where the TDS of water is more than 5g/l. between them is the transition area. Fig.2.

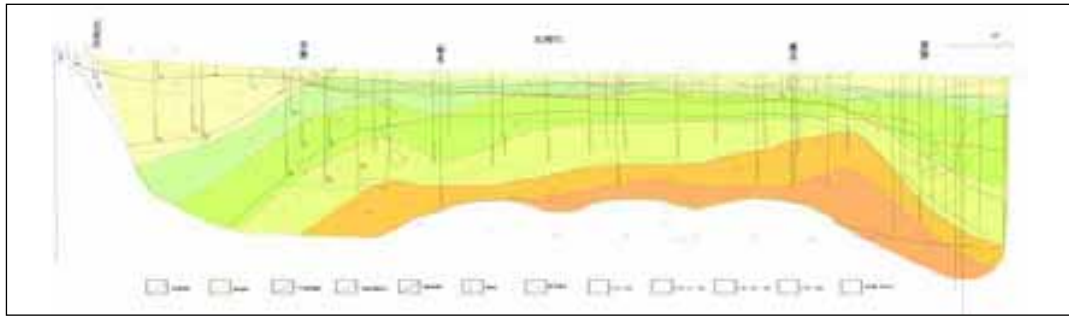


Figure 2: Hydrogeological cross section

The deep confined aquifers could not be recharge by rainfall directly. The flank groundwater flow would recharge these aquifers. The Isotopic data of water in deep aquifers show that the water flow from the front of mountains to the middle and coastal plain need about several thousands to more than 10 thousands years. In the condition of extensive exploitation, those aquifers are recharge by border shallow aquifers and aquitard. Exploitation is the mainly discharge of deep groundwater system. The main consist of pumping water are the storage in deep confined aquifers and neighbor aquitard. That is the causes of land subsidence. The chemical types of this groundwater are mainly Na-HCO<sub>3</sub>.SO<sub>4</sub> and Na.Mg-HCO<sub>3</sub>.

Situation	Plain in front Of Mountains	Middle plain	Costal plain
C (pmc)	24.50 ~ 111.07	6.29 ~ 18.40	2.44 ~ 18.52
$\delta^{18}\text{O}(\text{‰})$	-10.5 ~ -8.7	-12.5 ~ -10.2	-10.7 ~ -9.5
$\delta\text{D}(\text{‰})$	-72 ~ -65	-87 ~ -74	-81 ~ -75
Cl (mg/l)	5.57 ~ 62.30	1.64 ~ 329.6	242.70 ~ 524.7
$\delta^{18}\text{O}$ temperature	9.4 ~ 15.06	4.06 ~ 8.43	7.97 ~ 10.31
$^3\text{H}(\text{TU})$	6 ~ 47	1 ~ 3	1 ~ 6
$\delta^{13}\text{C}$ (PDP)	-10.39 ~ -9.28	-10.23 ~ -7.75	-11.46 ~ -7.92
TDS(mg/l)	342	908	1786
pH	7.7	7.95	7.9
Chemical type	HCO <sub>3</sub> -Na.Ca	Cl.HCO <sub>3</sub> -Na	Cl-Na
Vogel (ka B.P.)	10 ~ Modern	21 ~ 12	30 ~ 12

Table 1: Geochemical and Isotopic parameters of Groundwater in Deep confined aquifers

## Groundwater Resources

The assesment of groundwater resources is base upon an understanding of the recharge over a region and considering the environmental factors. The achievement of groundwater resources evaluation is as Table 2, the average annual fresh groundwater recharge in North China plain is  $19 \cdot 10^9 \text{m}^3$  per year. Thereinto the recharge for shallow aquifers is  $16.8 \cdot 10^9 \text{m}^3$  per year, Recahrge to deep confinded aquifers is  $2.4 \cdot 10^9 \text{m}^3$  per year. This typcal results in the exploitable yield being less than the recharge volum. They are restricted by the technical, economic and eco-environmental conditions. The rechrg to the deep confined aquifers is by the flow from the basin margin in the west, and by leakage from overlying aquifers. However the rate of horizontal flow is very slow and vertical leakage is little. Much of the groundwater in the deep confined aquifers can be considered to represent fossil water with limited recharge.

Sub systems		Area (Km <sup>2</sup> )	Annual preci.(mm)	Recharge (Mm <sup>3</sup> /yr)	Exploitable (Mm <sup>3</sup> /yr)
A	Luan river system	7000	552	1440	1238
B	Hai river system	75340	500	14400	13018
C	Ancient Yellow River system. system	56900	584	3280	3036
<b>Total (or average)</b>		<b>139240</b>	<b>548</b>	<b>19120</b>	<b>17292</b>

Table 2: Groundwater resources in North China Plain

Groundwater resources of the alluvial plain constitute the primary water supply for urban, industry as well as irrigation. In last 30 years, the exploitation and utilization of groundwater has been carried out extensively in this plain. The annual groundwater extractions is  $21 \cdot 10^9 \text{m}^3$  in 2000. Thereinto, those from shallow aquifer is  $17.8 \cdot 10^9 \text{m}^3$ , those from deep aquifer is  $3.3 \cdot 10^9 \text{m}^3$ . The groudwater usage is as Table.3. Groundwater is about 2/3 of total water supplied of the area. Groundwater over-exploitation is befallen in some area of the plain.

Province	Total	Industry	Agriculture	Civil	Other
Beijing	2487	436	1532	528	
Tianjin	555	15	316	105	119
Hebei	12862	1476	10136	125	
Shandong	2756	571	1827	358	
Henan	2538	294	1999	245	
<b>Total</b>	<b>21198</b>	<b>2792</b>	<b>15801</b>	<b>2486</b>	<b>119</b>

Table 3: Groundwater Usage in North China Plain (Mm<sup>3</sup>/yr)

## Groundwater related Ecological Issues

Groundwater has played a key role in the history and development in the plain. The huge extent of over-exploitation of groundwater in the alluvial plain has created a broad range of largely environmental problems. Long term groundwater overexploited especially in deep aquifers not only cause many bore to go dry but also cause many eco-environmental problems. Groundwater level both of shallow and deep aquifers in most part of the plain have declined more than 15 m during last 30 years. In some urban and irrigated area, the declined extent of groundwater level are ever large. Several ecological issues were occurred cause by groundwater overexploitation. The situations of land subsidence, sea water intrusion, water quality degradation are investigated and verify. The groundwater overexploited occurred in the area of Beijing city and Hebei Province. Continuance decline of groundwater level present to these region. Figure 3 shows the situation in Beijing downtown. The North China plain has witnessed the most excessive pumping of groundwater in the world and covers the largest subsidence area with the most funnels. The groundwater level in coastal region falls below sea level.

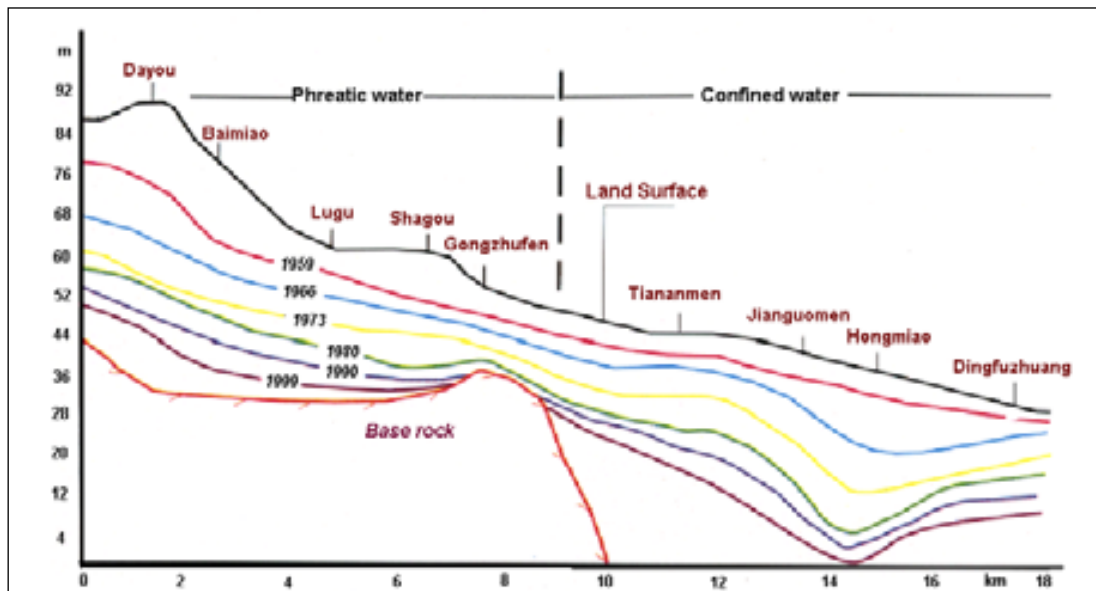


Figure 3: Groundwater level in Beijing Downtown

The deep confined aquifers could not be recharge by rainfall directly. The flank groundwater flow would recharge these aquifers. In the condition of extensive exploitation, those aquifers are recharge by border shallow aquifers and aquitard. The main consist of pumping water are the storage in deep confined aquifers and neighbor aquitard. That is the causes of land subsidence. In 2005, the areas of land subsidence more than 1000mm reach 8635 km<sup>2</sup>. The areas of land subsidence more than 500 mm reach 30080 km<sup>2</sup>. The most land subsidence in Beijing city is 0.79 m. The most land subsidence in Tianjin city is 3.18 m. The most land subsidence in Hebei Province is 2.45 m. The most land subsidence in Shandong Province is 0.94 m. The several areas of land are continuing developing. They are tending to gear into joint area in the plain.

Land subsidence due to groundwater withdrawal induces very serious economic and social problems. Subsidence in urban area, such as Tianjin and Cangzhou, effects are widespread and affect not only the nature structures but also the man-made ones. Damages could be

record but it is nearly impossible to establish their actual coast. Hazards are mainly structural damage, damage to well casing, lessened efficiency of storm-drainage facility, submergence of coastal lowland, etc. The disastrous of land subsidence are tide and waterlog due to less of land surface elevation. Relationship between Land subsidence and the groundwater level of deep aquifers has been root out as fig.4. We could find 50m and 70m of the depth of groundwater level is the key point of land subsidence. The aquifers dynamic pressure condition changed in evidence at those water levels.

For controlling subsidence, a monitoring networks focusing in North China plain is under establishing. It will monitor the rate of land subsidence as well as groundwater levels which covering 70000 km<sup>2</sup>.

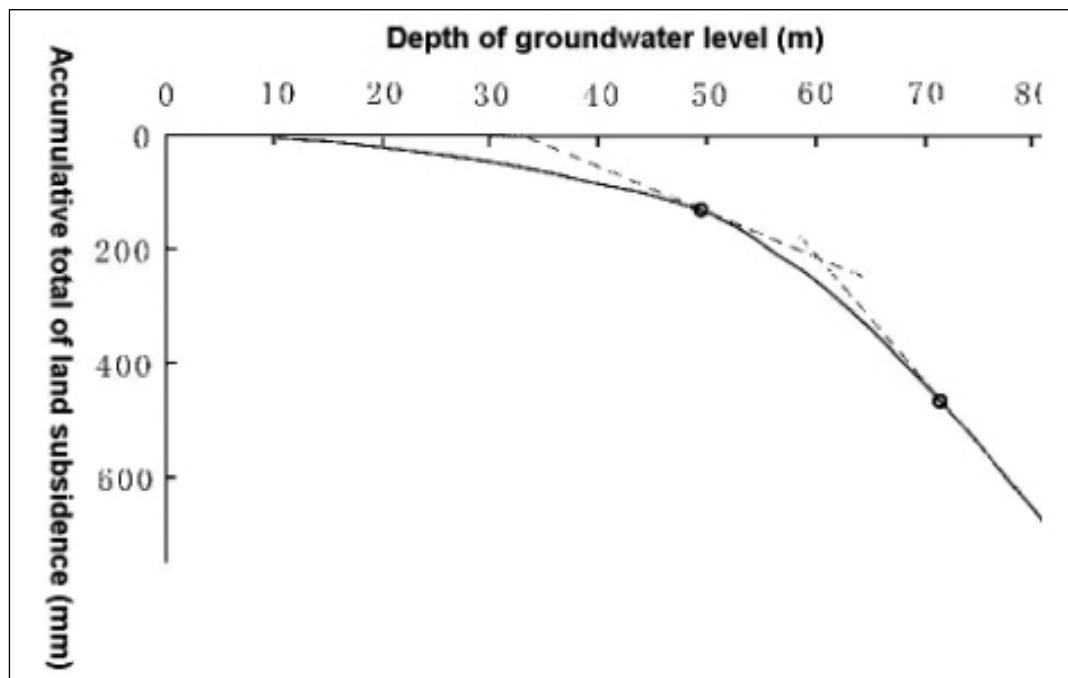


Figure 4: Relationship of Land subsidence and the groundwater level of deep aquifers

The shallow aquifers were polluted by the urban and industry waste water. The contaminated area is about half of the plain. The salted water have move down to the fresh water aquifers due to the excessive exploitation.

### Sustainable of Groundwater Usage

For the social – economical developpment in North China plain, one of the Chinese most important regions, sustainable of groundwater resources usage is integrant. The detail investigation on the aquifers has been taken. A numeric model with FEFLOW of WASY software for the plain is established. **All the groundwater models are basis on Darcy Law which was presented in 1856.** The 3-D model is used to simulate and forecast the situation both shallow and deep aquifers Fig.5. The data base of the aquifers were established. They are consistes of basic geograph information, geological information, hydrogeological condition information, groundwater quantity and quality information and dynamic monitoring informatin,etc. The data of year 2000-2003 were used to establish and calibrate the model. The hydrogeological



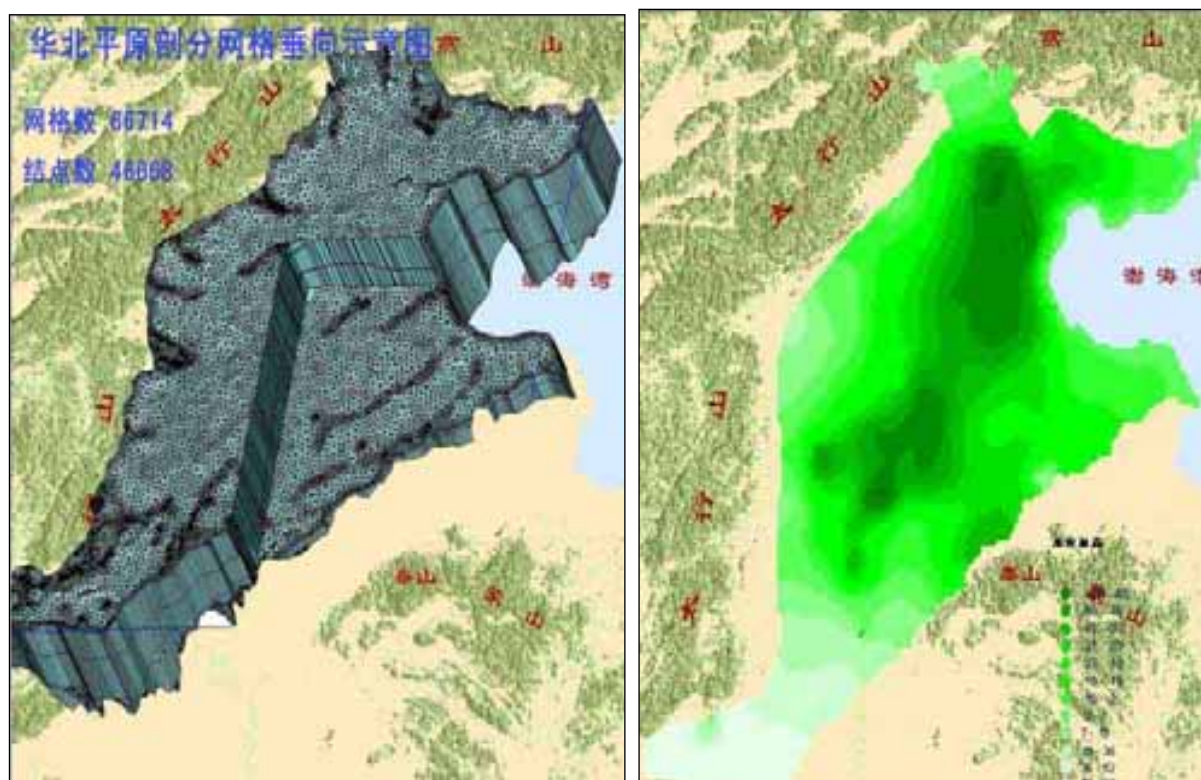


Figure 5: Numerical Model of North China plain

concept model are the whole plain with the area of 140000 km<sup>2</sup> and the aquifers depth to 550 m. Several measures for groundwater conservation are evaluated by the model.

The nature water circular have been breakaged by the surface reservoirs in the rivers upstream. Only in the flood seasons the alluvial aquifers could be recharged. The extracted groundwater are large than the recharge for the aquifers. Fig 6 shows the groundwater level in the plain front of Taihang Mountains could come back after recharged. Artificial recharge is the most important way for groundwater protection and aquifers recovery. Aquifer recharge enhanscement with excess surface runoff and urban wastewater are water resources safeguard measu- res. There are large area in front og mountains in the plain where coarse sands and gravel out- crop. The surface artificial recharge system would be efficient.

Reducing groundwater extractions, by a variety of means, will generally be the most cost – effe- tive method of solving groundwater relative eco-enviromental problems. The long-distance

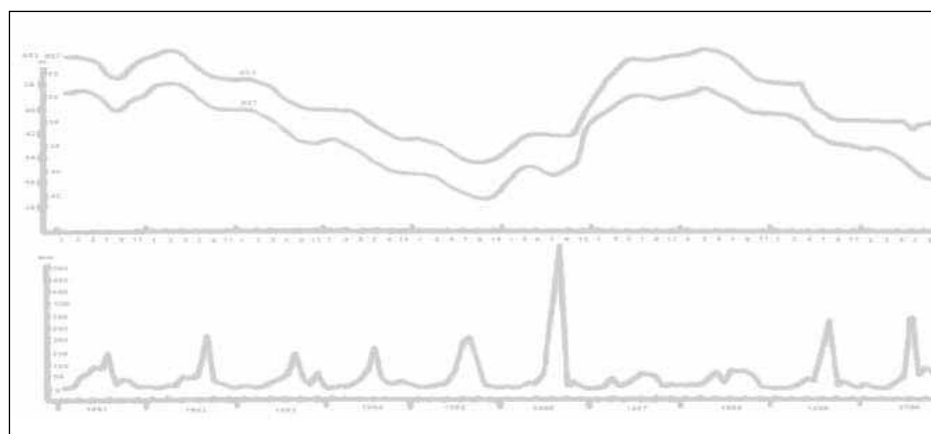


Figure 6: Groundwater level at the riverside and monthly precipitation

water transfer project from Yangtze river to North China plain will implement in 2010. Conjunct use of surface water and groundwater, the exploitation of groundwater in deep confined aquifers will decrease. Some surface run flow would be resume. And the environment of water could improve.

Agricultural sustainability in the North China Plain, is highly dependent on water resource availability. Over twenty percent of the area in the Plain is irrigated using groundwater. It is imperative that these practices tested in small plots now be demonstrated in commercial applications to conserve groundwater resources and maintain agricultural sustainability needed to feed China's increasing population. Reducing groundwater abstraction for irrigation is considered with water saving.

To make more sufficiency usage for local waste water and salted groundwater is a way for save fresh water. Treat with and Reused urban and industry waste water which amount is  $7 \times 10^9 \text{m}^3$  per year in this area have potential. There are some new groundwater well field could be for water supply meet an emergency. They must be regulating used with other water resources, such as surface reservoir and water transferred from other catchments.

Sustainable groundwater usage in North China plain could achieve in an integrated manner of all available management options.

## **Conclusion**

The alluvial aquifers in North China plain are an important source for water supply of the intensive development area. The detail hydrogeological investigation on the aquifers has been taken. Several eco-environmental issues have occurred due to groundwater over exploitation. Measures for sustainable of Groundwater usage have been evaluated and bring into effect. Those are Aquifer recharge enhancement, irrigate water saving, more for local waste water and salted groundwater sufficiency usage, etc.

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## DARCY 9

### Geochemical Modeling Through Groundwater Mineralization Appraisal: Sines Coastal Aquifer, SW Portugal

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#### Abstract

The Sines coastal sedimentary basin corresponds to a tecthonical ditch with a NE-SW orientation filled with Mesozoic and Cenozoic deposits. Two hydrogeological systems were identified: the Mio-Pliocene and the Jurassic. The aquifers recharge is made directly on the outcrop areas, although the Jurassic terrains receive also some contribution from the overlain Miocene layers. The main flow direction of Jurassic aquifer is E to W towards the Atlantic Ocean.

The groundwaters are mainly of the calcium-bicarbonate type related to the lithological composition of the reservoirs (calcareous and dolomitic units). Using mass balance model and statistics analysis it was proven that the water-rock interaction process is the major mechanism responsible for the groundwater salinity. If we assume the evolution from the Mio-Pliocene waters to Jurassic waters, it is expected that waters progressively increase the concentrations of chemical constituents. To evaluate this, using a simple mass balance model through the PHREEQC program were tested different scenarios in order to justify the groundwater mineralisation of both aquifers.

#### 1. Introduction

The growing request of good quality water for public, industrial and agricultural use is in nowadays a major concern for groundwater management and protection. The groundwater geochemical evolution have been recognized as being important tools in the resolution of problems such as identification of pollution sources, interrelationships between surface and groundwater, identification of salinity sources and in the appraisal of conceptual models of the systems. The region studied corresponds to the Sines coastal sedimentary basin where two hydrogeological systems were recognized: the Mio-Pliocene and the Jurassic. Both systems supply water to the entire region, which contains highly populated and industrialized areas, although in the remaining region agriculture represents an important activity. Some local losses in the water quality were identified which could be associated to human activities or due to the aquifer matrix lithology.

Water resources assessment and management require a multidisciplinary approach involving chemical, physical and geological data. In this context geochemical inverse modeling has been used in regional groundwater studies in order to identify the predominant reactions in the aquifer. However, this simple mass balance approach cannot be successfully applied to areas where groundwater mixing occurs. In order to address this problem multivariate mixing had been developed and applied in situations where different water types exist.

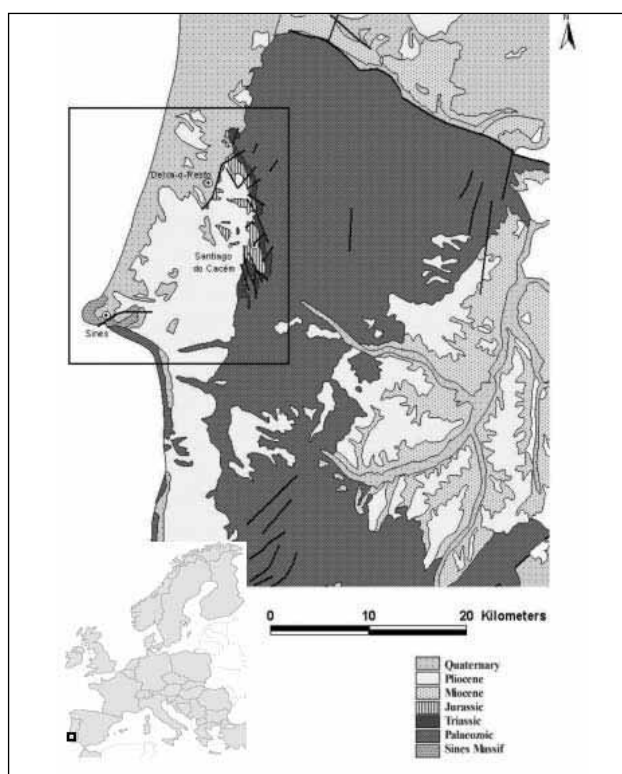


Figure 1: Location of Sines basin.

## 2. Geological and Hydrogeological Setting

The Sines sedimentary basin is situated in the Portuguese Atlantic coast and corresponds to a tectonic ditch with a NE-SW orientation filled with Mesozoic and Cenozoic deposits (Inverno, 1993) (Figure 1). The basin deposits have an angular contact with Paleozoic basement rocks in the E and S, with the Sines Subvolcanic Massif at the SW and with Quaternary and Tertiary deposits through the Deixa-o-Resto fault in the west. The local Mesozoic sequence begins with Triassic deposits consisting of sandstone, evaporite and carbonate series (Grés de Silves Formation) overlaid by tuff of the Volcanic-Sedimentary complex.

Carbonate layers with clastic rocks at the top compose the Jurassic sequence. The Liassic is represented by dolomite, dolomitic marl and oolitic limestone with an average thickness of 100 m. Oolitic limestone, microcrystalline limestone and rare dolomite and marl compose the Dogger, presenting a maximum thickness of 400 meters. The Malm with about 600 m is constituted by a sequence of conglomerates, limestone, clay and marl (Manuppela and Moreira, 1989).

Miocene deposits (clayey sandstone, marl and marly limestone), Plio-Pliocene detrital (sand and clay) and recent alluvial and dune deposits partially covered by the Mesozoic formations. Two hydrogeological systems were identified in the Sines basin: the Mio-Pliocene and the Jurassic areas (Figure 2). These hydrogeological systems supply the entire region, in which some areas are highly populated and industrialized. In the Mio-Pliocene system the recharge of the aquifer comes directly from the outcrop areas, while in the Jurassic areas the recharge occurs directly in outcrops of carbonate formations and furthermore receives some contribution from the overlain Miocene layers. The main discharge of the systems should be in the continental platform, although some small natural springs spout inland. These two aquifers seem to have a hydrological connection through recharge of the Jurassic aquifer through the Miocene layers.

In the Sines Basin the precipitation varies from 600 mm to 765 mm at Santiago do Cacém and the potential evapotranspiration is about 750 mm/year (Lavaredas and Silva, 1999a). Analyzing the precipitation records shows the influence of the topography in the amount of precipitation over Sines Basin. The values of mean annual precipitation increase to the interior where the altitude is higher (Grândola and Cercal Ridges of mountains).

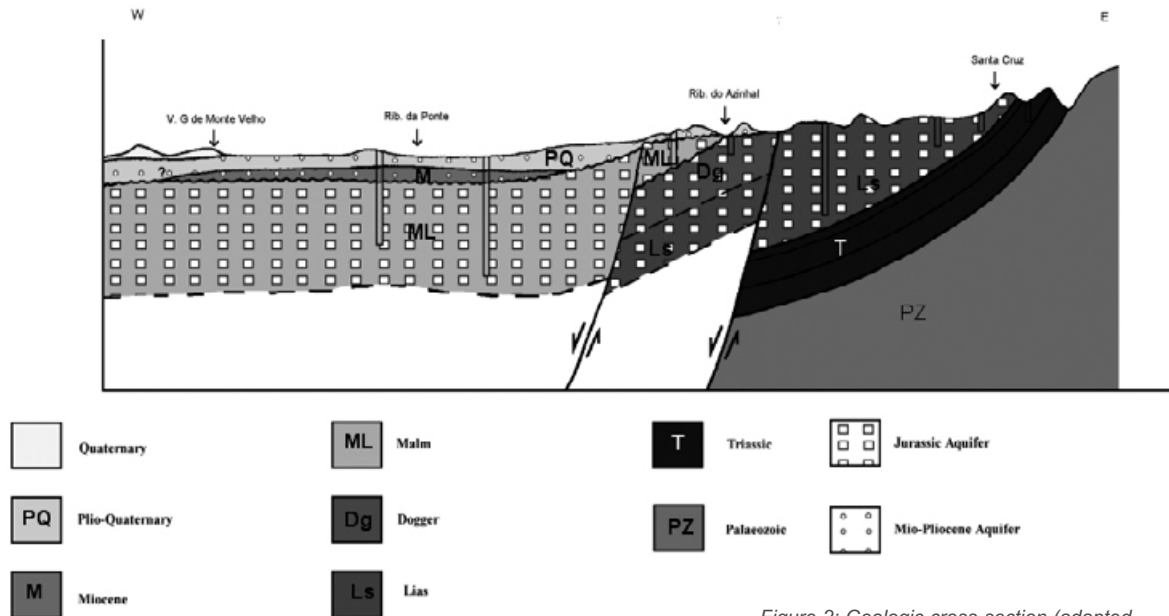


Figure 2: Geologic cross-section (adapted from Inverno et al, 1993).

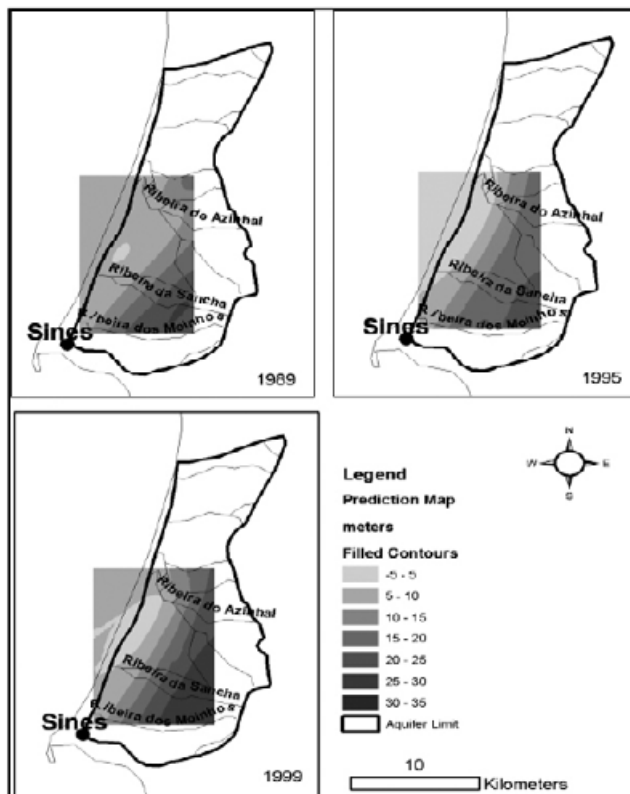


Figure 3: Sines basin piezometric map

The main groundwater flow direction of the Jurassic aquifer is E to W towards the Atlantic Ocean. In the central part of the area, near Santo André Lagoon, a concentration of wells supplying water to Santiago do Cacém city, yields a piezometric depression (Figure 3), although the system is not in stress and does not present “important” variations in time from one season to another. This could be a result of a recharge contribution from the Tertiary formations to the Jurassic system (Galego Fernandes, 2004a).

## 2. Field and laboratory methods

Five field campaigns were performed between 1997 and 2001 in the Sines area where a total of 40 points were sampled (dug wells, drill wells and springs). Groundwater samples were collected for physical-chemical analysis. A piezometric characterisation was also established. The physical and chemical analyses were performed in all water samples; major cations and anions and for some of the campaigns the content in Fe, Cu, Al and Mn were determined. Temperature (°C), pH and electrical conductivity ( $\mu\text{S}/\text{cm}$ ) were determined in situ at the time of the sampling. Total alkalinity was measured a few hours after the sampling by  $\text{H}_2\text{SO}_4$  titulation at 0.1 N until the pH value of 4.45

The following methods were used in chemical analyses performed at the Waters Laboratory of Centro de Geologia from the Universidade de Lisboa (FCUL) and at the Laboratório da Direcção Regional do Ambiente do Alentejo (DRAA): EDTA complexometry for Ca and Total Hardness; Mass spectrometry for Cl,  $\text{NO}_3$ ,  $\text{SO}_4$ , F, Br; atomic absorption for Na and K.

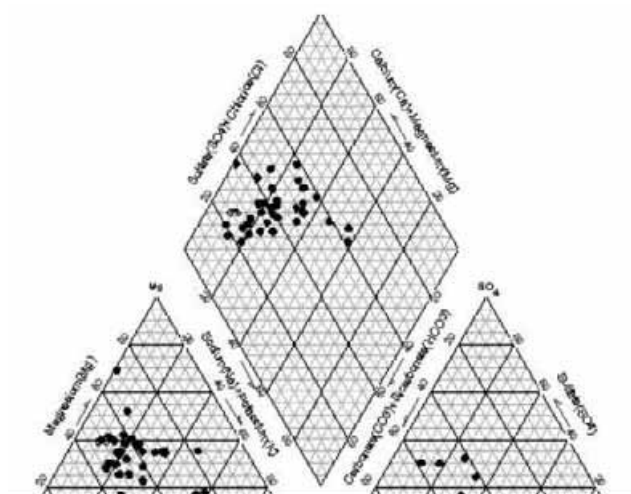
## 4. Hydrochemical features

Several hydrogeological and hydrochemical studies of the Sines basin, in order to evaluate its groundwater resources and to allow the chemical characterization and evolution along the flow paths have been performed (Lavaredas and Silva 1999a, 1999b, Galego Fernandes and Silva, 1999, Galego Fernandes et al., 2001a, 2001b, 2004b ).

We use physical and chemical data from the Sines basin groundwater system, which resulted in the most recent and more complete campaigns performed in the region between 1999 and 2001. The average, standard deviation, maximum and minimum values of the data from this period are given in Table 1.

1999			2001					
	Average	Standard Deviation	Max	Min	Average	Standard Deviation	Max	Min
EC ( $\mu\text{S}/\text{cm}$ )	729.2	258.3	1420	175	708.3	224.9	1179	235
pH	6.9	0.4	7.6	5.7	7.7	0.2	7.9	7.6
Na (mg/l)	37.9	16.1	82.3	0.04	n.a.	n.a.	n.a.	n.a.
Mg (mg/l)	30.8	13.9	57.3	5	n.a.	n.a.	n.a.	n.a.
K (mg/l)	2.8	1.4	7.9	0.8	n.a.	n.a.	n.a.	n.a.
Ca (mg/l)	65.9	28.2	120	5.75	67.0	27.3	101.6	4.8
$\text{HCO}_3$ (mg/l)	298.6	128.0	566	41	277.6	132.5	518	32
$\text{SO}_4$ (mg/l)	47.8	44.4	200.0	3.0	47.2	40.6	166.0	11.2
Cl (mg/l)	84.5	44.1	258.0	26.0	73.4	46.0	243.0	26.3
$\text{NO}_3$ (mg/l)	19.8	15.0	93.4	4.7	26.3	32.8	147.0	0.2
Fe (mg/l)	0.067	0.077	0.400	0.002	n.a.	n.a.	n.a.	n.a.
$\text{CO}_2$ (mg/l)	22.6	11.6	45.8	4.4	n.a.	n.a.	n.a.	n.a.
Cu (mg/l)	0.008	0.024	0.144	0.001	n.a.	n.a.	n.a.	n.a.
Al (mg/l)	0.083	0.098	0.597	0.007	n.a.	n.a.	n.a.	n.a.
$\text{PO}_4$ (mg/l)	0.033	0.031	0.130	0.002	n.a.	n.a.	n.a.	n.a.
Mn (mg/l)	0.010	0.020	0.119	0.002	n.a.	n.a.	n.a.	n.a.

Table 1: Comparison between 1999 and 2001 campaigns in Sines basin. To 1999 campaign  $n=38$  and to 2001 campaign  $n=20$ . n.a. – not analysed



The lithological composition of the aquifer's matrix is dominated by calcareous and dolomitic layers, recognized in the groundwater chemical evolution where the water-rock interaction processes are considered important in the definition of their calcium-bicarbonate type visible in a Piper diagram (Figure 4), in which dispersion in the cation (calcium and magnesium) content of the groundwater samples is shown.

Figure 4: Piper diagram showing the ionic composition of groundwater in Sines Basin from 1999 campaign.

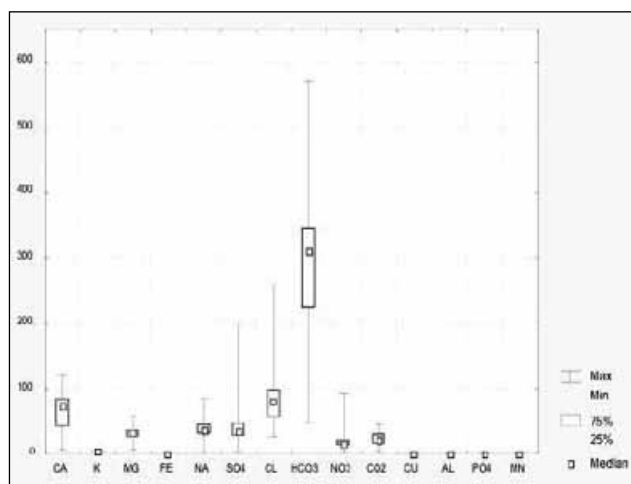


Figure 5: Box Plot of chemical analysis from 1999 campaign in Sines basin

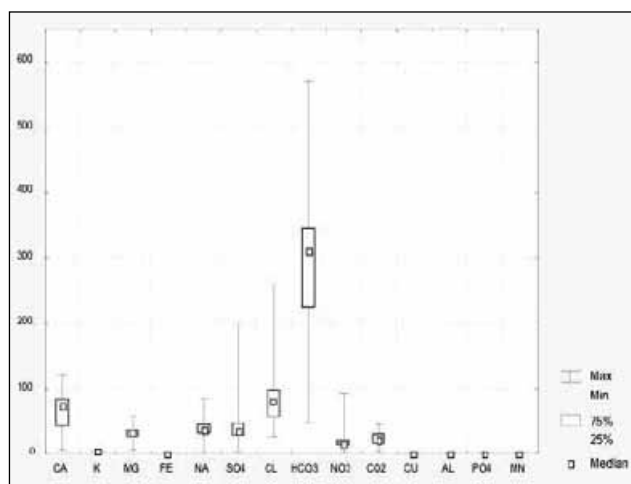


Figure 6: Box Plot of standardised parameters in Sines basin from 1999.

This groundwater evolution could be associated either to lithological heterogeneities within the sedimentary basin or whichever with human activities by the use of fertilizers/pesticides.

Boxplot of the chemical concentrations show that bicarbonate, calcium, sulphate, chloride and nitrate have the largest dispersions (Figure 5). The enrichment in chloride and sodium from values of 70 to 200 mg/l and 25 to 70 mg/l, respectively, is present in the waters located near the Moinhos River (in the S of the area). The increase in the salt concentration could be associated to different mechanisms: water-rock interaction processes, dissolution of Hetangian evaporites, mixture with actual seawater through the river substratum and/or mixture with ancient seawater trapped. The chloride, nitrate and sulphate content also show a significant difference between the medium and maximum values, mean values are near a quarter of the maximum values, suggesting local contamination inputs to the groundwater system. The wide range of values in the bicarbonate content, from 50 to 600 mg/l, is the result of the lateral geological variations of the layers conferring to the groundwater different concentrations of bicarbonate.

After the standardizing of the results (Figure 6), all the physical and chemical parameters from the statistical point of view have the same weight in the ground-

water evolution and characterization. For some parameters, such as  $\text{PO}_4$ , Al, Cu, Mn,  $\text{SO}_4$ ,  $\text{NO}_3$  and Fe, the median is close to the minimum which suggests the presence of an anthropogenic source to the aquifer system, probably indicating pollution input to the groundwater by agricultural or cattle breeding activities.

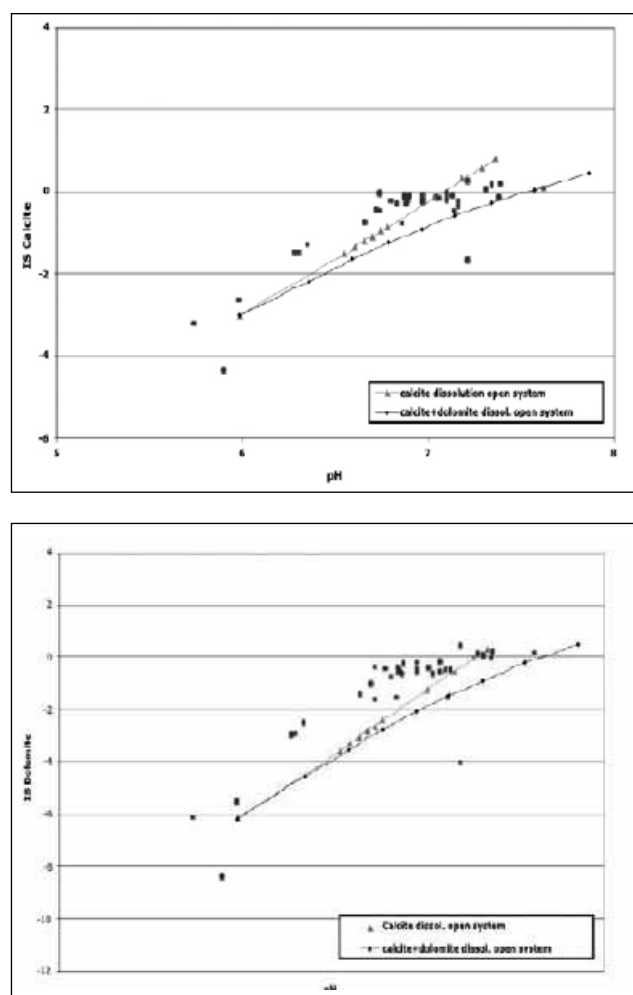


Figure 7: Calcite and Dolomite Saturation Index versus pH.

#### 4.1. Hydrogeochemical evolution of groundwater

If we assume the evolution from the Miocene waters to Jurassic waters, it is expected that waters progressively increase the concentrations of chemical constituents. The higher Ca and  $\text{HCO}_3$  concentration could be explained by the calcite and dolomite dissolution. Calculated saturation index (S.I.) indicated that the majority of groundwaters are in equilibrium with respect to calcite and dolomite (Figure 7). The progressively increasing pH values, Ca, Na,  $\text{SO}_4$  and  $\text{HCO}_3$  concentrations due to increased water rock interaction would ultimately result in saturation with respect to calcite and dolomite, materialised by the Jurassic waters that are in equilibrium or saturated in those minerals.

##### 4.1.1. Possible scenarios: calcite dissolution at open system or calcite and dolomite dissolution at open system

Using a simple mass balance model through the PHREEQC program, these two scenarios were tested. The reaction path was assumed to be such that Miocene waters observed at shallow depths evolved to more mineralised waters. We

considered a path that initiated in sample F5 and that was calculated the behaviour of groundwater mineralisation with different percentages of calcite dissolution.

Figure 8 shows the results of modelling, with calcite dissolution in open and calcite and dolomite dissolution at open system. Were also projected all the samples analysed to evaluate the behaviour of groundwater from the both aquifers. It is possible to notice the presence of a group of Jurassic waters that are projected along the line that represent the waters evolution in open system, indicated that probably Jurassic waters have an important contribution from the Miocene water-rock interaction.

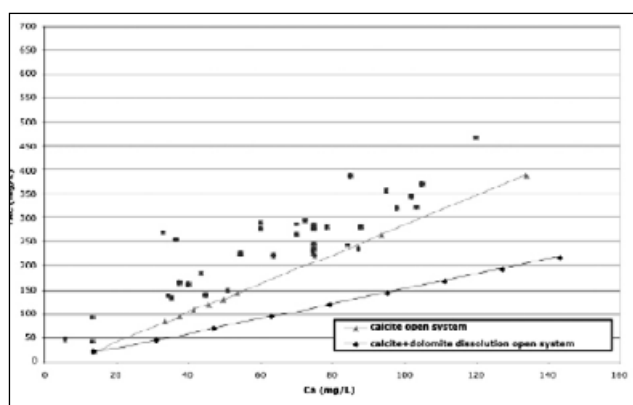


Figure 8: Results of the simple mass balance modeling, showing the relationship between TAC and Ca concentration.

#### 4.1.2. Mixing between Miocene and Jurassic waters

The samples F5 and F3 were considered as representative Miocene and Jurassic aquifers, respectively (Table 2). An ideal mixing solution with a given chemistry is calculated in accordance with the mixing ratio by using the program PHREEQC (Parkhurst and Appelo, 1999). The purpose of the modelling was to delineate the hydrogeochemical status of some Jurassic waters which are probably influenced by mixing. The results projected in a Piper diagram when compared with groundwaters samples from the both aquifers indicated that chemical mixing is also likely to be taking place in Jurassic aquifer (Figure 9).

	pH	T	EC	Ca	K	Mg	Fe	Na	SO <sub>4</sub>	Cl	HCO <sub>3</sub>	NO <sub>3</sub>	CO <sub>2</sub>	Cu	Al	Mn
F3	6,74	19,2	1093	120	3,28	42,75	0,01	53,5	42	88	570,96	37,9	45,76	0,00231	0,07632	0,0021
F5	5,98	19,8	246	13,25	3,43	5	0,13	29	3	49	48,8	20,6	18,92	0,00476	0,07856	0,00761

Table 2: Composition of F3 (Jurassic) and F5 (Miocene) groundwater. (EC -  $\mu$ S/cm, T- °C and remain parameters mg/L).

Under such conditions, mixing occurs simultaneous with geochemical reactions thereby influencing mass transfer; therefore, application of simple mass balance models only considering chemical reactions is not satisfactory. Therefore, is important consider the hydraulic mixing in the studied aquifers where is suggested that the geochemical reactions were less important than mixing in influencing the chemical composition of Jurassic groundwater.

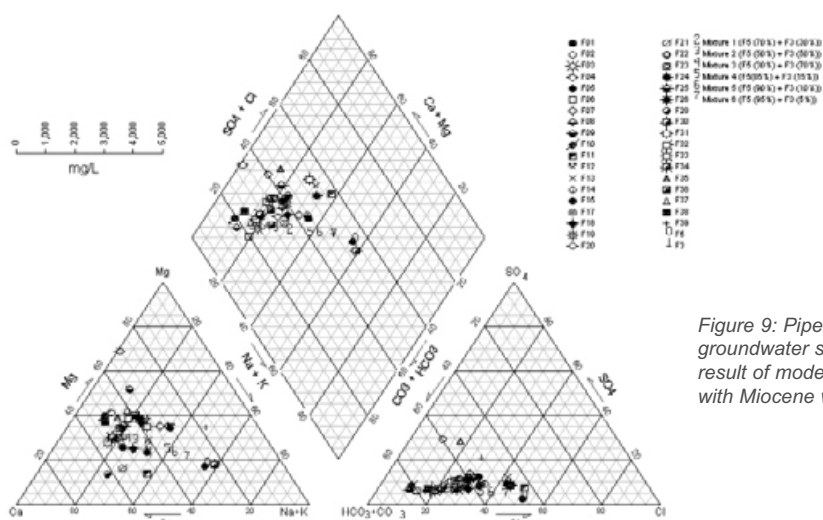


Figure 9: Piper diagram with groundwater samples and the result of modeling (mixing Jurassic with Miocene waters)



## 5. Conclusions

The hydrogeological system in the Sines basin supplies a highly populated region having industrial and agricultural activities. The amount of precipitation stores a consistent recharge, leading to an aquifer system that is not in hydraulic stress and does not present major temporal variations both in quantity and quality.

Simple mass balance modelling using hydrochemical data showed that Jurassic waters evolved from shallow groundwaters (Miocene aquifer) mainly by calcite and dolomite dissolution. Furthermore, mixing modelling suggested that the chemical composition of Jurassic groundwater is influenced by hydraulic mixing between a more mineralised Jurassic groundwater and a shallow Miocene groundwater with lower content in the major elements.

In Sines nowadays the protection limits for the groundwater quality are respected. However, through the use of qualitative and quantitative evaluations, some nitrate contamination problems are still identified as a result of some agricultural and cattle breeding activities, which lead us to suggest a rigorous control of possible contamination sources, such as effluent management and others.

## Acknowledges

P. Galego Fernandes acknowledges to FCT (Portugal) the Ph grant SFRH/BD/932/2000. The study was supported by FCT research project POCTI/35258/CTA/2000.

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## DARCY 11

### Modeling of chlorinated solvents transport and natural attenuation in groundwater

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#### Abstract

The objective of this study is to test different modeling approaches and the reliability of the codes used in water risk assessment for a site contaminated with chlorinated solvents. The final goal is to elaborate, within the framework of the TRANSPOL research program, a guideline that could be used as a scientist support for contaminated aquifers management. The models performed by 4 teams (ANTEA, ENSM, ENVIROS and INERIS) to simulate a contamination of groundwater by perchloroethene were compared. The total amount of perchloroethene discharged into the aquifer was unknown and a simplified conceptual model was considered. A first synthesis of the results obtained shows two principal difficulties : evaluate source concentration and simulate natural attenuation phenomenon (sorption/degradation). More accurate diagnosis is needed in order to reduce the uncertainties of model parameters.

#### 1. Context and Object

When applying a risk assessment approach to contaminated sites, of primary importance is the evaluation of the fate of pollutants in groundwaters and soils. This knowledge is based on the result of extensive investigations, available data from monitoring of pollutants in time and space and numerical modeling of the pollutants transport in the environment. In practice, results may vary greatly among users, according to the available data and the requested aims of the risk assessment.

The lack of a reliable methodology may impair high quality expertise. In this context, INERIS (the French National Institute for Industrial Environment and Risks, [www.ineris.fr](http://www.ineris.fr)) has developed a research program, TRANSPOL, to bring a better and common practice of the use of transport models for different groups of pollutants. The chosen way to reach this objective is based on the comparison of the methodologies used by private consultancies, universities and research centers.

This article presents results of a real case study, named Real Case 3, concerning chlorinated solvents fate, transport and natural attenuation in groundwater. The aim of this study is to develop a natural attenuation model to predict the fate and transport of chlorinated solvents and their degradation products in saturated groundwater systems.

## 2. Site description

A contaminated alluvial aquifer in northern Spain (cf. Figure 1), has been studied by ENVIROS since 2000. Figure 2 presents a conceptual cross section model of the site.

The site has a length of 1 000 meters along the direction of groundwater flow (S-N) and is 600 meters wide. A river crosses this site (Ter river).

The aquifer thickness is 16 meters including a 6 meters thick vadose zone. The sedimentary materials are unconsolidated and very heterometric (from clay to rolling cobbles), with an heterogeneous composition (from limestone and sandstone to metamorphic and igneous rocks).

perchloroethene (PCE) is the primary solvent contaminant that was originally disposed at this industrial site. However, concentrations of chlorinated solvent degradation products such as trichloroethene (TCE), cis-dichloroethene and trans-dichloroethene (cis-DCE, trans-DCE) were measured in the monitoring wells located downstream from the source location.

The observation well network is made up of 19 piezometers. 6 of these boreholes are pumping well (with pumping rate ranging between 1 100 to 70 000 m<sup>3</sup>/year – in PL2 pumping rate is unknown).

There are three potential recharge zones (Cf. Figure 1, irrigation zones are in green). The regional average natural net infiltration value is approximately 150 mm/y.

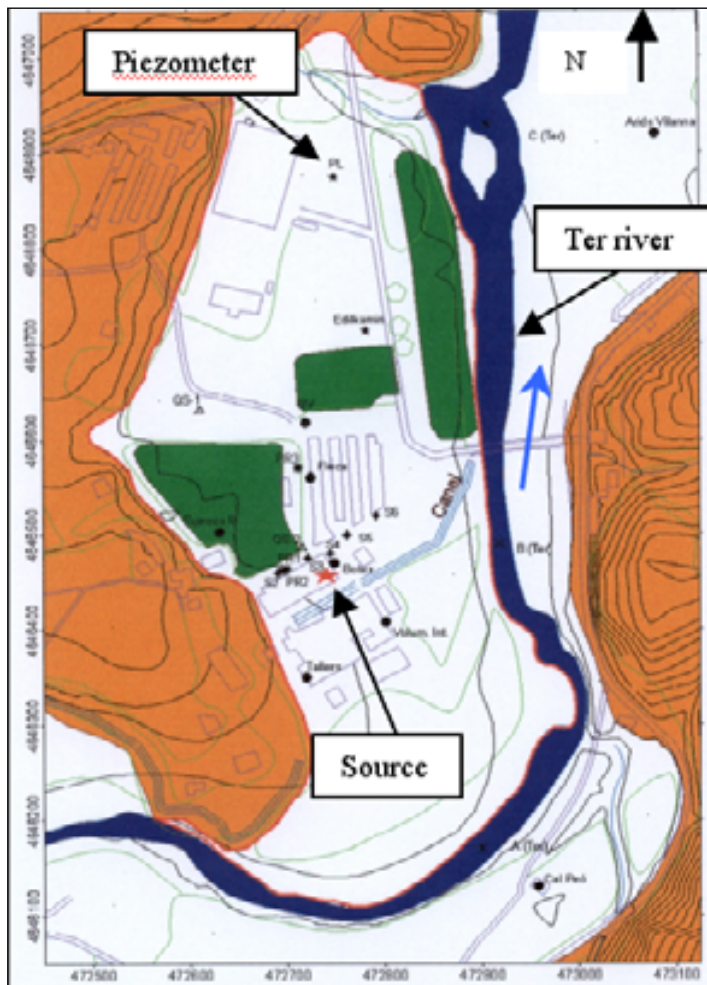


Figure 1: Site details and well locations (UTM coordinates)

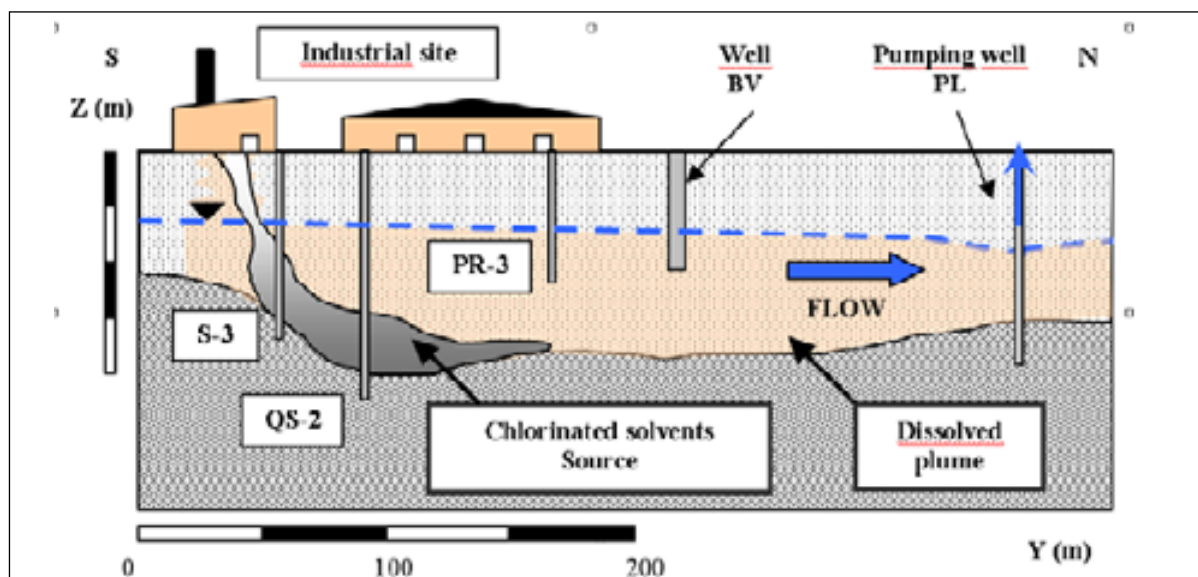


Figure 2: South – North section of the site

### 3. Conceptual model

At a first step, a workshop was held with all modellers to introduce the context (Cahier des charges n°1, Rollin & Bour, 2002), to identify the processes contributing to the behaviour of the pollutant, to select the hydrodynamic and transport parameters, the sources appearing to be the most appropriate..., as they would do in a proper risk assessment.

Conclusions of its workshop were given in a second “Cahier des Charges” (Rollin, 2003). It presents the conceptual model, initial conditions, calibration data (heads and concentrations values)..., these specifications are presented below. Some values and a range of variation were given as an indication. These values resulted from site investigation or from literature.

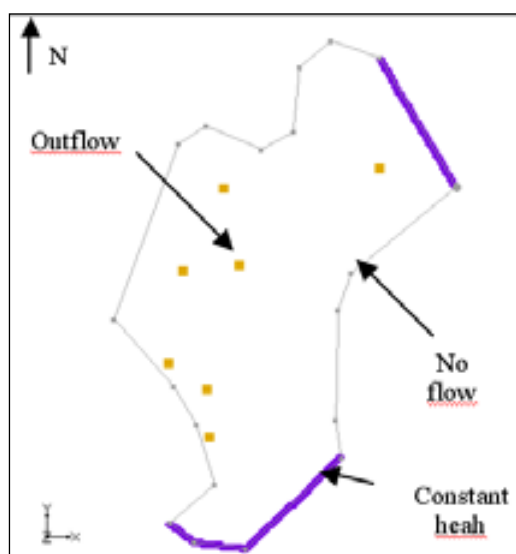


Figure 3: Modelled domain and boundary conditions

#### **Conceptual model for groundwater flow**

The boundary conditions are summarised on Figure 3. Flow conditions are assumed to be at steady state. The groundwater hydraulic head values at the model boundaries were based on measured data (december 2003).

The aquifer is modelled as a single, continuous, unconfined unit with spatially variable transmissivity values. The different transmissivity zones implemented in the model were based on pumping tests results and calibration of heads values.

#### **Conceptual model for contaminant transport**

The source of PCE is a modelled injection of mass straight to the saturated zone. The injection is located inside a 30 m diameter circle centred in the middle of the industrial building.

The total amount of PCE discharged into the aquifer is an unknown quantity, as it is often occurring on contaminated sites.

The time simulation is 10 years :

- initial time  $t_0$  (12 december 1995) : PCE concentration is zero ;
- $t_1$  (15 november 2000) : the plume is stabilised (measured concentrations -16 november 2000- were used to calibrate transport parameters) ;
- $t_0$  to  $t_1$  : the injection rate is constant during the first 5 years ( $R_1$  in kg/d) ;
- $t_1$  to  $t_2$  : the injection rate starts decreasing slightly from the beginning of the 6<sup>th</sup> year until the end of the 10<sup>th</sup> year.

High concentrations of PCE and chlorinated solvent degradation products such as trichloroethene, cis-dichloroethene and trans-dichloroethene were observed in the monitoring wells. Reductive dechlorination of chlorinated solvents is therefore suspected.

The kinetics of all the degradation reactions (cf. Figure 4) are assumed to be first order kinetics.



Figure 4: Anaerobic degradation pathway of chlorinated solvents

#### Groundwater flow simulations

The relationship between the aquifer and the river was not taken into account by all the teams. The groundwater flow codes were used to simulate the groundwater head distribution. The calibration results were assessed using the differences between calculated and observed heads in 16 piezometers. Errors in computed head values are listed in Table 2.

Table 3 presents the hydraulic conductivity values calibrated in the models.

Sorption processes could be taken into account. It was suggested to use the  $K_d$  approach. Values of transport parameters range are between different literature values and/or estimated values obtained by the concentrations calibration process:

- porosity ;
- dispersivity ;
- molecular diffusion ;
- sorption constants ( $K_d$ ) ;
- kinetic reaction rates of dechlorination.

	ANTEA	École des Mines de Paris	ENVIROS	INERIS
3D Flow Modeling	MARTHE - DF V. 6.3 (déc. 2002)	METIS - EF V1 (mars 2004) and MODFLOW 2000- DF V. GMS 4.0	TRANSIN- EF V. IV	MODFLOW 2000 - DF  V. GMS 5.0 (mai 2004)
3D Transport Modeling	MARTHE - DF V. 6.3 (déc. 2002)	Metamodel - kriging and RT3D - TVD V. GMS 4.0	TRANSIN - EF V. IV	RT3D - TVD V. GMS 5.0 (mai 2004)

EF: finite elements ; DF : finite differences ; TVD : total variation diminuting

Table 1: Teams and codes used in the intercomparison bench

## Groundwater flow simulations

The relationship between the aquifer and the river was not taken into account by all the teams. The groundwater flow codes were used to simulate the groundwater head distribution. The calibration results were assessed using the differences between calculated and observed heads in 16 piezometers. Errors in computed head values are listed in Table 2.

Table 3 presents the hydraulic conductivity values calibrated in the models.

	ANTEA	ENSMP	ENVIROS	INERIS
Mean error	0.04	0.14	0.09	0.04
Mean Abs. Error	0.05	0,06	0.04	0.03
Root mean Sq. error	0.002	0.004	0.002	0.001

Table 2: Hydrodynamic calibration – Error summary

Hydraulic conductivity range from 70 to 350 m/d. The final calibrated values are included in the range of values suggested in the specifications (results of investigations: 60 to 600 m/d). An anisotropy factor was tested by ENSMP and calibration results were better for piezometers near the source.

	ANTEA	ENSMP	ENVIROS	INERIS
Hydraulic conductivity (m/d)	109 and 150	150	73	350, 200 and 70
Recharge (mm/y)	146 irrigation zones	150 uniform	Not defined	150 irrigation zones
Pumping rate well PL2 (m <sup>3</sup> /d)	5	0,1	0	10

Table 3: Hydrodynamic calibration - Hydraulic conductivity

## Contaminant transport simulations

The models reproduced successfully the general trends of the contamination plumes but the time of peak arrival and the concentration at the observation points may vary more or less according to the use and the different features of the numerical codes. Results show that with such a simple conceptual model (homogeneous, isotropic and with a steady flow with steady boundary conditions), it is impossible to reproduce the oscillating concentrations observed. Thus the concentrations calibration objective was to fit the order of magnitude.

The transport parameters used in the models are summarised in Table 4. Transport properties were estimated based on literature values (for similar types of geologic materials) and calibration (using measured concentrations).

		ANTEA	ENSMP	ENVIROS	INERIS
PCE Injection rate R1(kg/d)		0,650	0,170	0,170	0,030
Source surface m <sup>2</sup>		707	100	91	25
Effective porosity n <sub>e</sub> (%)		10	30	10	20 and 30
Dynamic dispersivity	aL	30	22	10	20
(m)	aT	3	8,5	8	4
Molecular diffusion (m <sup>2</sup> /d)		Not defined	PCE, TCE DCE and CV 1x10 <sup>-4</sup>	PCE, TCE DCE and CV 1x10 <sup>-6</sup>	Not defined
Bulk density of aquifer (kg/m <sup>3</sup> )		1700	1600	Not defined	Not defined
Sorption coefficient Kd (m <sup>3</sup> /kg)	PCE	1,4x10 <sup>-4</sup>	9,4x10 <sup>-5</sup>	Not defined	Not defined
	TCE	5,8x10 <sup>-5</sup>	9,4x10 <sup>-5</sup>		
	DCE	5,2x10 <sup>-5</sup>	9,4x10 <sup>-5</sup>		
	CV	Not defined	9,4x10 <sup>-5</sup>		
First order degradation constant λ (d <sup>-1</sup> )	PCE	0,0004	0,0026	0,0030	0,0030
	TCE	0,0140	0,0001	0,0594	0,0020
	DCE	0,0007	0,0005	0,0174	0,0005
	CV	Not defined	0,0003	0,0300	0,0030

Table 4: Parameters selected for transport calibration

The differences in source volume are linked by the choice of its surface and by the injection rate considered (30 to 650 g/d). The variation of the extension of the source and the injection rate are different and influence the range of variation of PCE (TCE, DCE and VC) concentration in models.



Figure 5, Figure 6 and Figure 7 present PCE, TCE and DCE results for six piezometers distributed from source to downstream at 1800 days of simulation (calibration date).

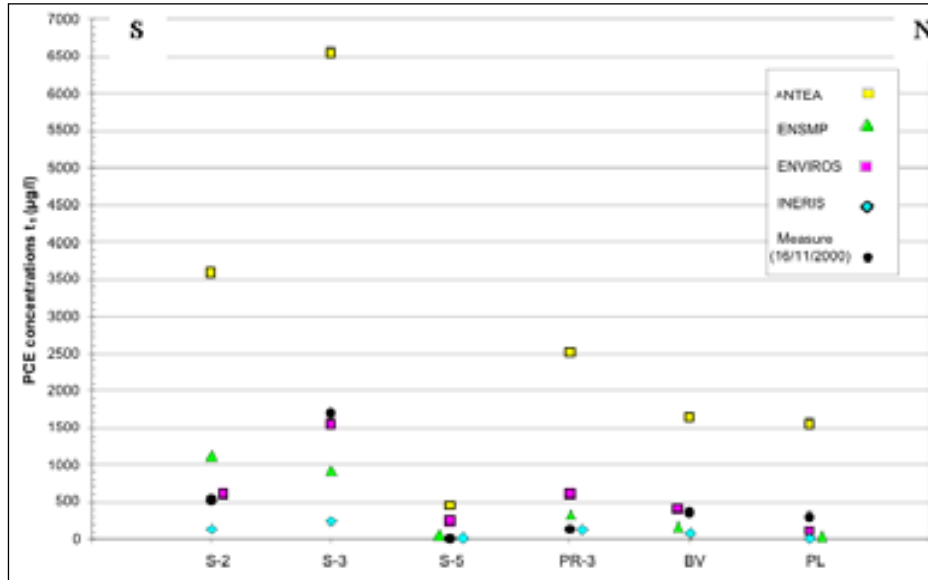


Figure 5: PCE concentrations (µg/l) at  $t_1$

The higher PCE concentrations are calculated by ANTEA. They consider higher PCE injection rate and source concentration, equal to the solubility (150 mg/l). This hypothesis may be justified by the fact that PCE concentrations are very high in the aquifer near the source (but solubility value is not reached in observation wells, maximum is 29 mg/l in S-2). ANTEA made the choice to calibrate, at a first time, concentrations with piezometers near the source.

Three others models give similar results for PCE except near the source.

Indeed PCE concentrations in S-2 and S-3 are less important for INERIS than ENSMP and ENVIROS. INERIS considers a smaller source concentration and calibrates concentrations principally on piezometers downstream the source. This assumption may be justified by the fact that piezometers downstream the source integrate multiple source information.

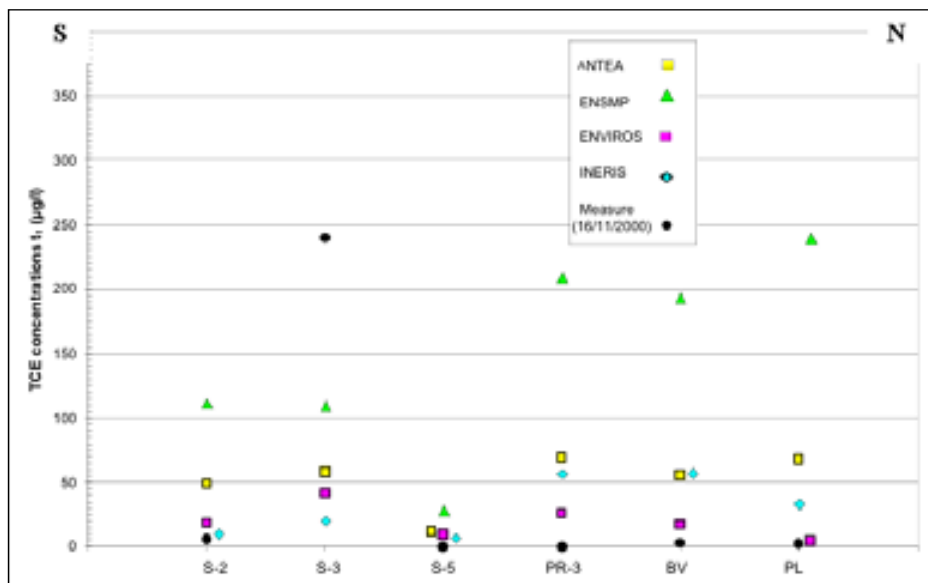


Figure 6: TCE concentrations (µg/l) at  $t_1$

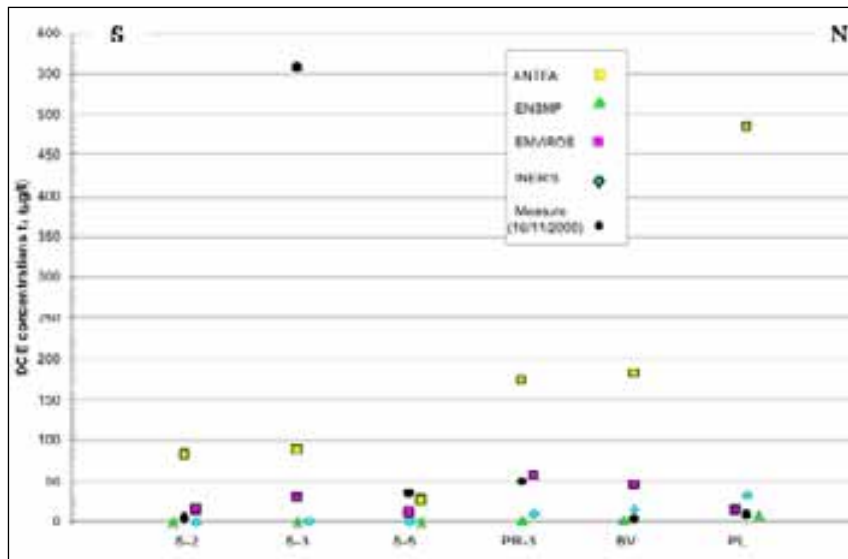


Figure 7: DCE concentrations (µg/l) at  $t_1$

Variations of TCE and DCE concentrations results compared to the measured values are mainly due to sorption and degradation conditions. Table 4 summarises the assumed values of sorption and degradation coefficients. Each team gave a different calibrated value.

The four teams considered degradation of chlorinated solvents but values of first order degradation constant are very different. For example in ENVIROS and INERIS models, the first order PCE degradation constant is about  $0.003 \text{ d}^{-1}$  (constant half life degradation : 230 d), it is about  $0.0026 \text{ d}^{-1}$  for ENSMP (267 d) but only  $0.0004 \text{ d}^{-1}$  for ANTEA (1733 d).

Close to the source area, concentrations observed of DCE is higher than the one of TCE. Thus in the developed models (except for ENSMP) the degradation factor of TCE is faster than the one of DCE.

Only two teams (ANTEA and ENSMP) considered sorption of chlorinated solvents. The retardation factor considered are 3.4 (PCE); 2 (TCE) and 1,9 (DCE) for ANTEA and 1.5 (PCE, TCE and DCE) for ENSMP

As shown in Figure 8, ANTEA privileges PCE sorption (with high PCE injection) and ENVIROS PCE degradation (with no sorption).

For ENVIROS, no retardation due to sorption processes has been considered. Then values of PCE mass out (by well or limits) and remaining in the model were lower than ANTEA values. The high degradation allows to calibrate concentrations despite a high injection rate.

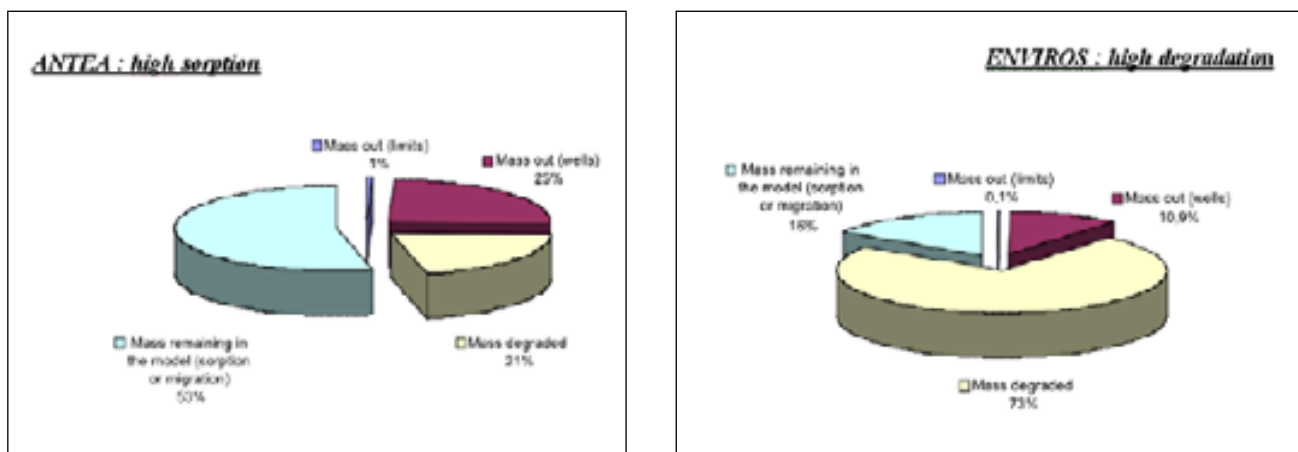


Figure 8: Comparison between ANTEA and ENVIROS PCE mass balance (kg) (0 to 1800 days)

## 5. Conclusion

Multi-species (PCE, TCE and DCE) models were used for modeling transport (homogeneous and isotropic) and natural attenuation processes occurring at a chlorinated solvents release site. Different codes have been used by four modeling teams (ANTEA, ENSMP, ENVIROS and INERIS). The models intercomparison methodology was based on comparison between flow and transport calibration results, calibration parameters values, hypothesis respected and natural attenuation phenomenon considered (particularly sorption and degradation).

Results show difficulty to evaluate :

- source concentration ;
- sorption and degradation.

A more accurate diagnosis is needed in order to reduce the uncertainty of model parameters and to try to improve the conceptual model. Thus, more accurate data were studying for the second semester 2005, concerning :

- the hydraulic conductivity ;
- the presents distribution of pollutants ;
- the location and rate of source term ;
- the degradation and sorption rate of each substance.

These new data will lead to realise a second phase of intercomparison to evaluate these parameters contribution to the new calibration results.

TRANSPOL results are presented on website : <http://transpol.ineris.fr/>

## Acknowledgements

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## DARCY 12

### Practical Application of Quasi-Static Stage of Ground Water in Low Permeability, Phreatic Aquifers in Hard Rock Terrain.

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#### Abstract

In many developing countries, whatever small quantity of water available from hand-dug wells in phreatic aquifers of low hydraulic conductivity is the lifeline for drinking water supply and small-scale irrigation for millions of the rural people. However, phreatic aquifers of low and very low hydraulic conductivity (K) have received much less attention in hydrogeological studies than the highly productive confined aquifers. These aquifers include sparsely fractured basalt and granite underlying a few meters thick cover of clayey weathered zone; alluvium with predominance of clay and silt; and marley limestone. Frictional forces play an important role in the regime of ground water flow and 'reservoir knowledge' is essential for managing exploitation and recharge augmentation in these aquifers. For the phreatic flow in small watersheds, the total head available for the flow as well as the gradient is often very small, especially in summer season. Under these conditions, the Darcy's Law could be written as:  $Q = K A (g - g')$

Where  $g$  is the gradient causing the flow and  $g'$  is the threshold gradient necessary to cause motion against the friction between the pellicular water and the water in slow motion, in the aquifer with low-permeability (K). When  $g$  becomes equal to  $g'$  the gravitational flow would stop but forces of transpiration by phreatophytic trees and evaporative forces at the wet patches at the exposed faces of the aquifer, would still cause some movement of water. This is the quasi-static stage of phreatic ground water in low permeability, water-table aquifers. During the summer season the natural springs at the exposed face of the aquifer may be reduced to only wet patches, but a little distance away from the exposure, the aquifer carries some water which may be used by digging a well for providing drinking water supply to a small hamlet. This paper discusses the practical applications of quasi-static stage under conditions of low values of K and horizontal variations in K.

#### Introduction

If all the strata were of very high porosity and of uniformly high hydraulic conductivity (permeability), any precipitation would have immediately infiltrated and the ground water resources would have drained into the sea within a very short time. The earth would have become a dry place indeed. Luckily, we have vertical variations in the permeability of strata giving rise to confined aquifers and horizontal variations in permeability controlling the movement of water from recharge area to discharge area. In a phreatic aquifer in a hard-rock terrain, comprising soft, weathered & fractured strata overlying an impermeable basement, the recharge area is spread all over the watershed. The recharge collected over the basin is guided towards lower elevations by the profile of underlying hard basement. Ground water discharge from a watershed occurs at the springs oozing out at the intersection of water table with ground surface, on the stream-bank or streambed, or as underflow below the streambed. Any horizontal variations in the permeability result in deflecting, bisecting or exposing the flow. This divides a watershed into smaller segments with smaller values of the hydraulic head operating the flow. Movement of phreatic ground water is under gravitational force and all loss of head along the

flow-path is due to frictional forces. A wooden block kept on an inclined plane would start sliding down, only when the angle of inclination of the plane becomes more than the angle of repose. During ground water movement, the frictional forces act between the moving water and the pellicular water adhering to the matrix. In the low-permeability strata the surface area on which these frictional forces act is much larger than that in the high permeability rocks. In phreatic flow in small watersheds, the total head available for the flow as well as the gradient is often very small, especially in summer season. Under these conditions, the Darcy's Law could be written as:

$$Q = K A (g - g')$$

Where Q is the volume of water flowing in cu. m per day, A is the area in sq. m, K is the hydraulic conductivity in m/day, g is the gradient causing the flow and g' is the minimum or the 'threshold' gradient required for overcoming the frictional forces in the low-permeability aquifer.

### Earlier Work

Mr. Daji G. Limaye, the author's father, being one of the pioneering hydrogeologists in India, observed during his field work in low permeability fractured basaltic rocks of western India (Deccan traps) that the dug-wells on a basaltic plateau could yield a small quantity of water in summer, even though the springs issuing out from the exposed face of the phreatic aquifer at the edge of a plateau were dry. This means that a dry, exposed face of a low-permeability phreatic aquifer does not necessarily mean a totally dry condition of the aquifer away from the exposure. This led him to think about the role of frictional force in low permeability phreatic aquifers (D.G.Limaye, 1949), which could stop the movement of ground water.

In the region of Monsoon rains like India, the rainfall occurs in four months (June to September) of rainy season, followed by four months of mostly dry winter and four months of hot, dry summer. In small watersheds or sub-basins, the value of gradient g causing the flow of ground water is high at the end of Monsoon rains but it gradually reduces towards summer, due to depletion of water table caused by natural outflow. Several dug wells pumping water during winter season also expand their area of influence and accelerate the depletion. In view of this, each dug well has a limit of expansion of its area of influence till the gradient of flow reaches the 'threshold gradient'. This sets up a limit for recoverable ground water in low-permeability basalt rocks of western India. (Limaye D G & Limaye S D, 1979)

However, when g becomes equal to g', only the gravitational force is balanced by the friction. Evaporation and transpiration forces are more powerful. The phreatic flow does not completely stop but attains a stage in which the flow is controlled by the evaporation and transpiration from the exposed portions of the phreatic aquifer. The phreatic ground water body thus reaches a 'quasi-static' stage.

### Practical Cases

Fig 1 shows a cross section along the gently sloping bed of a stream rising on a plateau and falling over its steeply sloping edge. The phreatic aquifer, comprising laterite, lateritic clay and fractured rock forms a cover over an impervious basement. The aquifer gets fully recharged during the Monsoon rains and water table at the end of the rainy season assumes position indicated by line (a). The spring (indicated by the arrow) issuing at the junction of the low permeability cover with the underlying hard rock drains ground water in the watershed during the

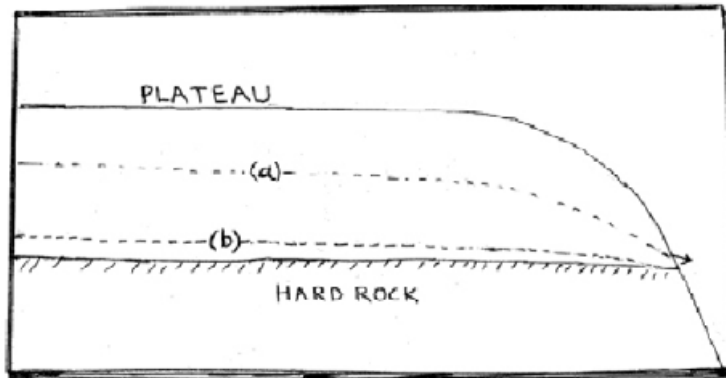


Figure 1: Spring draining ground water from a plateau

dry winter season. The water table recedes towards the base of phreatic aquifer, which often has a lower permeability. The discharge gradually reduces to a mere trickle by the beginning of dry & hot summer season. Line (b) indicates the depleted position of the water table by mid-summer, when the spring is just a wet patch, supporting some vegetation. A quasi-static stage is now reached as the gradient driving the ground water flow is at 'threshold value'.

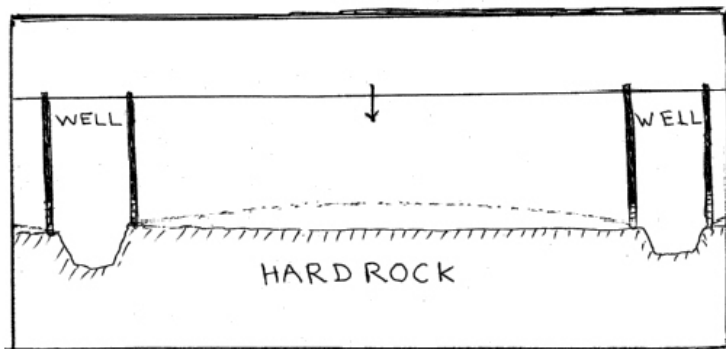


Figure 2: Arrow indicating a possible location for a new dug well between almost dry wells.

Sometimes, the strata exposed at the face of the spring are weathered into very low-permeability clayey formation, having a high capillary suction. If the total head driving the flow is less than the value of this capillary rise, then also a 'quasi-static' stage is reached. The tension-saturated capillaries support vegetation but prevent the delivery of water from the spring, at atmospheric pressure. However, away from the exposed face at this spring, the aquifer has some saturated thickness. If an

open well is dug into this small thickness of saturated aquifer it could yield about a few hundred litres per day. This negligible supply of water often proves to be a lifeline for a tribal village of ten to fifteen huts, perched on the plateau.

Another case in point is from a flat terrain with a saturated phreatic aquifer overlying an impervious basement (Fig. 2). Here, the ground water movement is slow due to flatness of the terrain. But ground water pumpage in winter season for domestic and irrigational use from a large number of dug wells causes depletion of the water table from its post-monsoon position. These dug wells penetrate through the phreatic aquifer and go a few metres deep into the hard basement rock. The masonry wall supporting the excavation in the upper soft strata has adequate number of holes to allow inflow of water from the phreatic aquifer. The incoming water gets stored in the bottom portion of the well and is conveniently pumped. Water level in the well is usually kept below the base of the phreatic aquifer so that the pressure of water accumulated in the well does not obstruct the delivery of water into the well. Wells, which have been over-pumped during the rainy season and in winter, reach their 'threshold gradient' quickly and become practically dry at the beginning of the summer, as shown in Fig. 2. Between two such dry wells, the aquifer has still some saturated thickness and could support a small yield in a newly dug well, at the location indicated by an arrow in Fig. 2. Instead of digging a new well, villagers often follow the wise practice of keeping some wells 'unused' during monsoon and winter season and bring them into use exclusively during summer season.

## **Conclusions**

Quasi-static stage of ground water is reached in low permeability phreatic aquifers when the gravitational force, acting through the slope of water table, is balanced by frictional force between the pellicular water & water free to move.

Evaporation and transpiration at the exposed faces of the phreatic aquifer are more powerful than gravitational force and cause some movement of water.

If clayey strata occur at the exposed face, strong capillary forces come into play. Discharge at atmospheric pressure from the spring, is not possible if the head in the phreatic aquifer behind the clayey strata is less than the height of capillary rise.

Quantity of water available in summer from these aquifers may be very small but it could be the lifeline for many rural people, especially in semi-arid, hard rock regions in India, as it saves for the village women the trouble of walking a few kilometers every day in hot summer to some distant source of polluted surface water to fetch drinking water supply for the family.

The area of influence of each dug well is limited. If recharge augmentation of phreatic aquifer is to be done during Monsoon rains, a large number of wells in the watershed are to be used as recharge points. Additionally, percolation tanks are also constructed by putting bunds across small streams so that a large area of the tank-bed is available for vertical infiltration of water being recharged.

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## Les très grands systèmes aquifères du Monde

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L'avancement des connaissances hydrogéologiques dans la plupart des pays, exprimé par de nombreuses monographies et cartographies de synthèse nationales et continentales, rend possible et opportune au seuil du XXI<sup>ème</sup> siècle une vision mondiale, comme en d'autres secteurs des Géosciences. Tout d'abord en se référant à une typologie des conditions hydrogéologiques primordiales, basée sur les principes de la légende internationale des cartes hydrogéologiques (AIH/UNESCO 1995), ce qui est le propos de la synthèse cartographique du projet «WHYMAP» initié par l'AIH, l'UNESCO et la Commission de la Carte Géologique du Monde (CCGM). Une vision des conditions hydrogéologiques mondiales peut aussi être structurale et mettre en évidence les systèmes aquifères de premier ordre dont la géographie est moins perçue et diffusée que celle des grands bassins hydrographiques.

De même que les écoulements d'eaux de surface sont organisés en bassins hydrographiques de toutes tailles et que quelques bassins fluviaux géants monopolisent une part importante de tout l'écoulement des terres émergées, les systèmes aquifères indétectables sont eux aussi d'étendues très variées et quelques grands systèmes rassemblent des parts notables des stocks et des écoulements d'eau souterraine mondiaux. Mais leur géographie est moins évidente et doit davantage être révélée par les études hydrogéologiques structurales.

Ces grands systèmes aquifères sont tous constitués par des roches sédimentaires et compris dans la classe «bleue» de la carte «WHYMAP» mentionnée plus haut.

37 systèmes aquifères de première grandeur, dont les étendues s'échelonnent de 100 000 à 2 000 000 km<sup>2</sup> ou plus, sont répartis sur tous les continents et en toutes zones climatiques. Leur situation est représentée en figure 1 et leurs principales caractéristiques sont résumées dans le tableau .

### Ces grands systèmes aquifères sont de trois types structuraux

I • Bassins sédimentaires généralement multicouches plus ou moins complexes, en fonction de leur structure inégalement accidentée et de leur constitution stratigraphique, qui peut s'étendre de l'Antécambrien au Quaternaire, et atteindre des puissances de plusieurs milliers de mètres (jusqu'à 20 000 m dans la plate-forme russe).

Ils sont composés par une alternance de couches très perméables et transmissives (formations détritiques – sables, grès...) n'interdisant pas des communications verticales («drainance») ou imperméables (roches salines), compliquée par des passages latéraux de faciès. Ils comportent une ou plusieurs couches aquifères à nappe libre et un nombre variable de couches aquifères à nappes captives en partie interconnectées, à eau souvent saumâtre ou salée en profondeur où le renouvellement est beaucoup plus faible et les temps de séjour sont les plus longs. C'est le type le plus répandu.

Les exemples sont nombreux : Grand Bassin Artésien d'Australie, Bassins Sahariens (SASS, Aquifère Nubien), Northern Great Plains Aquifer System d'Amérique du Nord (Canada, Etats-Unis), Bassin de Sibérie occidentale... Ces bassins peuvent se répartir suivant deux variantes structurales :

- Dans le modèle « parisien » dont le Bassin de Paris est un prototype classique, « les petits plats sont mis dans les grands... » : des auréoles sédimentaires aquifères affleurantes en périphérie, à nappes libres et sources de débordement, sont en continuité avec les aquifères profonds à nappes captives, parfois artésiennes ;
- Dans le modèle « pannonique », dont le Bassin de Hongrie est un exemple moins étendu, les couches supérieures recouvrent entièrement les aquifères profonds reconnus seulement par forage et moins facilement identifiables, et les échanges par drainage ou favorisés par des failles sont prédominants. Ces bassins sont souvent en même temps « artésiens » lorsqu'ils comportent des aires de jaillissement potentiel initial sur de grandes étendues par suite de conditions d'altitude et de pression de l'eau favorables qui en font des accumulateurs d'énergie appréciables.

II • Fosses d'effondrement subsidentes, à comblement principalement alluvial, à nappe libre mais pouvant être aussi multicouches et comporter plusieurs nappes captives, avec également des aires d'artésianisme.

Exemples : Central Valley de Californie, plaines du nord de Chine, Bassin Indo-Ganga – Brahmaputra en Inde.

III • Accumulations détritiques de piedmont de grandes chaînes montagneuses ; aquifères principalement à nappe libre.

Exemple : aquifère des High Plains (Ogallala) aux Etats-Unis.

Toutefois certains de ces grands aquifères présentés comme des systèmes uniques sont en fait des agrégats de systèmes aquifères contigus et similaires mais indépendants, comme l'Ogallala Aquifer des High Plains des Etats-Unis ou les Bassins de la plateforme de Russie.

Ces grands systèmes aquifères couvrent ensemble près de 35 millions de km<sup>2</sup>, près du quart des terres émergées. Ils doivent contenir la majeure partie des réserves d'eau douce souterraine continentales bien que tous n'aient pas fait l'objet d'estimation de réserve (cf. tableau 1). Aussi recèlent-ils l'essentiel des ressources en eau souterraine non renouvelables (réserves extractibles dans des conditions économiques et environnementales acceptables) reconnues et en partie en exploitation dans plusieurs pays en zone aride (Arabie Saoudite, Libye, Algérie principalement). Ils ont aussi été sujets à la plus grande partie des déstockages opérés au cours du XX<sup>ème</sup> siècle, soit du fait de surexploitation, soit par suite d'exploitation « minière » de ressources non renouvelables, qui doivent être globalement de l'ordre de 1 000 km<sup>2</sup> au minimum et qui ont entraîné d'amples dépressions, souvent supérieures à 100 m. Ces grands aquifères participent sans doute dans une moindre mesure à l'écoulement souterrain mondial (de l'ordre de 12 000 à 13 000 km<sup>2</sup>/an) car celui-ci est engendré essentiellement par les aquifères libres, dont beaucoup d'aquifères locaux à nappe phréatique des zones humides.

Les fonctions de ces grands systèmes aquifères dans le cycle des eaux continentales mondial et leur place dans l'économie de l'eau sont étroitement liées à leur position climatique.

En zones humides, ils participent à la régulation des écoulements de surface et ils sont largement exploités, voir surexploités, notamment en Chine, en Inde, aux Etats-Unis.

En zones aride et semi-aride, ils participent peu aux rares écoulements et leur exploitation mobilise surtout leurs ressources non renouvelables, notamment en Afrique saharienne, au Moyen-Orient et en Australie (où elle est maintenue très réduite).

En zone sub-arctique d'Europe et d'Asie septentrionales (Russie, Sibérie), les conditions de permafrost régnaient jusqu'à de grandes profondeurs (plusieurs centaines de m) « gèlent » leur fonction hydrologique et restreint beaucoup leur exploitabilité.

L'état inégal des recensements des prélèvements actuels d'eau souterraine, suivant les pays,

ne permet pas de chiffrer complètement la part de l'exploitation de ces grands systèmes aquifères dans l'exploitation d'eau souterraine mondiale estimée à environ 800 km<sup>2</sup>/an au moins. Quelques exemples peuvent seulement être cités (Tableau 2) : ils totalisent déjà quelques 130 km<sup>2</sup>/an, dont une vingtaine aux dépens de ressources non renouvelables (bassins du Sahara et d'Arabie) mais les intensités relevées sont très variées.

Enfin ces systèmes aquifères sont souvent - un sur deux - transfrontaliers ; leur étude comme la gestion de leurs ressources, renouvelables ou non renouvelables, posent des problèmes de coopération et de partage en partie similaires à celles des bassins hydrographiques pluri-nationaux, mais aussi plus spécifiques (transferts d'influence des exploitations).

Système aquifère	Indice du tableau 1	Pays	Date en km <sup>2</sup> /an	Prélèvements	Référence
Nubian sandstone aquifer system (NSAS) avec Post-nubian	1	Egypte, Libye, Soudan	2000	2,2	CEDARE/IFAD, FAO 2003
Système aquifère du Sahara septentrional (SASS)	2	Algérie, Libye, Tunisie	2000	2,5	OSS 2003
Murzuk Basin	3	Libye	2000	1,75	A. M. EL GHERIANI 2002 UNESCO/Projet ISARM 2004
Bassin Sénégal-Mauritanien	5	Mauritanie, Sénégal, Guinée, Bissau, Gambie	2000	0,26	UNESCO/projet ISARM 2004
Système aquifère Iullemeden –Irhazer	6	Algérie, Mali, Niger, Nigeria	2000	0,22	UNESCO/projet ISARM 2004
Bassin du lac Tchad	7	Niger, Nigeria, Tchad	2000	0,25	UNESCO/projet ISARM 2004
Central Valley California	16	USA	1990	20	USGS
Ogallala Aquifer	17	USA	2000	21,5	USGS
Arabian Aquifer System	22	Arabie Saoudite, Emirats Arabes Unis, Bahrein, Qatar	1995	15,2	FAO 1997 A.A. Ghum Alghamdi 2002
Indus Basin	23	Pakistan	2000	46,7	IGRAC/M.A. Kahlown 2004
Huang-Huai-Hai	29	Chine	1997	20	China Water Vision 2000
Bassin de Paris	32	France	2000	2	BRGM IFEN 2004
Great artesian Basin	3	Australie	2000	0,55	M.A. Habermehl, UNESCO, 2002

Tableau 2 – Prélèvements d'eau souterraine actuels dans quelques grands systèmes aquifères du Monde

Tableau 1: les très grands systèmes aquifères du >Monde

N° cf carte	Dénomination	Pays	Superficie 1 000 km <sup>2</sup>	Structure Hydrologique (P : puissance maximale en m)	Volume d'eau en réserve théorique 1000 m <sup>2</sup>	Flux moyen d'alimentation en km <sup>2</sup> /an	Références
1	Système aquifère nubien (NAS) : Système aquifère des Grès de Nubie (NSAS) Aquifère post-nubien (PNAS)	Egypte, Libye, Soudan, Tchad	2 199 dont 1 800 à eau douce	Multicouche Cambro-Ordovicien à Oligocène Grès continentaux prédominants P = 3 500 m	542 eau douce	~ 1	M. Bakhabakhi 2002 CEDARE/IFAD (FAO 2003) UNESCO / OSS 2005
2	Système aquifère du Sahara septentrional (SASS)	Algérie, Libye Tunisie	1 019	Multicouche Cambro-Ordovicien au Miocène Continental intercalaire et Complexe terminal P = 1 600 m	60	~ 1	OSS 2003, 2004 UNESCO/OSS 2005
3	Bassin de Murzuk-Djado	Libye, Algérie Niger	450	Multicouche Cambro-Ordovicien à Crétacé P = 2 500 m	4,8 en Libye	~ 0,15	UNESCO/OSS 2005
4	Bassin de Taoudenit Tanezrouf	Algérie, Mauritanie, Mali	2 000	Multicouche Infracambrien à Tertiaire (CT) P = 4 000	0,018 exploitable au Mali et en Mauritanie	~ 0,3 au Mali	UNESCO/OSS 2005
5	Bassin Sénégal-Mauritanien	Mauritanie, Sénégal, Gambie, Guinée Bisseau	300	Multicouche Aquifère principal : Maestrichtien P = 600 M	1,5	~ 9	B. Diagana 1997 UNESCO/OSS 2005
6	Système aquifère d'Iullemeden-Irhazer	Niger, Algérie, Mali, Nigéria	635	Multicouche Cambro-Ordovicien à Eocène 3 sous-bassins P = 1 500 m	10 à 15		A. DODO 1992 UNESCO/OSS 2005
7	Bassin du Lac Tchad	Niger, Nigéria, Tchad, Cameroun, RCA	1 917	Multicouche Continental intercalaire, Continental terminal et Plio-Quaternaire P = 7 000 m	0,6 au Niger (0,05 exploitable) ~ 0,4 exploitable au Tchad	3,6 au Niger	CBLT 1977 J.L. Schneider 2001 UNESCO/OSS 2005
8	Sudd-Basin Umm Ruwaba Aquifer	Soudan, Ethiopie	365	Multicouche Néogène-Quaternaire P = 3 000 m	0,11	0,34	ICID 1983 UN 1987 OACT 1993
9	Bassin d'Ogaden-Juba	Ethiopie, Somalie, Kenya	~ 1 000	Multicouche Nappes libres et captives P = 12 000 m		~ 10	UN 1987
10	Bassin du Congo	Congo RD, Congo, Angola, RC Afrique Gabon	750	Multicouche Mésozoïque ("Karoo") Quaternaire alluvial P = 3 500 m		~ 100	I. Zektser 2004 AAC 1993
11	Upper Kalahari Basin	Angola, Botswana, Zambie, Zimbabwe	~ 700	Multicouche Carbonifère, Crétacé (« Karoo ») à Néogène		~ 30 à 60	

N° cf carte	Dénomination	Pays	Superficie 1 000 km <sup>2</sup>	Structure Hydrologique (P : puissance maximale en m)	Volume d'eau en réserve théorique 1000 m <sup>2</sup>	Flux moyen d'alimentation en km <sup>2</sup> /an	Références
12	Lower Kalahari Basin	Afrique du Sud, Botswana, Namibie	~ 350	Multicouche « Karoo » à Néogène		~ 1 à 2	
13	Karoo Basin	Afrique du Sud	600	Multicouche Cambrien à Jurassique P = 7 000 m	3 à 5 (dolomites)	16 à 37	AAC 1993 I. Zektser 2004
14	Northern Great Plains Aquifer System (USA) / Interior Plains (Canada)	Canada, USA	~ 2 000	Multicouche Paléozoïque à Eocène			UN 1976 USGS 2003
15	Cambrian- Ordovicien Aquifer System (Central Region)	USA	250	Multicouche Cambro-Ordovicien			USGS 2003
16	Central Valley California	USA	80	Aquifère alluvial Quaternaire multicouche, à nappes libres et captives P = 600 m	1,73	~ 71	USGS
17	Orgallala Aquifer High Plains	USA	450	Alluvions tertiaires P = 150 m	~ 15	6 à 8	USGS
18	Atlantic and Gulf Coastal Plain Aquifers	USA, Mexique	1 150	Multicouche Paléozoïque à Tertiaire Ensemble d'aquifères contigus P = 12 000 m			USGS
19	Amazon Basin	Brésil, Colombie, Pérou, Bolivie Brésil	1 500	Multicouche Paléozoïque à Tertiaire P = 2 000 m	32,5		A. Rebouças 1988
20	Maranhao Basin	Brésil	700	Multicouche Ordovicien à Crétacé P = 3 000 m	17,5	4	A. Rebouças AIH 1976-1988
21	Guarani Aquifer (Parana & Chaco) ou Mercosul Aquifer System	Brésil, Argentine, Paraguay Uruguay	1 195	Multicouche Silurien à Crétacé P = 800 m Total basin : 5 000 m	57	234	A. Rebouças 1988-1976 L.M. Araújo & al. 1979
22	Arabian Aquifer System	Arabie Saoudite, Jordanie, Koweït, Bahrein, Qatar Pakistan	1 485 en Arabie Saoudite	Multicouche Cambrien à Néogène P = 6 500 m	2,185 en Arabie Saoudite	1,2	W. Abderrhaman UNESCO 2002 UN 1982
23	Indus Basin	Pakistan	~ 320	Aquifère alluvial à nappe libre P = 300 m		66(usable potentiel)	ICID 2000
24	Indo-Ganga- Brahmaputra Basin Bhabhar et Tarai Aquifers	Inde, Népal Bangladesh	~ 600	Aquifère alluvial à nappes libres et captives P = 6 000 m			

N° cf carte	Dénomination	Pays	Superficie 1 000 km <sup>2</sup>	Structure Hydrologique (P : puissance maximale en m)	Volume d'eau en réserve théorique 1000 m <sup>2</sup>	Flux moyen d'alimentation en km <sup>2</sup> /an	Références
25	West Siberia	Russie	3 200	Multicouche Paléozoïque à Crétacé p.p. sub-permafrost P = 6 000 m Eaux douces + eaux salées	1 000	82 sur 2,5 M km <sup>2</sup> ("predictive fresh grouwdwater field")	UN 1986 I. Zektser 2004
26	Tunguss Basin	Russie	1 000	Multicouche Cambrien à Trias. Sub-permafrost Eaux douces et eaux salées P > 4 000 m			UN 1986 I. Zektser 2004
27	Angara Lena Basin	Russie	600	Multicouche Cambrien à Jurassique Eaux douces et eaux salées P = 3 000 m		12,6	UN 1986 I. Zektser 2004
28	Yakut Basin	Russie	720	Multicouche Sub-permafrost Eaux douces et eaux salées Infra-Cambrien à Crétacé P = 12 000 m		18	UN 1986 I. Zektser 2004
29	North China Aquifer system (Huang-Huai- Hai Plain)	Chine	320	Aquifère alluvial Quaternaire multicouche Nappes libres et captives P = 1 000 m Artésianisme	0,018	49,2 (48,1 exploitable)	China Water Vision 2000 I. Zektser 2004
30	Song-Liao Plain	Chine	311	Aquifère alluvial quaternaire multicouche libres et captives P = 300 m		33,4 (23,8 exploitable)	I. Zektser 2004
31	Tarim Basin	Chine	520	Aquifère alluvial multicouche nappes libres et captives Artésianisme P = 1 200 m			
32	Bassin de Paris	France	190	Multicouche Trias à Néogène P = 3 200 m	0,5 à 1	20 à 30	NU 1990
33	Russian Platform Basins	Russie	~ 3 100	Ensemble de multicouches contigus Infra-cambrien à Quaternaire Sub-permafrost au N P = 20 000 m			NU 1990
34	North Caucasus Basin	Russie	230	Multicouche Carbonifère à Néogène P = 10 000 m			NU 1990
35	Pechora Basin	Russie	350	Multicouche Ordovicien à Tertiaire P = 3 000 m En partie sub-permafrost			NU 1990

N° cf carte	Dénomination	Pays	Superficie 1 000 km <sup>2</sup>	Structure Hydrologique (P : puissance maximale en m)	Volume d'eau en réserve théorique 1000 m <sup>2</sup>	Flux moyen d'alimentation en km <sup>2</sup> /an	Références
36	Great Artesian Basin	Australie	1 700	Multicouche Trias à Crétacé P = 3 000 m	20 8,7	1,1	M.A. Habermehl UNESCO 2002 Water Resources and Use, Australia, 2003
37	Canning Basin	Australie	430	Multicouche Dévonien à Crétacé P = 1 000 m			Lau & al. 1987 J.E. I. Zektser 2004



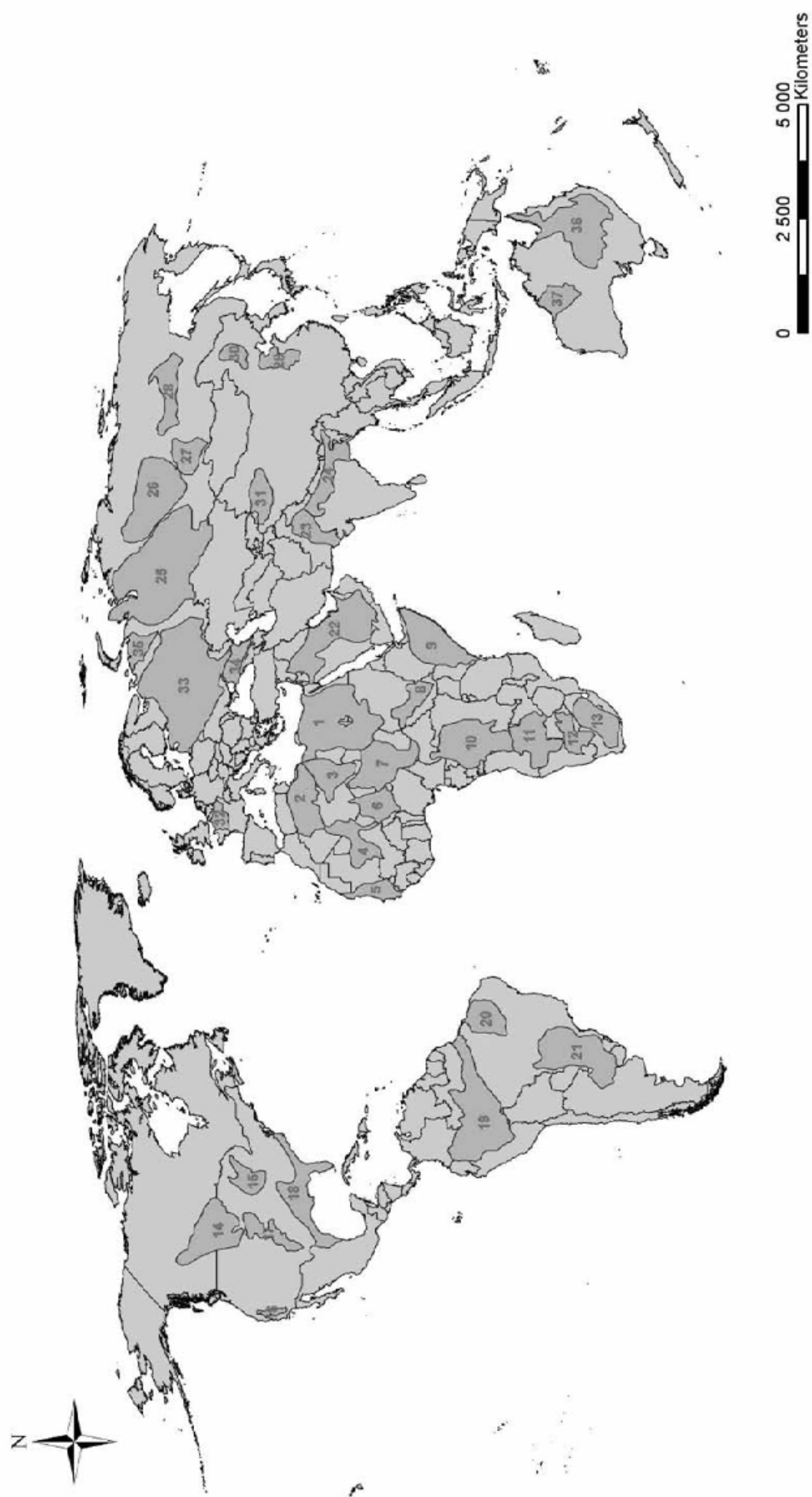


figure1: les très grands systèmes aquifères dans le monde

## DARCY 18

### **Can we identify vertical exchanges in multi-layered aquifer from groundwater chemistry ? A theoretical background with an application to the Aquitaine Basin.**

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#### **Abstract**

The interactions between aquifer and aquitards becomes more and more important for the management of large sedimentary multi-layer aquifer systems. In fact recent hydrodynamic modeling tend to outline the role of vertical leakage between superimposed aquifers. This led us to analyze in detail what could be the effects of exchange of matter between aquifers and aquitards. To explain the gradients several phenomena are studied : leakage, dissolution of minerals or ion exchange within an aquifer, and dissolution of minerals or ion exchange from an overlying aquitard. Each process are studied and compared. It is shown that, given the assumptions made, the influence of each process can be differentiated where the aquifer-aquitard system is well enough characterized. Our work suggests that the composition of major aquitards may have a significant effect on the chemistry of the aquifer water.

#### **Introduction**

In regional sedimentary basins, several aquifers, isolated by aquitards of variable thickness are often found (Raoult et al., 1998 ; Taigbenu and Onyejekwe, 2000 ; Mehta et al., 2000). Several studies, using for instance noble gas concentration (Castro et al., 2000), <sup>36</sup>Cl (Love et al., 2000), or CO<sub>2</sub> fluxes (Chiodini et al., 1999) have shown that vertical fluxes exist within these aquitards. In order to understand better the exchange of matter between aquifer and aquitard we suggest a method based on the chemical composition of the groundwater.

The chemical composition of groundwater in such systems results mainly from water-rock interactions and transport of elements. Interactions include congruent or non-congruent dissolution of minerals, precipitation, adsorption or ion exchange whereas the transport of species may result from advection, dispersion and/or diffusion. Water facies are based on the concentration of major elements in solution. Na, Cl and SO<sub>4</sub> can reach high concentrations in groundwater as the minerals containing these ions are highly soluble. Ca and Mg concentrations often lie between these two endpoints as they are often controlled by equilibrium with carbonate minerals. Our approach will be centered on the elements showing high concentrations and the corresponding minerals.

Several geochemical studies suggest a smooth evolution of the groundwater chemical composition along the flow direction (Hiscock et al., 1996). Concentration variations are often justified by mixing of two aquifers or dissolution of minerals within the aquifer (Appelo and Postma, 1993). Such a mixing can significantly modify the groundwater composition only where important fluxes from two aquifers of very different composition converge, which is fairly rare. Besides, in an ideally homogeneous aquifer the dissolution of minerals should lead to

concentrations close to the solubility value. However, for ions like Cl, Na or SO<sub>4</sub>, the ground-water solutions are undersaturated with respect to Cl, Na or SO<sub>4</sub> bearing minerals, in most aquifers. Moreover the highly soluble minerals delivering these ions by dissolution are often not found in most of the considered aquifers (Plummer et Sprinkle 2001). Therefore, the dissolution process cannot easily justify the smooth spatial variations of concentration in a homogeneous aquifer and needs clarification.

## Modeling strategy and assumptions

We use an idealized aquifer system that includes two types layers : an aquifer of high or intermediate permeability and an aquitard of low to very low permeability. The aquifer is assumed to consist mostly of sand. The aquitard might be pure clay or clay including layers of evaporites or other minerals. The physical characteristics of each medium (porosity, permeability) are considered to be homogeneous and isotropic. The flow conditions are also considered constant : a known velocity in a regular flow field is assumed in the aquifer ; the flow in the aquitard is assumed to be zero and with no density effect. To develop the steady state equations, we consider that the mass of selected elements is almost infinite by setting boundary conditions at infinite distance. The mass balance limits are then analyzed in the discussion section.

Both aquifer and aquitard may include minerals that can dissolve as well as a portion of 'inert' minerals (e.g quartz). As we consider easily soluble minerals, the thermodynamic equilibrium between water and sediment is considered to be reached everywhere (i.e. local equilibrium assumption). Moreover, the minerals are assumed to be evenly distributed in space.

So the different processes are :

- Dissolution in a homogeneous aquifer
- Influence of leakage
- Simple diffusion from aquitard
- Dissolution in the aquitard and diffusion
- Ion exchange and diffusion

We try to describe how the various interactions between aquifers and aquitards systems influence groundwater chemistry. The ions released by diffusion from the aquitard may arise from three different sources : brine as pore water in the aquitard, dissolution of salts and ion exchange. These sources, combined with diffusion, are analyzed separately.

We have considered simplified conditions with homogeneous aquifer or aquitard layers and regular boundary conditions. These hypothetical conditions may not exist in any real aquifer system but they make the basis for any further analysis. In order to get closer to real conditions, we investigate in this section two directions.

Is the longitudinal gradient of concentration resulting from one process can be so different from others ? and be recognized directly ?

What is the duration of the presented processes and their respective boundary conditions, that may separate the processes along the geological time scales ?

## Longitudinal gradients of concentration

Several processes delivering ions to solution were investigated. In a completely homogeneous aquifer, and assuming local equilibrium, dissolution from minerals present in the aquifer may lead to abrupt spatial variation of concentration close to the location of the dissolution

front (Lasaga, 1998). This implies that salts of S and Cl will not remain in an aquifer over geological time scales. Diffusion from an aquitard containing brine in its pore volume will lead to a slow accumulation of ions in the aquifer along the flow direction. Dissolution of mineral phases existing in the aquitard will generate the same type of concentration gradient except that it may remain over a longer timescale due to the larger amounts of matter available in the solid phase. Exchange between aquifer water and the CEC of clays embedded in the aquitard will result in a diffusion process from the clays but with higher amounts of ions in the solution and a depletion of bivalent cations in the aquifer. Leakage may lead to a non negligible flux of water from the aquitard and thus, if this water is saturated with one mineral, it will generate large concentration variations over short distances.

Under the boundary conditions of interest, the four investigated processes : diffusion, dissolution and diffusion, leakage, and ion exchange + diffusion, all lead to a linear increase in groundwater concentration distribution with distance. The only criterion to determine the presence, or predominance, of one process will thus be to assess the average increase in the  $C/C_{eq}$  ratio in the aquifer with distance down flow. The importance of the parameters values will thus be investigated in order to determine if the  $C/C_{eq}$  ratio can be used to distinguish processes. This is done in the following section.

### Varying parameters

Any one of the processes described above will be detected only where the concentration of an element in the aquitard pore water is significantly higher than the concentration prevailing in the aquifer.

The case of leakage is original as concentrations depend, among other parameters, on the area and permeability of the zone where the aquitard head is higher than that in the aquifer. It is difficult to give any general value for the extent and properties of the leakage zone. The resulting concentrations increase with the length of the leaking zone. The major parameter in this approach is the vertical permeability of the aquitard, which may vary over more than three orders of magnitude. This value is very difficult to estimate at the regional scale. However the problem has to be considered from the point of view of aquifer management. Keeping this approach in mind, leakage is of interest only where it can affect significantly the fluxes within the aquifer. For the average properties that we considered, values of leakage greater than  $0.5 \text{ mm.y}^{-1}$  will significantly modify the aquifer flow (Fig. 1). By considering this limit we obtain the range of concentrations shown in Fig. 2.

In the case of diffusion, only a few parameters influence the computed concentrations. The major role is played by the diffusion coefficient which is often unknown, mostly because of unknown tortuosity. However, even if the coefficient is varied between  $5.10^{-4}$  to  $10^{-2} \text{ m}^2.\text{y}^{-1}$  the diffusion by itself still gives the lowest concentrations among all the processes investigated. Increase in  $D$  is in fact partly compensated for by a decrease in the concentration gradient in the aquitard ; if  $D$  increases by a factor of 20, the resulting concentration increases only by a factor of 3. The diffusion flux is also sensitive to the aquitard porosity, a change in porosity by a factor 2 leading to a change in concentration by a factor of 1.6. However the total porosity of a clayey aquitard is unlikely to vary outside the range of 0.2 to 0.4 and this parameter plays a secondary role compared to the variation of the diffusion coefficient.(a) Boundary conditions

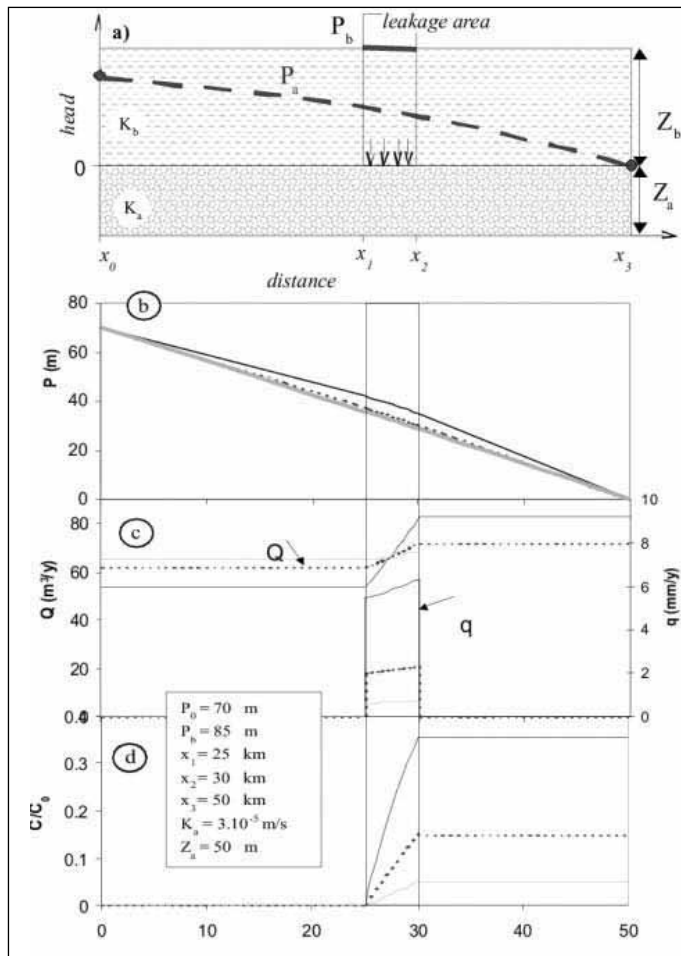


Figure 1: Influence of leakage.

for the analysis of leakage.  $P_a$  is the head in aquifer,  $P_b$  is the head in the aquitard at the ground surface, with leakage occurring only between  $x_1$  and  $x_2$ ,  $K_a$  and  $K_b$  are the permeabilities, and  $Z_a$  and  $Z_b$  are the thickness of the aquifer and aquitard respectively.

(b) Distribution of head values with distance. (c) Distribution of the flux along the aquifer.

(d) Evolution of the  $C/C_0$  ratio, where  $C$  is concentration in the aquifer and  $C_0$  is concentration in the aquitard. Thick line,  $Z_b = 250$  m,  $K_b = 10^{-9}$  m s<sup>-1</sup>; dashed line,  $Z_b = 750$  m,  $K_b = 10^{-9}$  m s<sup>-1</sup>; thick shaded line,  $Z_b = 250$  m,  $K_b = 10^{-10}$  m s<sup>-1</sup>.

More parameters affect the situation where mineral dissolution exists; the major ones being diffusion coefficient again, aquifer thickness and the percentage of mineral in the aquitard solid phase. Due to the dissolving minerals, the diffusion flux remains higher than for the case considered in the previous paragraph. It can be seen in Fig. 3 that after 1 My the  $C/C_{eq}$  ratio (where  $C_{eq}$  is the concentration in the aquitard) is equal to 0.28 for  $x/v = 10$  ky;

while after the same duration and distance, the  $C/C_0$  ratio (where  $C_0$  is the concentration in the aquifer) when only diffusion is active is 10 times lower. The influence of the diffusion coefficient is more important. An increase in a factor of 20 in the diffusion coefficient value leads, in the presence of dissolution, to an increase of the concentration by a factor of 4.5. The major unknown will often be the amount of highly soluble minerals in the aquitard at the regional

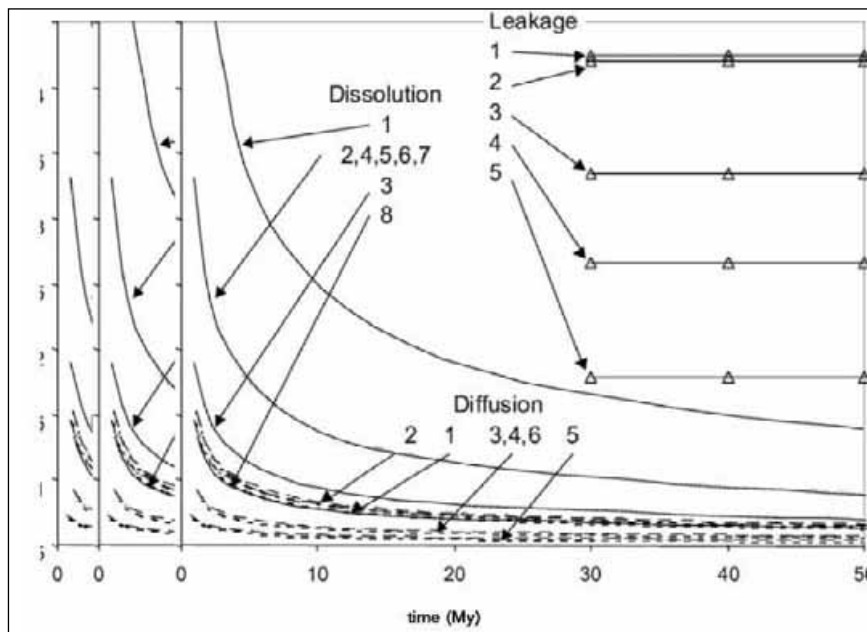


Figure 2: Variation of concentration with time in millions of years, for each of the modeled processes.

scale. The presented approach apply only where the diffusive properties are close to the clay's ones, i.e. where the evaporite fraction is lower than 10 to 20%. A different approach should be considered in case of pure layers of evaporites identified within the aquitard. A change in a factor 10 for the mineral fraction (1 to 10%) leads to a change in a factor of 3 for the resulting concentration. Assuming complete mixing, the aquifer thickness does not influence the resulting concentration because the diffusive flux decreases for an increasing concentration in the aquifer.

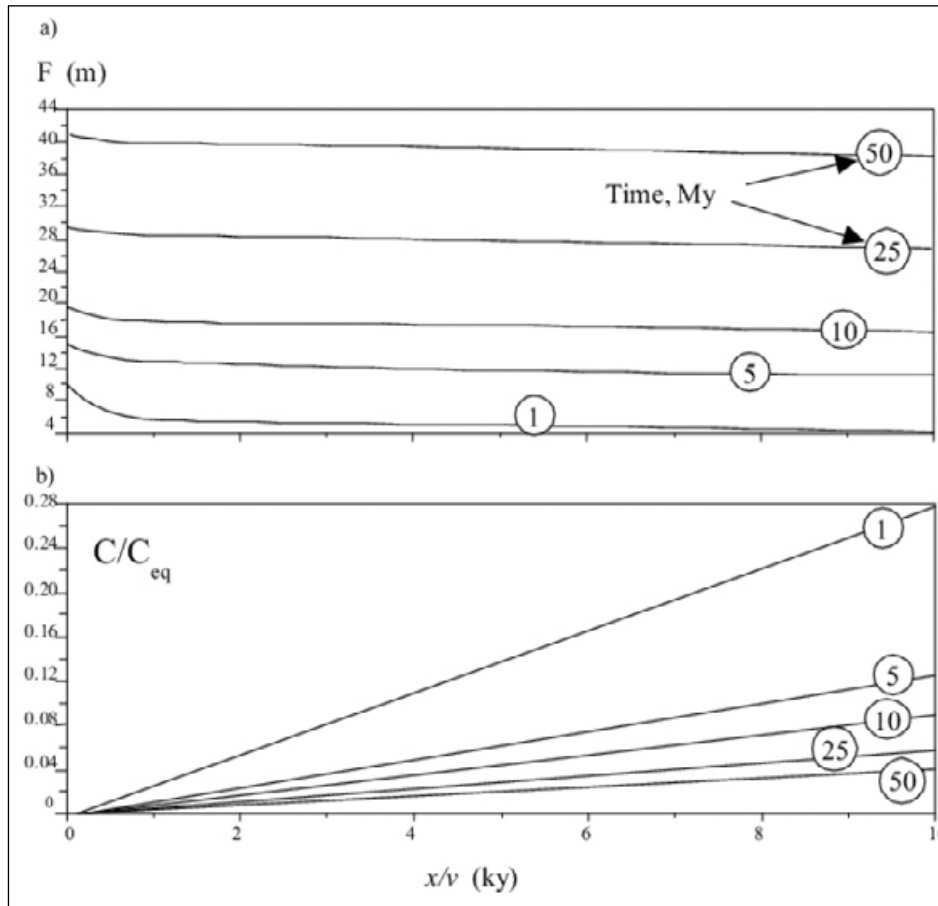


Figure 3: Dissolution and diffusion from the aquitard, vertical position of dissolution front and concentration in the aquifer.  
 (a) Vertical position of the dissolution front ( $F$  in m)  
 (b) average normalized concentration ( $C/C_{eq}$ ) and along normalized time ( $x/v$ ) for several time periods of dissolution: 1, 5, 10, 25, and 50 Myr.

Ion exchange in an aquifer of the type considered here will be completed typically in 5 to 15 pore volumes. However, ion exchange and diffusional transport from an adjacent aquitard may well have an important effect of aquifer groundwater chemistry over geological time scales. This process can be identified by considering ion ratios, and in this sense absolute concentrations do not have to be compared with those developed by the other mechanisms. In the systems considered, Na concentrations in the aquifer ground waters are strongly affected by Ca availability. This availability will vary considerably with the amount of calcite present. In addition, the presence of thick interbedded clay layers can lead to a dramatic decrease of flow rate locally within the aquifer. In this case, a specific analysis must be conducted by using the real local pore velocities in the aquifer. This may lead to a much longer time scale of influence of such exchanging layers on the composition of the aquifer water. It appears that concentrations delivered by a significant leakage are always higher than that observed for any other processes.

## Temporal evolution

When varying parameters, we considered that an infinite amount of matter was available in the aquitard. However the amount of matter available to maintain the aquitard-to-aquifer fluxes is not infinite. We calculated for leakage, diffusion and diffusion+dissolution the duration that the minerals or solutes may remain within the aquitard ('flushing time'). The estimated duration is obtained by the ratio of the amount of matter present in the aquitard to the flux leaving to the aquifer. For diffusion alone, the time is obtained when 95% of the amount is depleted. The parameters were varied as above, and the resulting variation in the results is shown by an error bar in the estimated time.

Fig. 4 shows that the 'flushing time' is determined largely by the considered process. Where a 1000 m thick aquitard is present, the ion concentrations in groundwater may remain stable for at least 150 My for all processes. For a 100 m thick aquitard, some of the processes studied can lead to a depletion of salts within the aquitard. If soluble minerals such as gypsum or halite are present in the aquitard, their effect may influence ion concentration in the aquifer over a long time, i.e. from 100 to 750 My. On the contrary, if concentrated solutions are present in the aquitard without soluble minerals, the effect of diffusion will remain in the aquifer only for 7 to 26 My. Leakage may deplete the soluble minerals in the entire aquitard after a duration of 8 to 45 My. The prediction for the leakage duration must be considered with a lot of care. In fact, the leakage intensity is largely dependent on the difference between the ground level and the piezometric surface. Because of climate change, this gradient may vary drastically across time scales of tens of thousands years. It might thus be difficult to make reliable predictions on the duration of the leakage effect. For ion exchange, the flushing time might be longer than for diffusion alone, but it will also depend on the amount of calcium transported to the exchange area, which may vary according to local conditions in the considered aquifer. This may lead to an ion exchange effect active for long duration (10's My) only at places where the aquifer flow is slow.

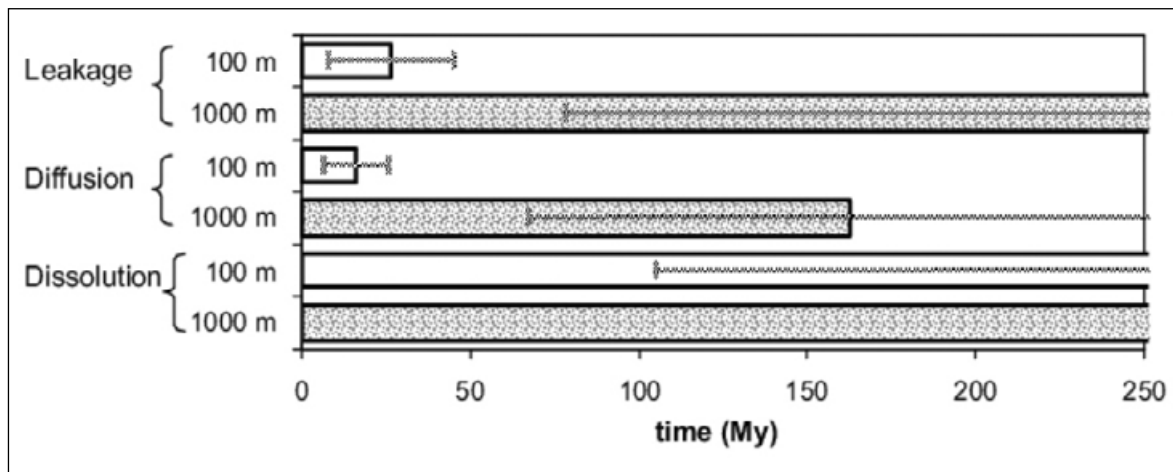


Figure 4: Estimates of the time to deplete an aquitard layer of its soluble components (minerals and pore water), using two thickness: 100 and 1000 m.

## Heterogeneity

Up to now we have considered the simple case of a homogeneous aquifer having 10's of m thickness bounded by 100's m thick aquitards. In most aquifers, deposits are complex (Koltermann and Gorelick, 1995) and layers of low permeability are interbedded within sand. Thus we will now consider applying to 'real' world, i.e. more complex deposits. In fact the equations remain the same but now apply to thin zones with a change in the boundary conditions. The highly soluble mineral content in these thin clay layers are assumed to be the same as in previous sections and will, sooner or later, be exhausted. Our interest will thus be focused on the lifetime of minerals in the clay zones.

Where minerals are present in the clay layers, the lifetime of this source of salts can be approximated as the time when the dissolution front reaches the mid-thickness of the clay layer. For sand and clay layers of 2 m thickness, the clay layer will be depleted over a 2 km length, after a duration of 0.1 My. Therefore, interbedded clay sources may not remain active more than 1 My in most situations.

For diffusion alone, the case is more complex because there is a change in boundary conditions : when diffusion in a clay layer occurs in both directions, there is a zero flux across the central plane at the middle of it. This gives a more complex solution than eq.10. To solve it, we used the solution of Sudicky and Frind. (1982). Several calculations show that the lifetime of solutes within the clay layers is small. For instance, with a zero flux boundary condition at 1 m in both sand and clay layers, depletion over 25 km will last only approximately 12 ky with  $v = 5 \text{ m.y}^{-1}$ ,  $w_b = 0.4$  and  $w_a = 0.2$ . Therefore, thin clay layers do not seem to be significant diffusion sources over geological time scales.

Although interbedded clay layers might be rapidly depleted of their ion content, they may isolate several parts of the aquifer. These barriers can lead to different ion concentrations for each layer of the aquifer, that are often observed in the field (McMahon, 2001). Despite the vertical heterogeneity of concentrations, a detailed analysis of the formulae developed for thick aquitards shows that the average concentration in the aquifer is the same in a homogeneous aquifer and in an aquifer including interbedded clay layers.

For ion exchange, simple mass balance calculations show that the flux of Ca can be an important limiting factor and that clay layers embedded within the aquifer can remain active exchangers for several My. However, this behavior largely depends on the amount of calcite present in sediments that is difficult to estimate.

## Conclusion

Throughout this paper we tried to estimate the effects of aquifer/aquitard interactions on the resulting concentration gradients in the aquifer. This theoretical approach indicates that quite complex boundary conditions can be simplified in many instances and lead to analytical solutions. Whilst these solutions must be calculated numerically, these formulae help to understand the roles of the different variables and make sensitivity analysis easier than would be the case with numerical models. This approach shows the very different patterns resulting from leakage, dissolution, diffusion and ion exchange. The results may help to understand better the evolution of chemistry in deep ground waters.

Calculations on leakage showed that at places where leakage is significant for the global flow in the aquifer system, it may lead to important changes in concentration in the aquifer, provided that mineralized solutions exist in the aquitard. Therefore where hydrodynamic modeling of an aquifer system suggests the existence of leakage, this can be verified by analyzing the concentration gradients of several ions. Diffusion itself seems to play a secondary role, except in a young aquifer or aquitards deposited under brine conditions. However diffusion limits the



flux of matter through the aquitard and thus slows the dissolution or ion exchange fluxes from the aquitard. That is why these processes can be identified even tens of My after burial, even though aquifer groundwater might have been renewed a thousand times. Ion exchange should now be viewed with an emphasis on aquitard CEC. The role of ion exchange from the aquitard should be considered where ion exchange is recognized in ground waters from an aquifer of substantial age.

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