

## MODELING OF CHLORINATED SOLVENTS TRANSPORT AND NATURAL ATTENUATION IN GROUNDWATER

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**Theme B** : Functions and values of Soil-Water systems ; Understanding of Processes

**PhD work** : no

**Poster**

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### 1. Context and Object

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.

This work was realised within the framework of the research program TRANSPOL. This program is run by INERIS (the French National Institute for Industrial Environment and Risks, [www.ineris.fr](http://www.ineris.fr)). It was created 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 document presents results of a real case study, named Real Case 3. It concerns chlorinated solvents fate, transport and natural attenuation in groundwater. INERIS provided the four modeling teams with a document containing specifications (conceptual model and calibration data).

### 2. Site description

A contaminated alluvial aquifer in northern Spain (cf. Figure 1 and Figure 2), has been studied by ENVIROS since 2000. Figure 2 is 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. 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

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).

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

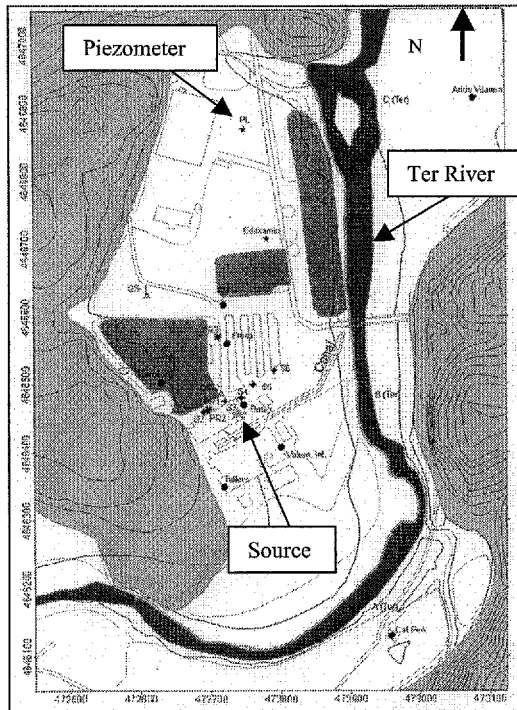


Figure 1 : Site details and well locations (UTM coordinates)

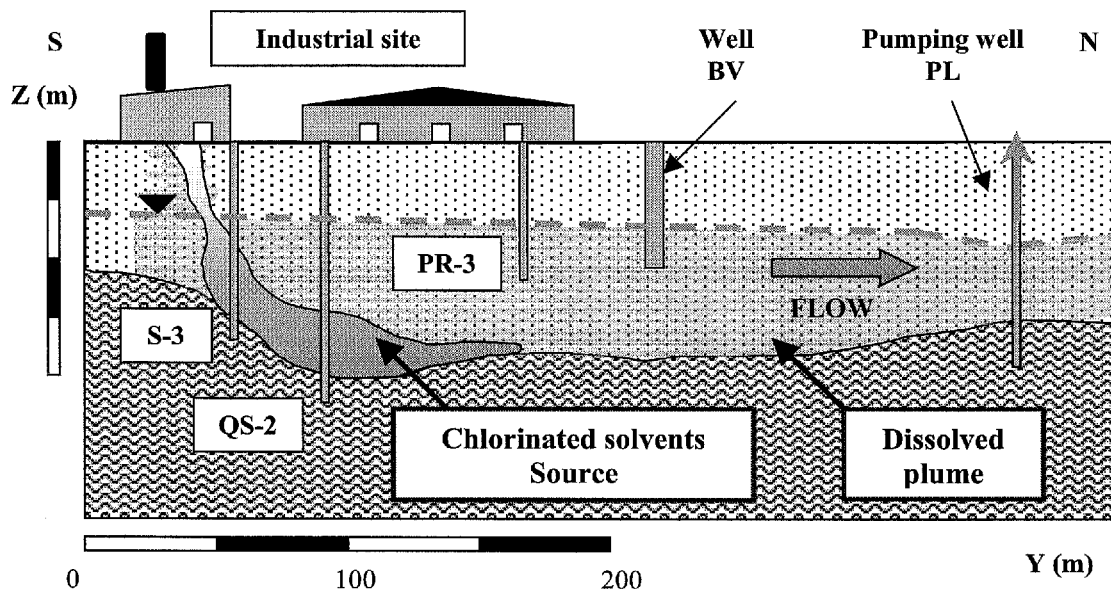


Figure 2 : South – North section of the site

### 3. Conceptual model

The four teams used the same data to simulate flow and transport. Specifications were given to the teams presents conceptual model, initial conditions, calibration data (heads and concentrations values). Models represent an homogeneous and isotropic aquifer.

#### Conceptual model for groundwater flow

The boundary conditions are summarised in Figure 3.

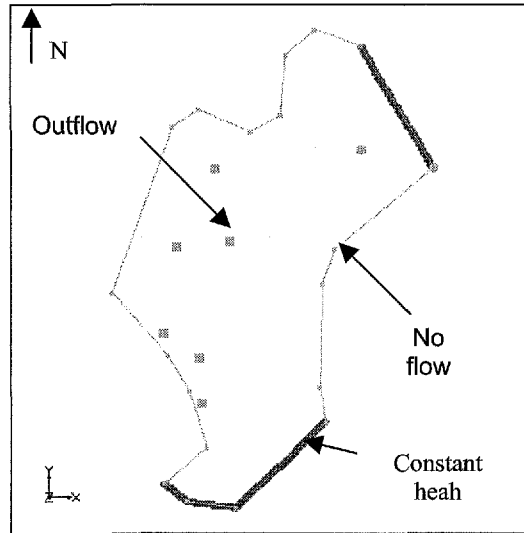


Figure 3 : Modelled domain and boundary conditions

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 an 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 at contaminated sites.

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 nov. 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 therefor 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

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 ( $\lambda$ ).

#### 4. Results and comparison

The models intercomparison methodology is based on comparison between :

- ✓ flow (head) and transport (concentrations) calibration results ;
- ✓ calibration parameters values ;
- ✓ hypothesis respected ;
- ✓ natural attenuation phenomenon considered (particularly sorption and degradation).

Different codes have been employed (cf. Table 1). The Transport codes allow to consider natural attenuation phenomenon like sorption and degradation.

	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 diminishing

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

	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

Hydraulic conductivity range from 70 to 350 m/d. The final calibrated values are included in the range of values suggested in the specifications (60 to 600 m/d).

An anisotropy factor was tested by ENSMP. Calibration results were better for piezometers near the source.

### Contaminant transport simulations

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

The models reproduced successfully the general trends of the contamination plumes but the time of peak arrival and the concentration at the observations points may vary more or less according to the use and the different features of the numerical codes. Results show that with such a 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.

Figure 5 presents PCE results for six piezometers distributed from source to downstream.

The higher concentrations are calculated by ANTEA (higher source concentration, cf. Table 4, calibration with piezometers near the source). Three others models give similar results except near the source (concentrations in S-2 and S-3 are less important for INERIS, smaller source concentration and calibration with piezometers downstream the source).

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

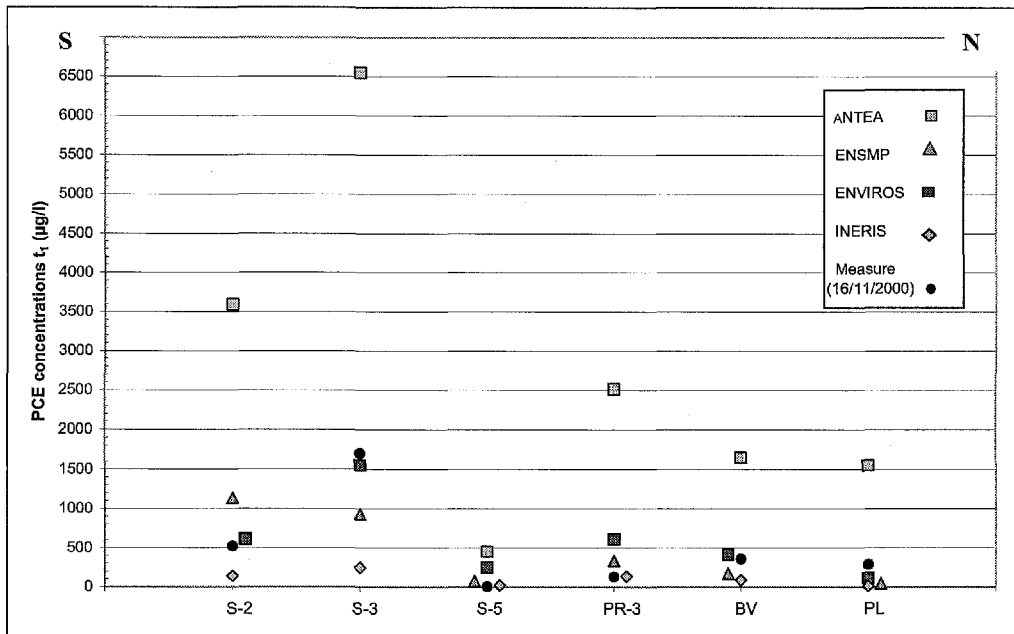


Figure 5 : PCE concentrations ( $\mu\text{g/l}$ ) at  $t_1$

		ANTEA	ENSMP	ENVIROS	INERIS
PCE Injection rate $R_1(\text{kg/d})$		0.650	0.170	0.170	0.030
Source surface ( $\text{m}^2$ )		707	100	91	25
Effective porosity $n_e$ (%)		10	30	10	20 and 30
Kinematic dispersion (m)	$\alpha_L$	30	22	10	20
	$\alpha_T$	3	8.5	8	4
Molecular diffusion ( $\text{m}^2/\text{d}$ )		Not defined	PCE, TCE, DCE and CV $1 \times 10^{-4}$	PCE, TCE, DCE and CV $1 \times 10^{-5}$	Not defined
Bulk density of aquifer ( $\text{kg}/\text{m}^3$ )		1700	1600	Not defined	Not defined
Sorption coefficient $K_d$ ( $\text{m}^3/\text{kg}$ )	PCE	$1.4 \times 10^{-4}$	$9.4 \times 10^{-5}$	Not defined	Not defined
	TCE	$5.8 \times 10^{-5}$	$9.4 \times 10^{-5}$		
	DCE	$5.2 \times 10^{-5}$	$9.4 \times 10^{-5}$		
	CV	Not defined	$9.4 \times 10^{-5}$		
First order degradation constant $\lambda$ ( $\text{d}^{-1}$ )	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

## Sorption and biodegradation

Table 4 summarizes the assumed values of sorption and degradation coefficients. Each team gave a different calibrated value.

The four teams considered degradation of chlorinated solvents. For ENSMP, ENVIROS and INERIS models the first order PCE degradation constant is about  $0.003 \text{ d}^{-1}$  (constant half life degradation : 230 d). Close to the source area concentrations observed of DCE is higher than the one of TCE. Thus in the models developed (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 transport conceptual model reproduced successfully the concentration trends without taking into account sorption processes.

As shown in Figure 6, ANTEA privileges PCE sorption and ENVIROS PCE degradation. 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.

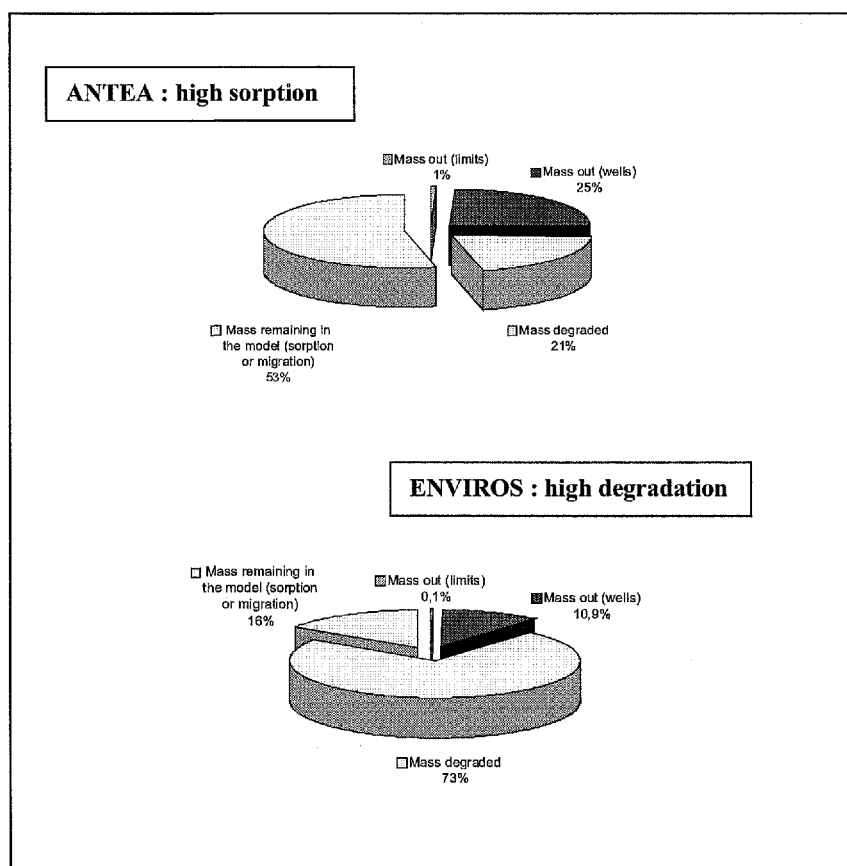


Figure 6 : Comparison between ANTEA and ENVIROS PCE mass balance (kg) (0 to 1800 days)

## 5. Conclusion

Multi-species (PCE, TCE and DCE) model was used for modeling transport (homogeneous and isotropic) and natural attenuation processes occurring at a chlorinated solvents release site. Different codes have been employed 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 ;
- ✓ natural attenuation parameters (sorption and degradation).

A more accurate diagnosis is needed in order to reduce the uncertainty of model parameters. Thus more appreciate data would be studying for this year, concerning :

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

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

### **Acknowledgements**

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### **References**

Dan, A. ; Goblet, P. (2004) – Programme TRANSPOL II (INERIS 2003). ENSMP-CIG-LHM/RD/04/18.

Goblet, P. (2002) – Programme METIS : simulation d'écoulement et de transport miscible en milieu poreux et fracturé – Rapport technique LHM/RD/02/05, Ecole des Mines de Paris.

Mac Donald, M. G. ; Harbaugh, A. W. (1988) – A modular three dimensional finite difference groundwater model (MODFLOW) – U. S. Geological Survey Techniques of Water Resources Investigations, Book 6, 586 pp.

Medina, A. ; Alcolea, A ; Carrera, J. – Modelos de flujo y transporte en la geosfera : El Código TRANSIN.

Medina, A. ; Carrera, J. ; Alcolea, A. ; Castro, L, F – Modelos de flujo y transporte en la geosfera : Código TRANSIN IV.

Poirot, N. ; Schwartz, J. (2004) – Impact d'un déversement de composés chlorés sur la qualité des eaux souterraines – TRANSPOL II - Cas Réel n°3. ANTEA- A33548/A.

Quiot, F. (2004) – Modélisation hydrogéologique d'une nappe alluviale polluée par des solvants chlorés TRANSPOL - Cas Réel n°3. INERIS-DRC-04-55503/DESP-R01.

Rollin, C. ; Bour, O. (2002) – TRANSPOL II Cahier des charges pour la réalisation d'un modèle numérique (CdC n°1). Cas réel n°3 : impact d'un déversement de composés chlorés sur la qualité des eaux souterraines – INERIS-DRC-02-25294/DESP-R18.

Rollin, C. (2003) – TRANSPOL II Cahier des charges pour la réalisation d'un modèle numérique (CdC n°2). Cas réel n°3 : impact d'un déversement de composés chlorés sur la qualité des eaux souterraines - INERIS-DRC-03-46524/DESP-R01.

Ruiz, E. ; Jordana, S. ; Guimerà, J. (2004) – Simulations of the impact of a spill of chlorinated compounds on groundwater quality – TRANSPOL II - CR-3. ENVIROS R-2225-r1.

Thiéry, D. (1994) – Logiciel MARTHE, version 6.1 – Rapport BRGM R38108 HYT/DR/94.