3D characterization and modeling of a chlorinated solvents contamination in a complex alluvial aquifer to assess the remediation potential of Monitored Natural Attenuation

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Remediation with MNA = today & tomorrow

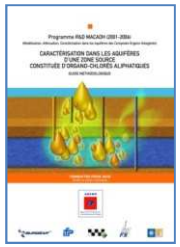
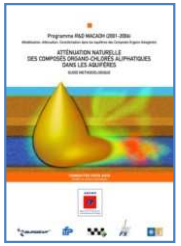
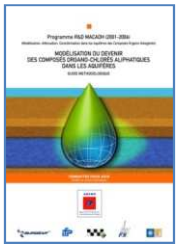
- Today's evaluation of MNA potential
  - Characterize hydro-geological structures and flow patterns
  - Quantify contaminants mass in the source
  - Characterize and quantify attenuation due to NA processes in the source and plumes (groundwater and gaseous)
- Future evaluation of MNA potential
  - Build a model based on today's characterization
  - Calibrate and run prospective scenario

➢ **Need to overcome recurrent problems to insure the model predictions**

- Complex geology & transient flows
- DNAPL heterogeneous distribution
- Numerous NA processes

Framework of the present study

- ATTENA research project (ADEME, 2009-2012)
  - BRGM, INERIS, APESA, TOTAL Petrochemicals, ArcelorMittal Real Estate, RHODIA, BURGEAP → www.attena.org
  - Develop tools, demonstrate, and give a French technical framework for MNA remediation concerning petroleum hydrocarbons, PAHs & chlorinated solvents
  - **BURGEAP = demonstration study on Site 1bis (chlorinated solvents), implementation of the MACAOH protocols**
- MACAOH research project (ADEME, 2001-2006)
  - BURGEAP, IFP, IMFS/IFARE, IMFT
  - Chlorinated solvents = **source characterization**, **NA evaluation** and **modeling**
  - 3 technical guides :

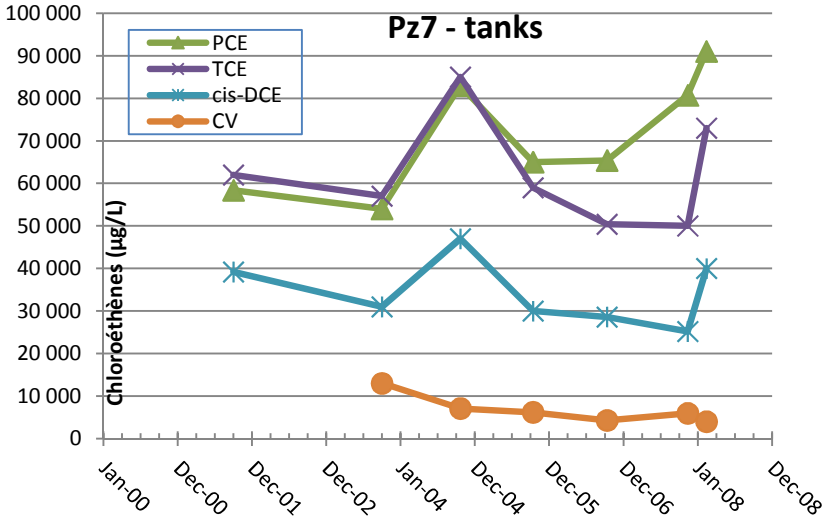




http://www2.ademe.fr/servlet/KBaseShow?sort=-1&cid=96&m=3&catid=10143

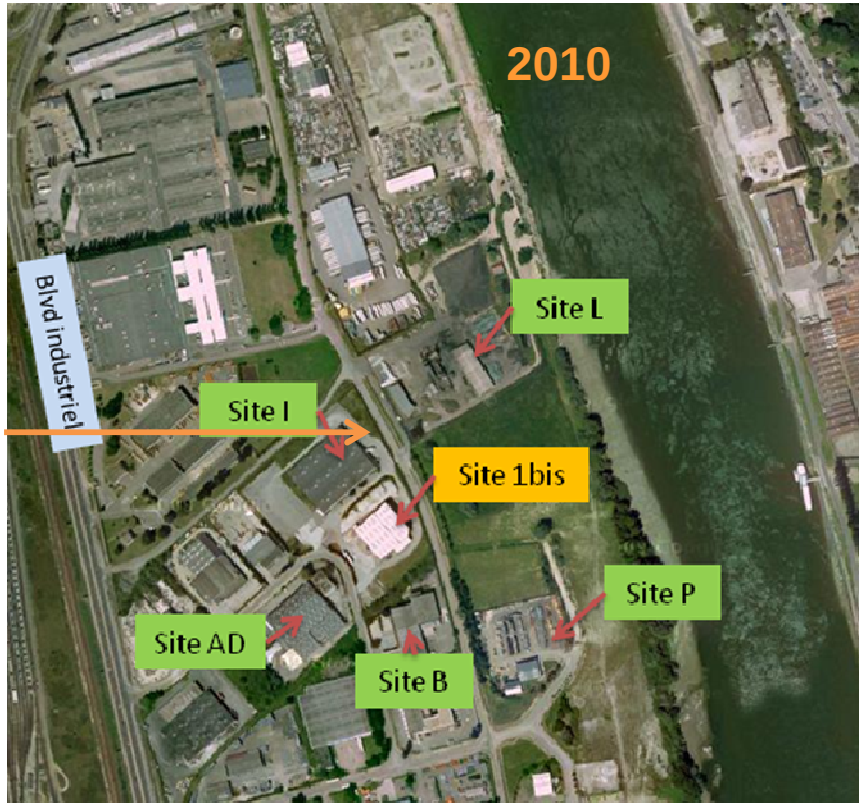
Site 1bis = activity, context, previous data

- Storage facility since 1970 (agricultural lands before)
  - 1970-1988 = above ground tanks = solvants
  - 1970-1997 = building = powders and salts
  - **Spill (mid-80s) = 80m³ (PCE or TCE) from tank-train**

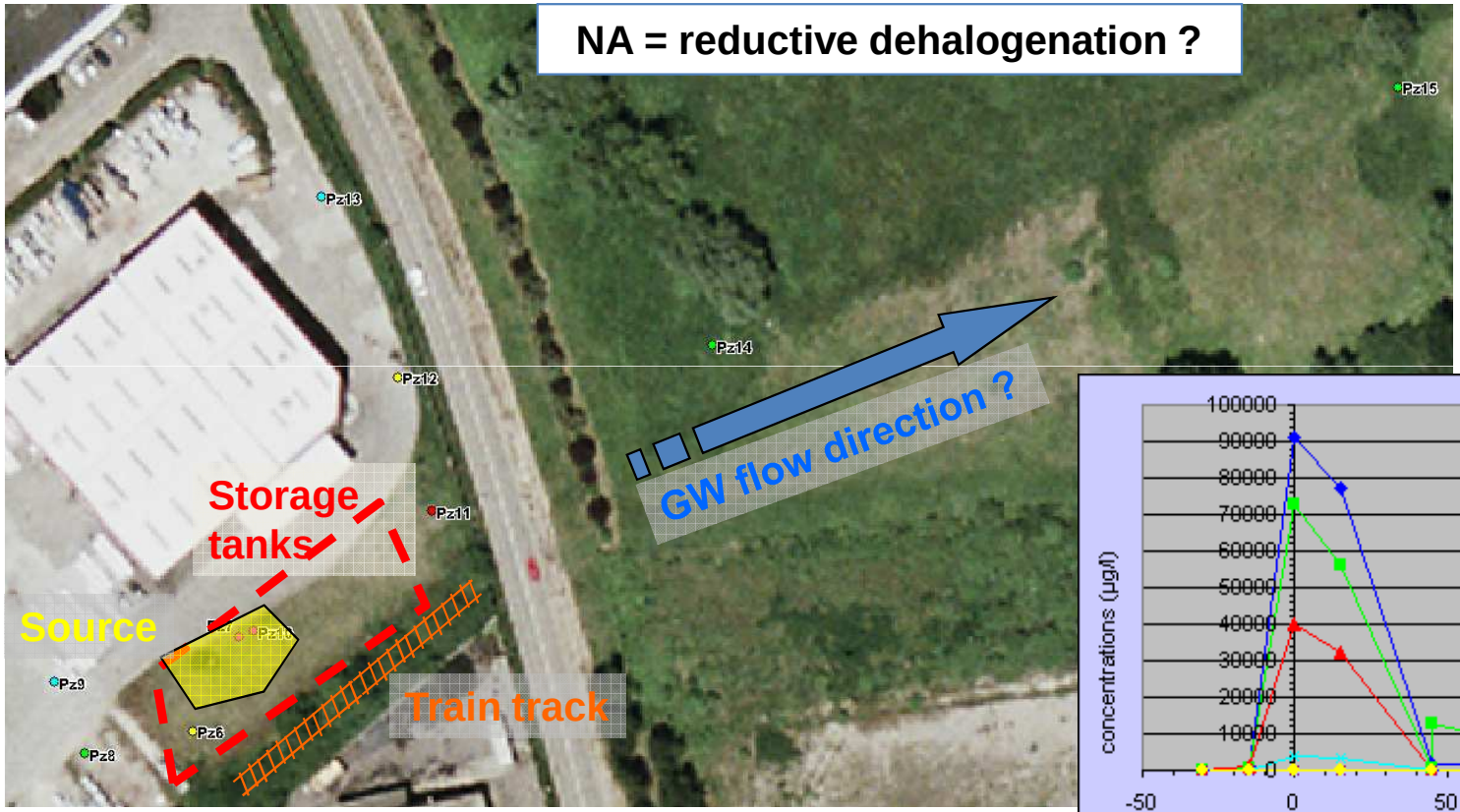
- Previous studies (2000-2008)
  - GW monitoring since 2000 :
    - **Stable concentrations in source zone**

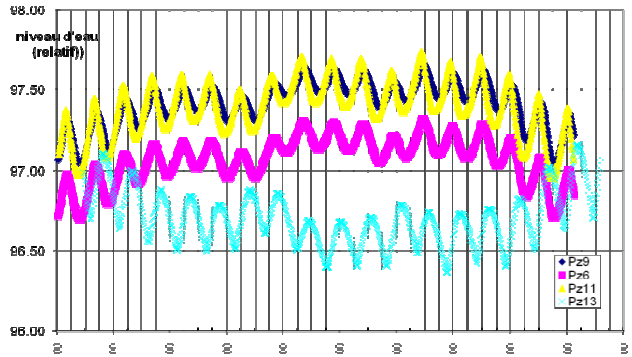


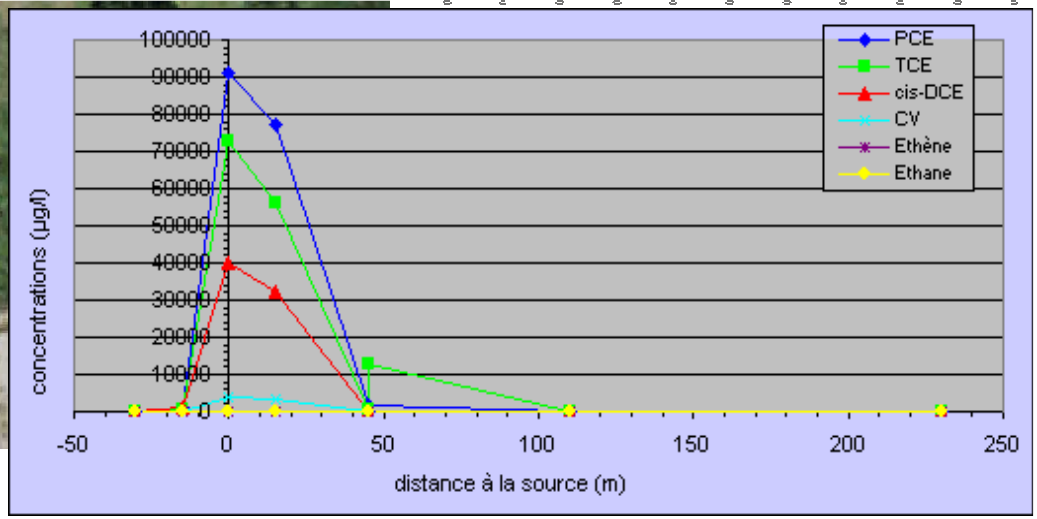
    - Few wells beyond site limits
  - Soils and soil-gas measurements
  - Geology and water table measurements
  - NA parameters measurements in GW

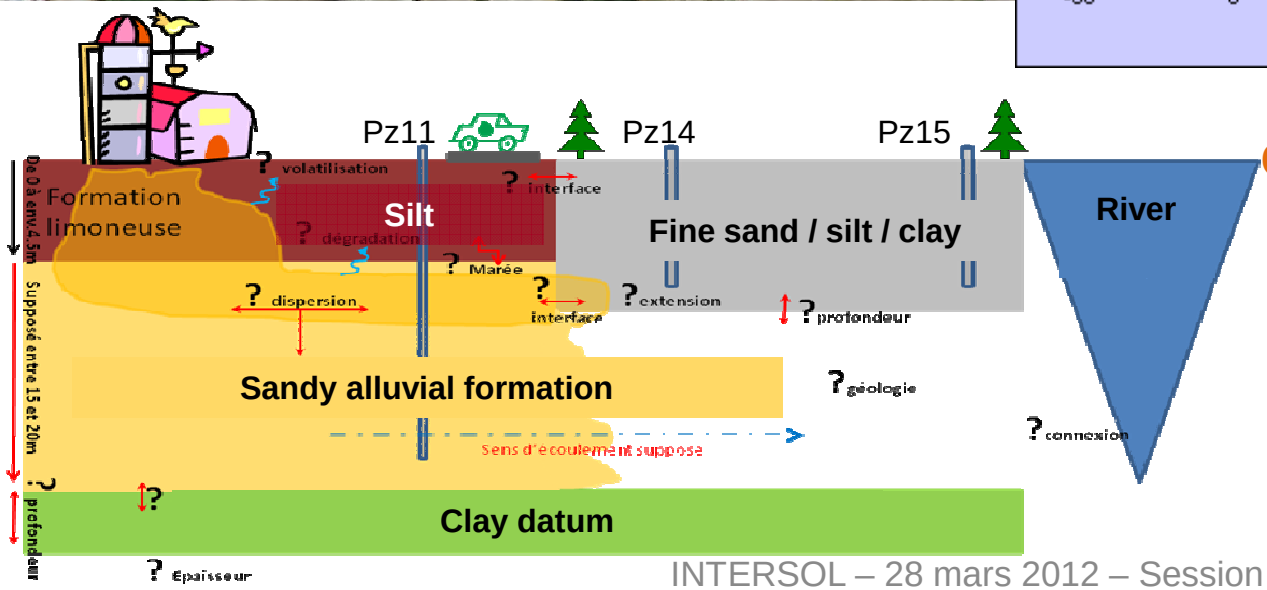


Site 1bis = first assessment







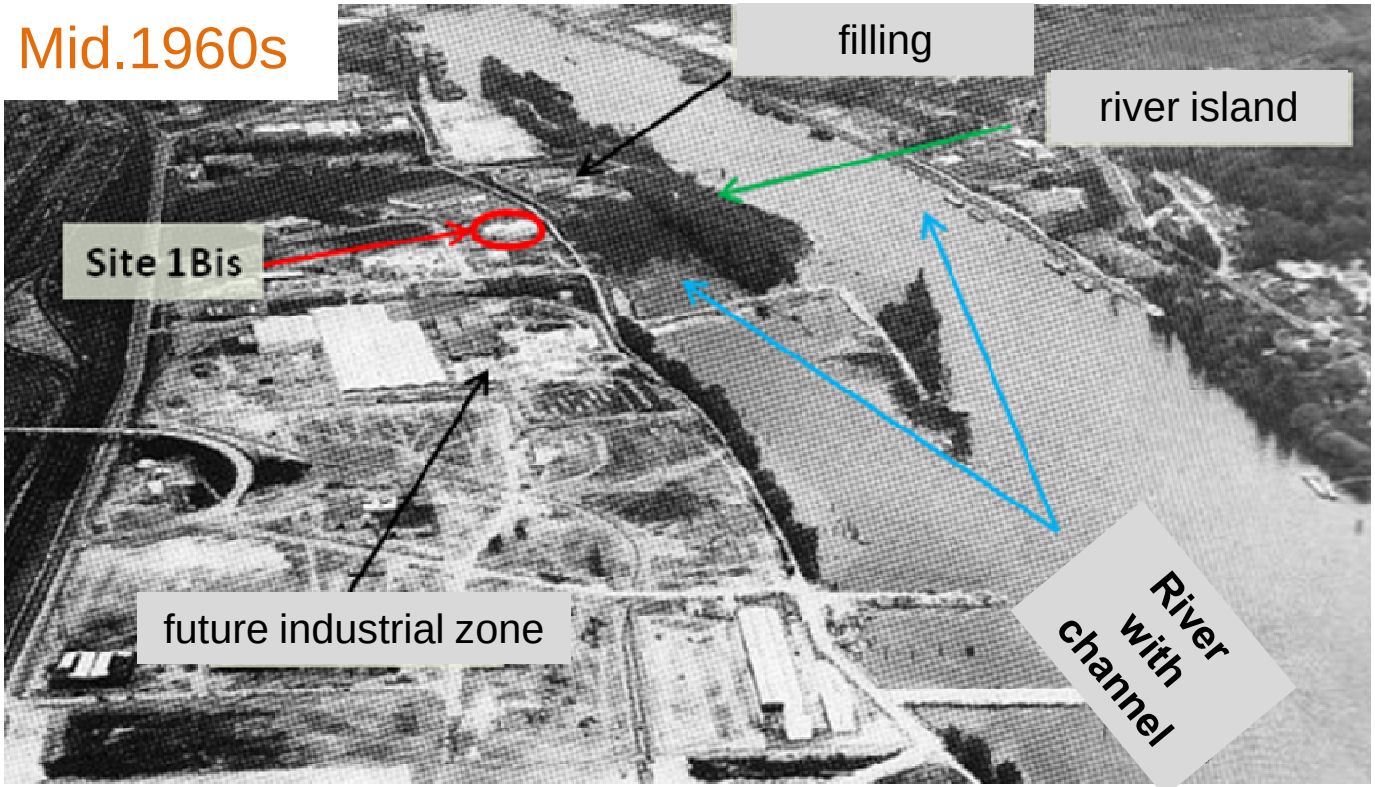


Conceptual model lacks

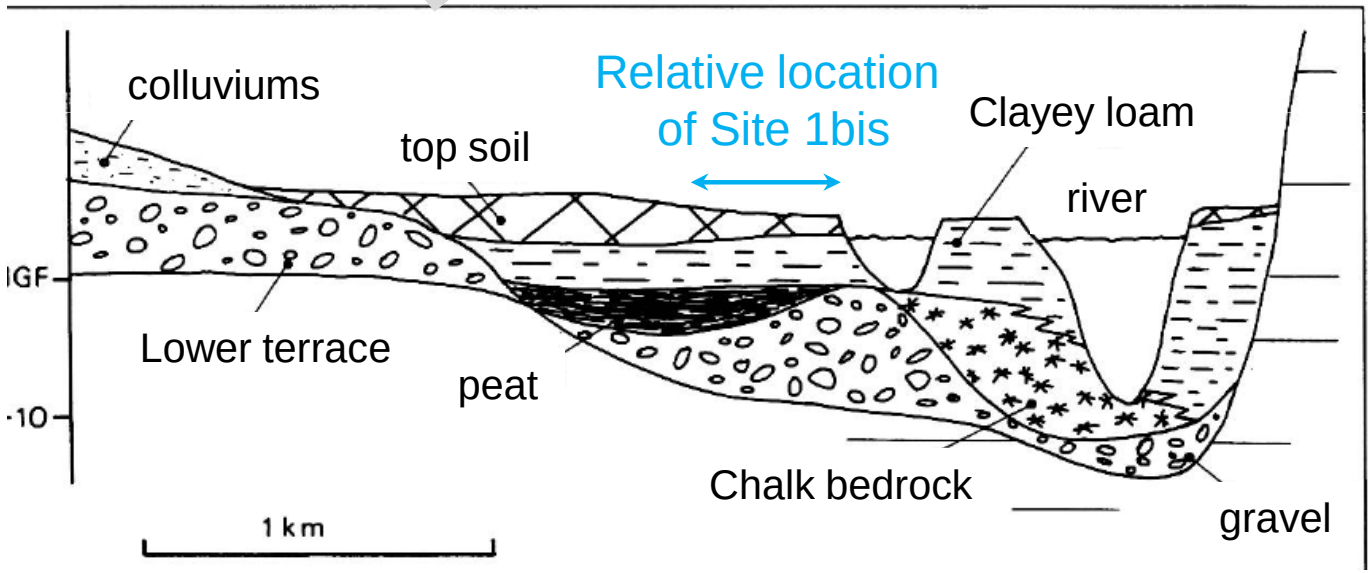
- Lithologies description
- GW flow directions
- GW plumes extension (x, y, z)
- NA processes parameters
- GW / river exchange …

Hydrogeology - update

Mid.1960s



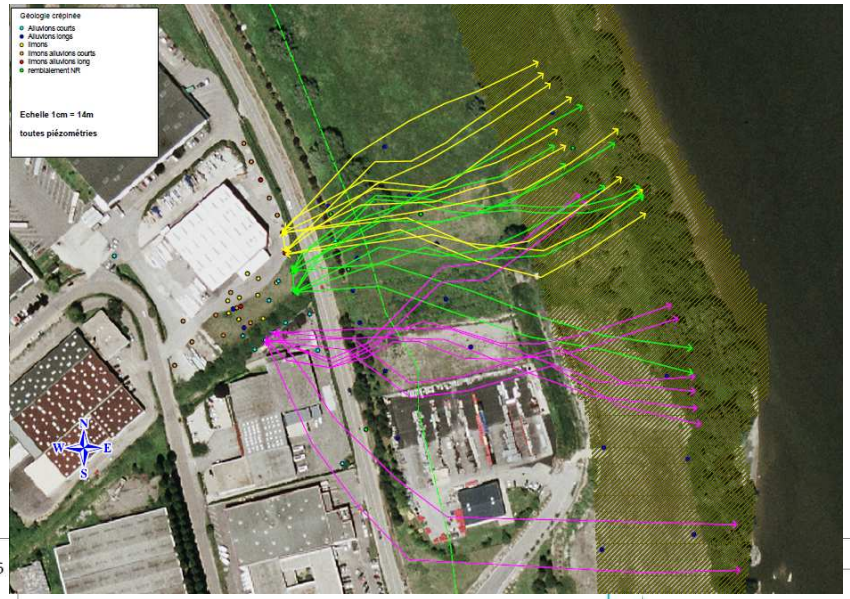
Near location hydrogeological study

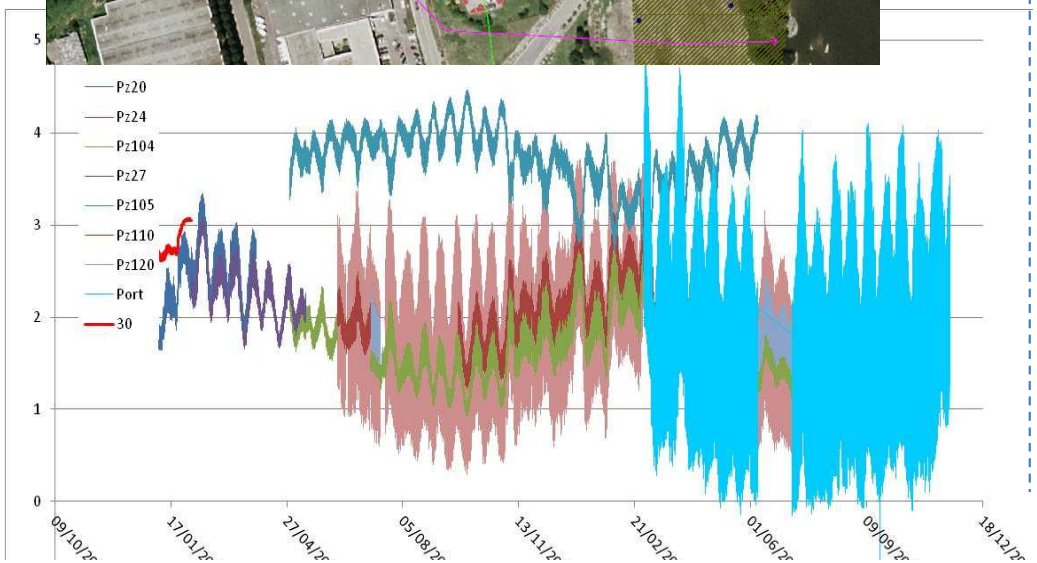


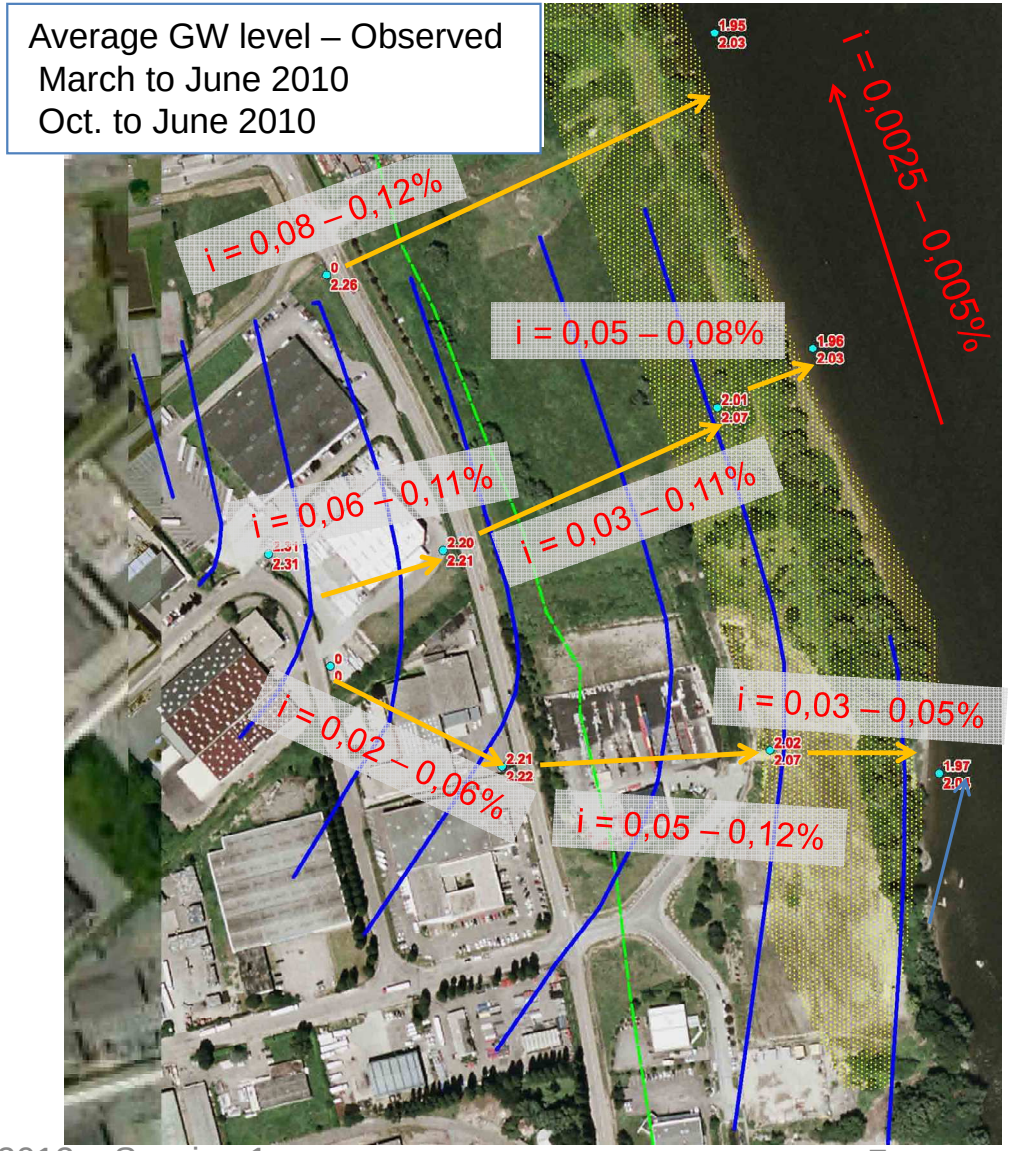
Groundwater flow paths

- Tidal effects
- Changing flow directions
- Reverse flow (25% of the time)

Define a mean GW flow path for the average GW levels







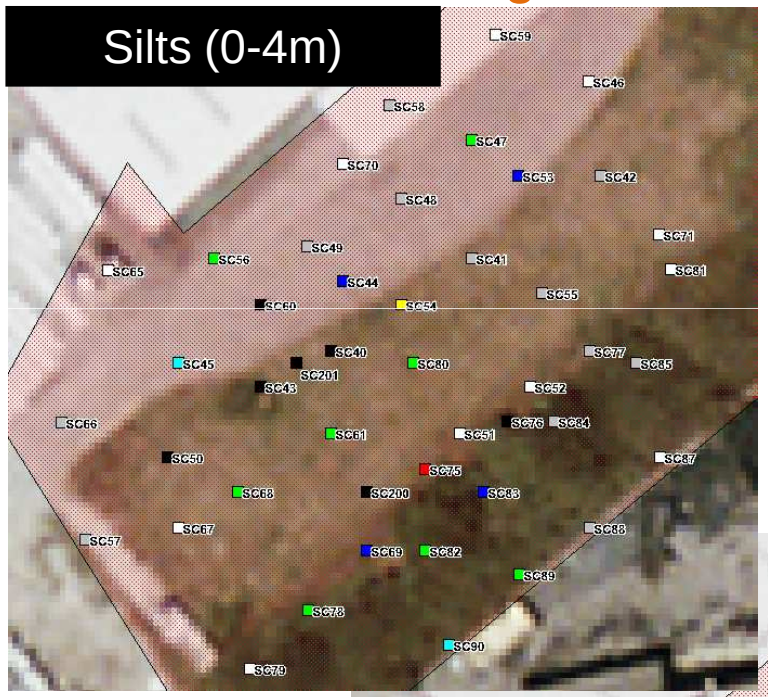
Source characterization (1/2)

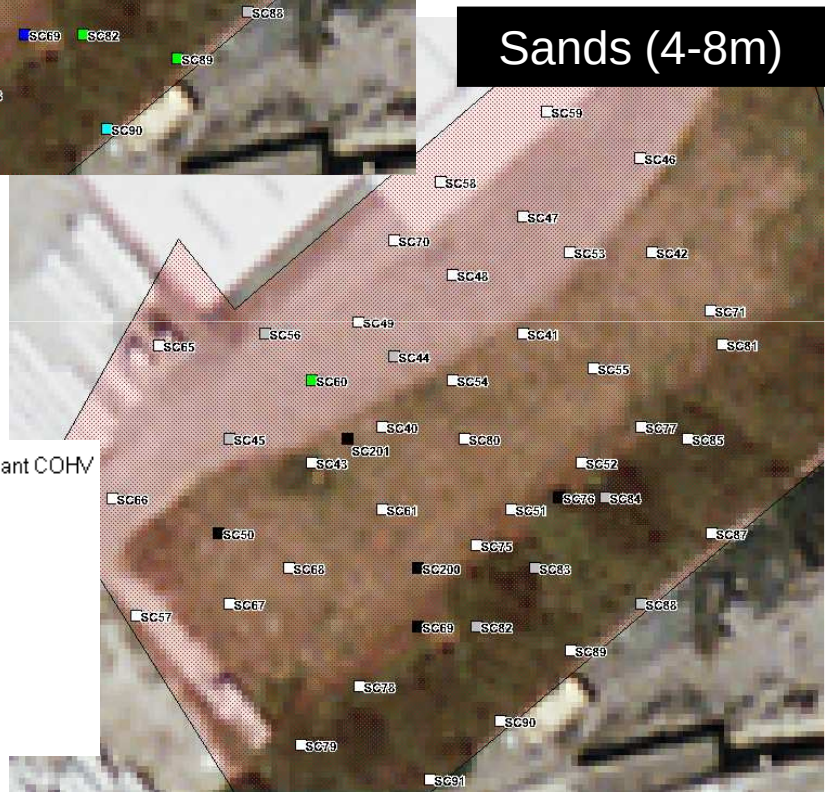
1. Screening: GW concentrations

Octobre 2008: Somme des chloroéthènes

- 100 000 à 280 000µg/l
- 25 000 à 100 000µg/l
- 10 000 à 25 000µg/l
- 1 000 à 10 000µg/l
- 100 à 1 000µg/l
- 10 à 100µg/l
- 1 à 10µg/l
- N.A

2. Boreholes drilling





Sondages carottés: Géologie Sable: polluant COHV

- 1 000 à 12 900mg/kg M.S
- 590 à 1 000mg/kg M.S
- 470 à 590mg/kg M.S
- 360 à 470mg/kg M.S
- 180 à 360mg/kg M.S
- 85 à 180mg/kg M.S
- 40 à 85mg/kg M.S
- 10 à 40mg/kg M.S
- 1 à 10mg/kg M.S
- 0,1 à 1mg/kg M.S
- Non Atteint / <LQ

Source characterization (2/2)

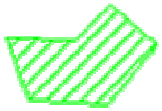
3. Compute NAPL occurrence threshold from soil concentrations (mg/kg DW)

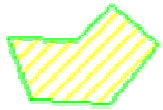
- Equilibrium computation (NAPLANAL®)
- For each soil formation & contaminant

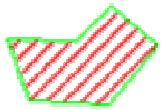
	Silts						
PCE+TCE Molar fraction	**470/671**						
	PCE	TCE					
	94%	6%					
"Kerosene" Molar fraction	**110/140**						
	aroC10/C16	aroC16/C20	aliC8/C10	aliC10/C12	aliC12/C16	aliC16/C35	
	5,7%	0,6%	1,6%	74,0%	16,0%	2,1%	
Cutting oil Molar fraction	**607/822**						
				aliC10/C12	aliC12/C16	aliC16/C35	ali>C35
				0,6%	0,7%	93,0%	5,4%
Porosity	0,35/0,4						
foc	0,01/0,014						
Water content	0,2/0,345						

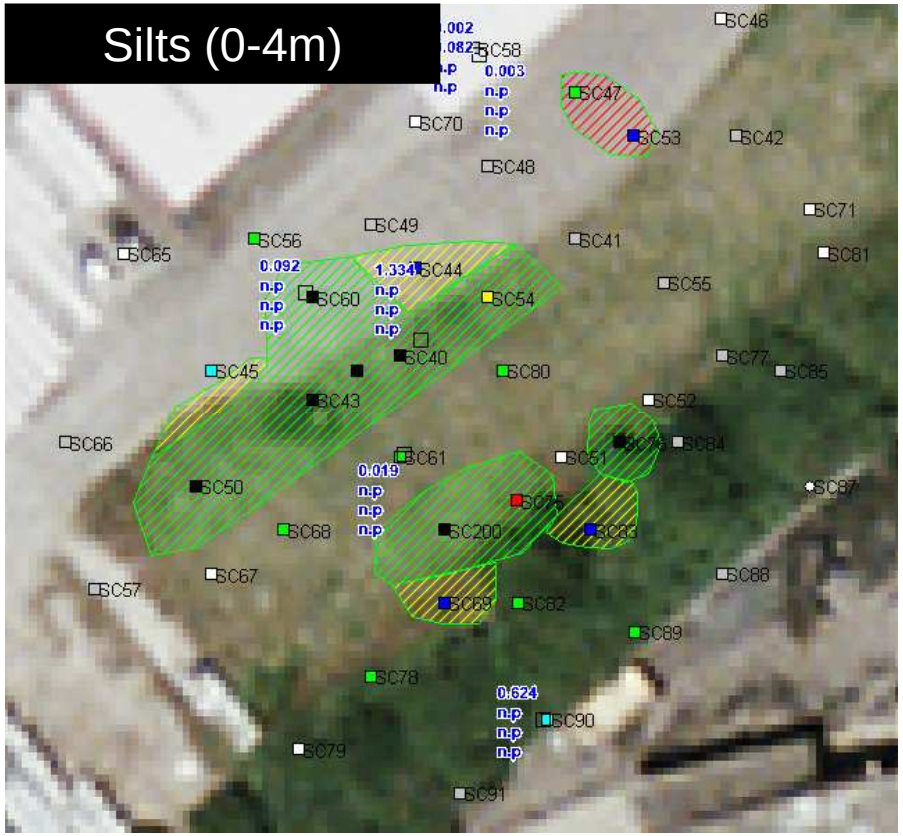
	Sandy alluvial formation				Clay datum	
PCE+TCE Molar fraction	**39/85**				**362/591**	
	PCE	TCE			PCE	TCE
	97%	3%			24%	76%
"Kerosene" Molar fraction						
Cutting oil Molar fraction	**31/61**					
	aliC10/C12	aliC12/C16	aliC16/C35	ali>C35		
	0,6%	0,7%	93,0%	5,4%		
Porosity	0,1				0,15/0,2	
foc	0,00075/0,002				0,003/0,005	
Water content	0,1				0,15/0,2	

4. Delineation of sources and NAPL saturation computation

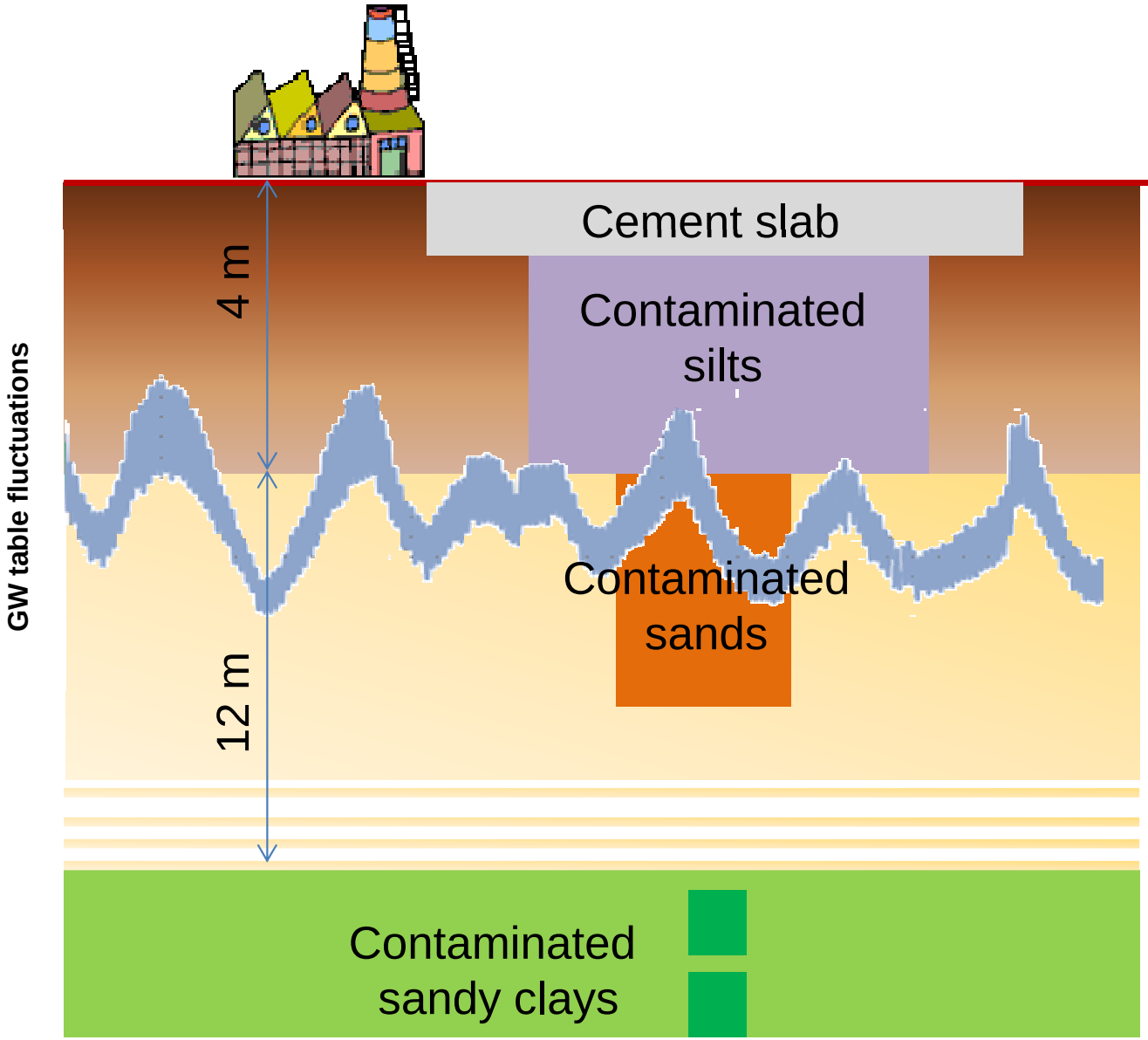

Source zone in silts


Potential source zone in silts


Sand lens



Contaminants mass balance in the source



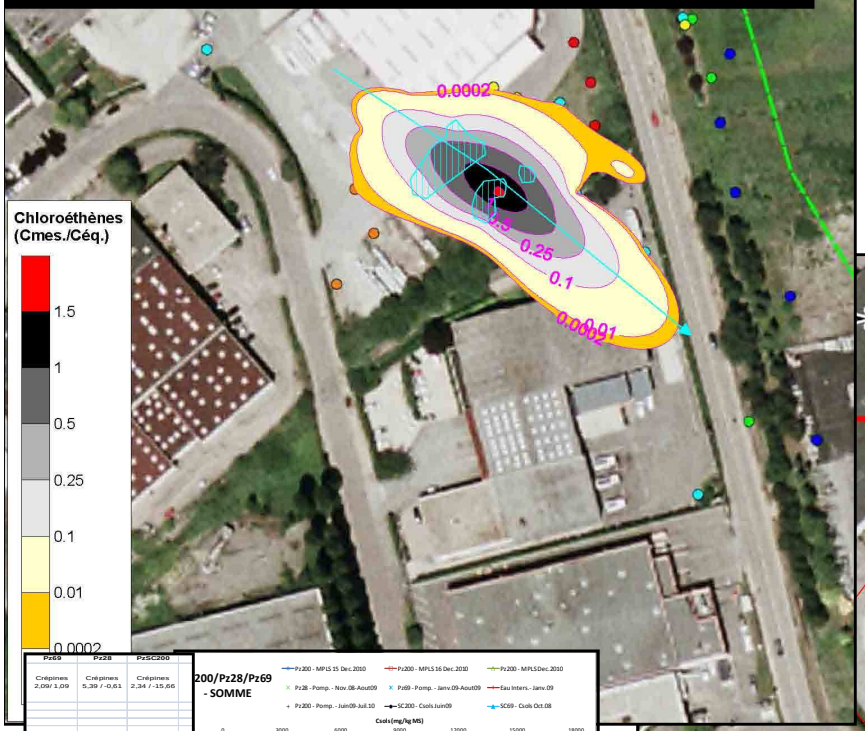
Silts : C11
330 à 410m² contaminated over a 0.2 to 3.2m depth
Cl-VOC : 5 à 20 Tons (240 samples)
Cutting Oil : 0.9 à 1.9 Tons
& "Kerosene" : 100 kg (73 samples)
Cl-Benzenes : 360 kg (48 samples)

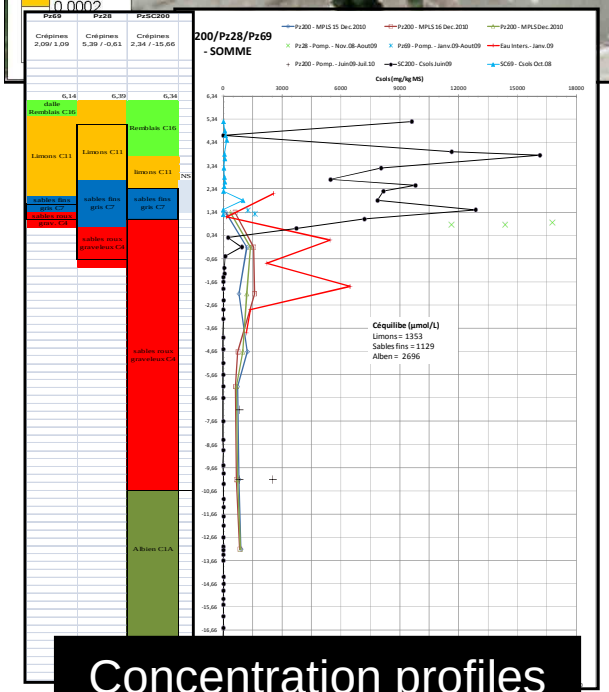
Fine & medium sands : C7
160 à 320m² contaminated over a 3.2 to 4.7m depth
Cl-VOC : 2 à 7 Tons (93 samples)
Cutting Oil : 1 à 2 Tons (52 samples)

Sandy clay : C1A
>10m² contaminated over 7m depth
Cl-VOC > 50 kg (48 samples)

Contaminants plumes - observed

Fine / medium sands (4-8m)





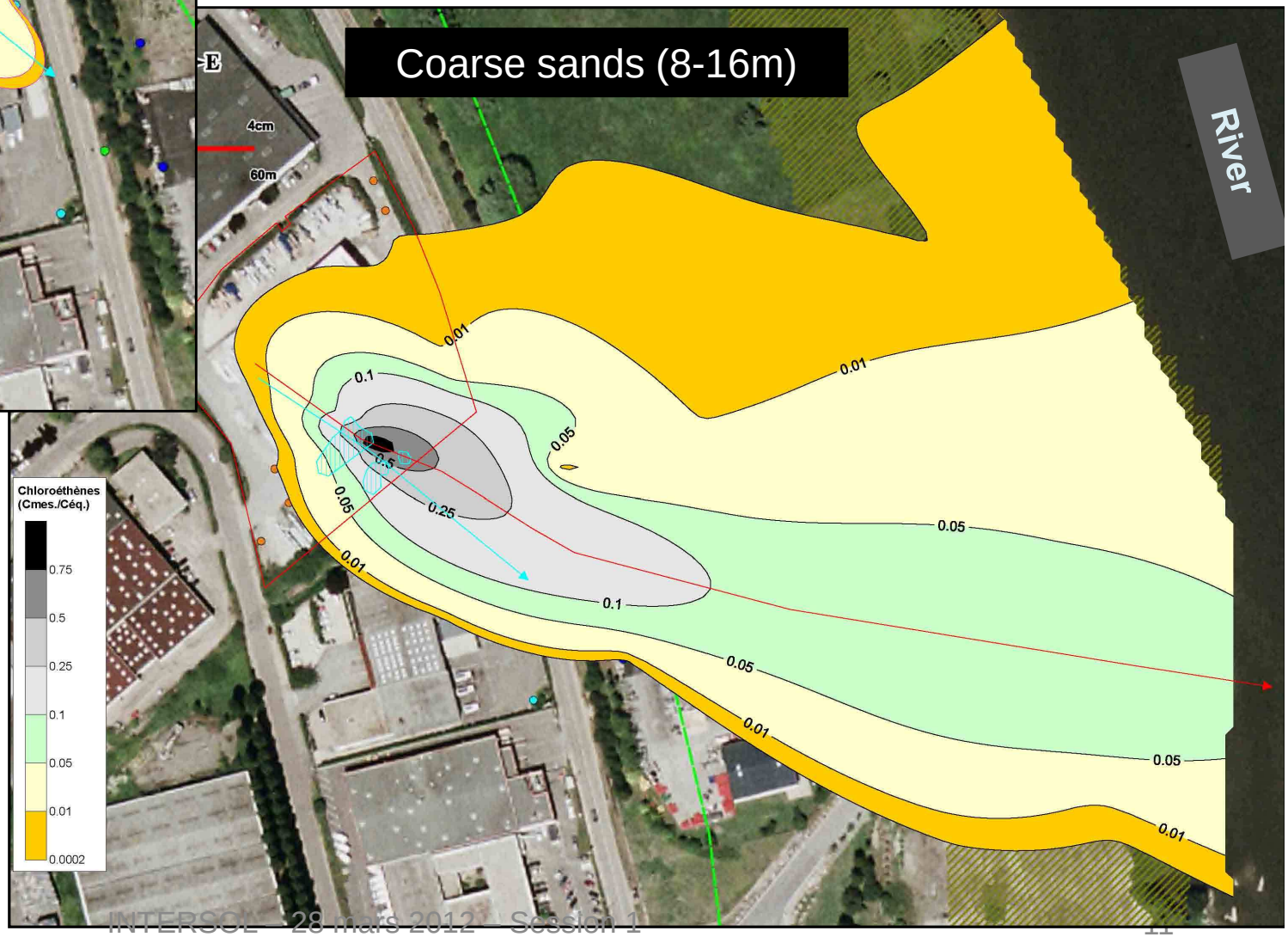
Concentration profiles

Sum of Chloro-ethenes (% equilibrium Conc.)

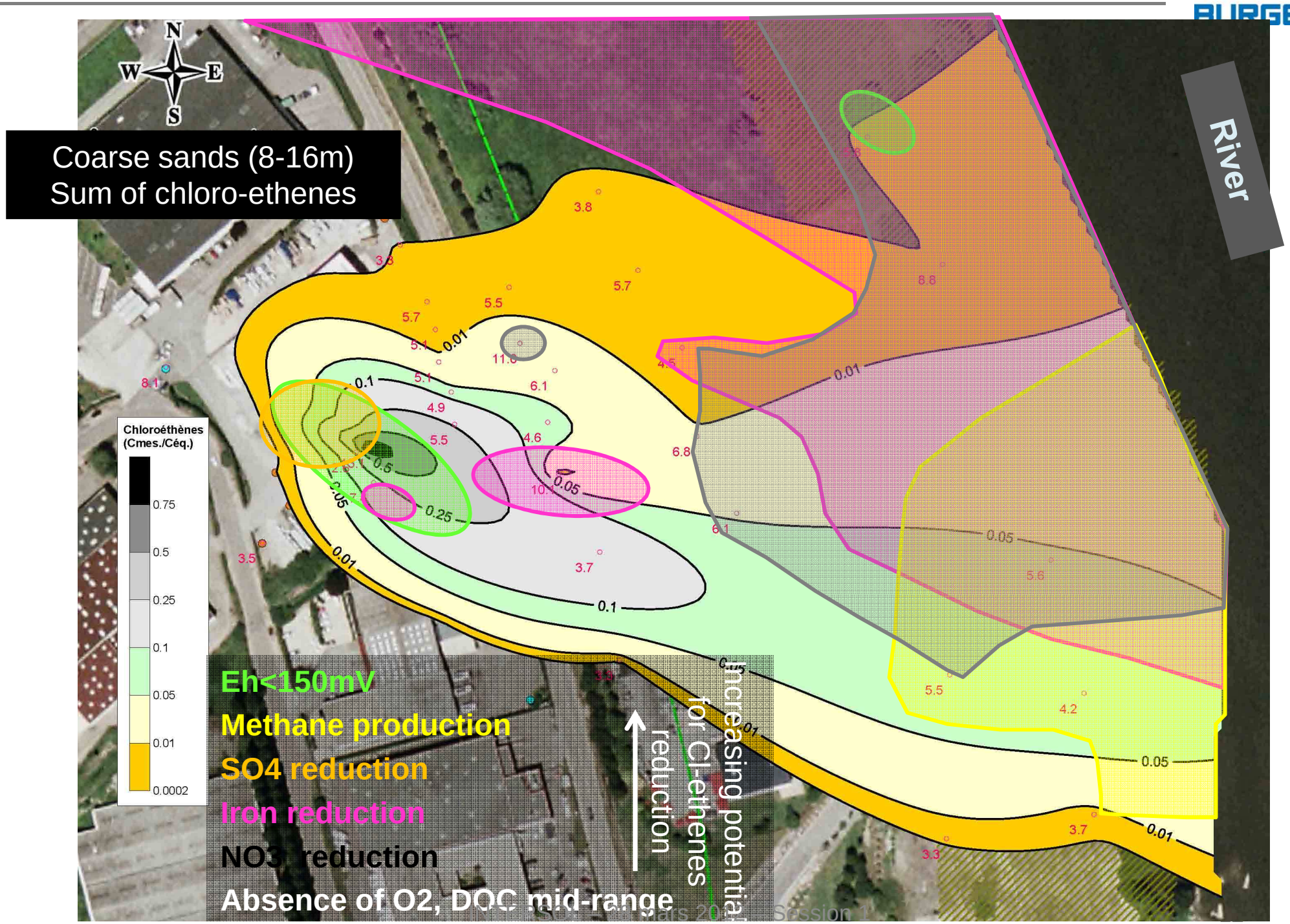
Average conc. over 3-year monitoring period

2-layer plume in sandy alluvial formation

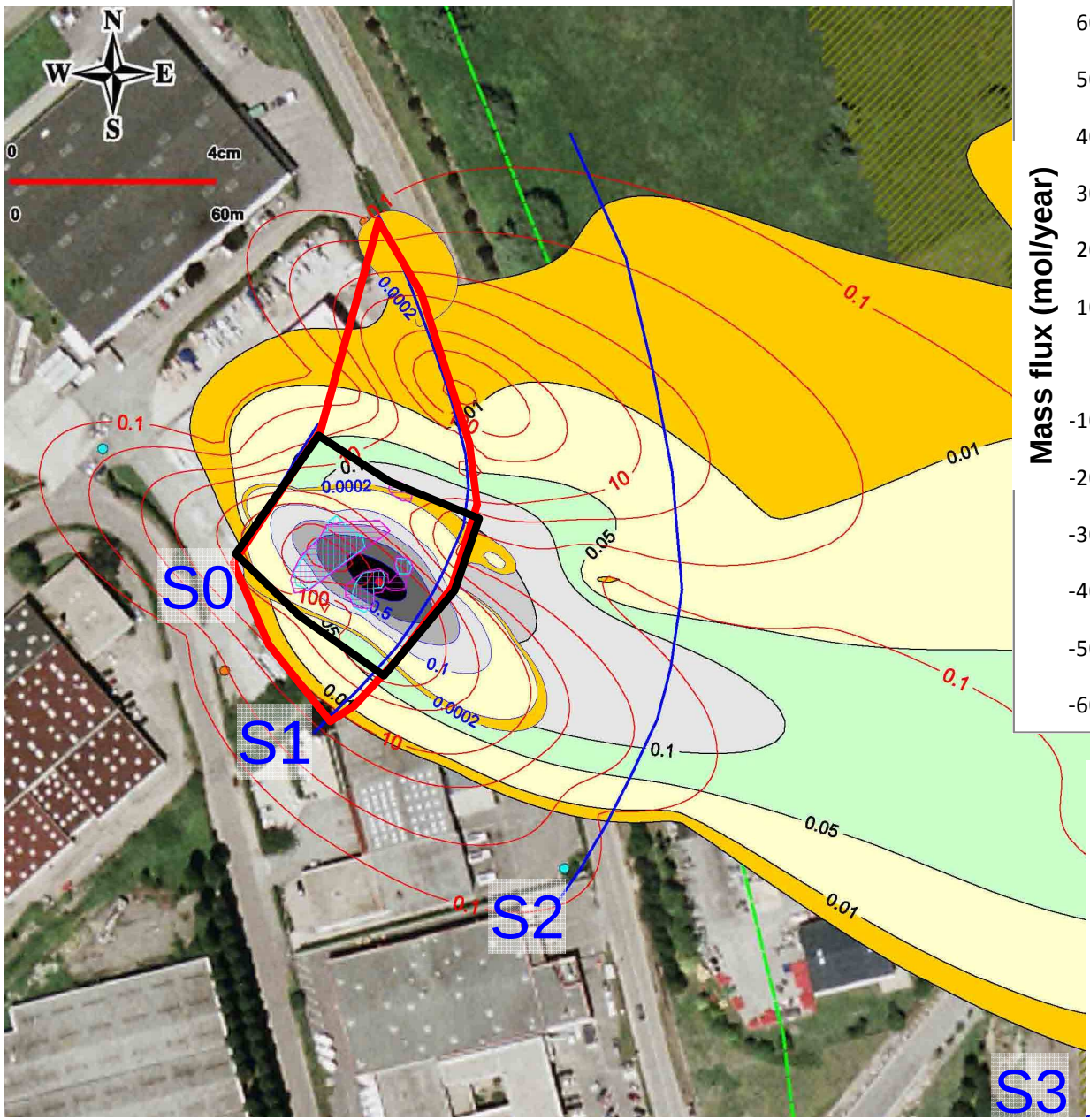
Coarse sands (8-16m)

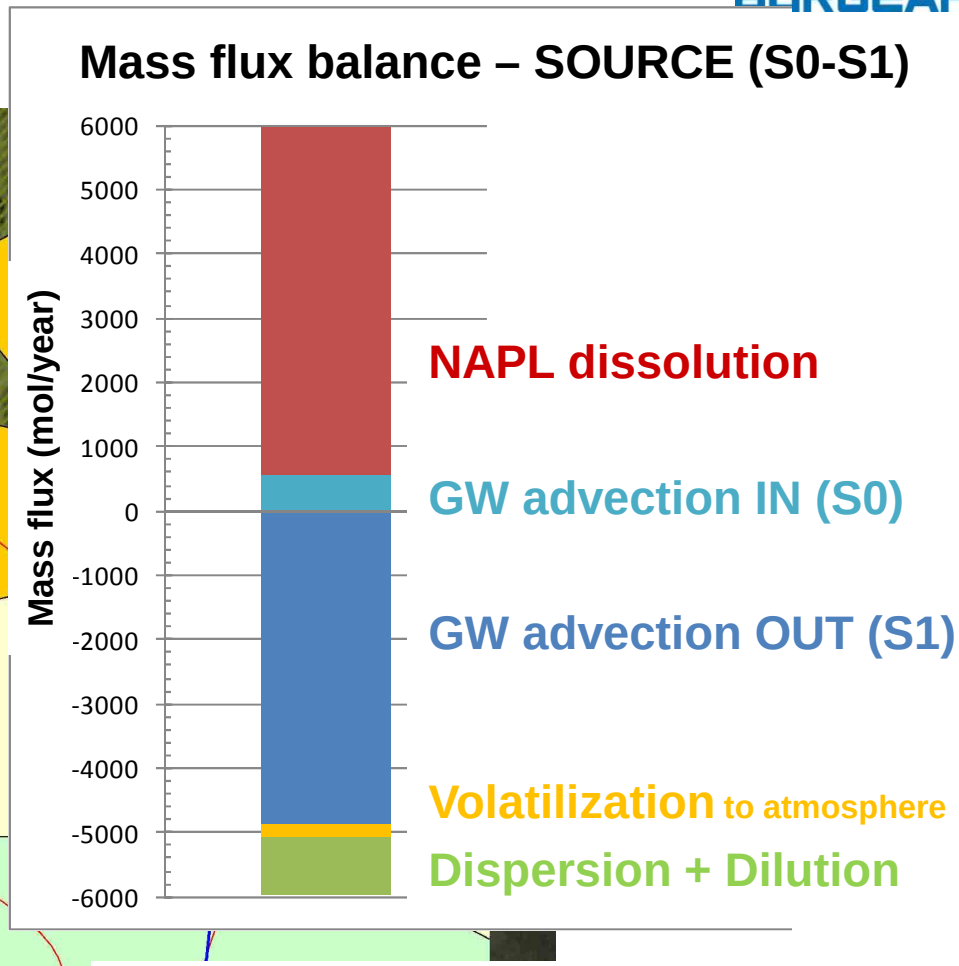


Biodegradation conditions - observed



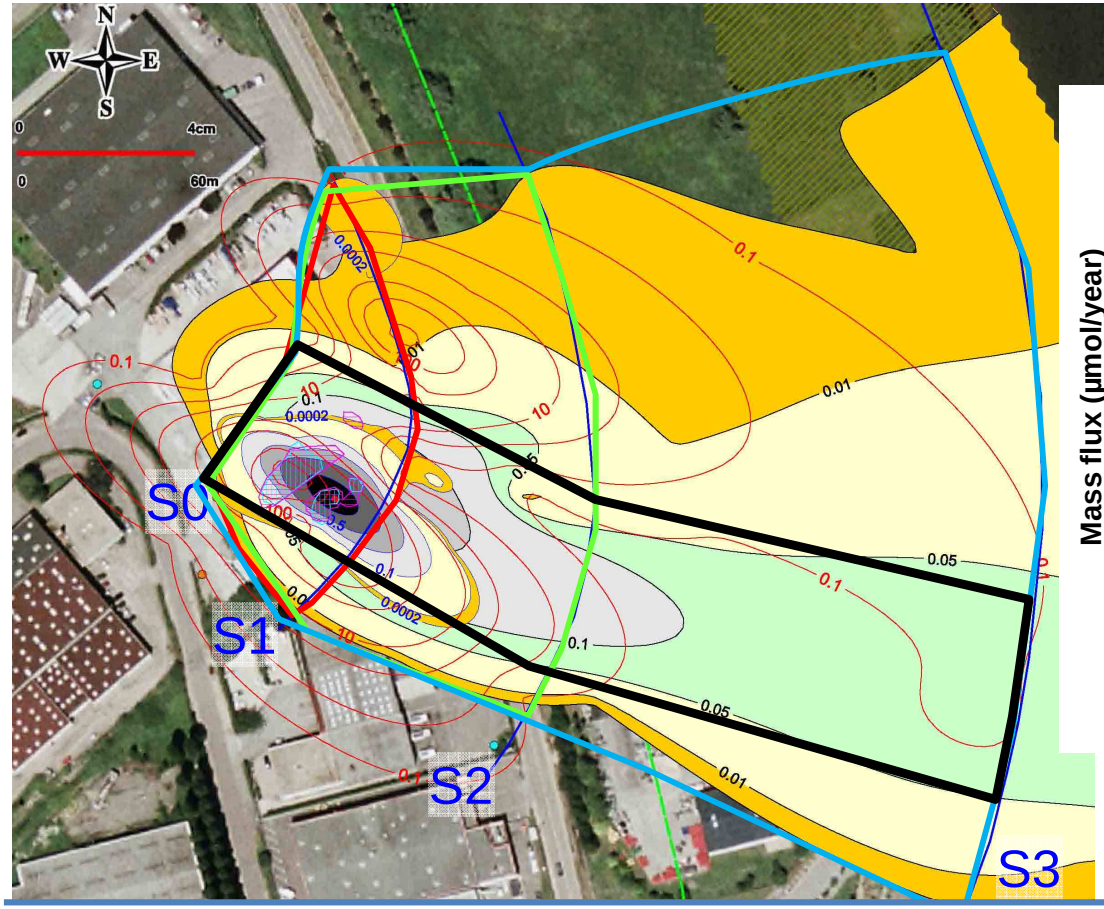
Mass fluxes balance – source zone



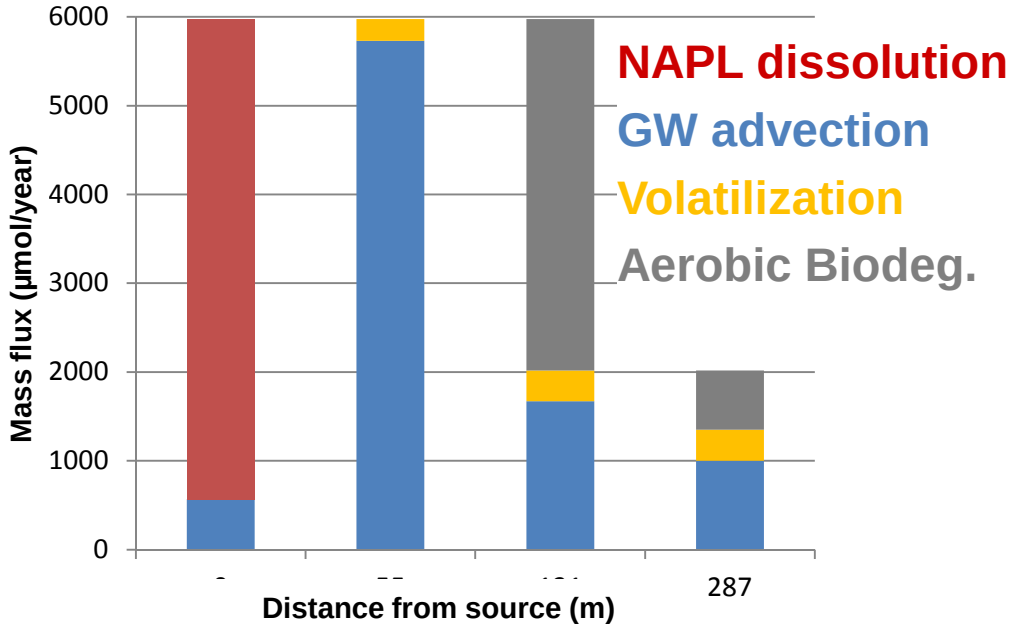


- GAIN : 91% is NAPL dissolution
- LOSS : 15% is Disp.+Dilution
  3% is volatilization
- Supposing no aerobic biodegradation in the total volume (red shape from S0 to S1)

Mass fluxes balance – GW plume

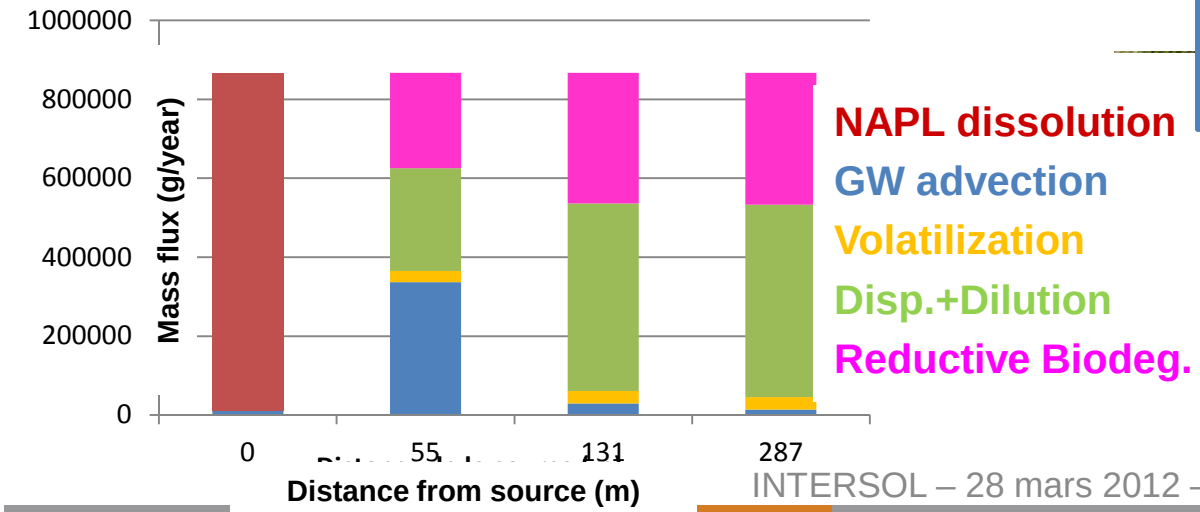


Sum of Chloro-ethenes (µmol/year)



Aerobic biodegradation flux

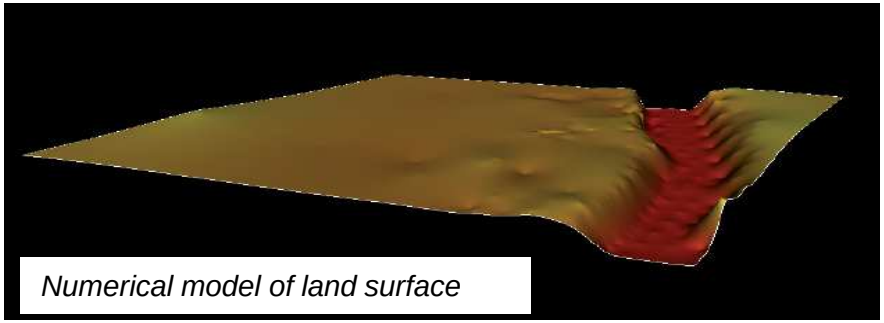
- 66% of IN-flux from x=55m to x=131m
- 11% of IN-flux from x=131m to x=287m



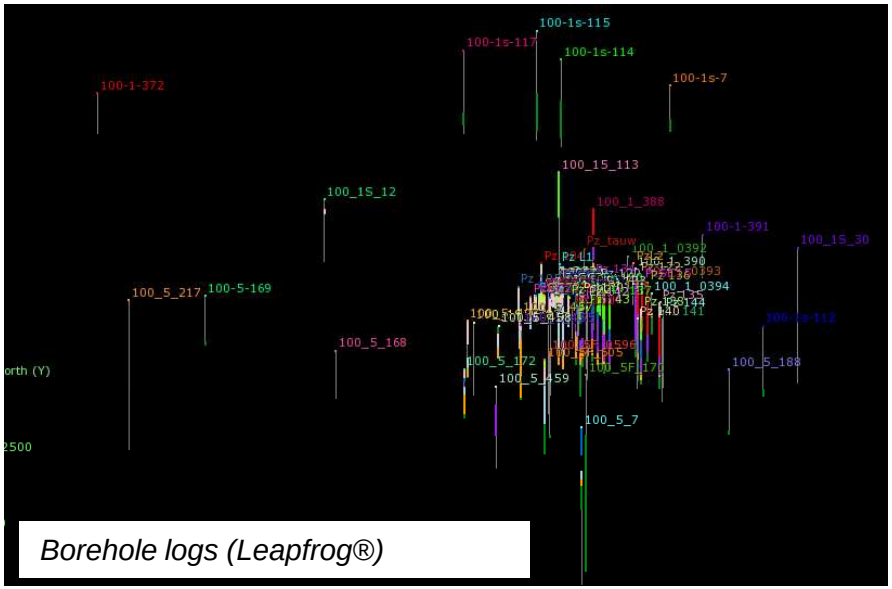
PCE (g/year)

- Anaerobic biodeg. = 25 to 30%
- Disp.+Dilution = 25 to 60%
- Computation of $\lambda_{biodegradation}$

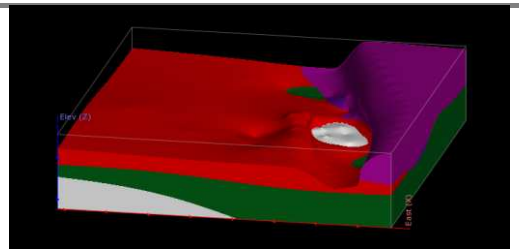
Geological model construction



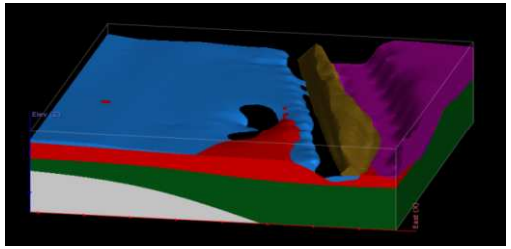
Numerical model of land surface



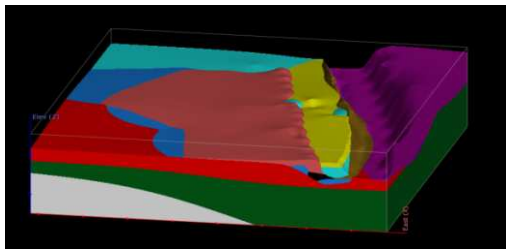
Borehole logs (Leapfrog®)



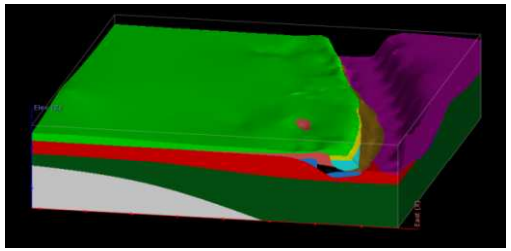
Deposition of C6 (coarse sand)



Erosion after deposition of C8+C9 (peat and clay)

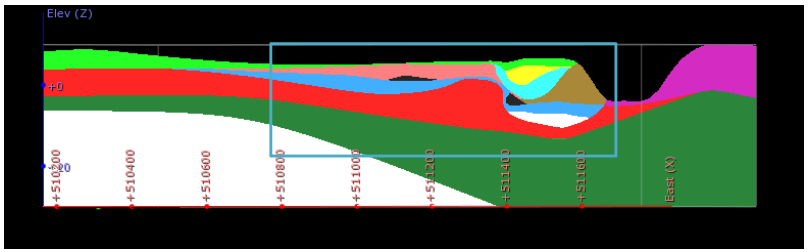


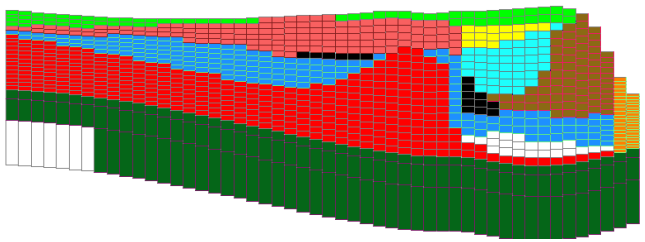
Deposition of C15 (channel fill material)



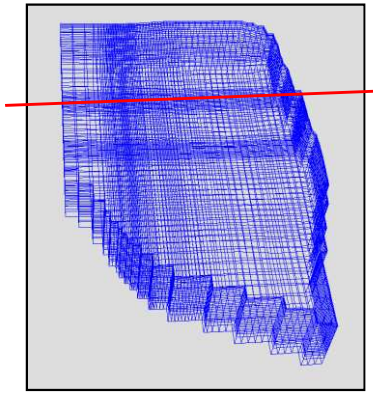
Deposition of C16 (top soil)

FINAL MODEL

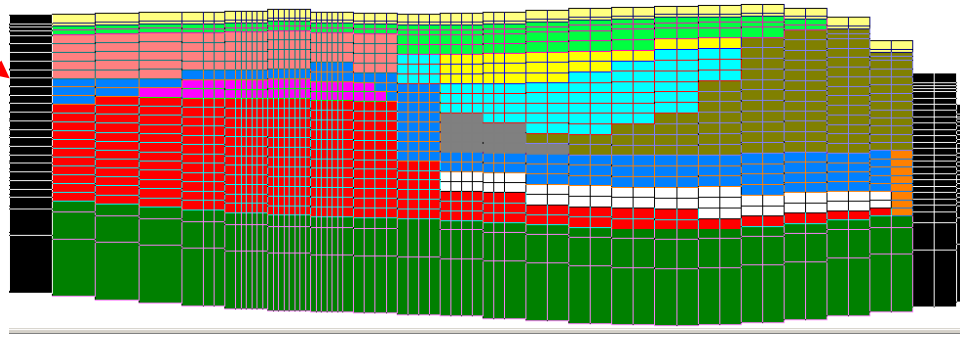




GW flow model (Modflow®)



Grid : horizontal (2.5m to 20m)



Grid : vertical layers

Atmosphere = 2 layers (25 & 75 cm)

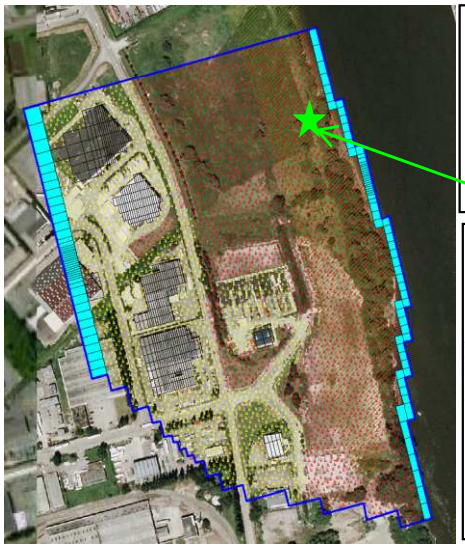
Aquifer = 21 layers (80cm)

Datum = 3 layers of sandy clays (1m, 2.5m, 5m)

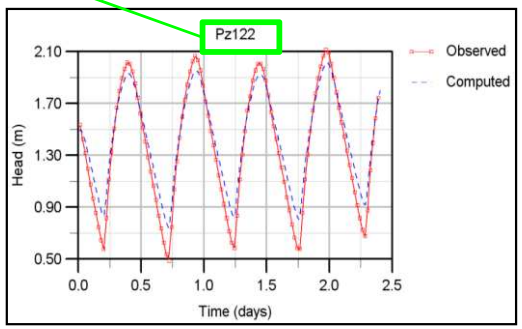
Total of ~ 92300 grid blocks

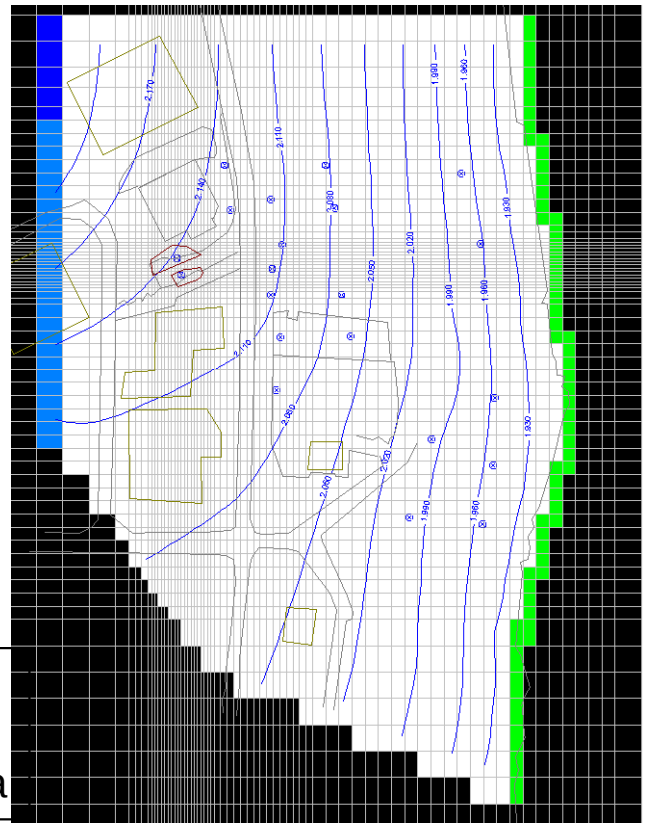
K values from field tests

formation	nb mesures	centile 10	médiane	centile 90
C4	39	3,8E-04	2,4E-03	1,7E-02
C6	6	3,5E-04	1,6E-03	6,8E-03
C7	10	4,2E-05	1,9E-04	2,0E-03
C9	1		6,8E-06	
C11	4	7,5E-06	1,4E-05	3,6E-05
C13/C15	2	7,3E-05	7,6E-05	7,9E-05
C15	1		8,6E-05	



Recharge = 300 mm/year
Fixed heads = up- & down-gradient
River conductance = model calibration to tidal fluctuations (Pz122)



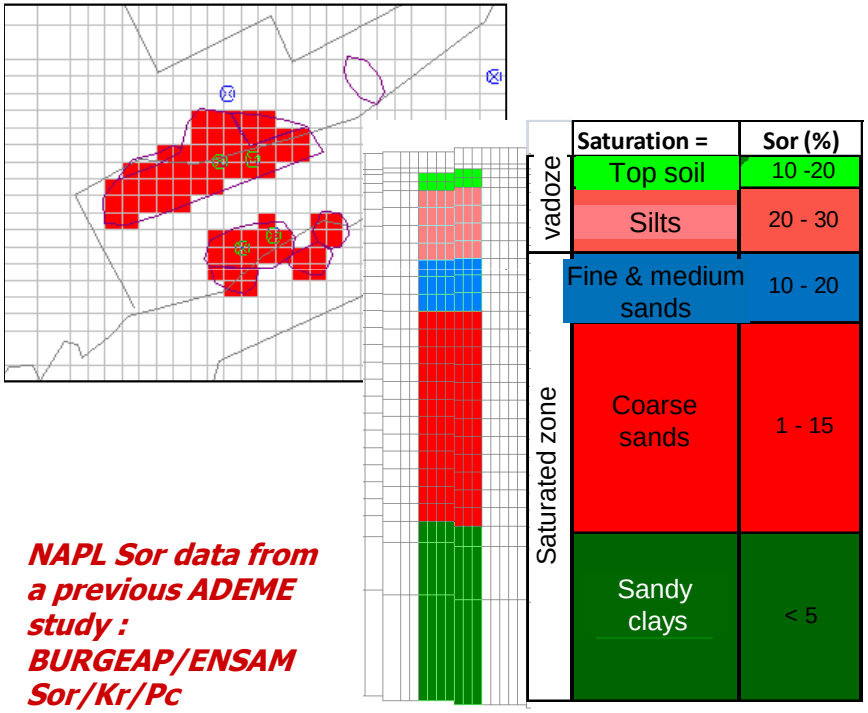


Average steady state flow fitted to observed data

Contaminants fate model (SURFACT®)

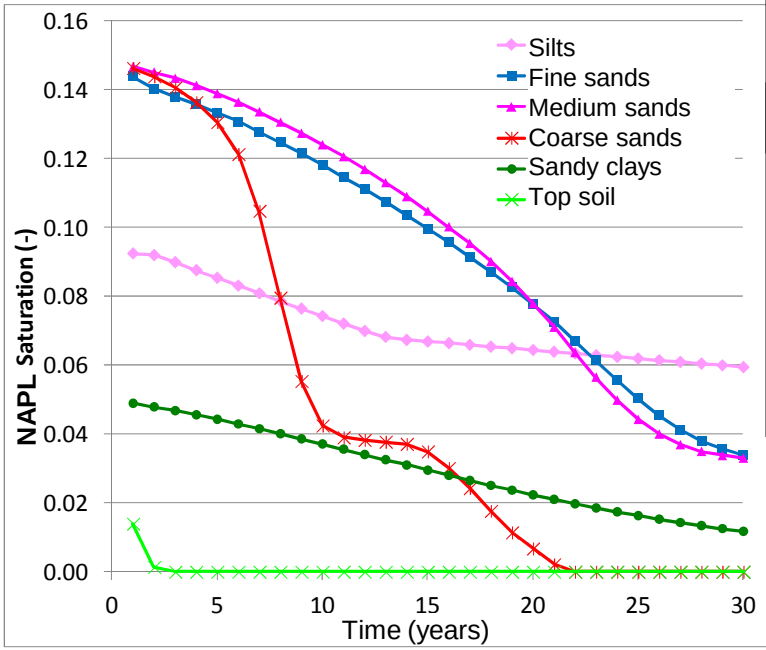
- Source = NAPL (PCE/TCE)
- Modeled plumes : PCE, TCE, cis-DCE, VC & Chloride
- Transport model : advection + dispersion in GW, diffusion in gas (vadoze zone & atmosphere)
- Phases mass transfers at equilibrium (NAPL dissolution & volatilization)
- Linear adsorption
- 1st order biodegradation (anaerobic / aerobic zones)

SOURCE Initial state (t0 ~ 1980)

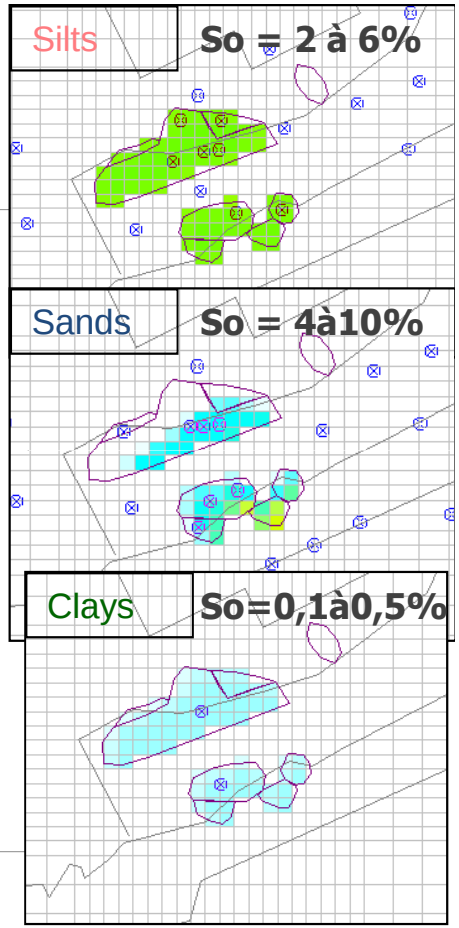


NAPL Sor data from a previous ADEME study : BURGEAP/ENSAM Sor/Kr/Pc

SOURCE Fitted state (t0 + 30 years ~2010)

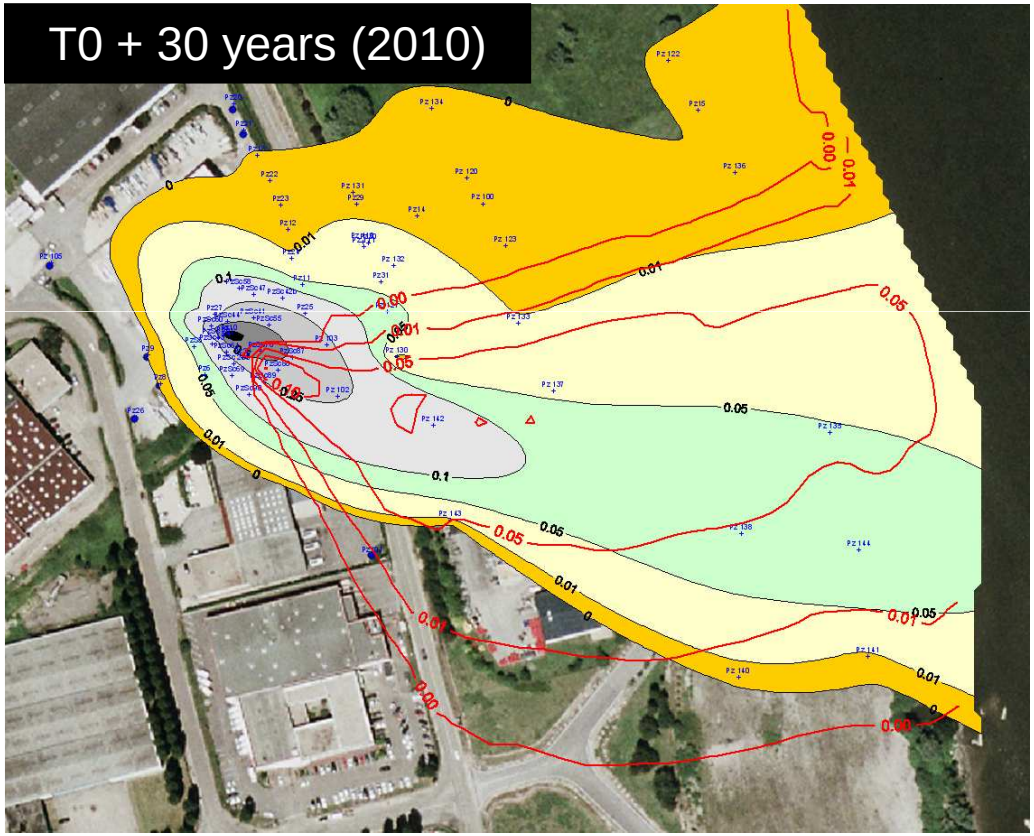


NAPL saturations observed



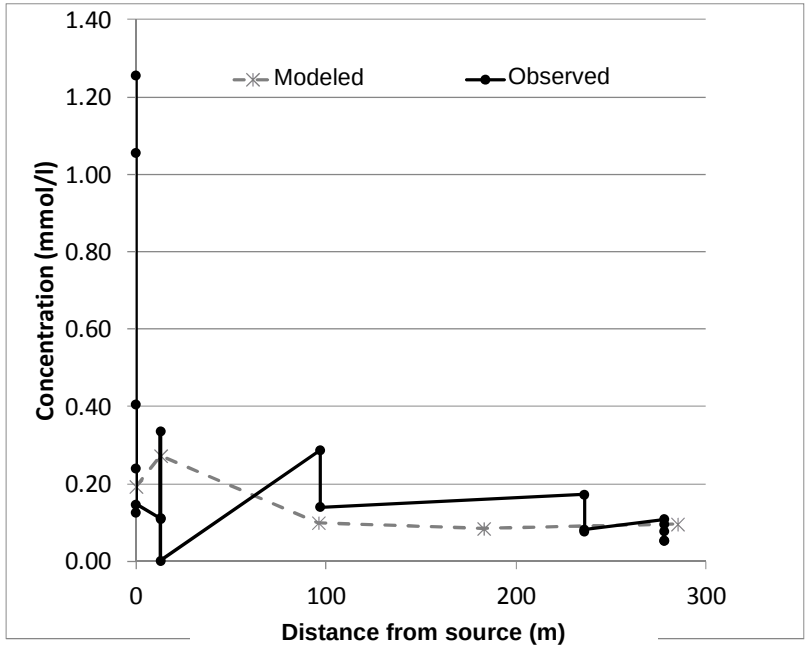
Contaminants model : calibration

Sum of chloro-ethenes (% equilibrium concentration) in coarse sands



PLUME Fitted state (t0 + 30 years ~ 2010)

Sum of chloro-ethenes (mmol/L)

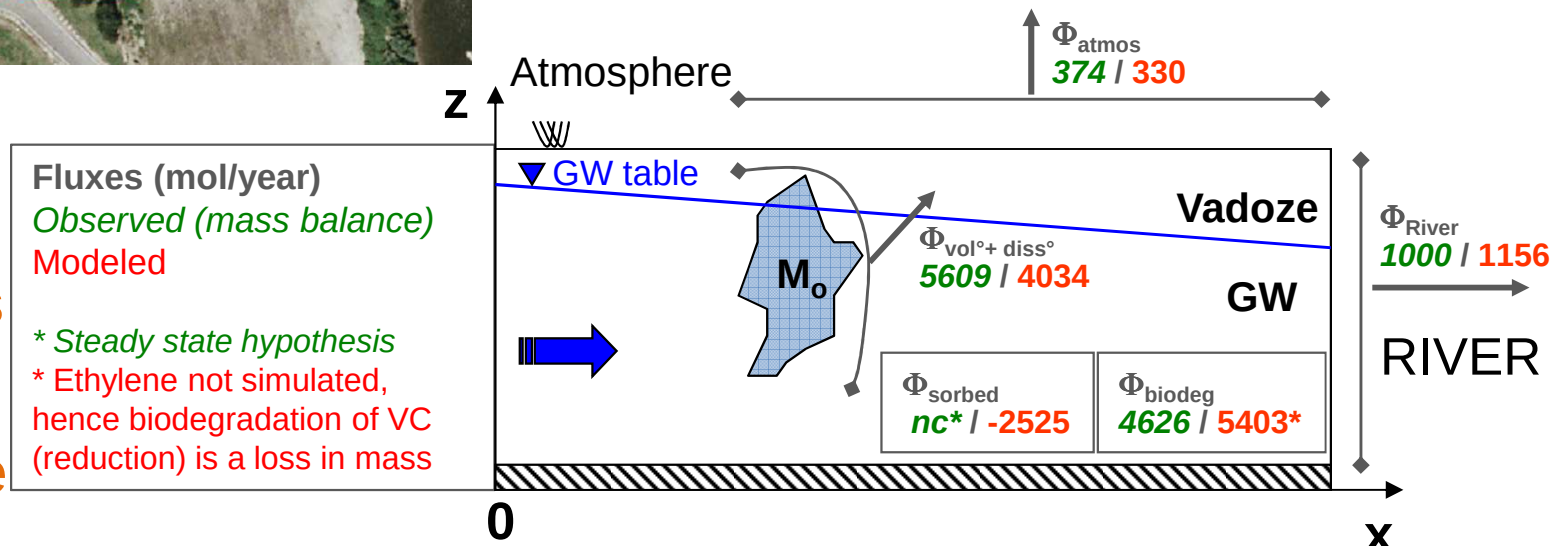


Good agreement in both

- GW concentrations

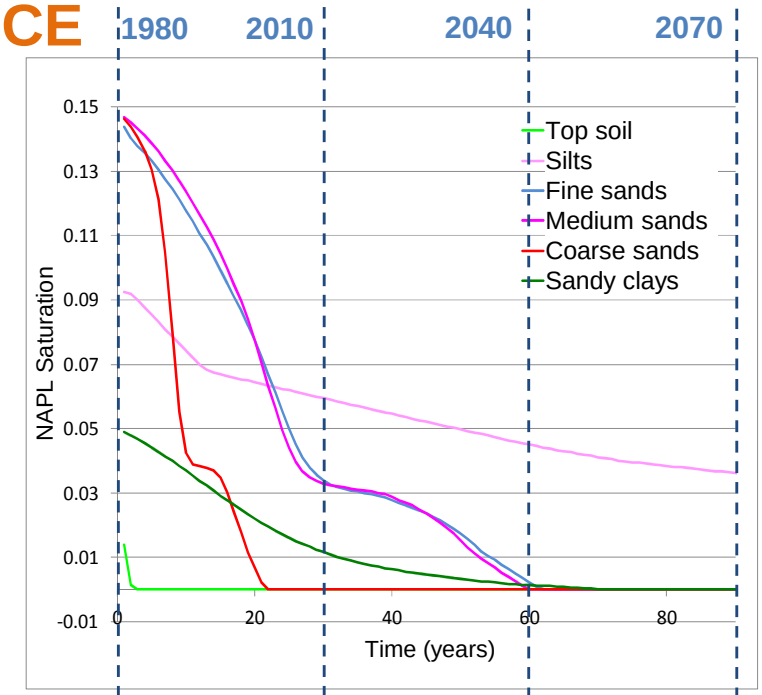
&

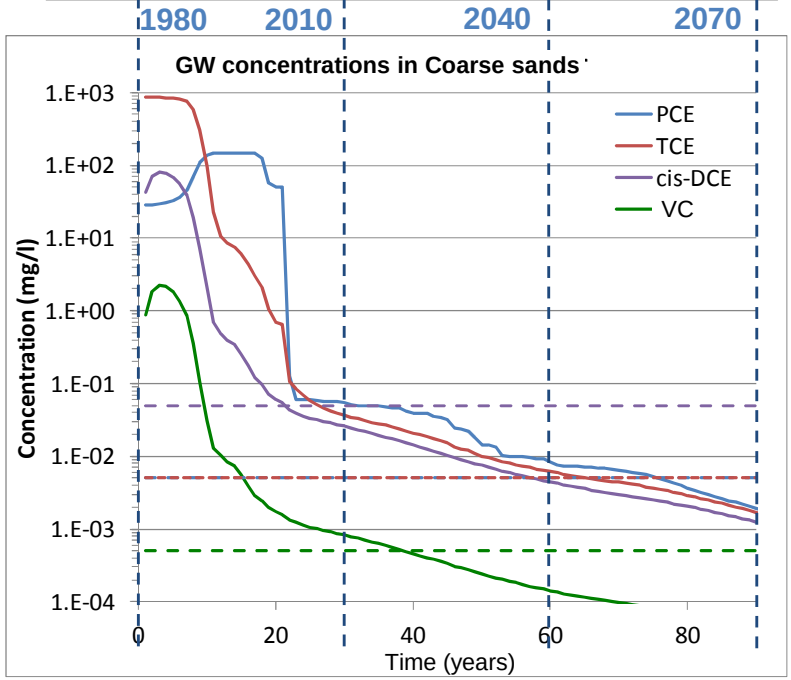
- overall flux balance



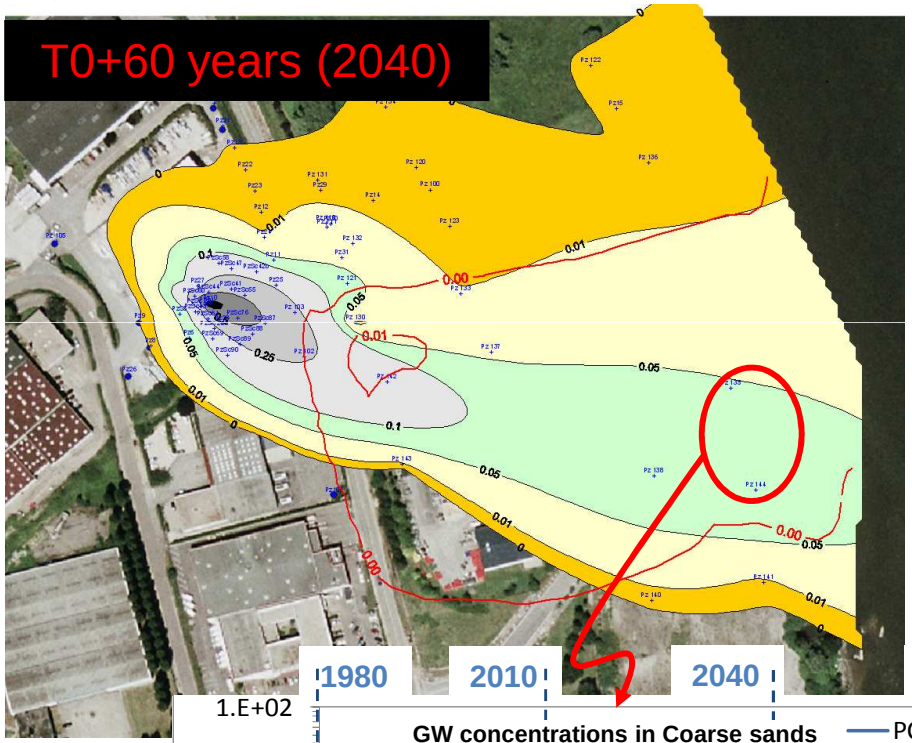
Contaminants model : MNA prediction

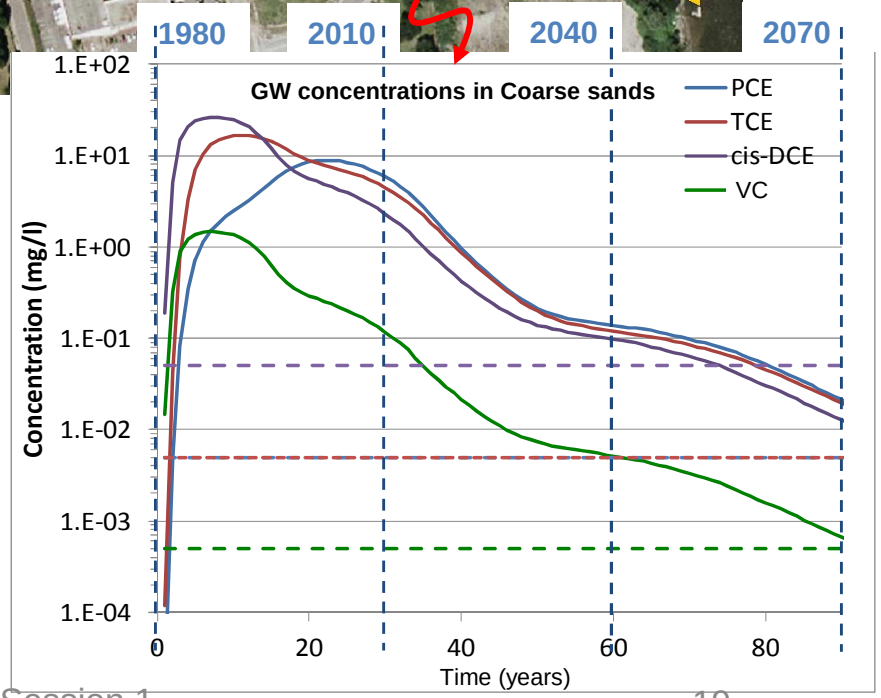
SOURCE





PLUME





Conclusions

- Today (2010)
  - Source = ~17 tons of NAPL (PCE / TCE) in silts / fine & medium sands / clay

    Dissolution is the main NA process
  - Multi-layer aquifer + transient flows
  - Plumes = Concentrations >> MCLs

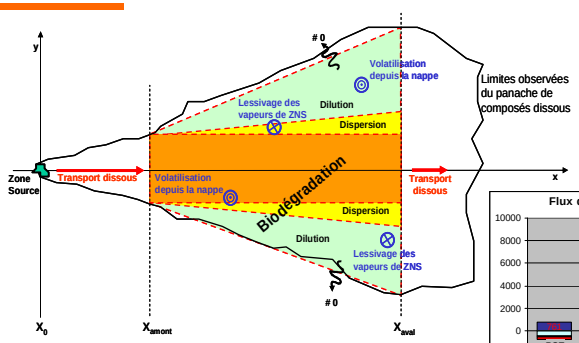
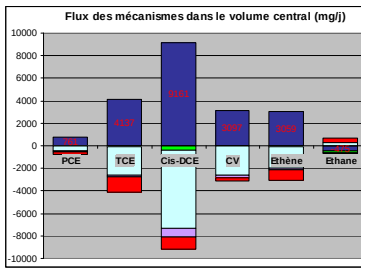
    Biodegradation & Dispersion+Dilution are the main NA processes
- In 30 years from now
  - Source = ~10 tons of NAPL in silts only
  - Plume concentrations in coarse sands (main alluvial formation)
    - On site (near source) ≤ MCLs
    - **Downstream (near river) >> MCLs** **PCE+TCE # 200 µg/L, MCL = 10µg/L**
- Remediation plan
  - **MNA does not achieve MCL within 30 years near River (neither within 60 years)**
  - REMEDIATION (evaluation stage not yet complete)
    - Source = 0 to 8 m depth, excavation and / or ZVI soil mixing -> lab & field pilots
    - Plume = MNA after source treatment ? -> 1st evaluation with numerical model

Acknowledgements

- J. Chastanet, T. Gleize and J.-M. Côme, BURGEAP
- ADEME
- P. Renard, University of Neuchâtel / CHYN
- G. Verreydt, VITO

Thank you for your attention

- **Available soon : <u>mass flux evaluation software</u>**

  great analytical tool for

  - quantification of NA processes
  - 1st estimation of numerical model parameters