MODELING OF CHLORINATED SOLVENTS TRANSPORT AND NATURAL ATTENUATION IN GROUNDWATER

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Abstract

The objective of this study is to test differents 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, ENSMP, 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 contamined 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) 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^3/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.

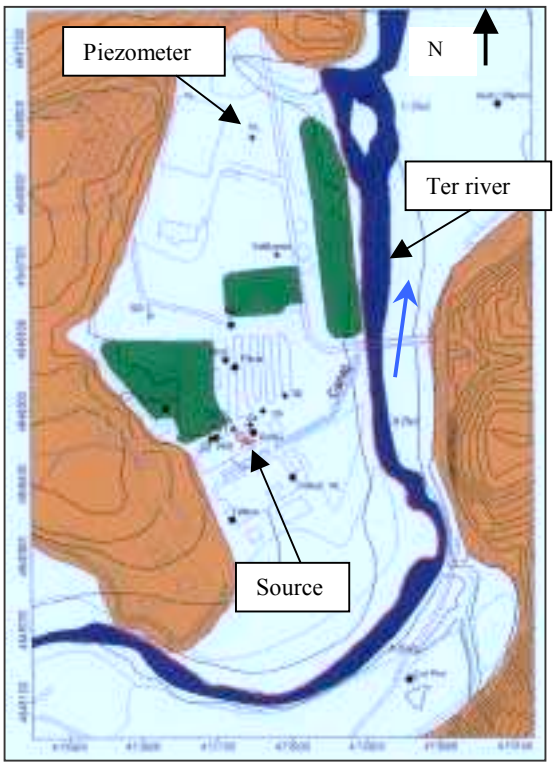


Figure 1 : Site details and well locations (UTM coordinates)

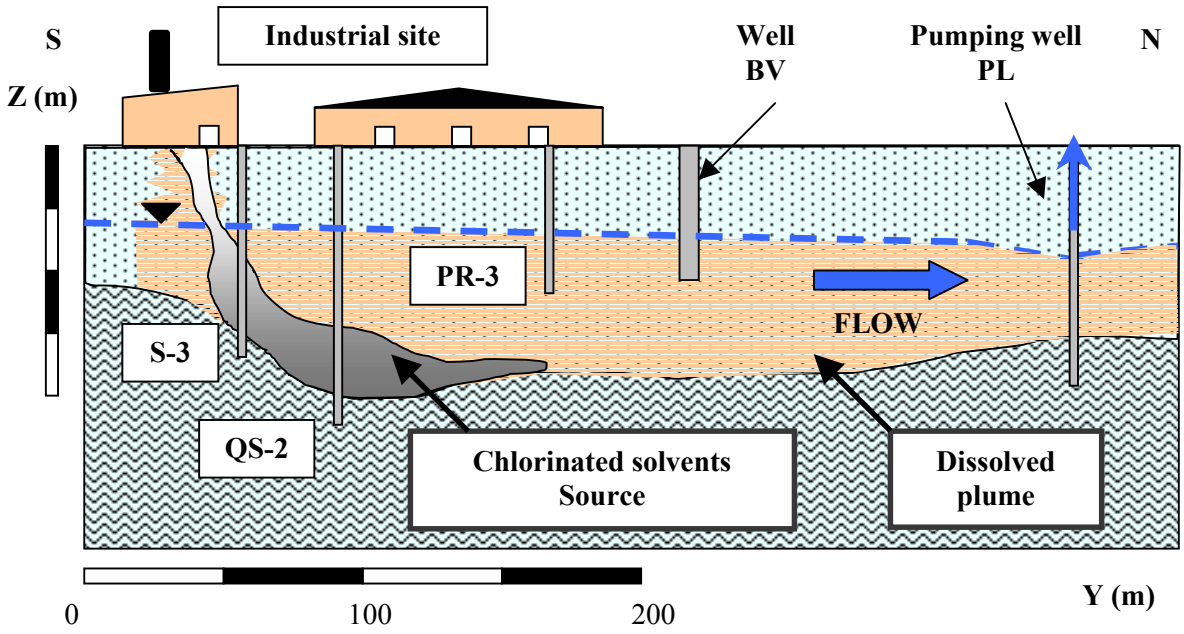


Figure 2 : South – North section of the site

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.

Conceptual model for groundwater flow

The boundary conditions are summarised on Figure 3.

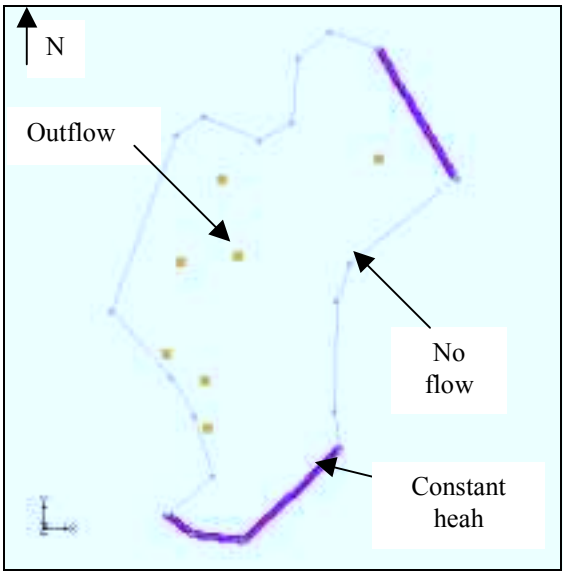


Figure 3 : Modelled domain and boundary conditions

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 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 occuring 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 (R1 in kg/d) ;
- t_1 to t_2 : the injection rate starts decreasing slightly from the beginning of the 6th year until the end of the 10th 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.

PCE ⟶ TCE ⟶ DCE ⟶ VC (Vinyl Chloride)

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 (λ).

4. Results and comparison

The models intercomparison methodology is based on a comparison between :

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

Four teams were involved in the benchmarking process. Different numerical commercial or developed internally codes have been used (cf. Table 1). All the transport codes allow to consider sorption and degradation (natural attenuation phenomenon).

Table 1 : Teams and codes used in the intercomparison bench

	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

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.

Table 2 : Hydrodynamic calibration – Error summary

	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 3 : Hydrodynamic calibration - Hydraulic conductivity

	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^3/d)	5	0.1	0	10

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.

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).

Table 4 : Parameters selected for transport calibration

		ANTEA	ENSMP	ENVIROS	INERIS
PCE Injection rate R1(kg/d)		0.650	0.170	0.170	0.030
Source surface (m²)		707	100	91	25
Effective porosity n_e (%)		10	30	10	20 and 30
Dynamic dispersivity (m)	α_L	30	22	10	20
	α_T	3	8.5	8	4
Molecular diffusion (m²/d)		Not defined	PCE, TCE, DCE and CV $1x10^{-4}$	PCE, TCE, DCE and CV $1x10^{-6}$	Not defined
Bulk density of aquifer (kg/m^3)		1700	1600	Not defined	Not defined
Sorption coefficient K_d (m^3/kg)	PCE	$1.4x10^{-4}$	$9.4x10^{-5}$	Not defined	Not defined
	TCE	$5.8x10^{-5}$	$9.4x10^{-5}$		
	DCE	$5.2x10^{-5}$	$9.4x10^{-5}$		
	CV	Not defined	$9.4x10^{-5}$		
First order degradation constant λ (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

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).

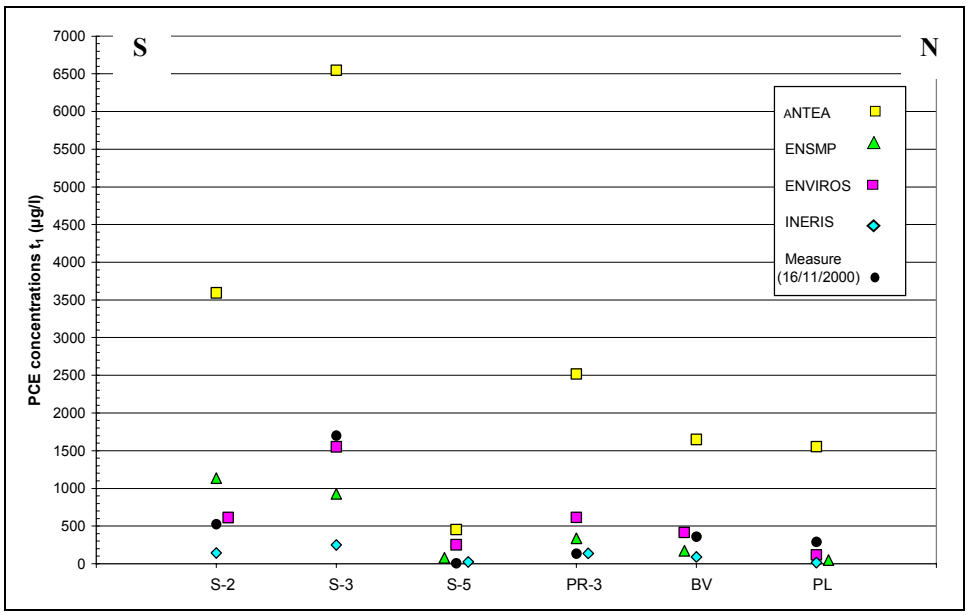


Figure 5 : PCE concentrations (µg/l) at t_1

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.

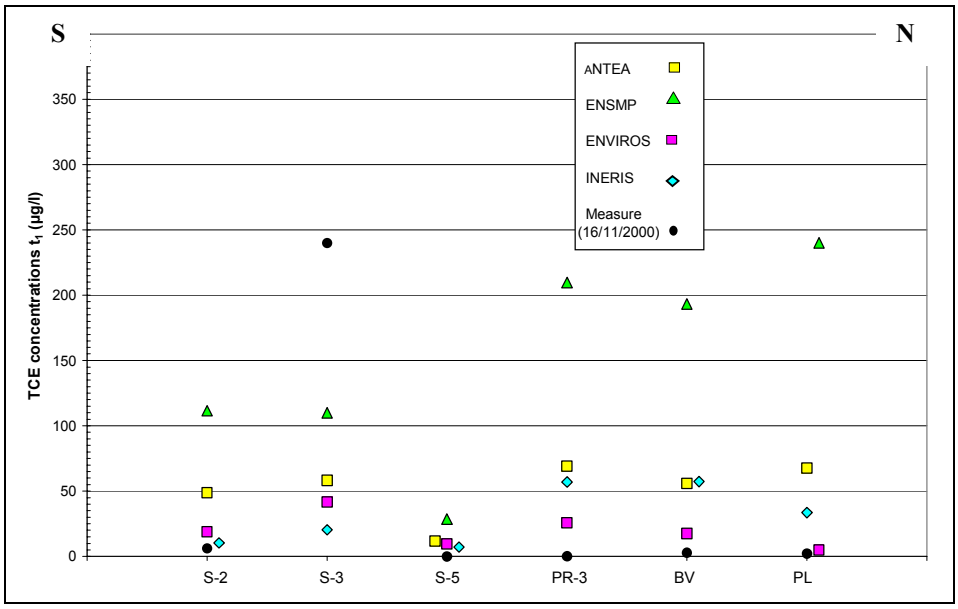


Figure 6 : TCE concentrations (µg/l) at t_1

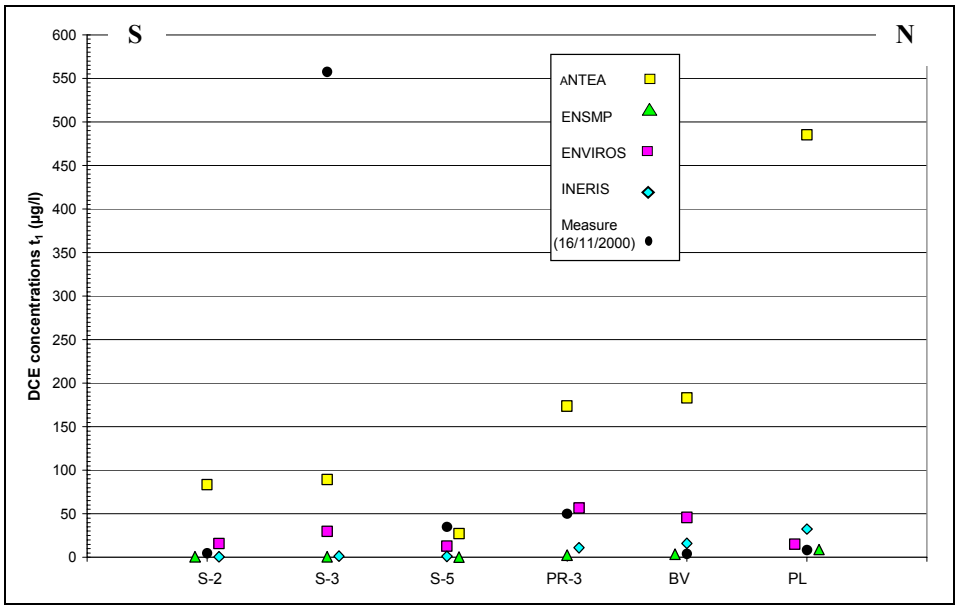


Figure 7 : DCE concentrations (µg/l) at t_1

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 d^{-1} (constant half life degradation : 230 d), it is about 0.0026 d^{-1} for ENSMP (267 d) but only 0.0004 d^{-1} for ANTEA (1733 d).

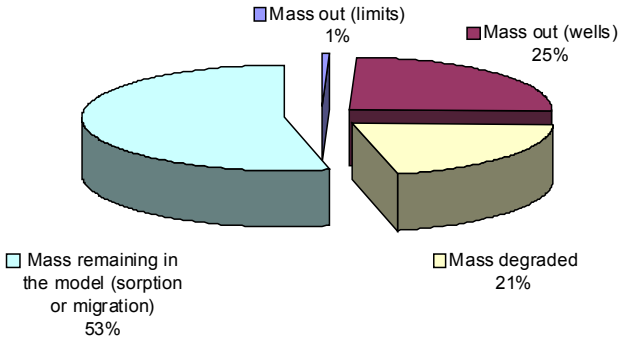
Close to the source area, concentrations observed of DCE is higher than the one of TCE. Thus in the developed models (expect for ENSMP) the degradation factor of TCE is faster than the one of DCE.

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.

ANTEA : high sorption



ENVIROS : high degradation

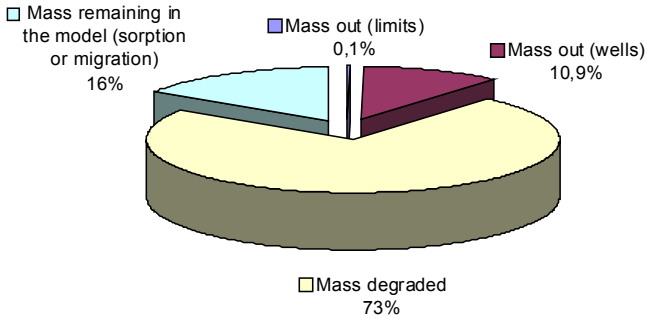


Figure 8 : Comparison between ANTEA and ENVIROS PCE mass balance (kg) (0 to 1800 days)

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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