Groundwater risk assessment for a Polycyclic Aromatic Hydrocarbons (PAH) contaminated site ; benchmarking and validation of numerical transport models

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Groundwater risk assessment for a Polycyclic Aromatic Hydrocarbons (PAH) contaminated site; benchmarking and validation of numerical transport models

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Abstract

The objective is to test the modelling approaches and the reliability of the codes used in water risk assessment. The final goal is to elaborate, for each group of pollutant, guidelines that could serve as a scientific support for pollutant transport modelling in groundwater and soil.

The models performed by 5 teams to simulate a contamination of soils and groundwaters by PAH at a disused coke plant site were compared. Hydrogeology is characterised by a superficial and a chalk aquifer, the latter being confined under a 2 meter thick clay layer. The source of contamination was determined by 40 soil sampling points. Total PAH concentrations in the soils ranged from 3 to 80000 mg/kg. 18 observation wells were implemented to monitor the aquifers. Total PAH concentrations in the groundwaters ranged from 0,1 to 40000 µg/l. A first synthesis of the results obtained leads to the following:

- naphthalene was chosen as a tracer by all 5 teams;
- hydrodynamic parameters vary from one model to another. More investigations are carried out to reduce uncertainties;
- the partition coefficient of naphthalene in the different layers is unknown, which leads to high uncertainties. Batch tests are currently being carried out ;
- the number and extension of the sources considered by the teams are different. Thus, modellers have to be involved in the diagnosis phase;
- biodegradation is an important factor to consider even though few values are available in the literature concerning anaerobic aquifers. A sensitivity analysis of the degradation constant has to be performed.

The paper presents the available data used for modelling, a summary of the 5 team results and preliminary practical guidelines for PAH transport modelling.

1 Introduction

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 (a) the results of extensive investigations at a specific moment in time, (b) data available from monitoring of pollutants in time and space and (c) numerical modelling of the transport of pollutants in the environment. In practice, the techniques 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 has developed a research program, based on comparisons of modelling approaches, in order to elaborate guidelines that could provide a scientific support for the modelling of each group of pollutant.

The approach we have selected goes further from the mere validation of numerical codes, since the results of a model not only depend on the way a code is used and results interpreted, but also on the quality of the input parameters and data. The comparison of the results and the search for the points leading to differences will allow to determine the minimum soil, aquifer and pollutants characteristics to take into account in the modelling. The proposed comparison relies on several teams treating identical cases according to their own approaches and modelling techniques. Each case is transposed into a report integrating available data from the site and specifying the type of expected results.

2 Study area

The site of interest is a former coke plant closed 40 years ago. The site, along a river, covers a surface of 10 hectares. Contamination of soils and groundwater has resulted from the disposal of tar residues.

2.1 Geology

The plant was built on an heterogeneous filling material composed of sand, silt and bricks to a depth of about 1 to 5 m, placed over fine clayey sands. Under this superficial layer, gravels in a sandy matrix are found. The width of this superficial aquifer varies between 1,6 and 5,8 m. The chalk aquifer, whose roof is 13 to 15 m deep, is separated from the deposits by a 2 m width confining layer of clay (called 'argile de Louvil') composed of very fine clayey sands. The following figure displays a SSW-NNE geological cross-section of the site.
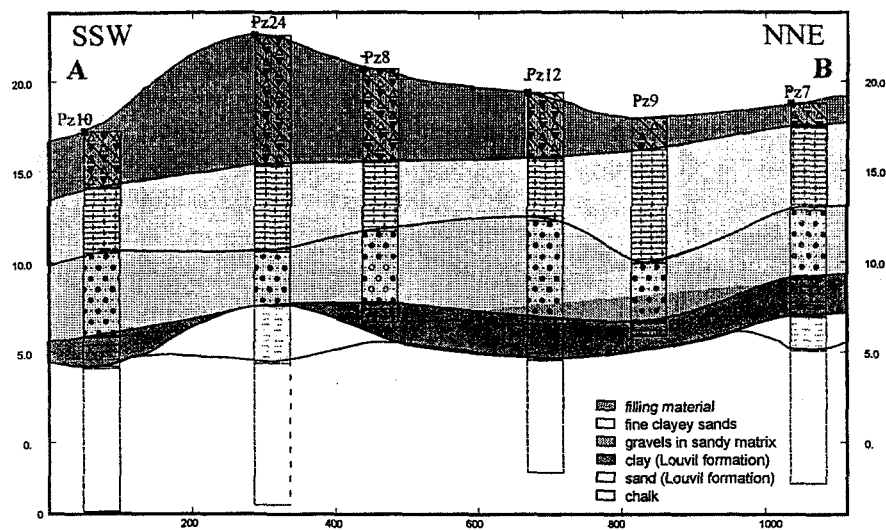
Figure 1: Geological cross-section of the site.

2.2 Hydrogeology

Two aquifers may be distinguished : the superficial deposits and the chalk formation. The recharge of the chalk aquifer occurs to the north where the chalk outcrops. This aquifer is the main resource for drinking water in the area. The superficial water table flows from NW towards SE and the hydraulic gradient ranges from 5.10^{-3} and 10^{-3}. The chalk aquifer is confined, due to the presence of the clayey layer and the flow direction is NE towards SW. The hydraulic gradient is $2,8.10^{-3}$. Water-table surfaces are depicted in Figure 3.

3 Field investigations

3.1 Characterisation of the pollution

3.1.1 Soils
40 analysis of sampled soils (Fig. 3) have been carried out and lead to the following remarks : (a) soil pollution is located in the areas where extractors, tar oils reservoirs, oil distillation equipment were present. Total PAH concentrations range from 100 to 80 000 mg/kg, (b) contamination is principally located in fine silty sands between 3 and 6 m deep. This soil pollution is in direct relation with the contamination of the superficial aquifer, (c) pollution is mainly represented by 2 to 3 cycles PAH (naphthalene, acenaphthene and phenanthrene).

3.1.2 Groundwater
5 observation wells were drilled to the chalk aquifer (PZ7, PZ10, PZ12, PZ13 and PZ24) and 13 to the superficial one. Locations of the wells and of the coke plant equipment are shown in Figure 2.
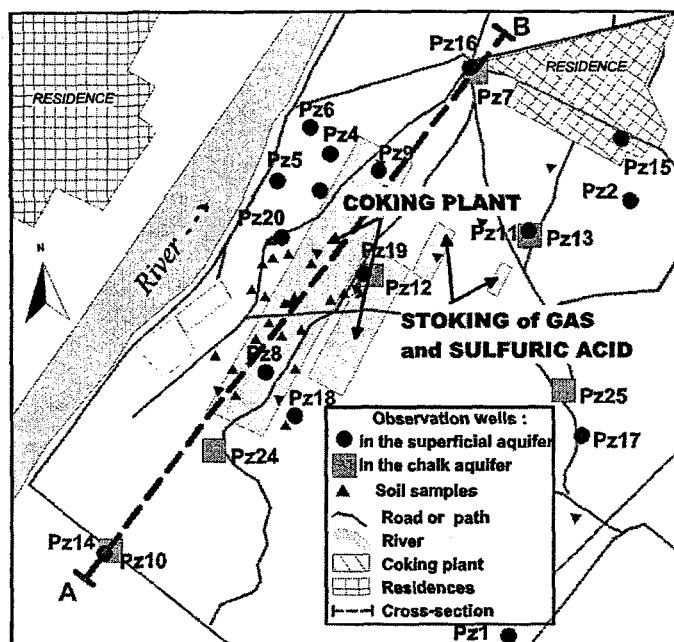
Figure 2: Locations of the observation wells and of the coke plant equipment.

The chalk aquifer observation wells reach a depth of 21 m. They were drilled in two steps to avoid contamination of the deep aquifer. All the monitoring wells have been sampled. The superficial aquifer is heavily contaminated ; high indices of pollution are found in the observation wells located at the former coke plant location (PZ8, PZ20, PZ22). Concerning the chalk aquifer, a slight contamination is encountered in the monitoring wells : PAH concentrations range from 0,1 to 2 µg/l but the drinking water level for the 6 WHO-PAH is not reached (Fig. 3).

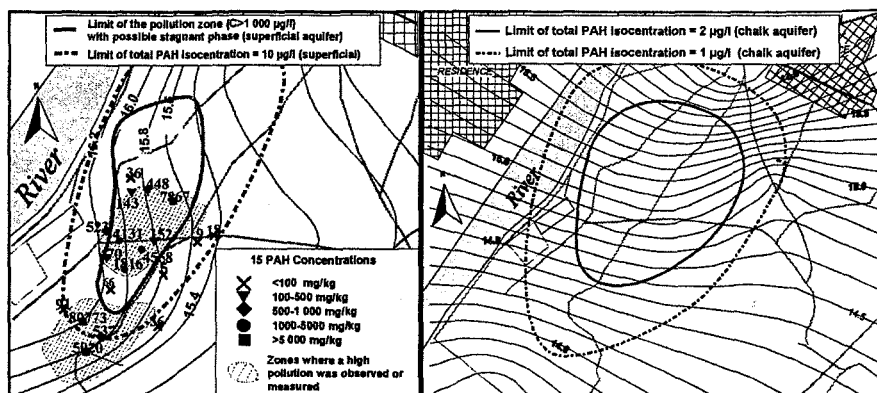

Figure 3 : Measured PAH concentrations in soils and groundwaters.

3.2 Hydrodynamic parameters

Lefranc permeability tests were carried out to determine the permeability of the superficial aquifer. The average values are respectively $3,1.10^{-5}$, $1,3.10^{-5}$ and $4,2.10^{-5}$ m/s in PZ16, PZ18 and PZ19. A test was also carried out for the clay layer. The values of permeability obtained are $1,6.10^{-9}$ m/s before saturation and $4,7.10^{-9}$ m/s after saturation.

4 Proposed data for the modelling

5 teams participated in the benchmarking process. The features of the selected codes are listed below :

Team	code	method of resolution	references
INERIS	Modflow coupled to Mt3d, interface GMS 2.0	Flow : finite differences	[1], [2], [3]
		Transport : mixed eulerian lagrangian approach	
		Resolution : MOC*, MMOC**, hybrid MOC/MMOC	
BRGM	Misp	Analytical resolution	[4], [5]
FSSI	Visual Modflow 2.81, Mt3d	Flow : finite differences	[6]
		Transport : mixed eulerian lagrangian approach	
		Resolution : MOC*, MMOC**, hybrid MOC/MMOC	
ANTEA	Marthe v5.4	Flow : finite differences	[7]
		Transport : finite volumes method, MOC, random walk method	
CNRSSP	Feflow 4.7	Flow : finite elements	[8]

(*) MOC : method of characteristics

(**) MMOC : modified method of characteristics

Table 1 : Specifics of the codes selected by the teams.

Data submitted to the modellers have been presented as results from a site diagnosis. This procedure allows the modeller to select the hydrodynamic and transport parameters, the sources appearing to be the most appropriate, according to its experience, as he would do in a proper risk assessment. However, some values and a range of variation have been given as an indication. The values proposed to the modellers resulted either from site investigation or from literature. The parameters that were fixed are relative to the substances : their solubility and their partition coefficient K_{oc}.

Parameter	Gravels		Clay		Chalk	
	Initial value	Range	Initial value	Range	Initial value	Range
Permeability [m/s]	$2,5.10^{-5}$	$10^{-5}-5.10^{-5}$	5.10^{-9}	$10^{-8}-10^{-9}$	5.10^{-3}	$10^{-3}-10^{-2}$
Longitudinal dispersivity [m]	40	20-60			70	40-100
Transversal dispersivity [m]	10	0-20			20	5-40
Total porosity [-]	0,30	0,2-0,4	0,20	0,3-0,5	0,20	0,15-0,25
Specific yield [-]	0,2	0,15-0,25	0,01	0,01-0,02	003	0,01-0,05
Density [g/cm³]	1,7	1,6-1,8	1,4	1,3-1,5	1,8	1,7-1,9

Table 2 : Proposed values for the modelling exercise.

5 Results and discussion

Calibration of the flow model was performed by considering the water table levels and by setting constant head boundary conditions. Calibration of the transport model was performed by assuming that the pollution started 40 years ago at the dismantling of the coke plant and by comparing the calculated values to the measured concentrations in the monitoring wells. Parameters values and hypothesis selected by the modellers are displayed in Table 3.

After 200 years, in the chalk aquifer, estimated naphthalene concentrations differ by more than two orders of magnitude in some of the observation wells : breakthrough curves in PZ10 are displayed below.
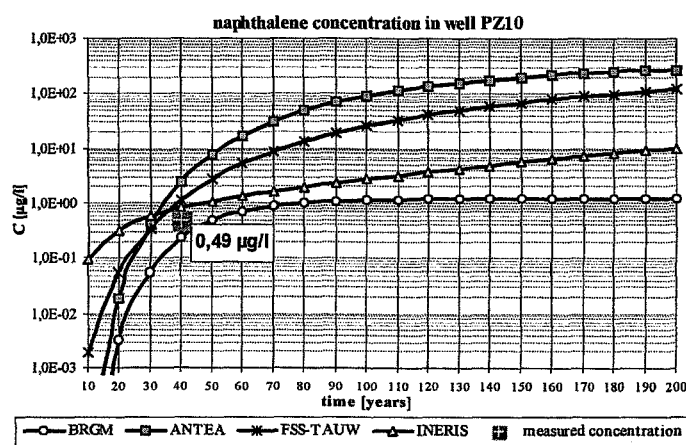

Figure 4 : Calculated concentrations in the chalk aquifer (obs. PZ10).

		INERIS	BRGM	FSS-TAUW	ANTEA	CNRSSP
Numerical model		MODFLOW / MT3D (with GMS 2.1)	MISP	Visual MODFLOW / MT3DMS	MARTHE v5.4	FEFLOW v4.7
Tracer		Naphthalene	Naphthalene	Naphthalene	Naphthalene	Naphthalene
Hypothesis used for the source		Continuous source (naphthalene solubility)	Continuous source (naphthalene solubility)	Continuous source (naphthalene solubility)	Continuous source (naphthalene solubility)	Equilibrium concentration fixed at the source
Surface of the source (m²)		300 × 80	100 × 50	50 × 30 & 80 × 40	100 × 100 & 30 × 30	40 × 40 & 60 × 20 & 110 × 25
Transport in the clay layer		2 layers : leakage over all the area	2 layers :leakage over the source surf.	3 layers	3 layers	3 layers
[R] (*)	gravel	23,7	7,5	25,3	1,6	31,6
	clay	-	-	46,5	1,63	78,0
	chalk	37,0	9,2	5,5	43,3	49,6
Recharge		No	No	Only at the source	Over all the area	Over all the area
K (clay layer) (m/s)		5 10⁻⁹	5 10⁻⁸	3 10⁻⁹	10⁻⁹	5 10⁻⁹
α_L (m)	gravel	40	35	40	40	20
	clay	-	0,25	5	0,4	1
	chalk	70	70	70	70	10

Table 3 : Hypothesis selected by the teams for the modelling.

(*) : R = 1+ $\frac{\rho_a K_d}{\vartheta}$ where ρ_a is the apparent density of the soil, K_d the distribution coefficient and θ the total porosity of the soil.

K = permeability ; α_L = longitudinal dispersivity

All the teams have selected naphthalene as a tracer of the groundwater pollution. This choice may be explained taking into account the mobility, solubility and representativity of this substance in the source (40 to 75 % of the total PAH mass. All the calculations have been performed by assuming that naphthalene is present in the soluble phase.

The modellers have considered a constant naphthalene concentration equal to the solubility of naphthalene, which means that the pollutant stock is important enough to assume the presence of a continuous source during 200 years. This hypothesis may be justified by the fact that naphthalene concentrations are very high in the soils and in the superficial aquifer (the solubility value of this substance is reached).

The differences encountered in the results are explained by the following points :
✓ the numbers and extension of the sources considered by the teams are relatively different, though the diagnosis was the same.
✓ flow calibration was not the same for all the teams : the lack of data concerning flow rates and aquifer pumping lead to uncertainties concerning the couple (permeability-recharge) obtained after calibration. A two-fold increase of both parameters values has no effect on the calculated water table levels.
✓ Table 3 brings to the fore the large dispersion of the retardation coefficient values selected for the modelling exercise. This is the parameter presenting the highest impact on the pollutant fate in groundwater. Data available in the literature does not allow a proper calibration of the concentrations values.
✓ biodegradation phenomena were not taken into account in the modelling exercise. Whereas the upper aquifer exhibits aerobic to semi-aerobic conditions, the lower aquifer is anaerobic. The evaluation of the actual literature on PAH degradation has shown that extensive knowledge is available on the aerobic biodegradation of single PAH compounds by bacteria and fungi. However, the literature concerning natural anaerobic degradation of PAH under the chalk aquifer conditions is scarce. Some few results from recent literature suggest that biodegradation of PAH occurs under nitrate- and sulfate-reducing conditions.

6 Conclusions and further work

In order to reduce the uncertainties, a second report integrating the results from recent investigations has been sent to the teams involved in the project, in order to improve the models.
Pumping tests have been carried out to calibrate more precisely the flow model. The synthesis of the results has shown the relevance of the K_d value selection. Therefore, batch measures for PAH adsorption are currently being carried out for the three geological formations present at the site. In addition to a sensitivity analysis for the biodegradation rate, INERIS is now performing laboratory tests

(microcosms, column tests) to determine whether biodegradation occurs at the site or not. The results are promising since biodegradation was observed in laboratory in the site conditions, i.e. sulfato-reducing conditions with bacteria isolated from the site. In situ tests, by the mean of stable isotope measurements will be performed to estimate the in-situ biodegradation rates.

Finally, we will focus on the tracer choice. Naphthalene may be used as a basis to validate the models ; however, it does not give any indication concerning a quality criteria since it does not belong to the 6 WHO-PAH. Further work will be conducted to extrapolate the results obtained for naphthalene to the other PAH, and to develop a specific risk assessment approach.

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