Natural attenuation of contaminants in aquifer

Advanced Environmental Technology
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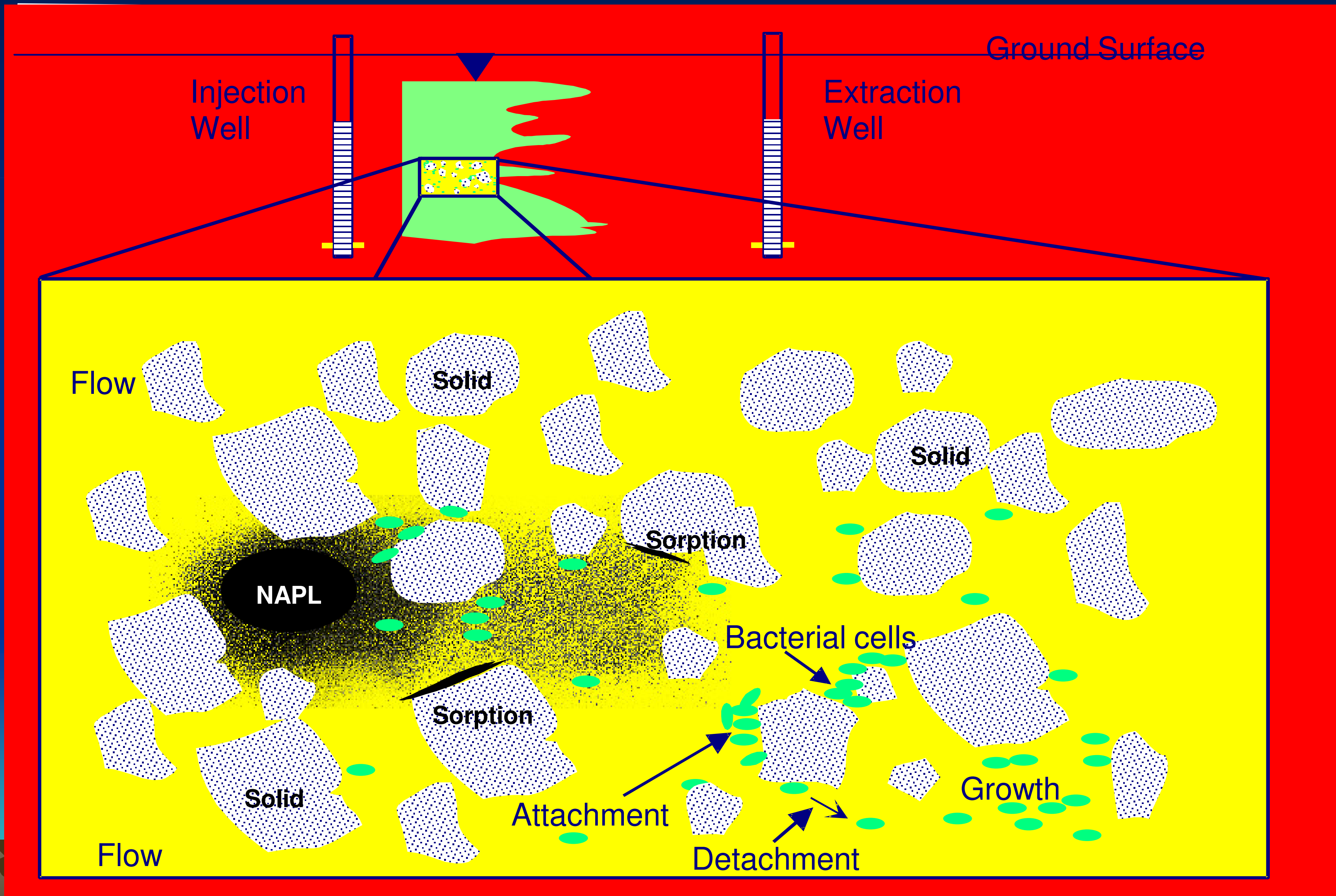
Theoretical Part

Processes that can be Modeled with RT3D



- Natural attenuation of contaminants in aquifers relay on natural processes to achieve remediation goals in a time frame that is approximate to other more active remediation methods

- Natural attenuation as method of aquifer remediation comprises of different *physical, chemical and biological* processes that act under favorable circumcises to reduce contaminant mass, concentration and toxicity without human intervention

These in-situ processes includes:

- ❖ Dilution of concentrations due to recharging with fresh water (precipitation, the river recharge….)
- ❖ Advection
- ❖ Hydrodynamic dispersion
- ❖ Adsorption
- ❖ Volatilization
- ❖ Biodegradation
- ❖ Abiotic transformation

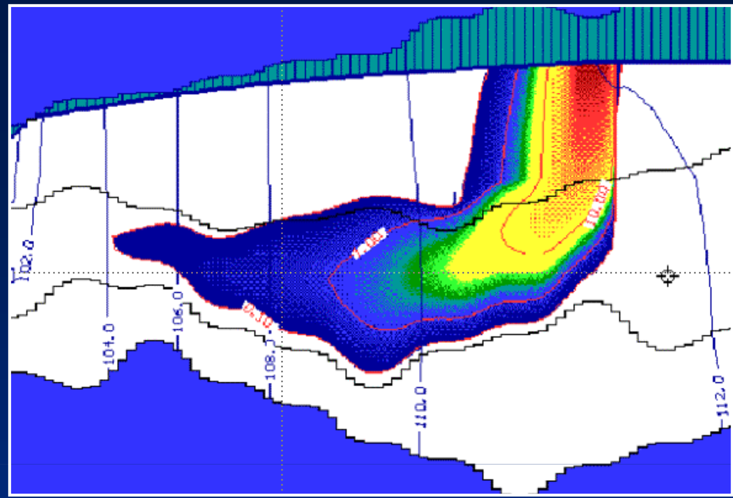
Natural attenuation nondestructive processes – they lower the concentrations but do not destroy the contamination, mass of contamination in aquifer remains the same

- Dilution of concentrations due to recharging with fresh water (precipitation, the river recharge….)
- Advection
- Hydrodynamic dispersion
- Adsorption

Natural attenuation destructive processes – they lower the concentrations but also the mass of contamination by destroying it

- Biodegradation
- Chemical (abiotical) transformation
- Radioactive decay
- Volatilization

Advection-Dispersion Equation solved by MT3D



$$\frac{\partial}{\partial x_i}\left[D_{ij}\frac{\partial C}{\partial x_j}\right] - \frac{\partial}{\partial x_i}(v_i C) + \frac{q_s C_s}{\theta} - \lambda\left[C + \frac{\rho_b S}{\theta}\right] = R\left[\frac{\partial C}{\partial t}\right]$$

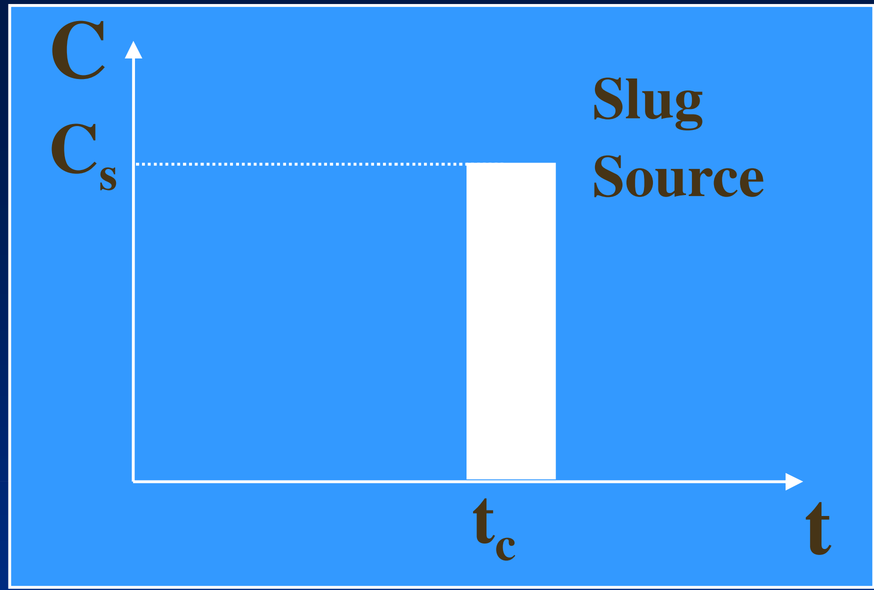
Dispersion — Advection — Sink/Source — Reactions — Retardation

- **Only advection part solved differently by the different methods**

Transport Mechanisms

Advection

$$-\frac{\partial}{\partial x_i}(v_i C)$$

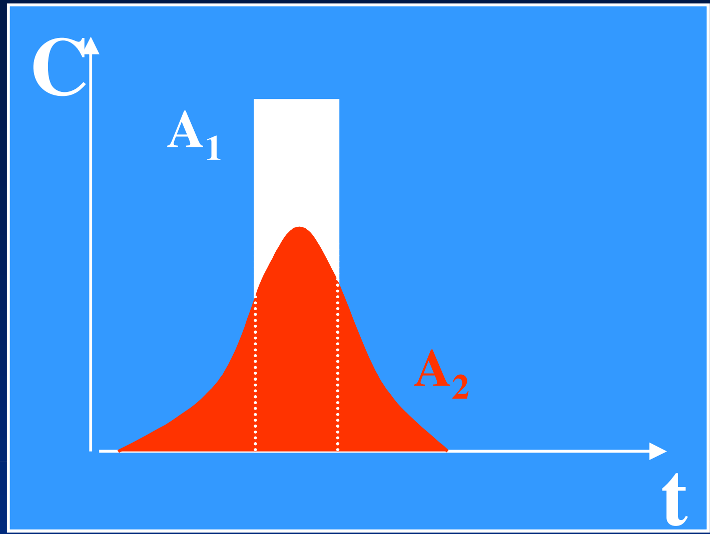


- Transport of dissolved solute at the same velocity of groundwater flow (t_c = Distance/v_i)
- The dominant mechanism for most practical plume migration problems
- MT3D calculates v_i using heads and K's from the MODFLOW modeling results

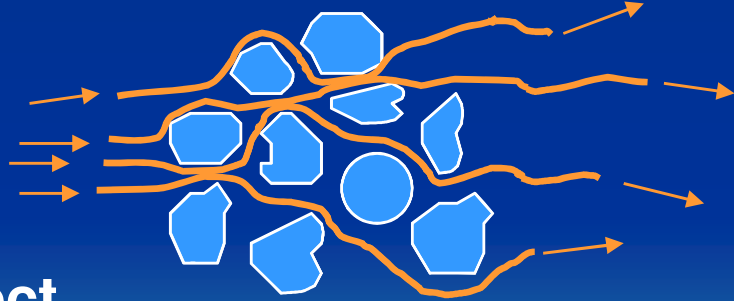
Transport Mechanisms

Dispersion

$$\frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial C}{\partial x_j}\right)$$



- Dissolved solute spreads more than predicted by advection alone (total mass constant, $A_1 = A_2$)
- Pore-scale mechanical dispersion of solute molecules, and molecular diffusion due to concentration gradients
- Scale dependent
- In theory, with a micro-scale grid and perfect information, we would not need dispersion
- Mechanisms well understood, but remains a difficult term to accurately measure

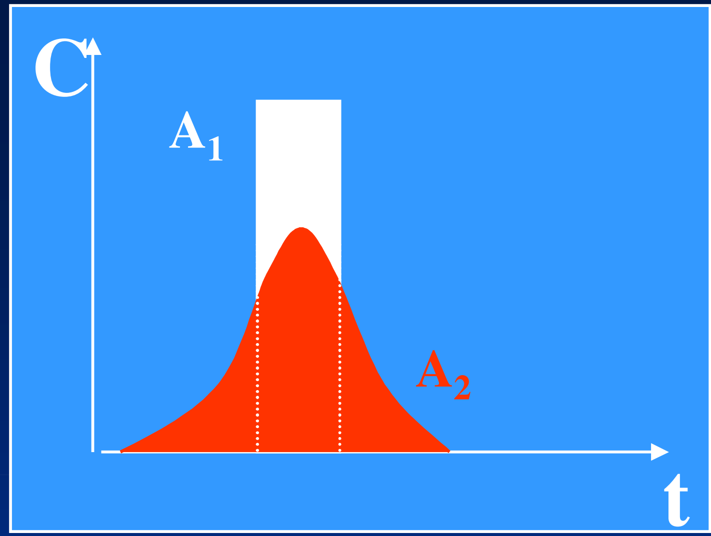


Transport

Mechanisms

Dispersion

$$D = f(\alpha_i\ , v_i, Diffusion)\ [L^2/T]$$



- **MT3D requires dispersivity (α) values and simulated flow velocities (*v_i* from MODFLOW model) to calculate the Dispersion terms.**
- **Longitudinal Dispersivity (α_L) [L]**

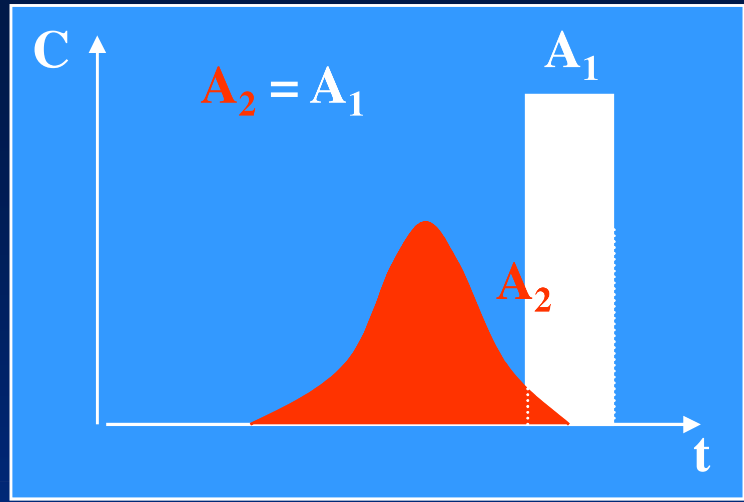
  Typically α_L is 0.1 m < α_L < 100 m

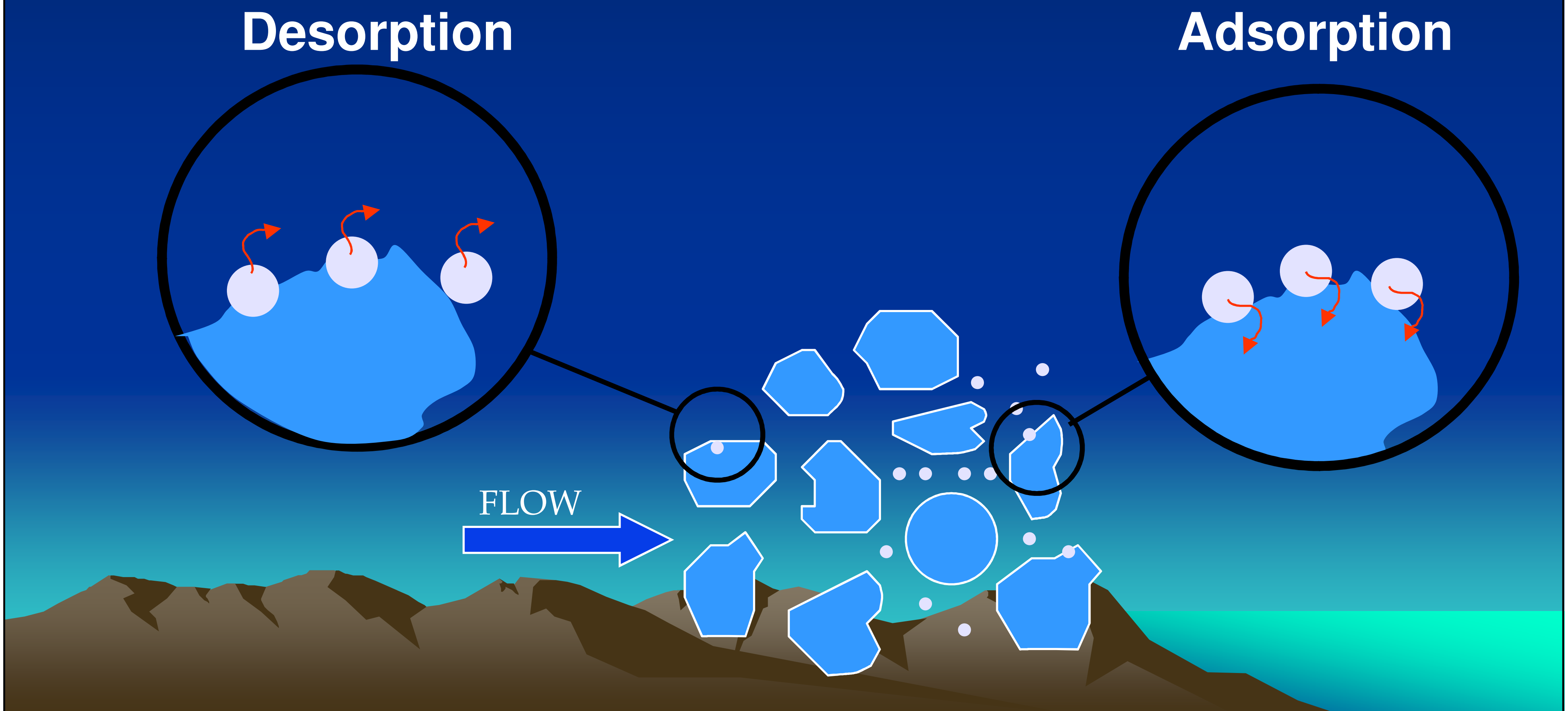
  or 0.03 - 0.05 x plume length
- **α_L/α_T ratio – Typically 0.1 α_L**
- **α_L/α_V ratio – Typically 0.01 α_L**
- **Diffusion (D^*) [L^2/T] – usually insignificant**

Transport Mechanisms

Retardation

$$R\frac{\partial C}{\partial t}$$

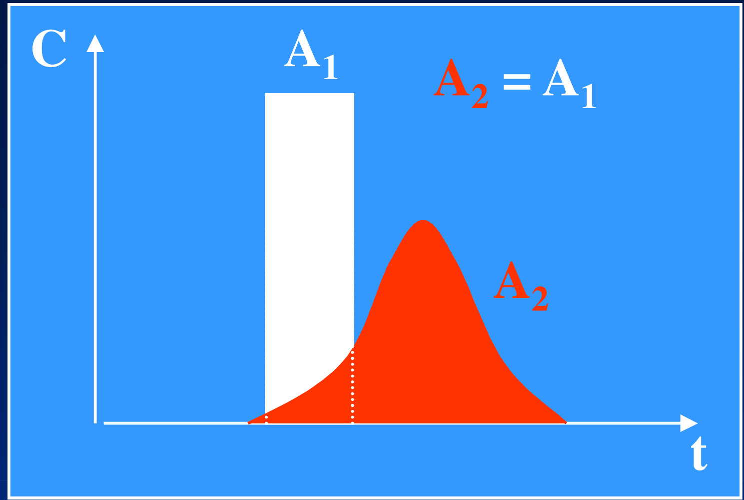




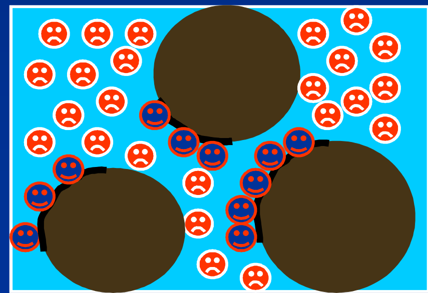
Transport Mechanisms

Retardation

$$R \frac{\partial C}{\partial t}$$



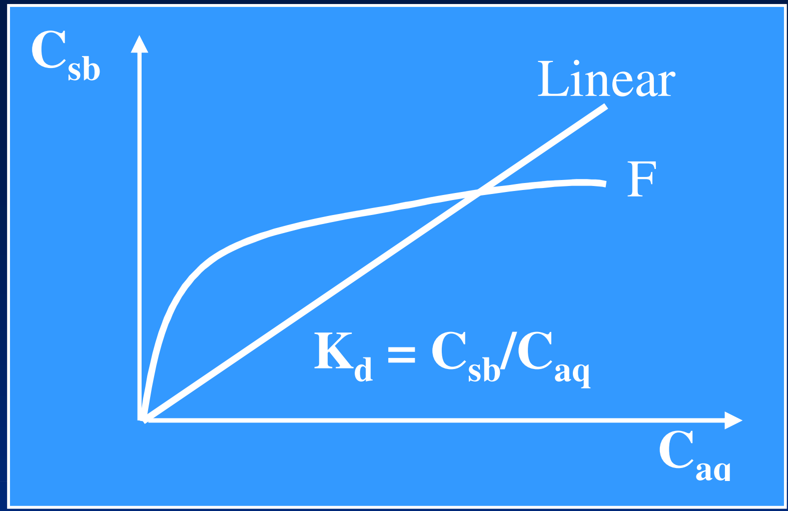
- Adsorption caused by the affinity of hydrophobic organic solutes to bind with the organic coating of soil particles
- Equilibrium partitioning between solid phase and liquid phase
- As liquid phase concentration falls adsorbed molecules dissolve back into solution
- Retardation = transport delay caused by this partitioning



Transport Mechanisms

Retardation

$$R_{Linear} = 1 + \rho_b \frac{K_d}{\theta}$$

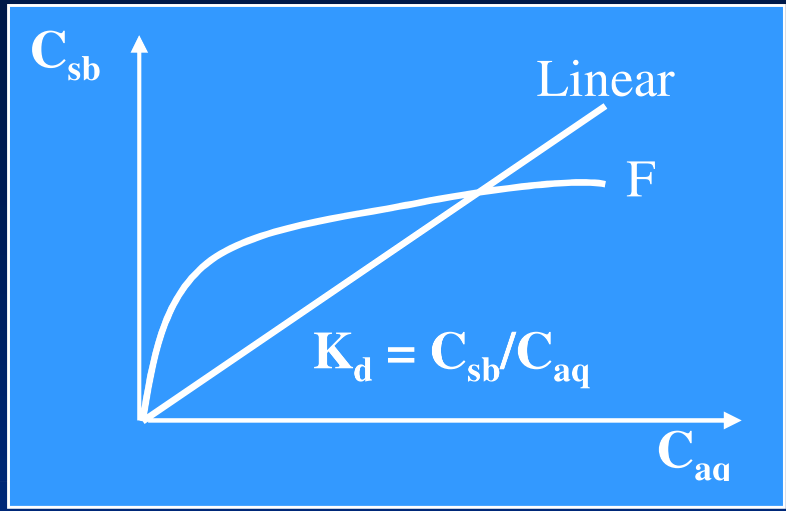


- Retardation a function of the amount of solute adsorbed vs. the amount in solution = isotherm
- Linear isotherm (most common)
  - Constant ratio of Conc. adsorbed vs. Conc. Dissolved = K_d
  - K_d a function of contaminant (K_{oc}) and soil (f_{oc})
- Non-linear isotherms (e.g. Freundlich and Langmuir)
  - Variable ratio of Conc. adsorbed vs. Conc. Dissolved
  - Often there is a maximum adsorbed conc. as dissolved concentrations become very high

Transport Mechanisms

Retardation

$$R_{Linear} = 1 + \rho_b \frac{K_d}{\theta}$$



- Linear and non-linear isotherms assume instantaneous sorption/desorption
- MT3DMS and MT3D99 now allow kinetic mass transfer

  → First-order, kinetic sorption/desorption

  Same as Linear isotherm but has a first-order rate constant

  → First-order, kinetic dual-domain mass transfer

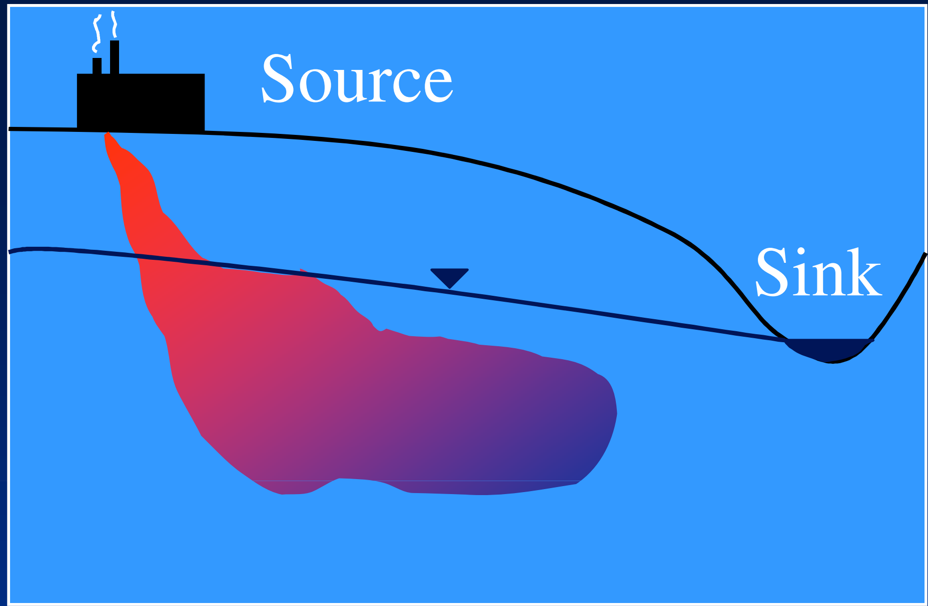
  Simulates diffusion into secondary porosity via a first-order rate constant

Transport

Mechanisms

Sources/Sinks

$$+ q_s \frac{C_s}{\theta}$$



- Dissolved solute concentration entering/leaving the model domain through sources/sinks

- MT3D boundary conditions allow both spatially distributed sources/sinks and point sources/sinks
  - Constant Conc. Source (Type I - Dirichlet)
  - Point Source Conc. (Type II - Neuman)
  - Recharge/Evapo. Source (Type III - Cauchy)

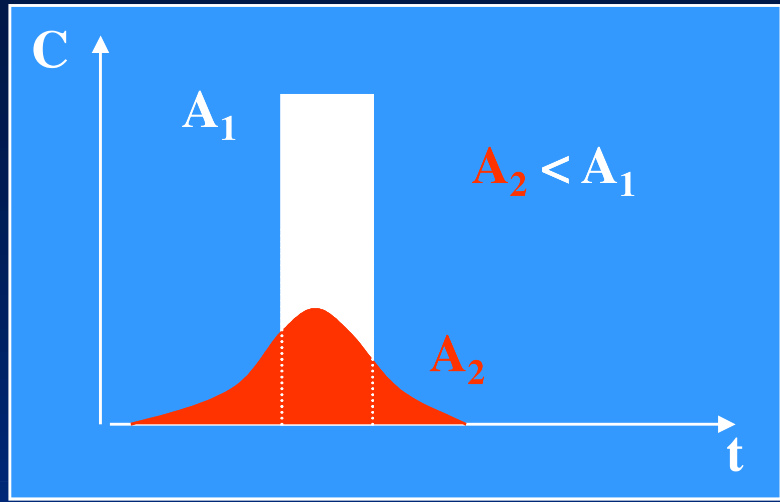
- Input for MT3D is concentration
  → Flow (q_s) from MODFLOW

Transport

Mechanisms

Reactions

$$-\lambda_d C \quad -\lambda_s \rho_b \frac{S}{\theta}$$



- **Simplest reaction is first-order irreversible decay**

  $C_t = C_o\, e^{-\lambda t}$ $\quad\quad$ λ = degradation rate [1/day]

  assumes reaction not limited e.g. by oxygen

  half-life ($t_{1/2}$) = time for C_t/C_o to equal 1/2 = ln(1/2)/–λ

- **For first-order decay MT3D requires:**

  soil dry bulk density (ρ_b [M/L^3])

  degradation rate for the dissolved solute (λ_d [T^{-1}])

  degradation rate for the sorbed solute (λ_s[T^{-1}])

Advective-Dispersive Transport Equation

Solution Techniques

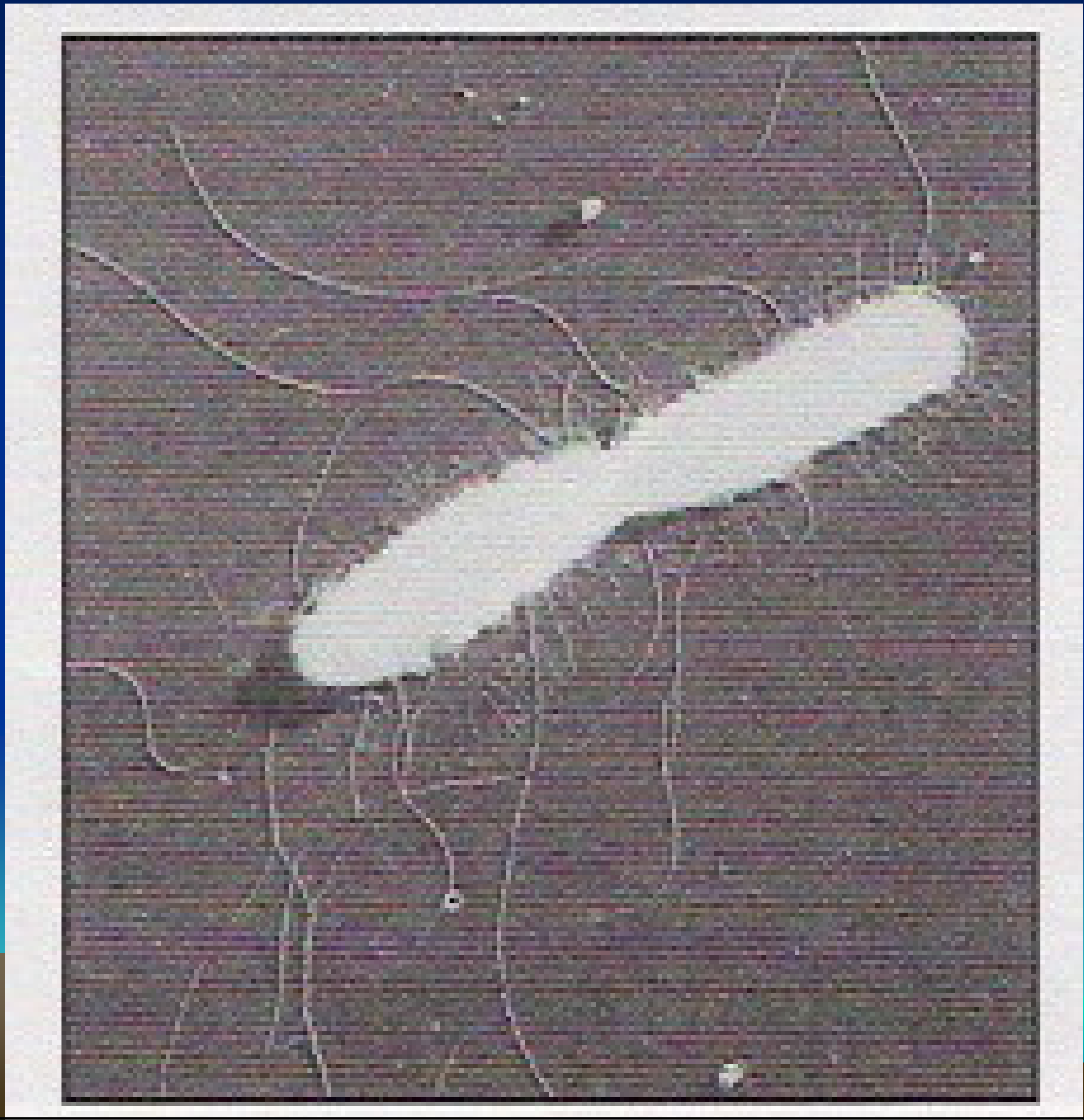
$$\frac{\partial}{\partial x_i}\left[D_{ij}\frac{\partial C}{\partial x_j}\right] - \frac{\partial}{\partial x_i}(v_i C) + \frac{q_s C_s}{\theta} - \lambda\left[C + \frac{\rho_b \bar{C}}{\theta}\right] = R\left[\frac{\partial C}{\partial t}\right]$$

- Finite Difference
- MOC (Method of Characteristics)
- MMOC (Modified Method of Characteristics)
- HMOC (Hybrid Method of Characteristics)
- Explicit 3rd-order TVD (ULTIMATE)

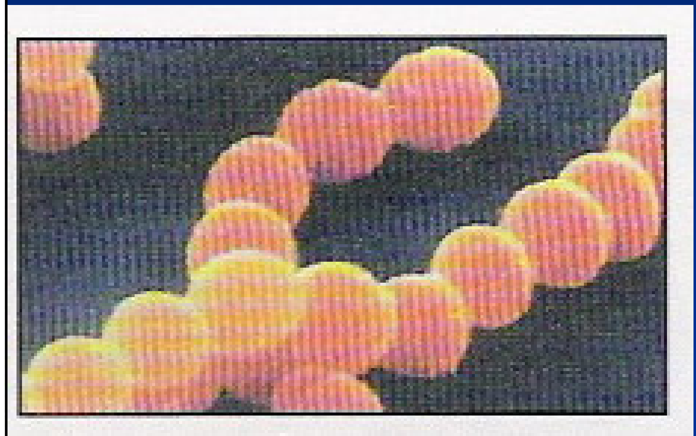
Biodegradation

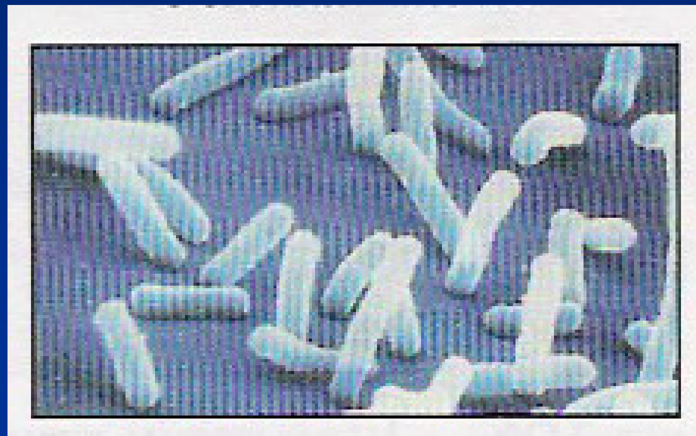
- Biodegradation is a process where hydrocarbons and other contaminants are used as source of food and energy for bacteria and fungi (for grow and reproduction). As the end result contaminants are transformed into CO_2 and water.

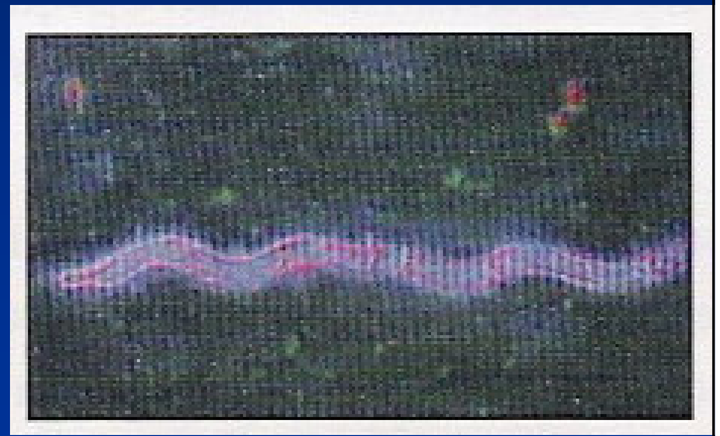
Bacteria pictured by 3D microscope



Bacteria morphology







Sperical shape **Rod shape** **Spiral shape**

Contaminant	Microorganism	Biodegradation Potential
Benzene	*Pseudomonas putida, P. rhodochrous, P. aeruginosa,Acinetobacter sp., Methylosinus trichosporium OB3b, Nocardia sp., methanogens, anaerobes*	Moderate to High
Toluene	*Methylosinus trichosporium OB3b, Bacillus sp., Pseudomonas putida, Cunninghamella elegans, P. aeruginosa, P. mildenberger, Pseudomonas aeruginosa, Pseudomonas sp., Achromobacter sp., methanogens, anaerobes*	High
Ethylbenzene	*Pseudomonas putida*	High
Xylene	*Pseudomonas putida, methanogens, anaerobes*	High
Jet fuels	*Cladosporium, Hormodendrum*	High
Kerozine	*Torulopsis, Candidatropicalis, Corynebacterium hydrocarboclastus, Candidaparapsilosis, C. guilliermondii, C. lipolytica, Trichosporon sp., Rhohosporidium toruloides, Cladosporium resinae*	High

Biodegradation of hydrocarbons – BTEX *(mineralization)*

- ***Aerobic biodegradation***

$$C_6H_6 + 7.5O_2 = 6CO_2 + 3H_2O$$

On a mass basis ratio between O2 and benzene = 240:78 = 3.08:1 which means that 3.08 mg of O2 is destroyed to mineralize 1 mg of benzene

- ***Anaerobic biodegradation - denitrification***

$$6NO_3^- + 6H^+ + C_6H_6 = 6CO_2\ (g) + 6H_2O + N_2\ (g)$$

On a mass basis ratio between NO3 and benzene 372:78 = 4.77:1

- ***Anaerobic biodegradation – Fe (III) reduction***

$60H^{+}+ + 30Fe(OH)_3 + C_6H_6 = 6CO_2 + 30\ Fe_2^{+} + 78H_2O$

On a mass basis ratio between Fe2+ (produced) and benzene = 21.5:1

- ***Anaerobic biodegradation – sulfate reduction***

$7.5H^{+} + 3.75SO_4^{2-}- + C_6H_6 = 6\ CO_2\ (g) + 3.75H_2S^0 + 3H_2O$

On a mass basis ratio between SO4 and benzene = 4.6:1

- ***Anaerobic biodegradation – metanogenezis***

$$C_6H_6 + 4.5H_2O = 2.25CO_2 + 3.75CH_4$$

On a mass basis ratio between CH4 and benzene = 0.77:1

Amount of energy that is produced during biodegradation

Proces	ΔG_r (kJ/mol benzene)
Aerobic respiration	-3202
Denitrification	-3245
Fe^{3+} reduction	-2343
Sulfato (SO4) reduction	-514
Metanogenezis	-136

Fundamental concepts of Natural Attenuation ….

- During last decade significant advance was made in understanding the natural processes that contribute to natural attenuation
- Intensive field investigation and desk studies have led to technical protocols and improved mathematical models

Fundamental concepts of Natural Attenuation ….

- Implementation of N.A. is not “do-nothing” approach, this method of remediation requires:
- Complex investigation with aim to prove that natural processes rolled out in aquifer;
- Detail scientific documentation of processes in aquifer and prognosis how this processes can change;
- Long term monitoring to prove that this remediation technique is efficient;
- Alternative plan of remediation in a case that N.A is no more efficient

Influence of geochemical condition on biodegradation

- Biodegradation will occur only if geochemical conditions are favorable
- During biodegradation significant changes of geochemical condition occurs
- When evaluation natural attenuation it is important to predict future geochemical conditions that are favorably for biodegradation

Field investigation work

- One of the challenges in natural attenuation studies is to properly characterize geochemistry of groundwater
- "low-flow" sampling techniques are necessarily to obtain valid samples of dissolved O2 and other electron acceptors, pH, eH….

Field Application

Advanced Groundwater Technology AGT

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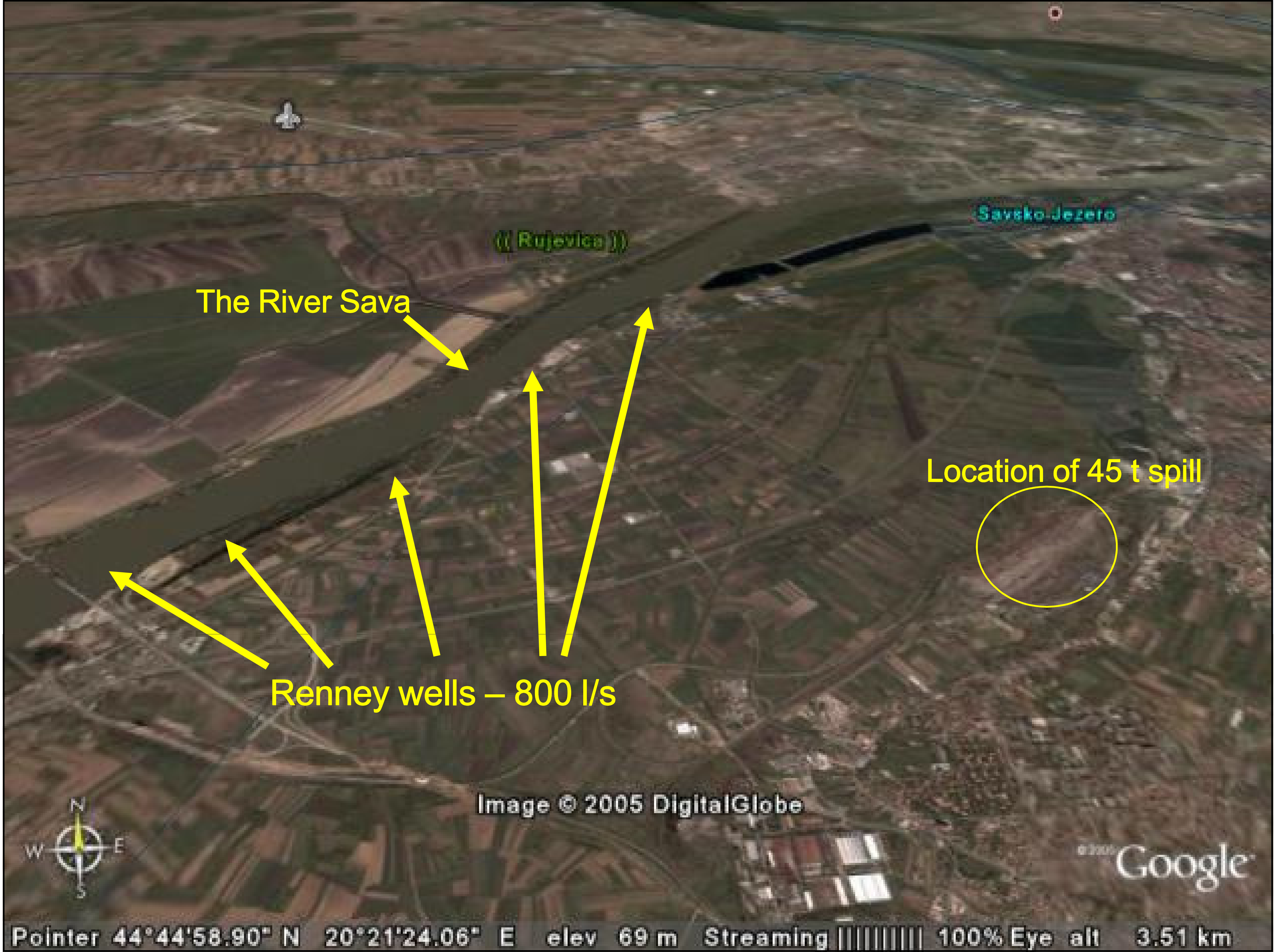

Savsko Jezero
Rujevica
The River Sava
Location of 45 t spill
Renney wells – 800 l/s
Image © 2005 DigitalGlobe
Google
Pointer 44°44'58.90" N 20°21'24.06" E elev 69 m Streaming |||||||||| 100% Eye alt 3.51 km


Location of 45 t spill
Image © 2005 DigitalGlobe
N
W
E
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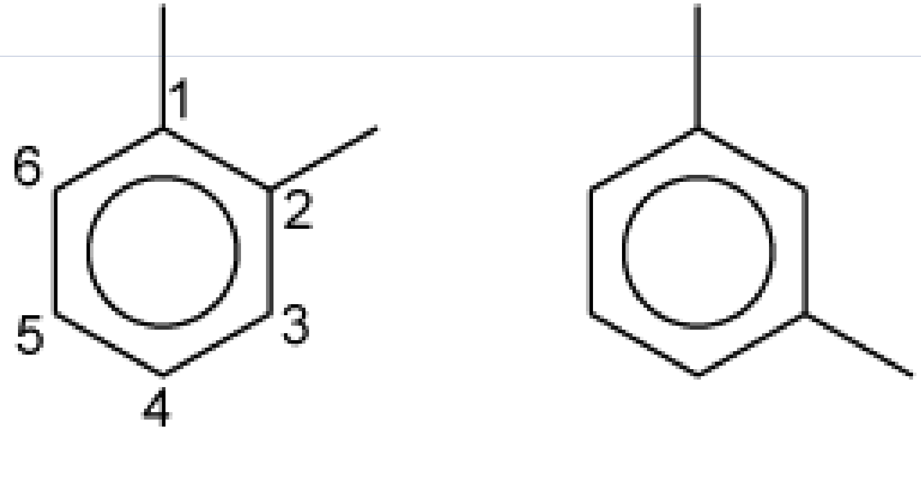
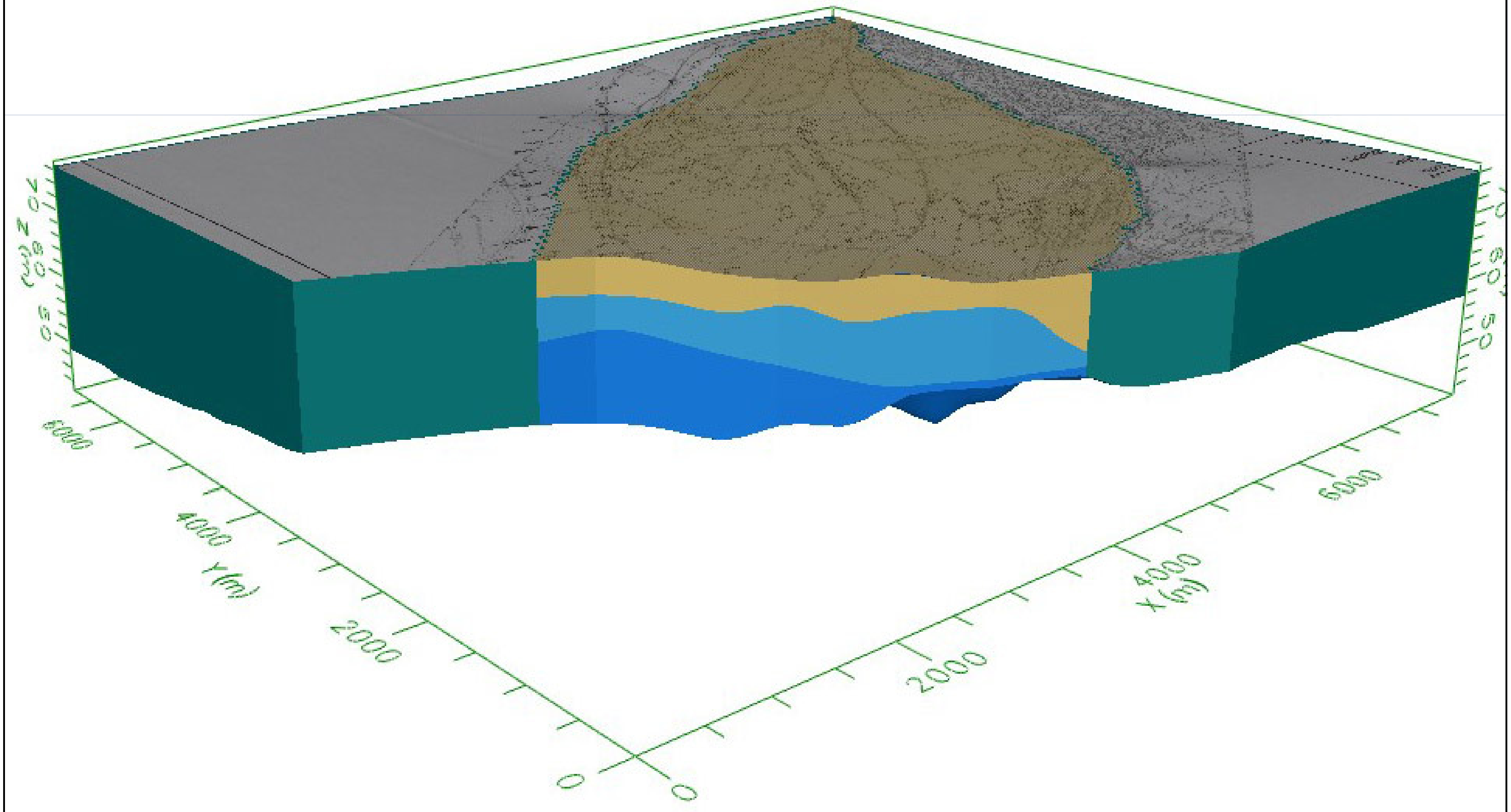
Googl
Pointer 44°44'35.20" N 20°22'53.55" E elev 70 m Streaming |||||||||| 100% Eye alt 2.10 km

Xylene – contaminant, spill of 45 tones

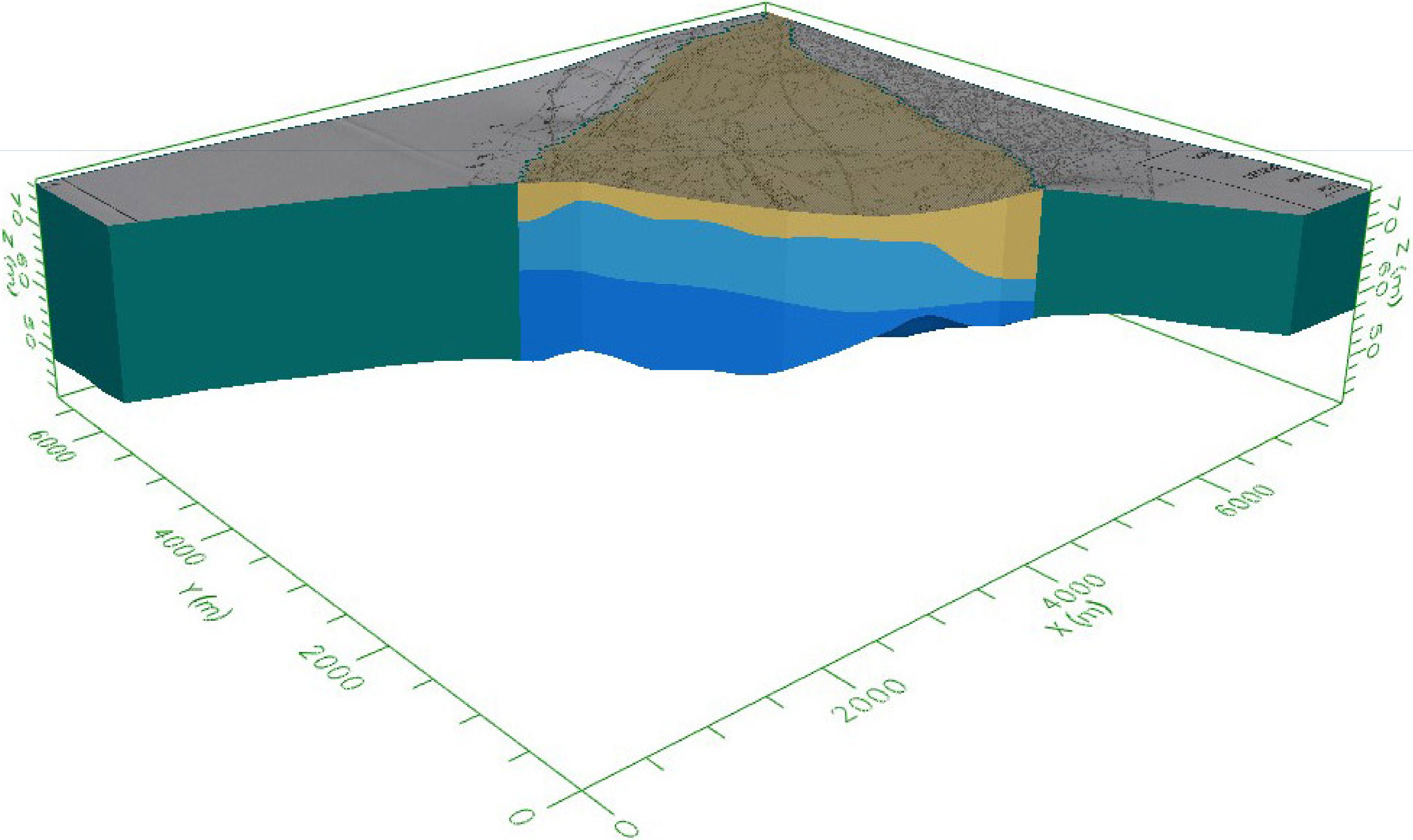


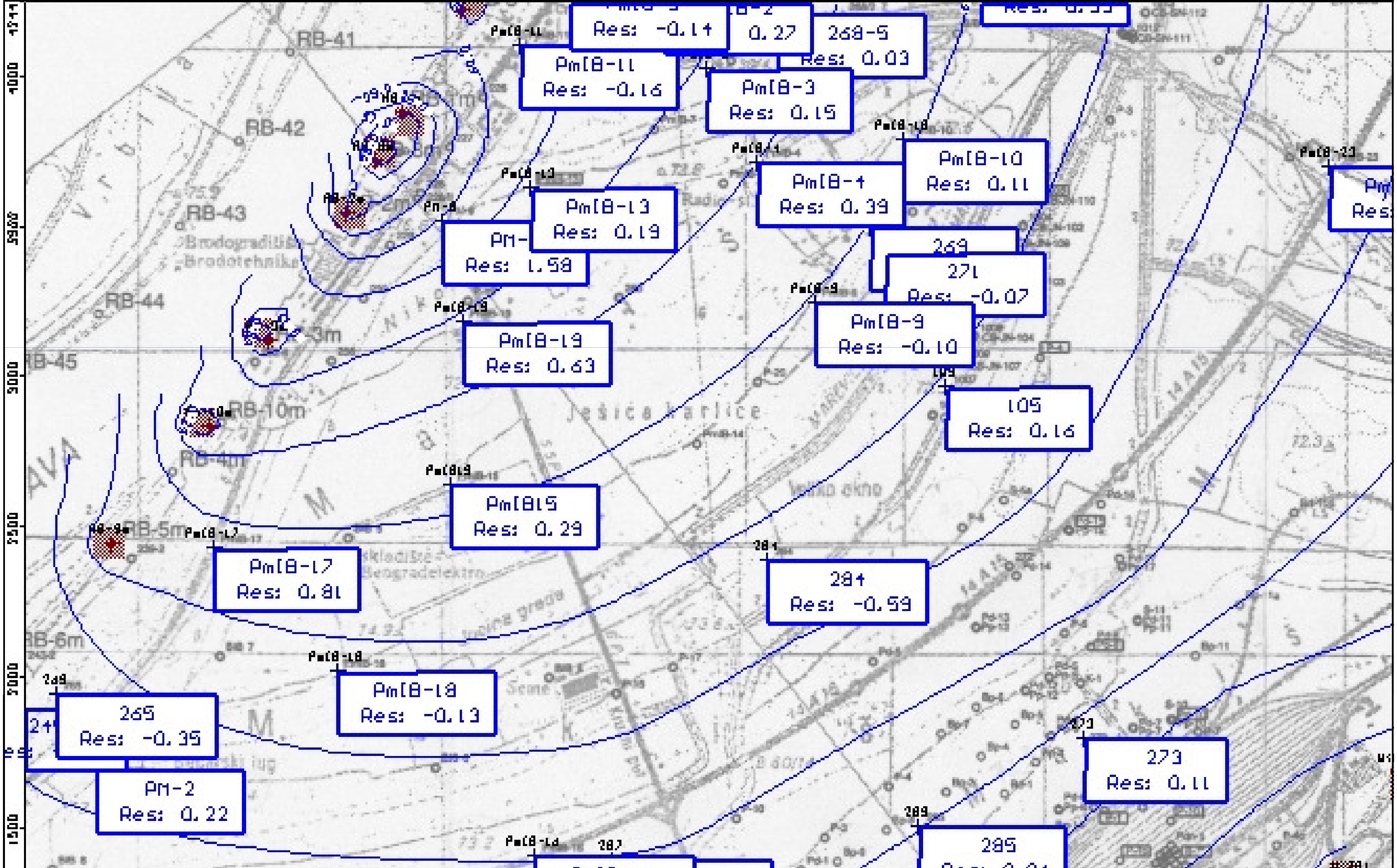
1,2-dimethylbenzene (*ortho*-xylene) 1,3-dimethylbenzene (*meta*-xylene) 1,4-dimethylbenzene (*para*-xylene)

3D Geological model



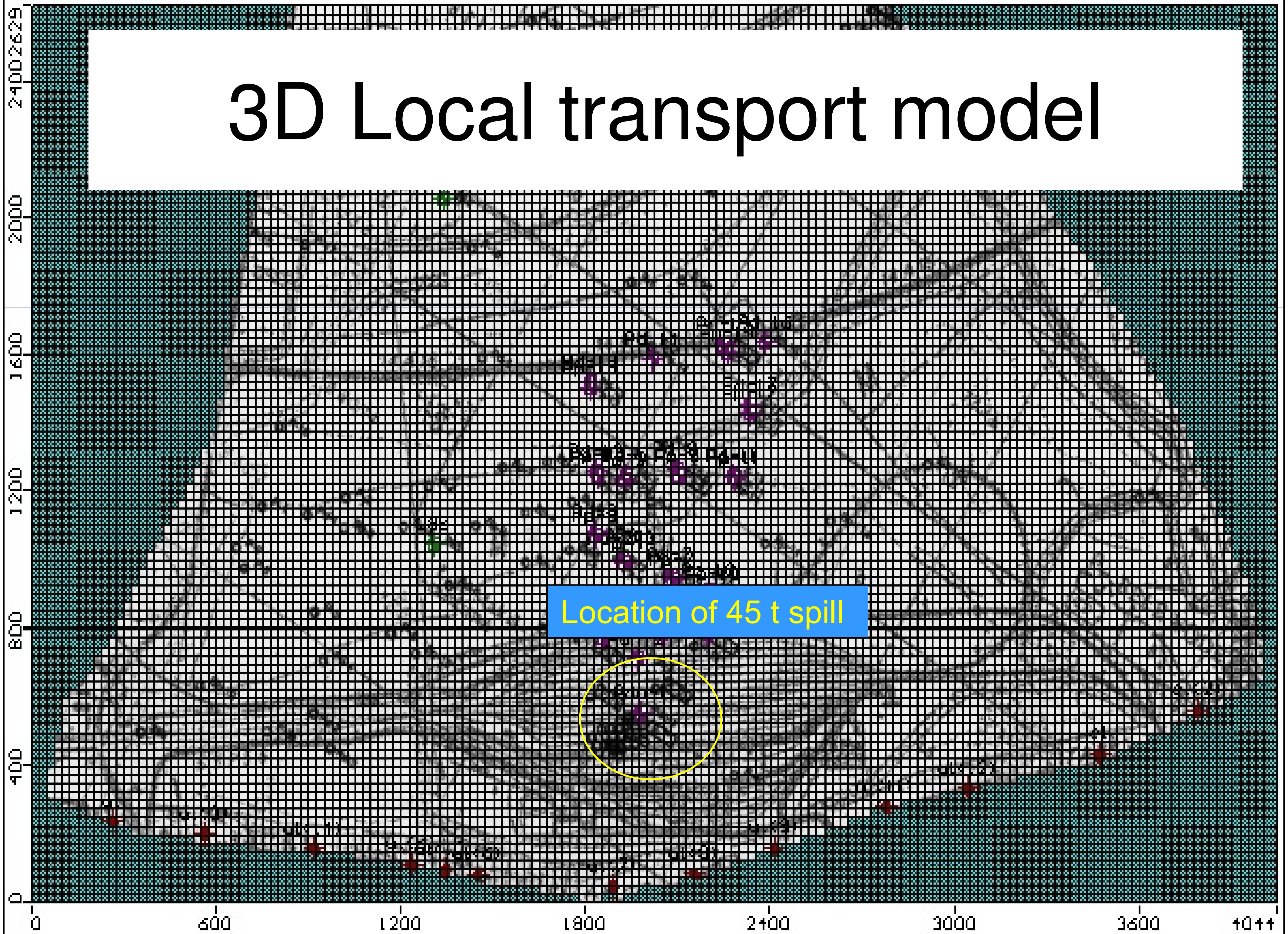
3D Geological model



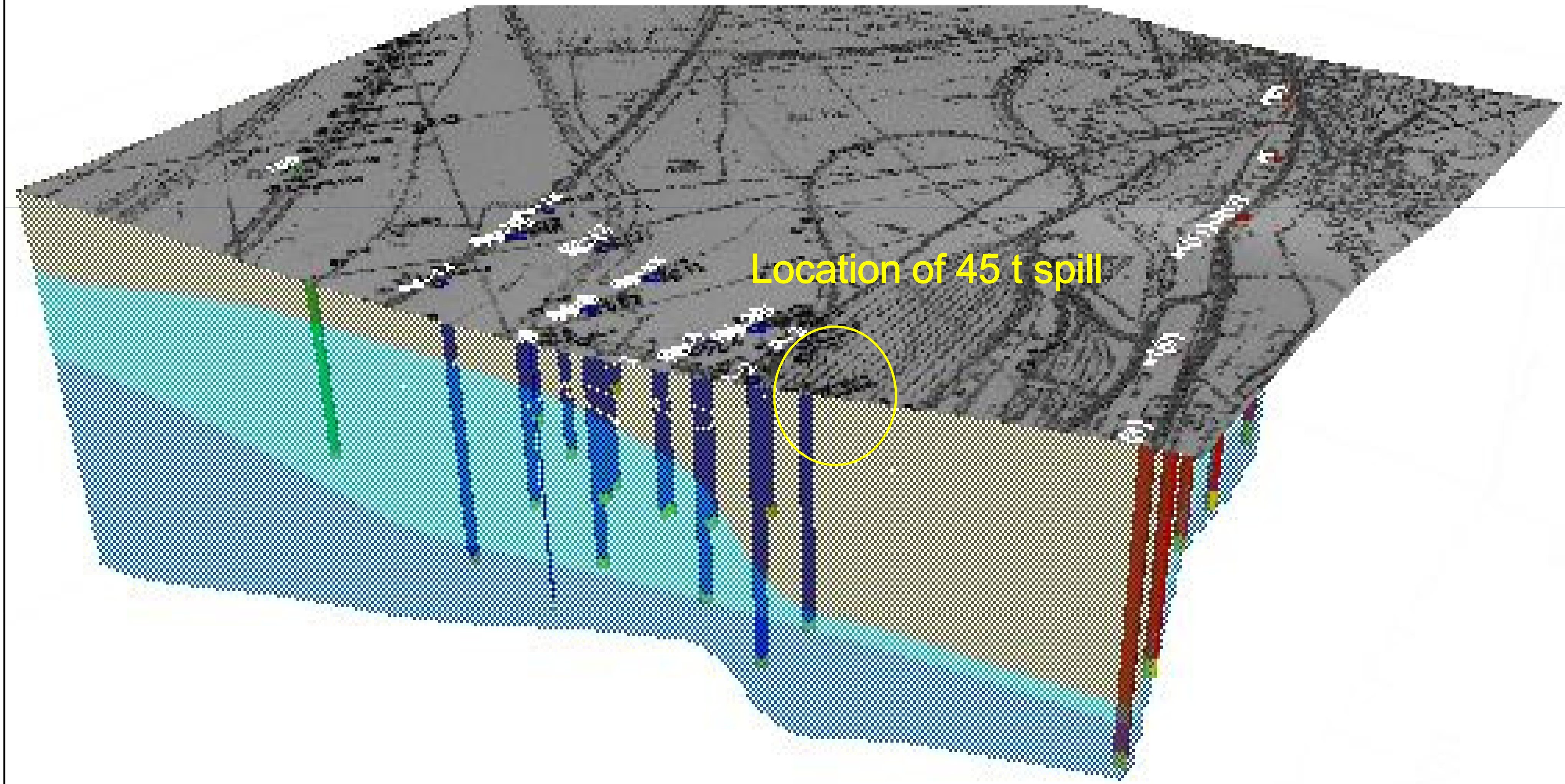


3D Hydrodynamic model

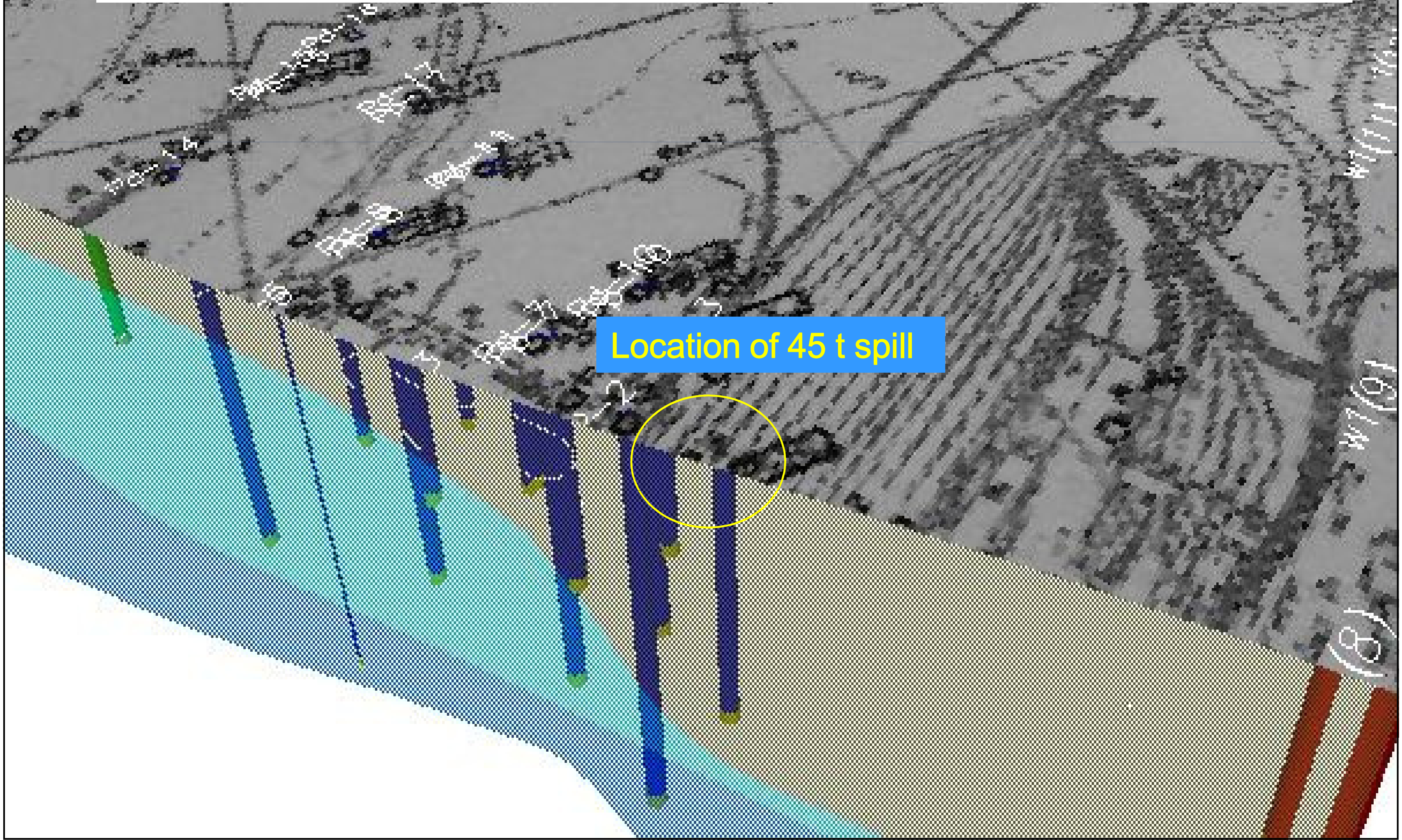
3D Local transport model



3D Local transport model



3D Local transport model

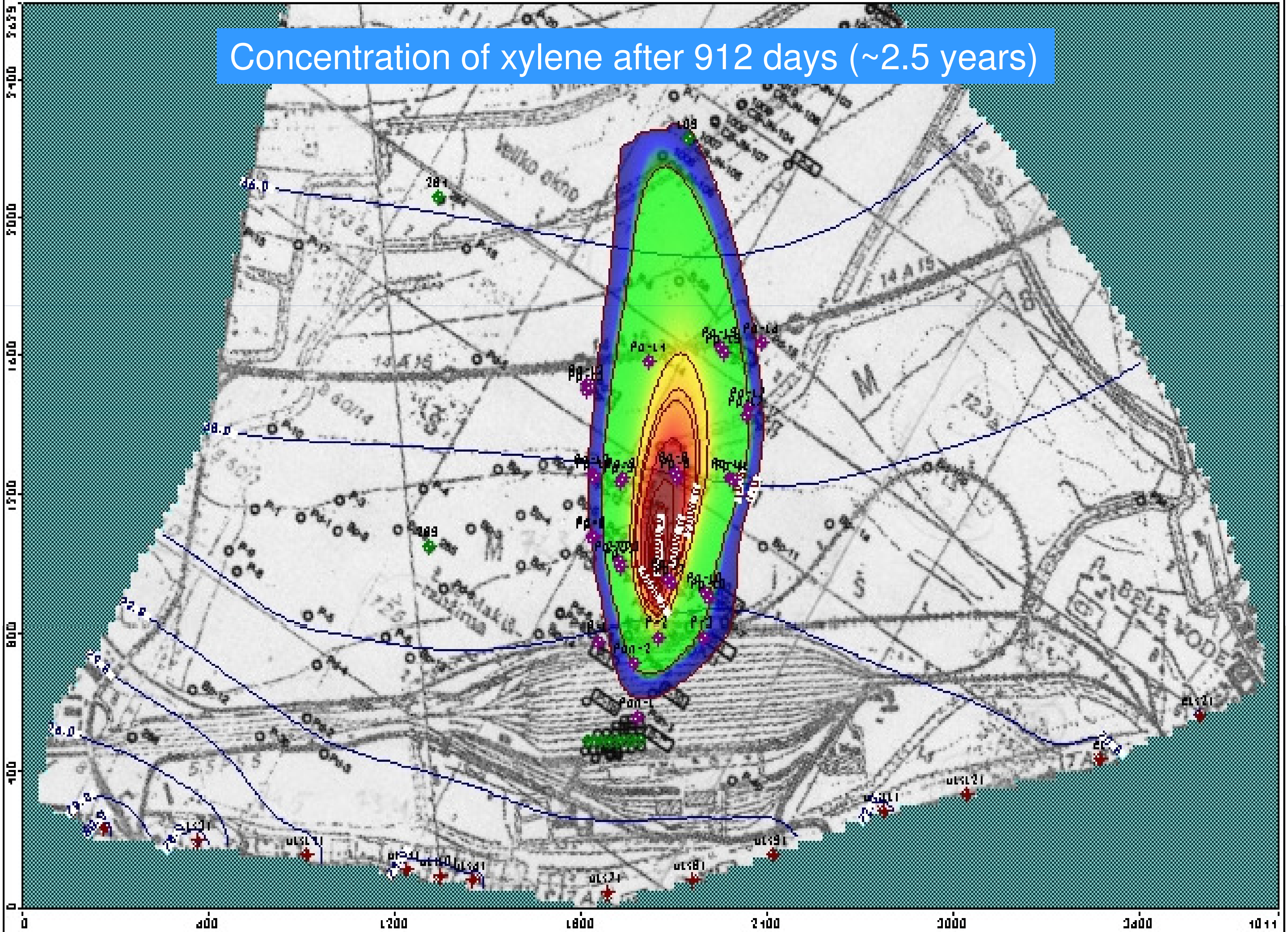



Canals where the xylene spilled into and via which xylene is introduced into aquifer
Image © 2005 DigitalGlobe
N
W
E
S
Google
Pointer 44°44'42.08" N 20°22'42.72" E elev 68 m Streaming |||||||||| 100% Eye alt 703 m

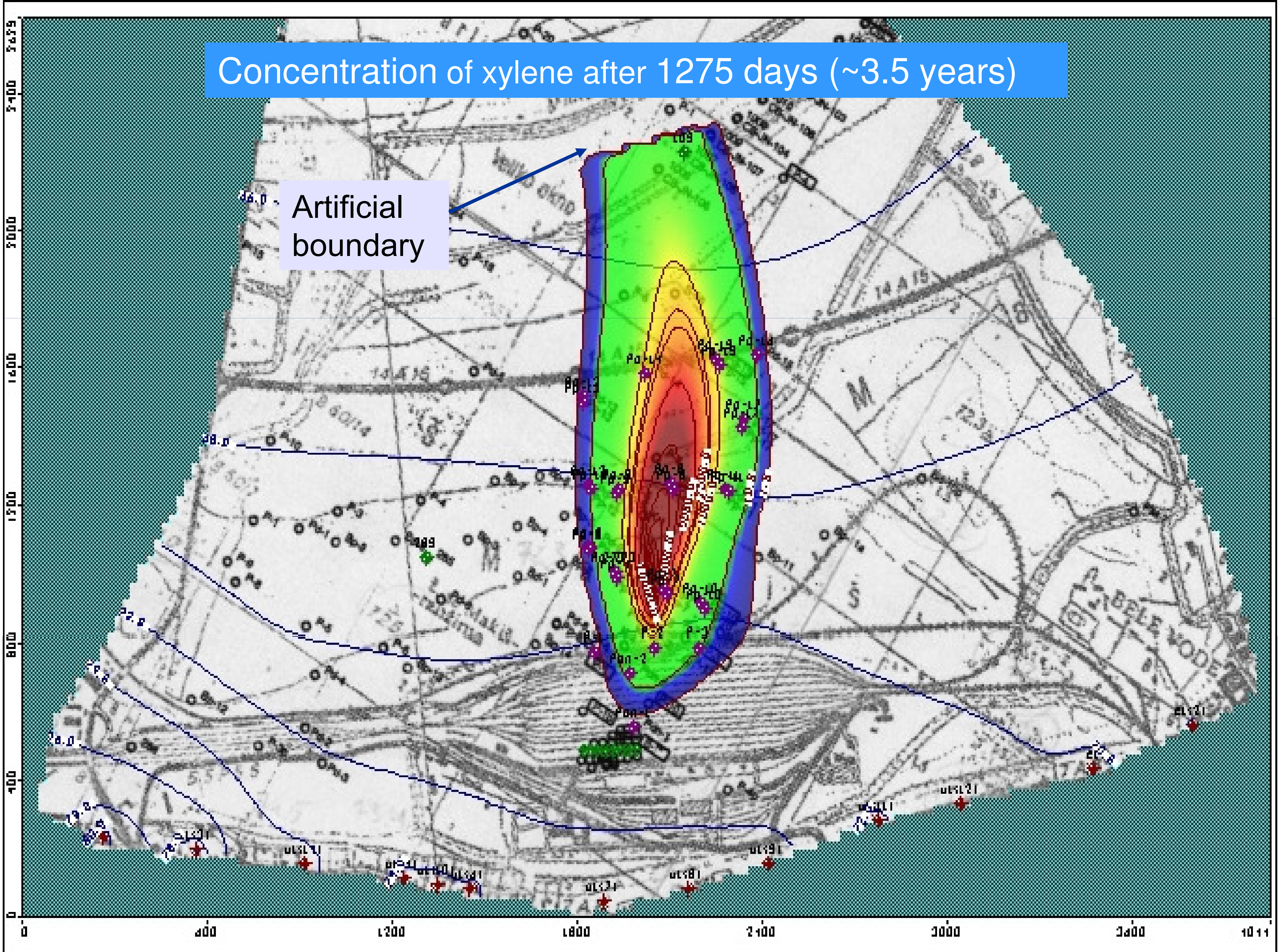

Canals where the xylene spilled into and via which xylene is introduced into aquifer
Image © 2005 DigitalGlobe
Pointer 44°44'42.55" N 20°22'35.95" E elev 69 m
Streaming |||||||||| 100%
Eye alt 677 m

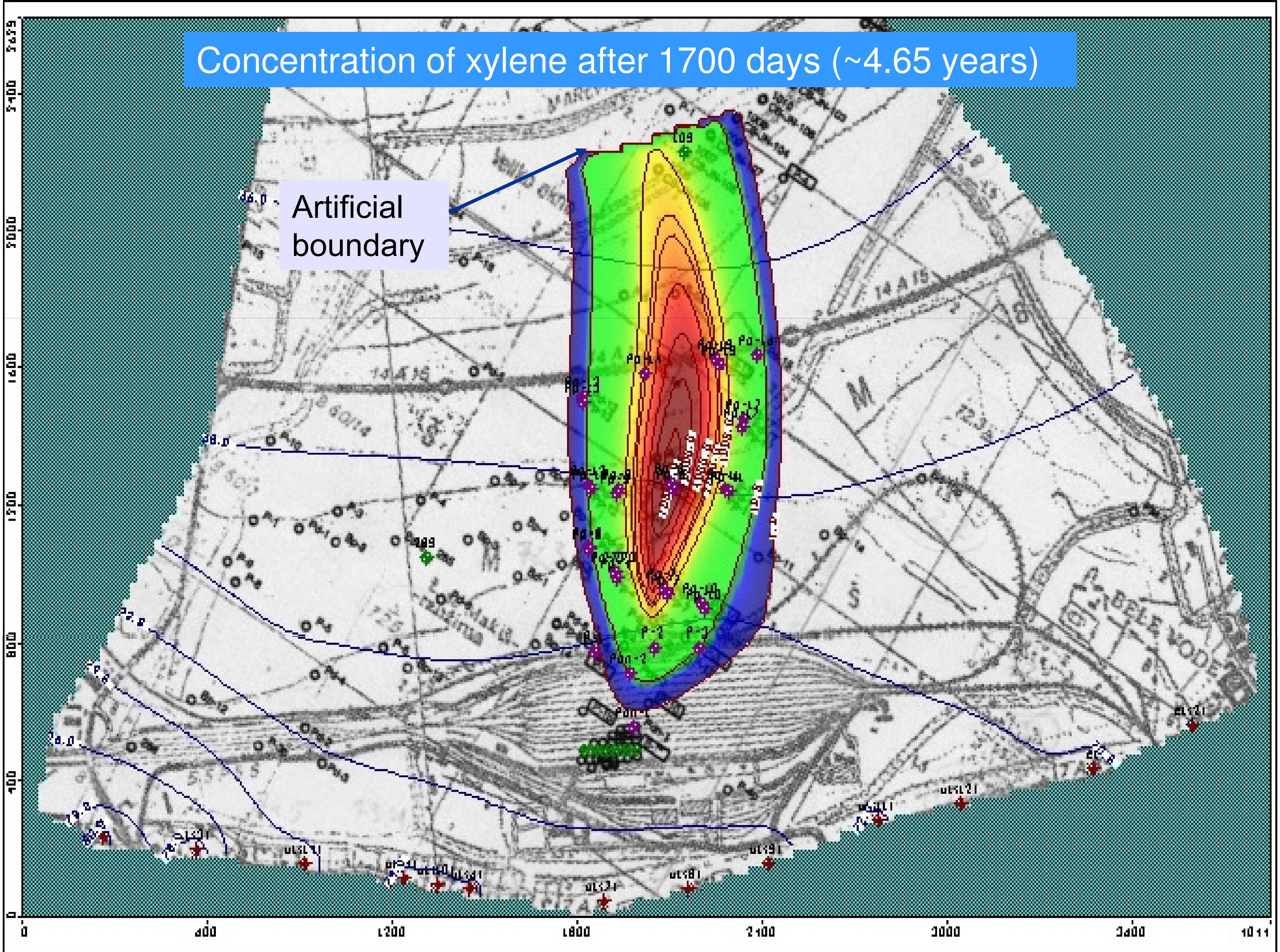
Movement of dissolved xylene without processes of adsorption and biodegradation – advection and dispersion only

Concentration of xylene after 912 days (~2.5 years)

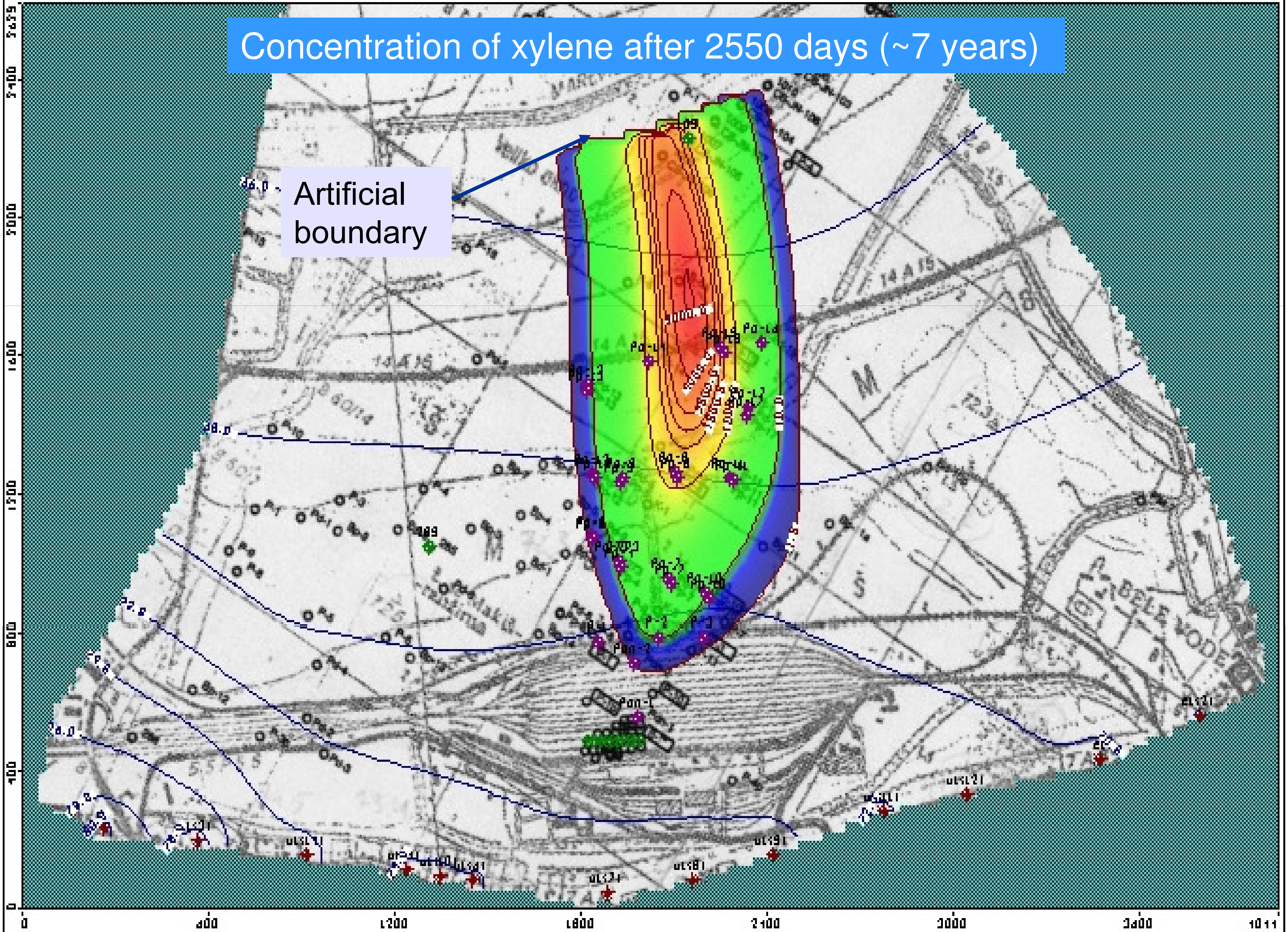


Concentration of xylene after 1275 days (~3.5 years)



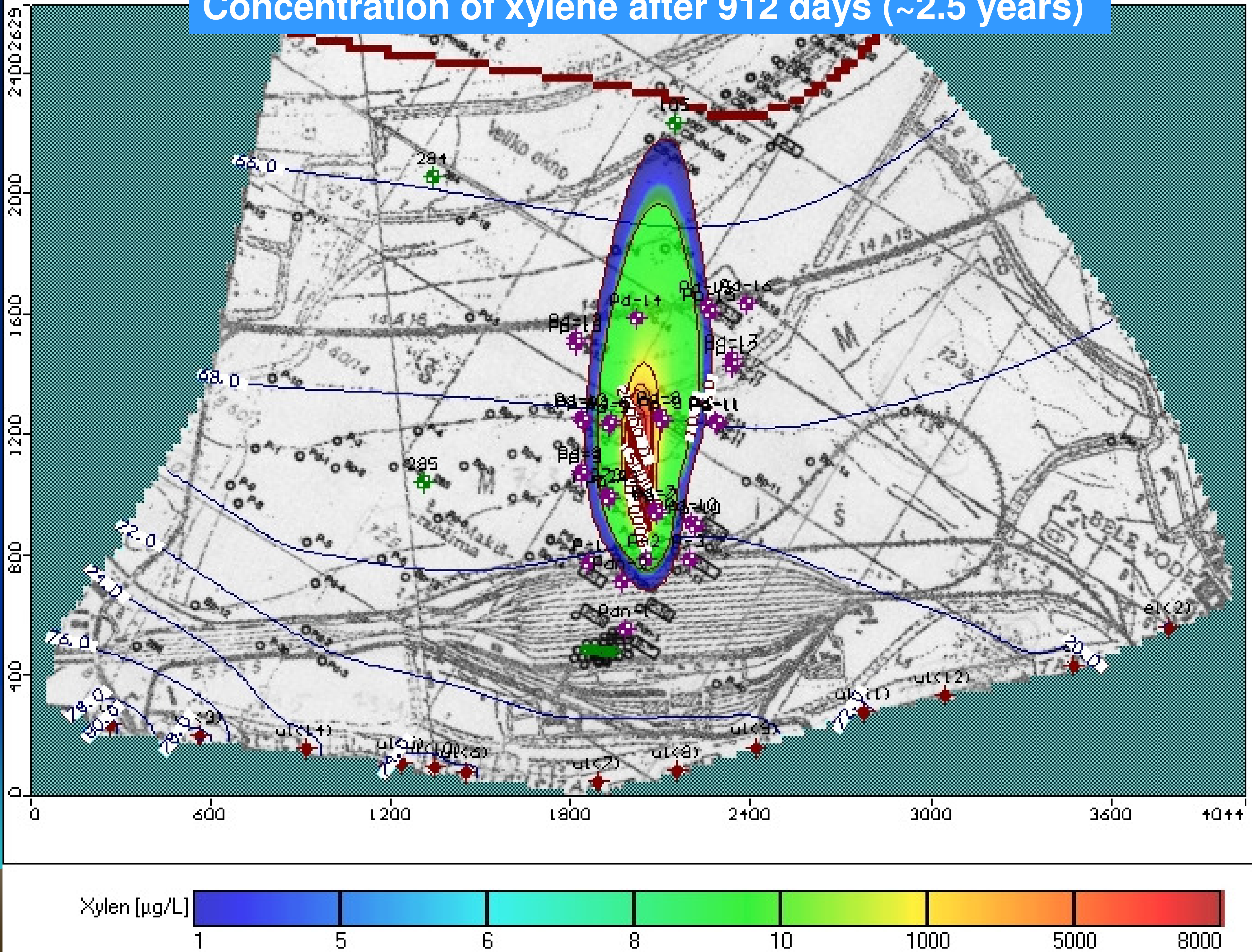

Concentration of xylene after 1700 days (~4.65 years)
Artificial boundary

Concentration of xylene after 2550 days (~7 years)

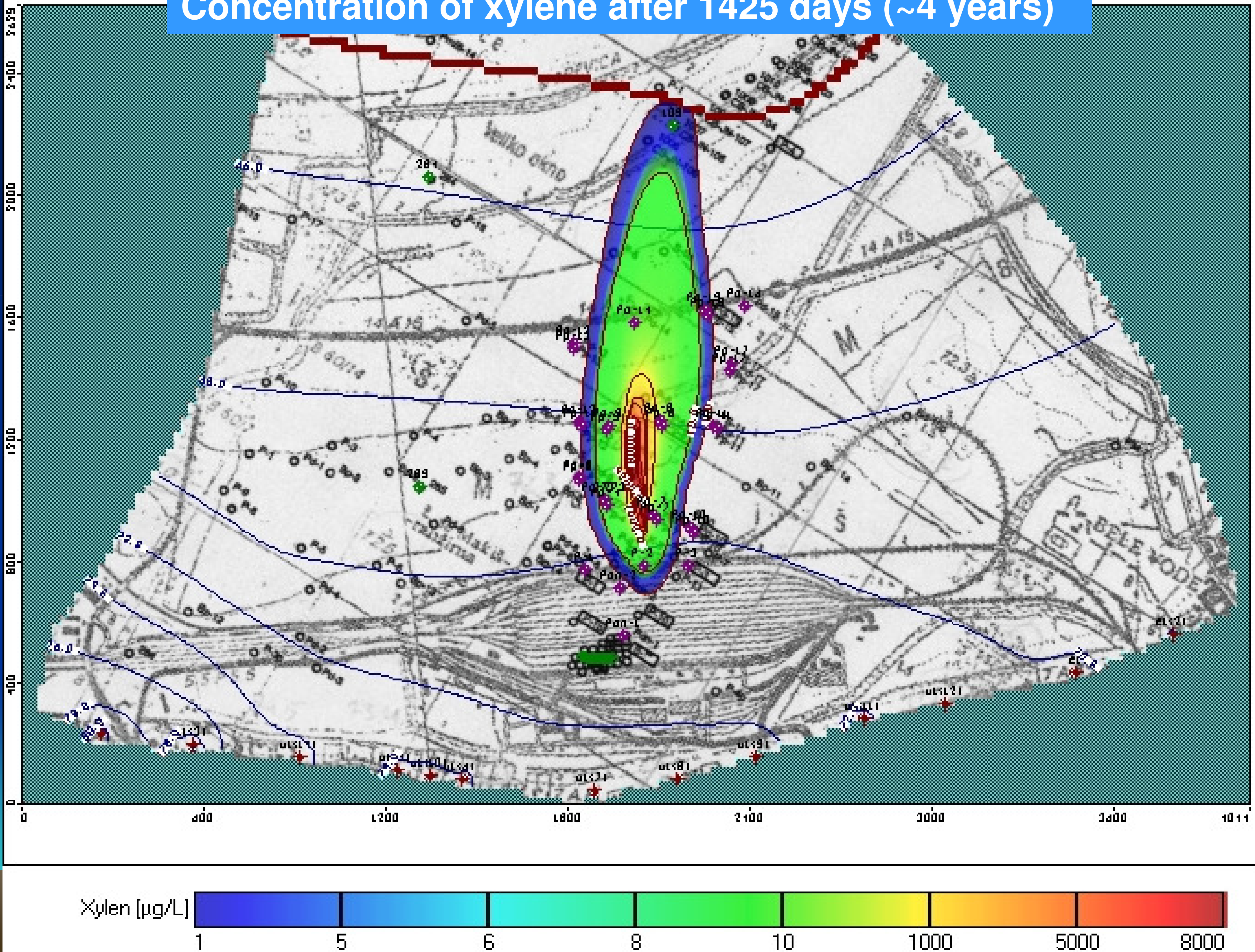


Movement of dissolved xylene with advection, dispersion and microbial biodegradation

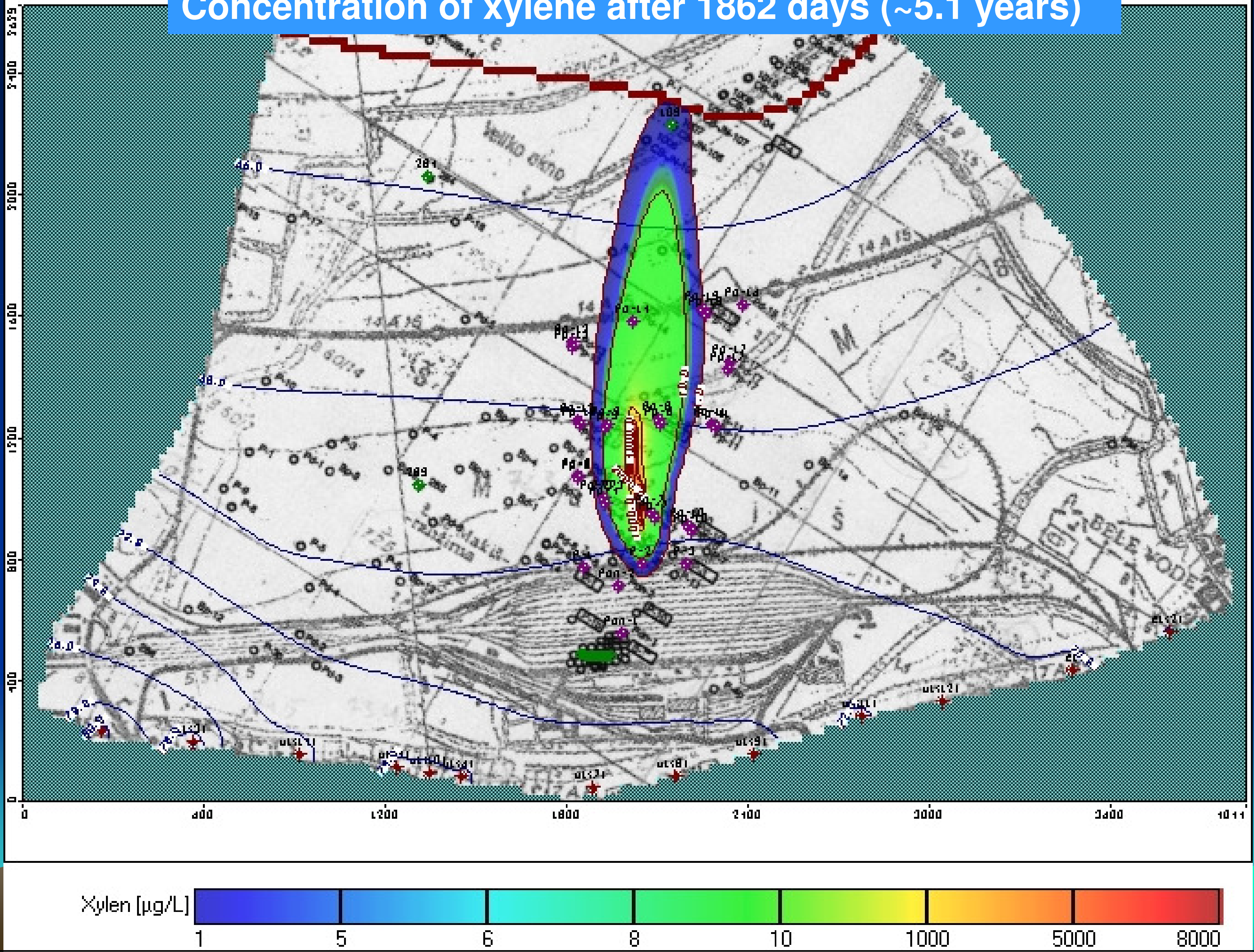
Concentration of xylene after 912 days (~2.5 years)



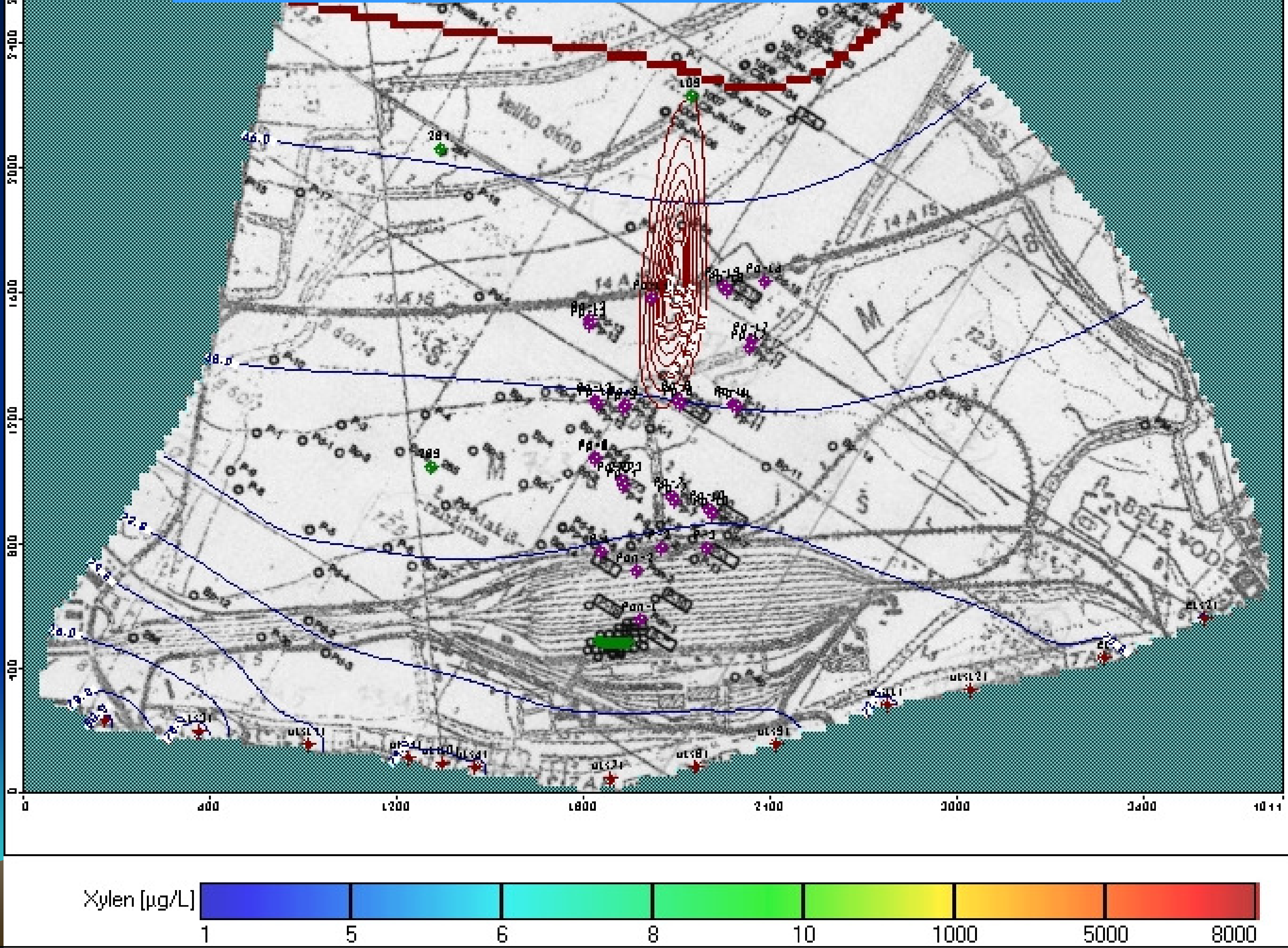
Concentration of xylene after 1425 days (~4 years)



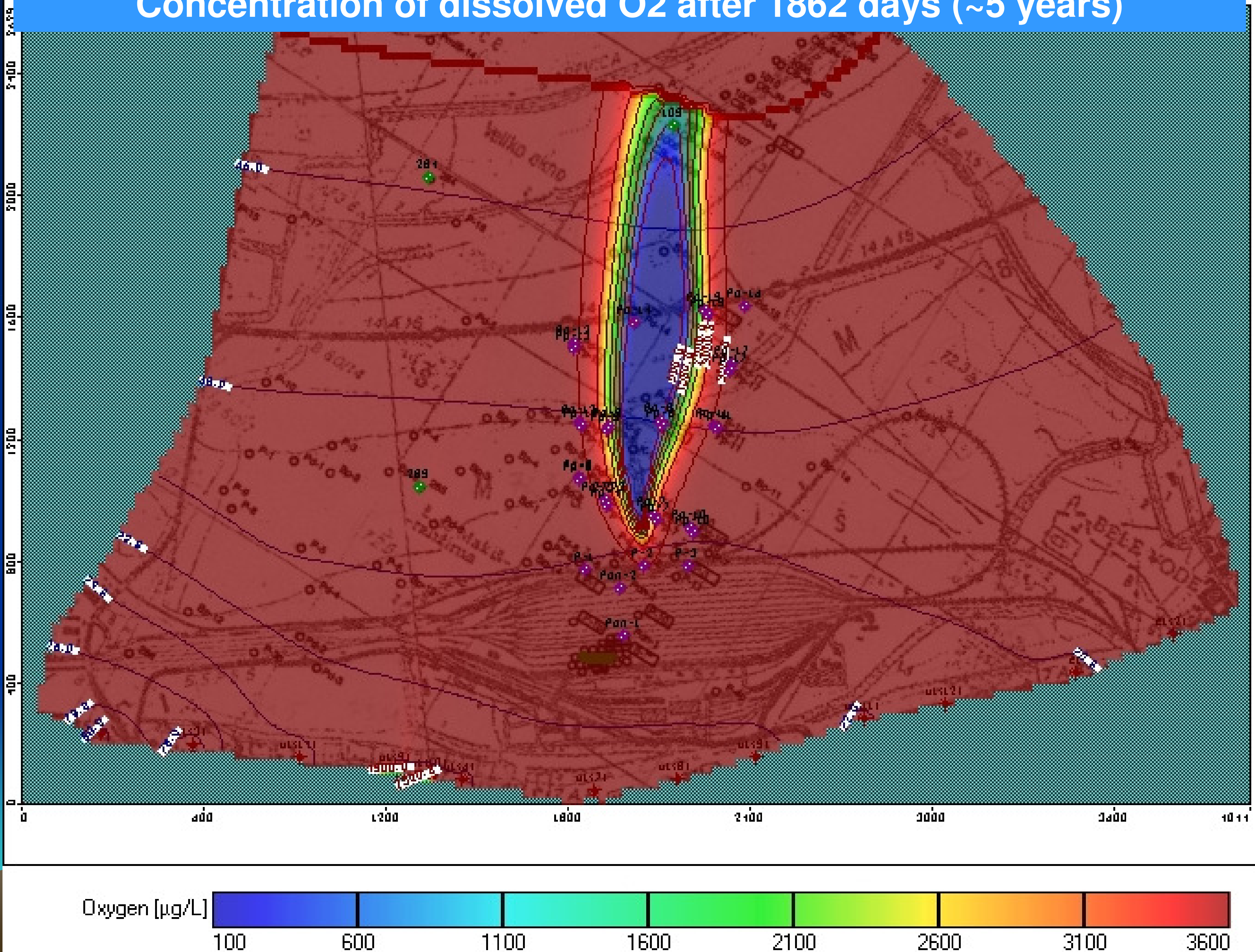
Concentration of xylene after 1862 days (~5.1 years)



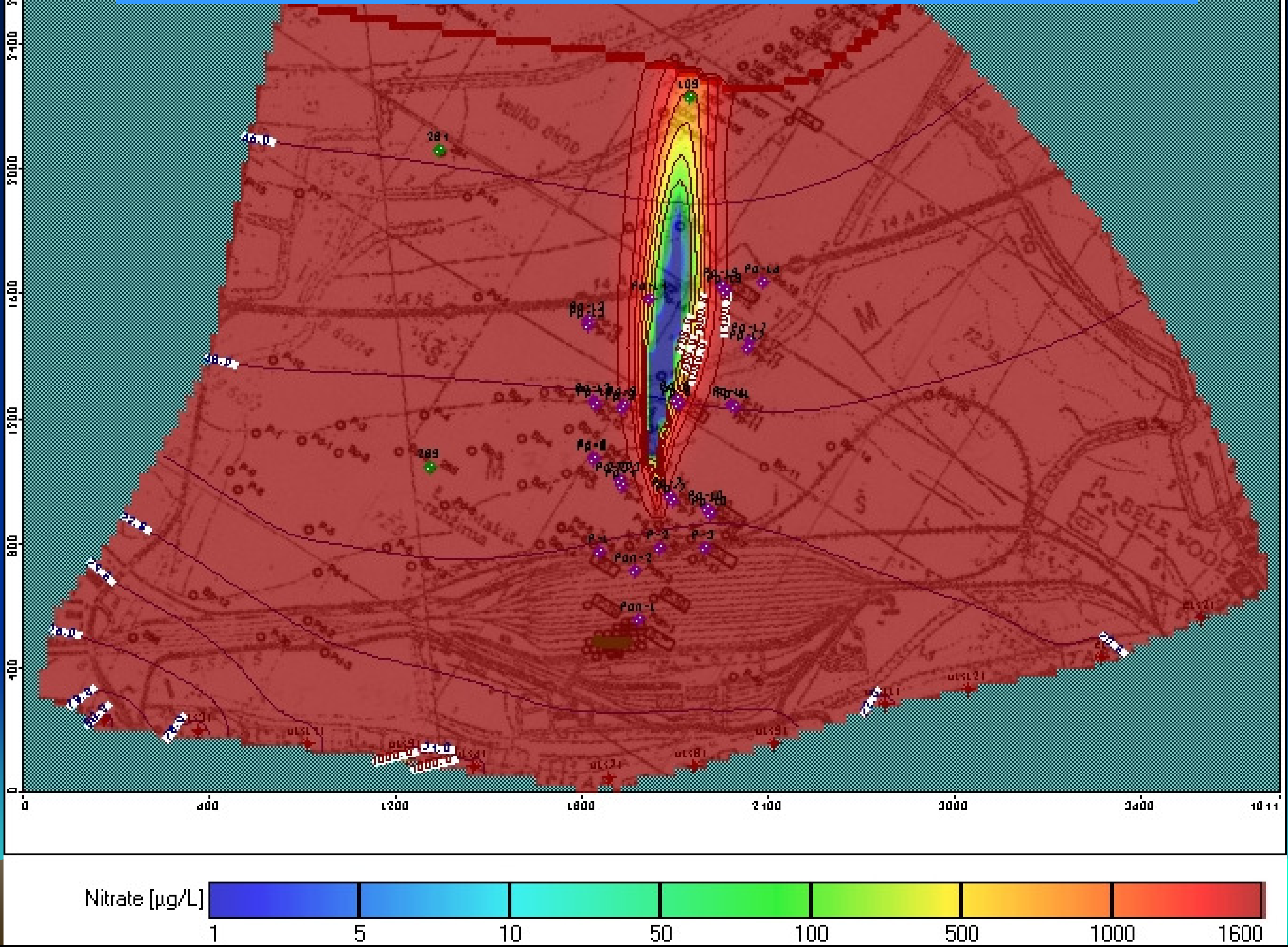
Concentration of xylene after 2550 days (~7 years)



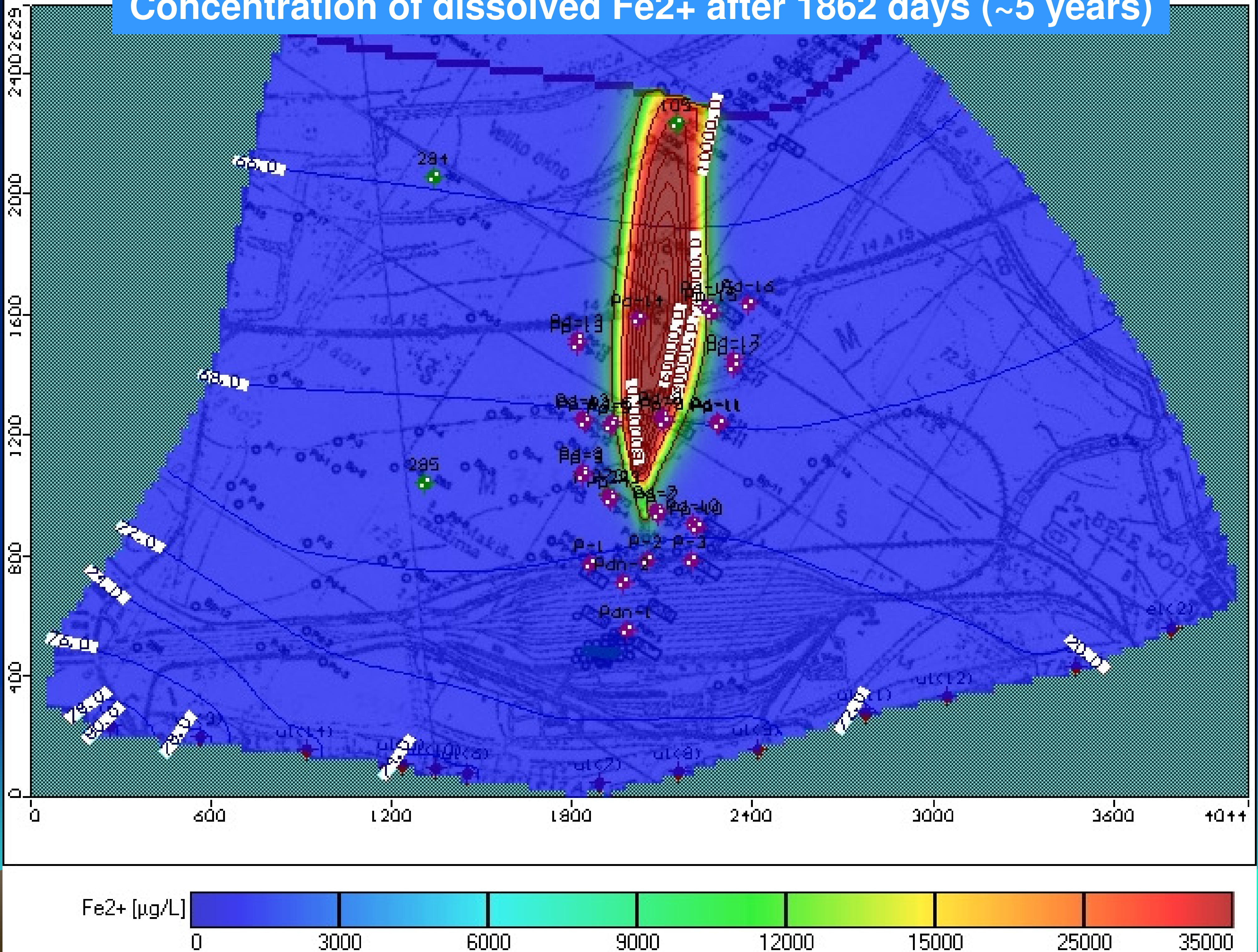
Concentration of dissolved O2 after 1862 days (~5 years)



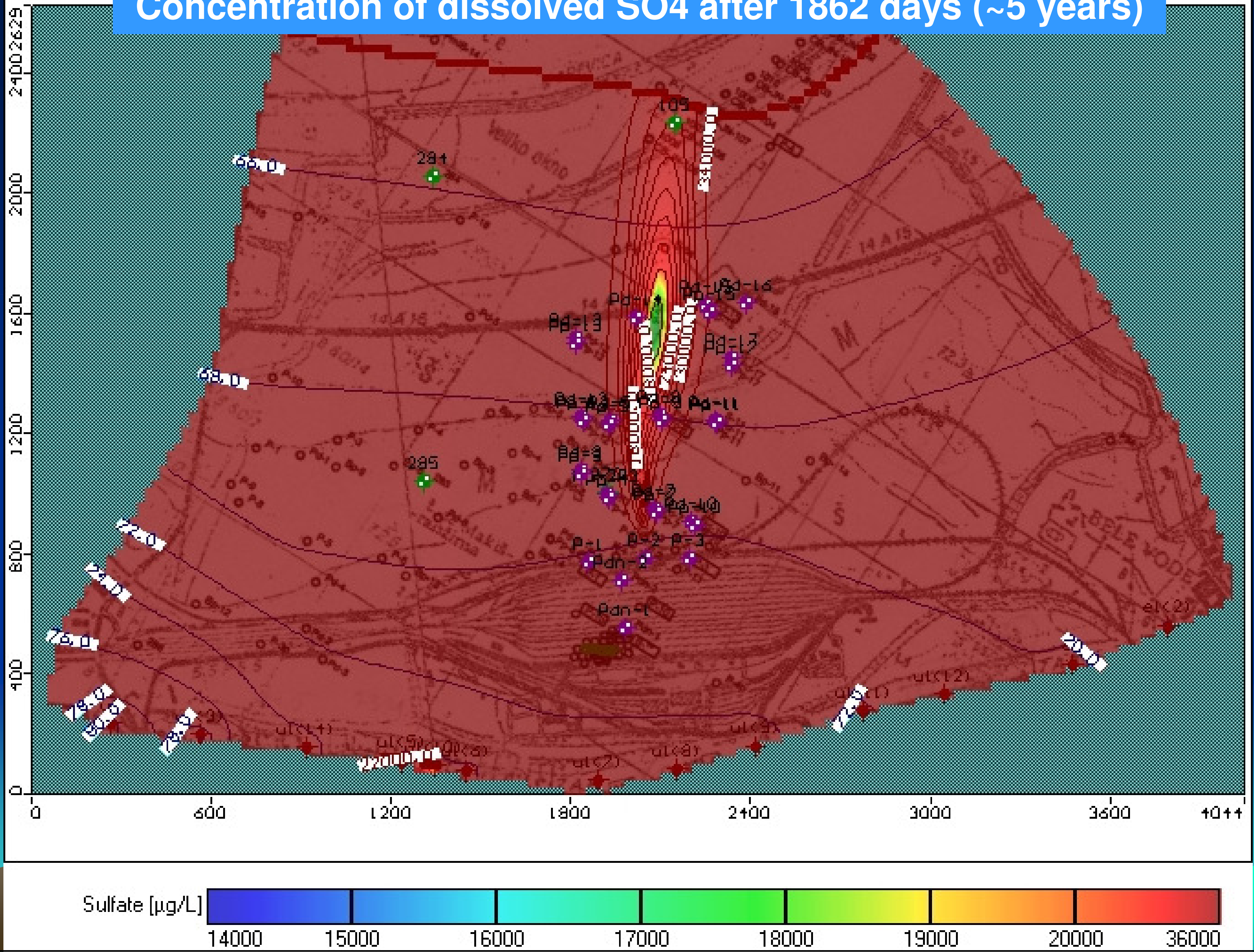
Concentration of dissolved NO3 after 1862 days (~5 years)



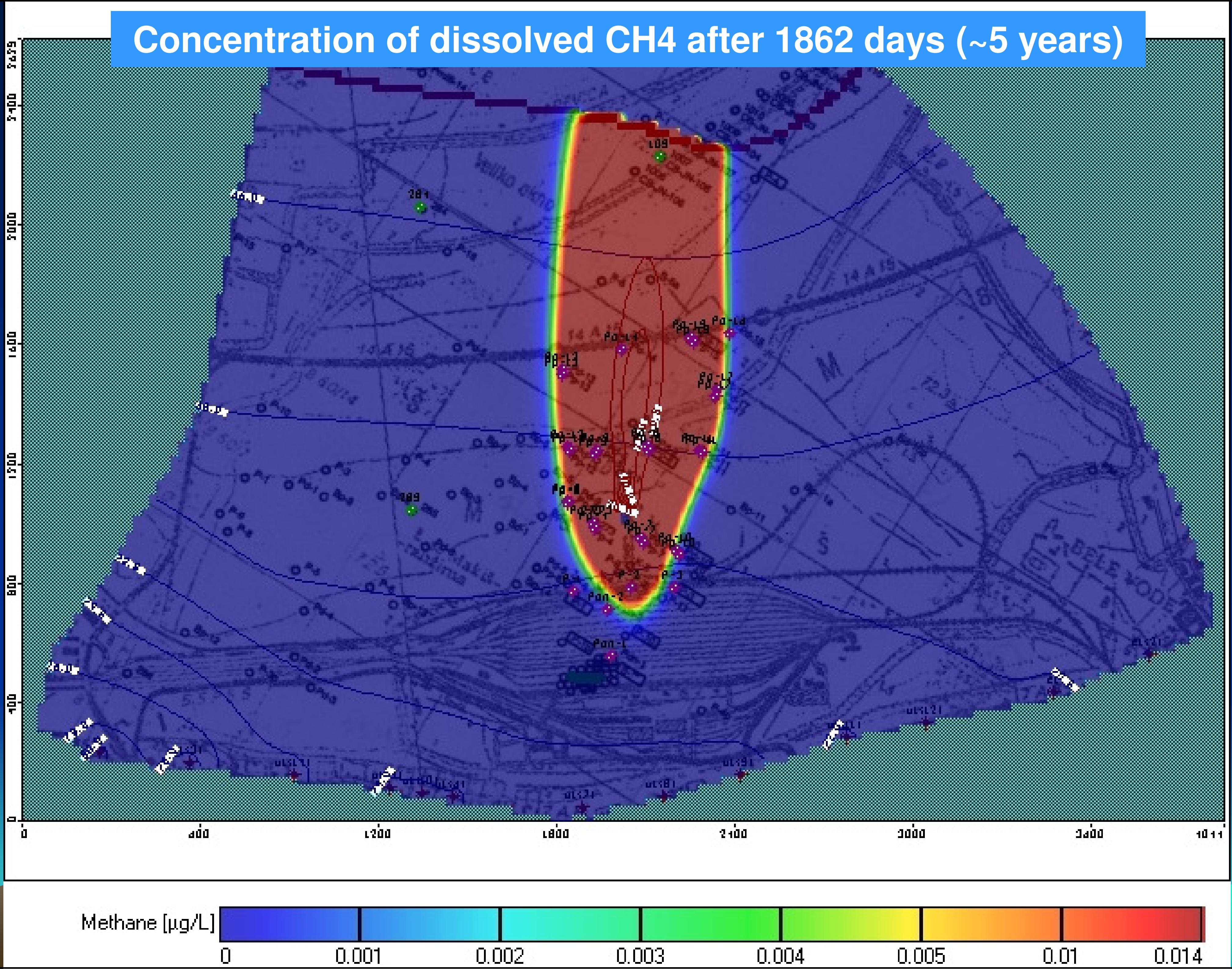
Concentration of dissolved Fe2+ after 1862 days (~5 years)



Concentration of dissolved SO4 after 1862 days (~5 years)

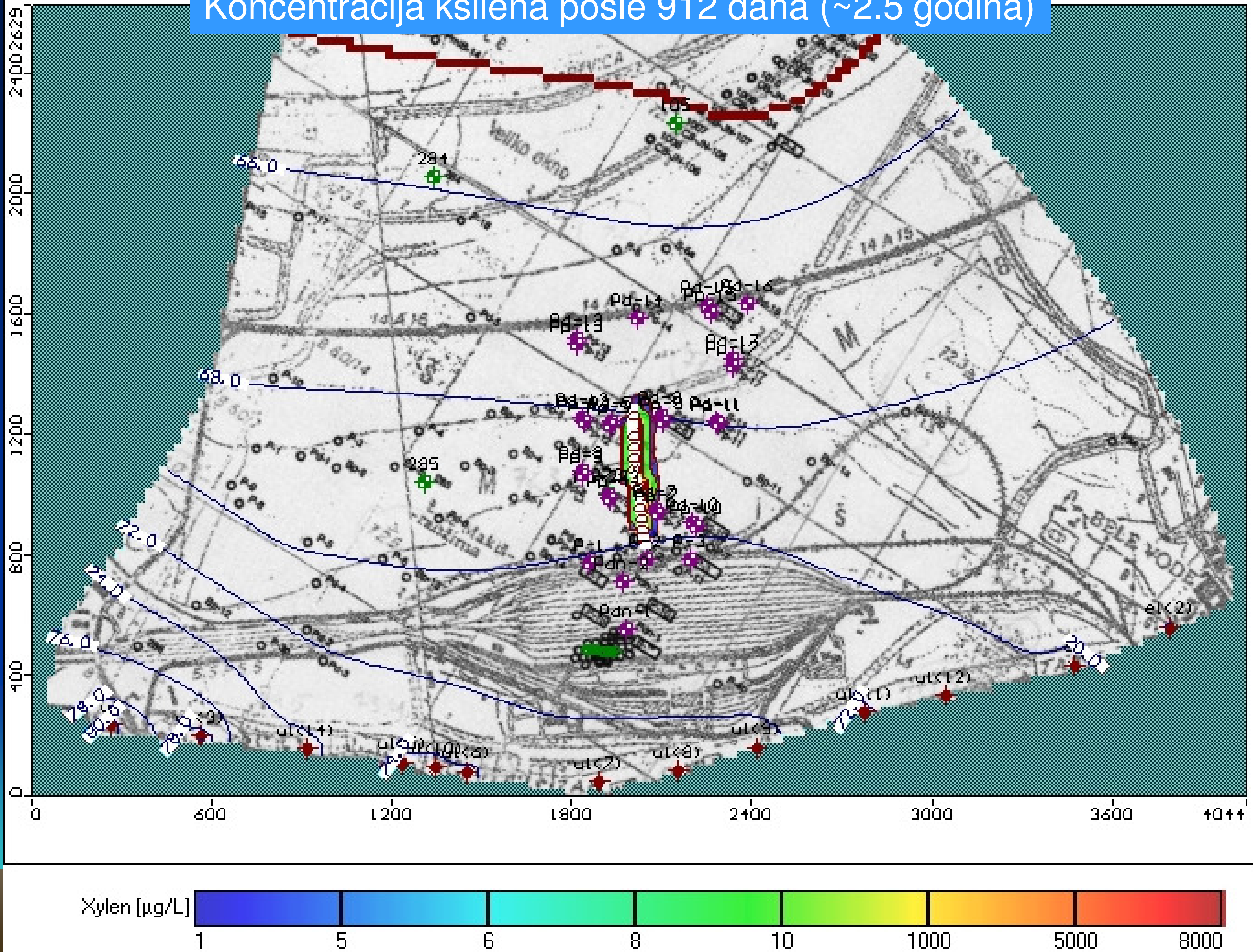


Concentration of dissolved CH4 after 1862 days (~5 years)

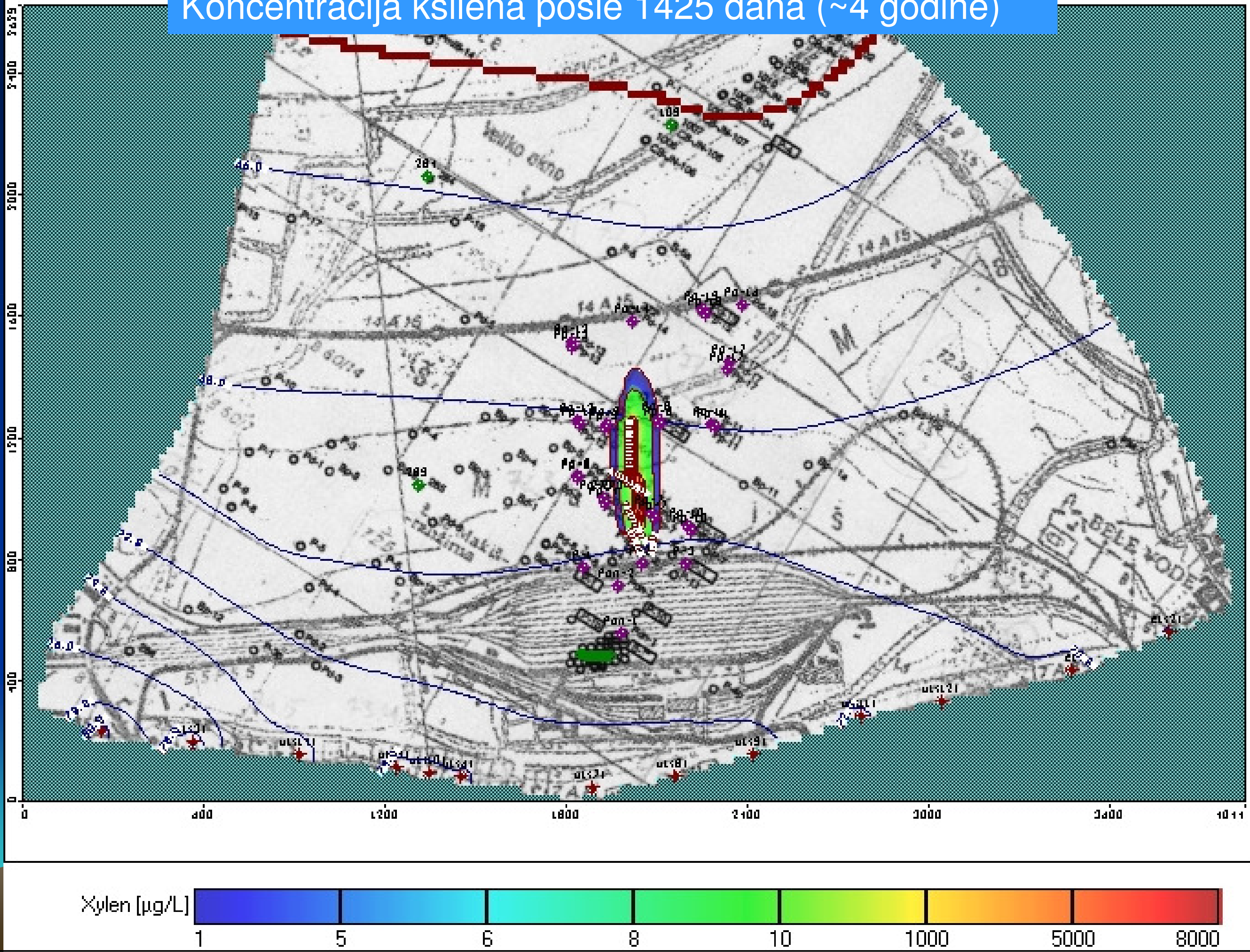


Movement of dissolved xylene with advection, dispersion, adsorption and microbial biodegradation – high Kd

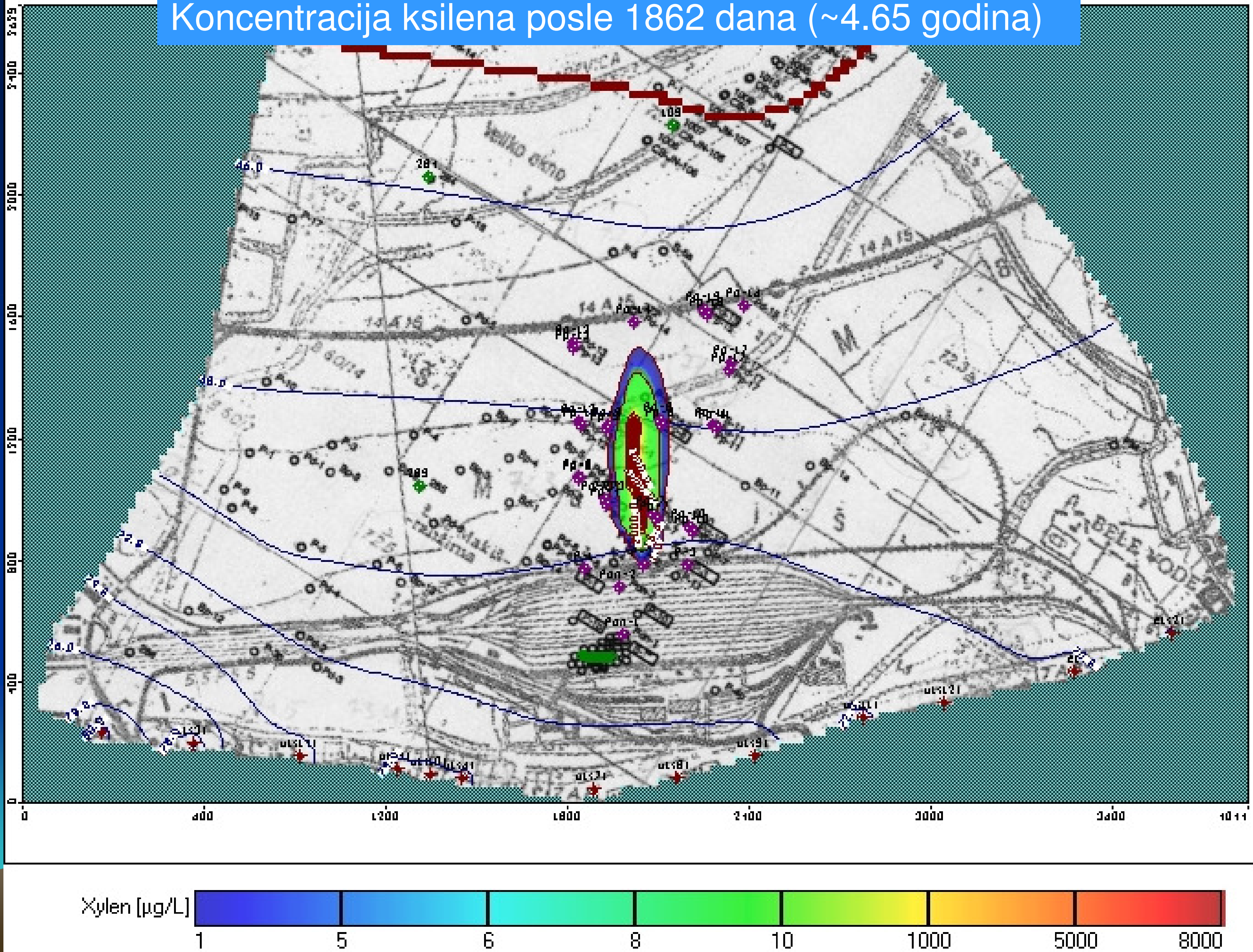
Koncentracija ksilena posle 912 dana (~2.5 godina)



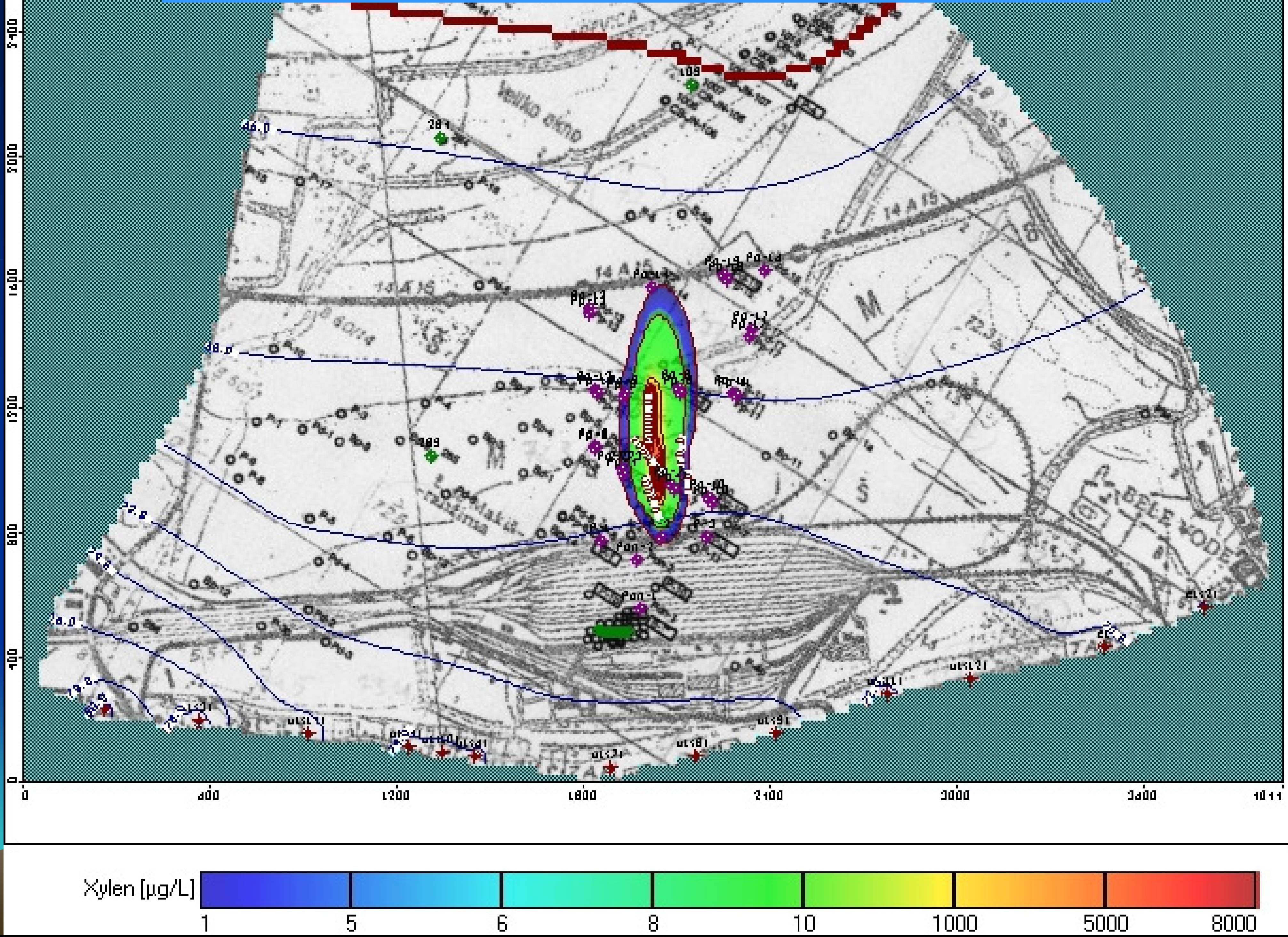
Koncentracija ksilena posle 1425 dana (~4 godine)



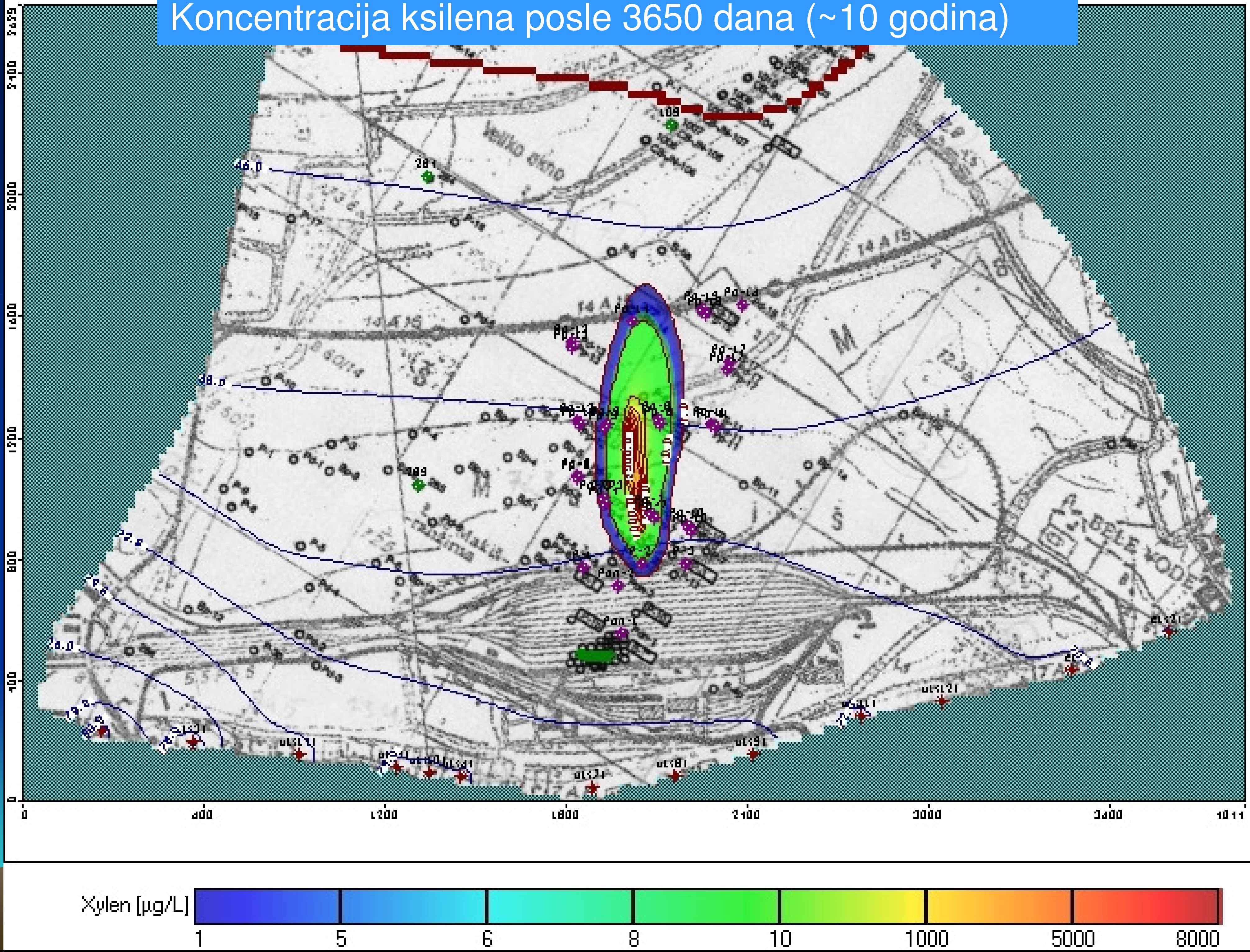
Koncentracija ksilena posle 1862 dana (~4.65 godina)



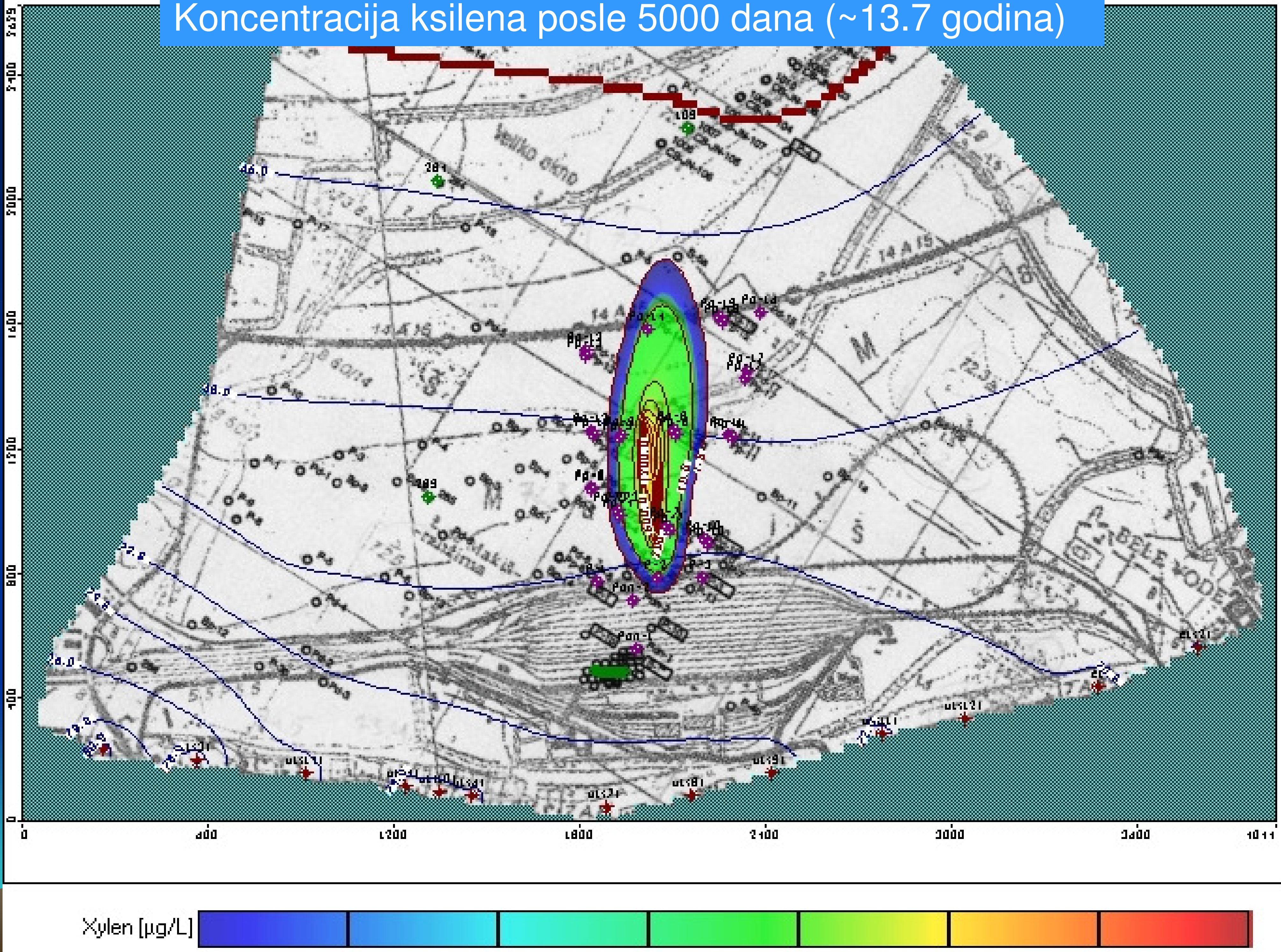
Koncentracija ksilena posle 2550 dana (~7 godina)



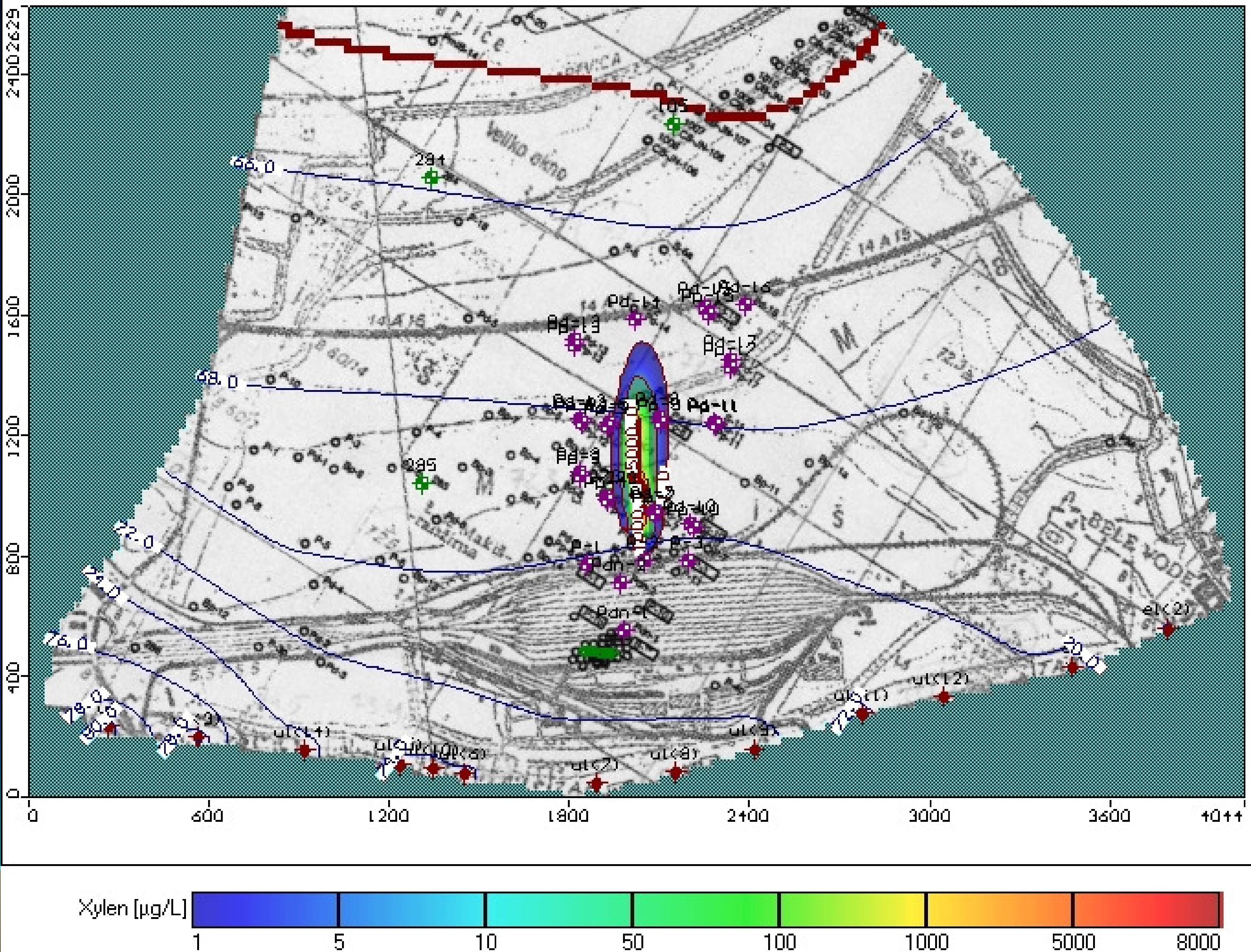
Koncentracija ksilena posle 3650 dana (~10 godina)

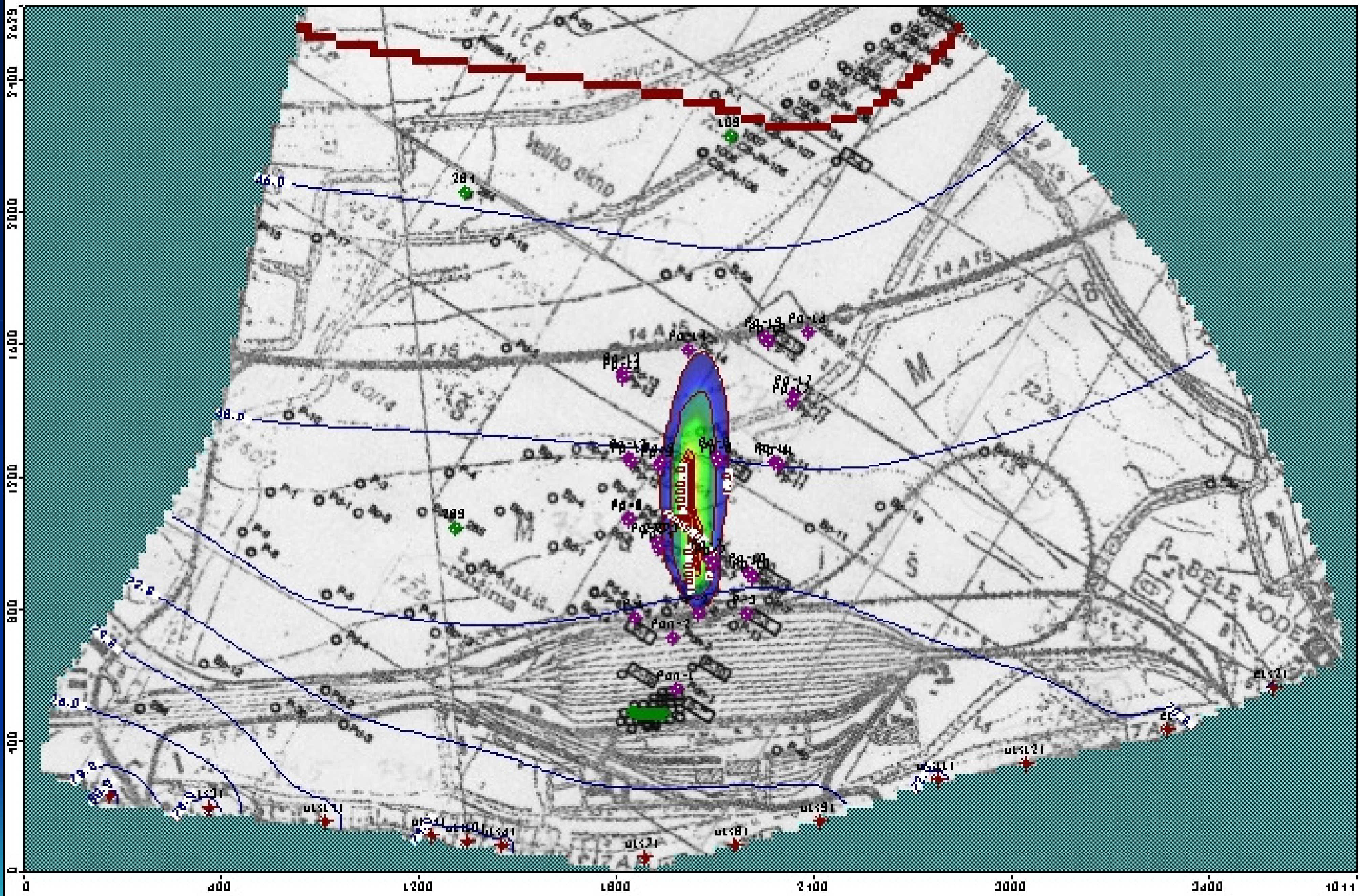


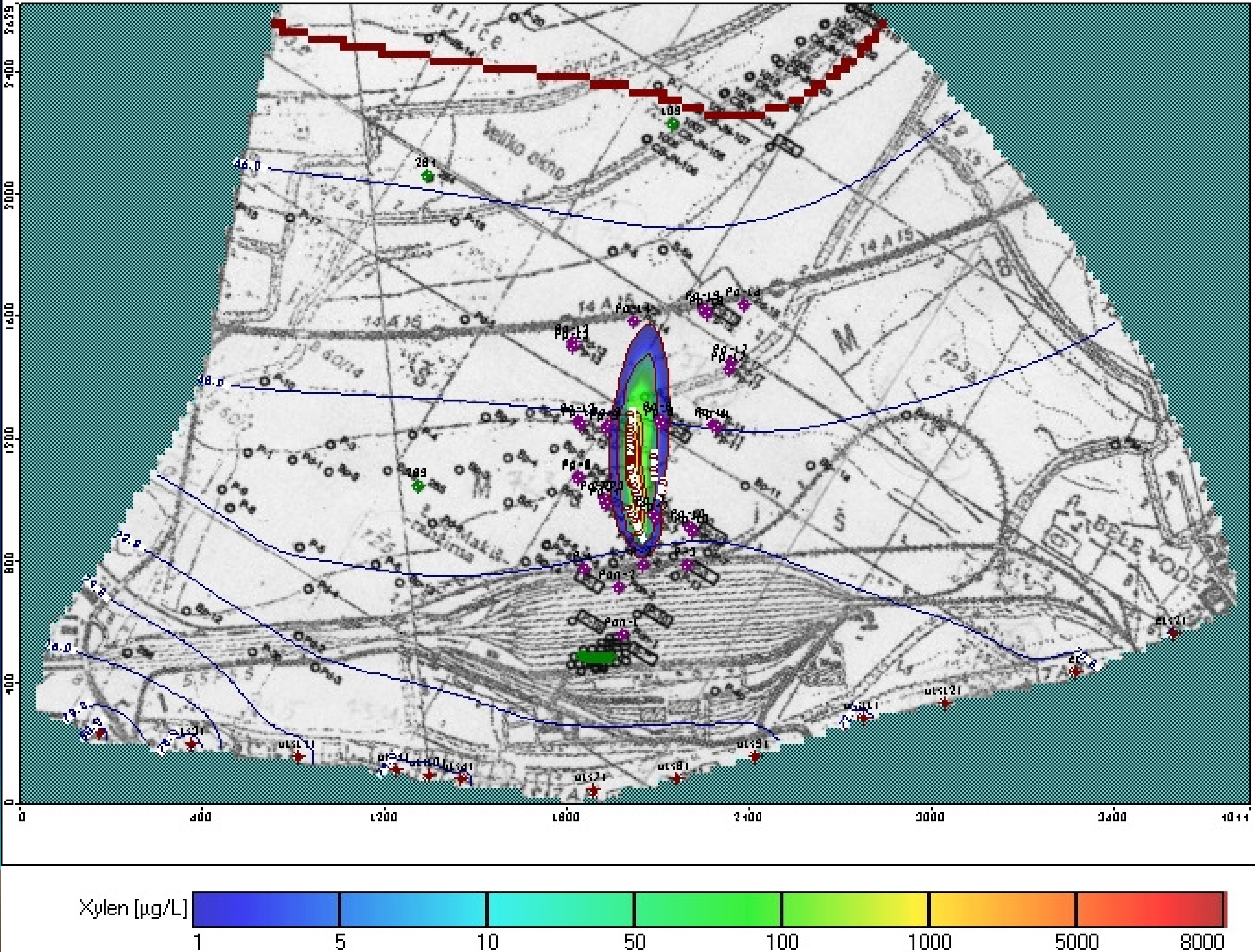
Koncentracija ksilena posle 5000 dana (~13.7 godina)

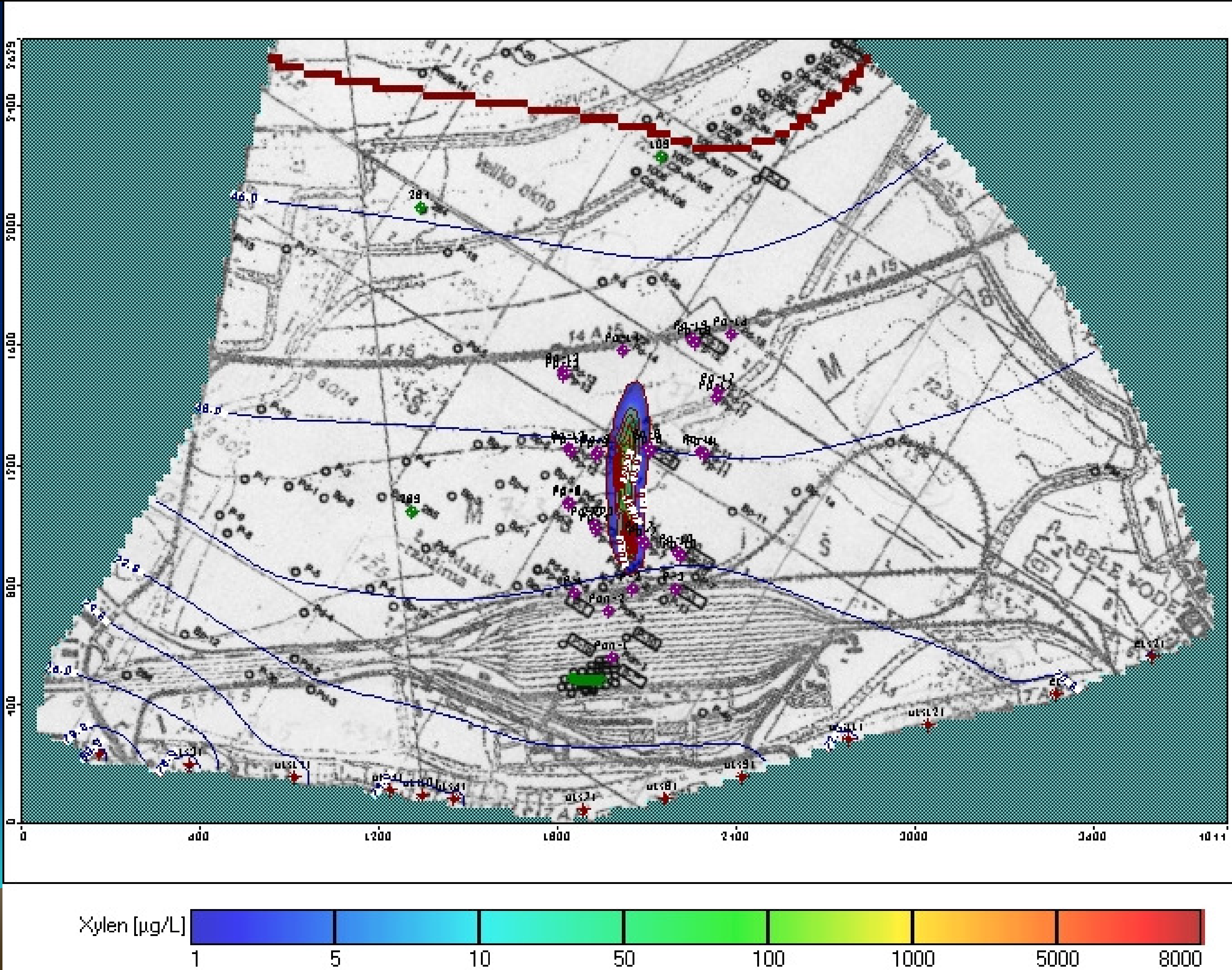


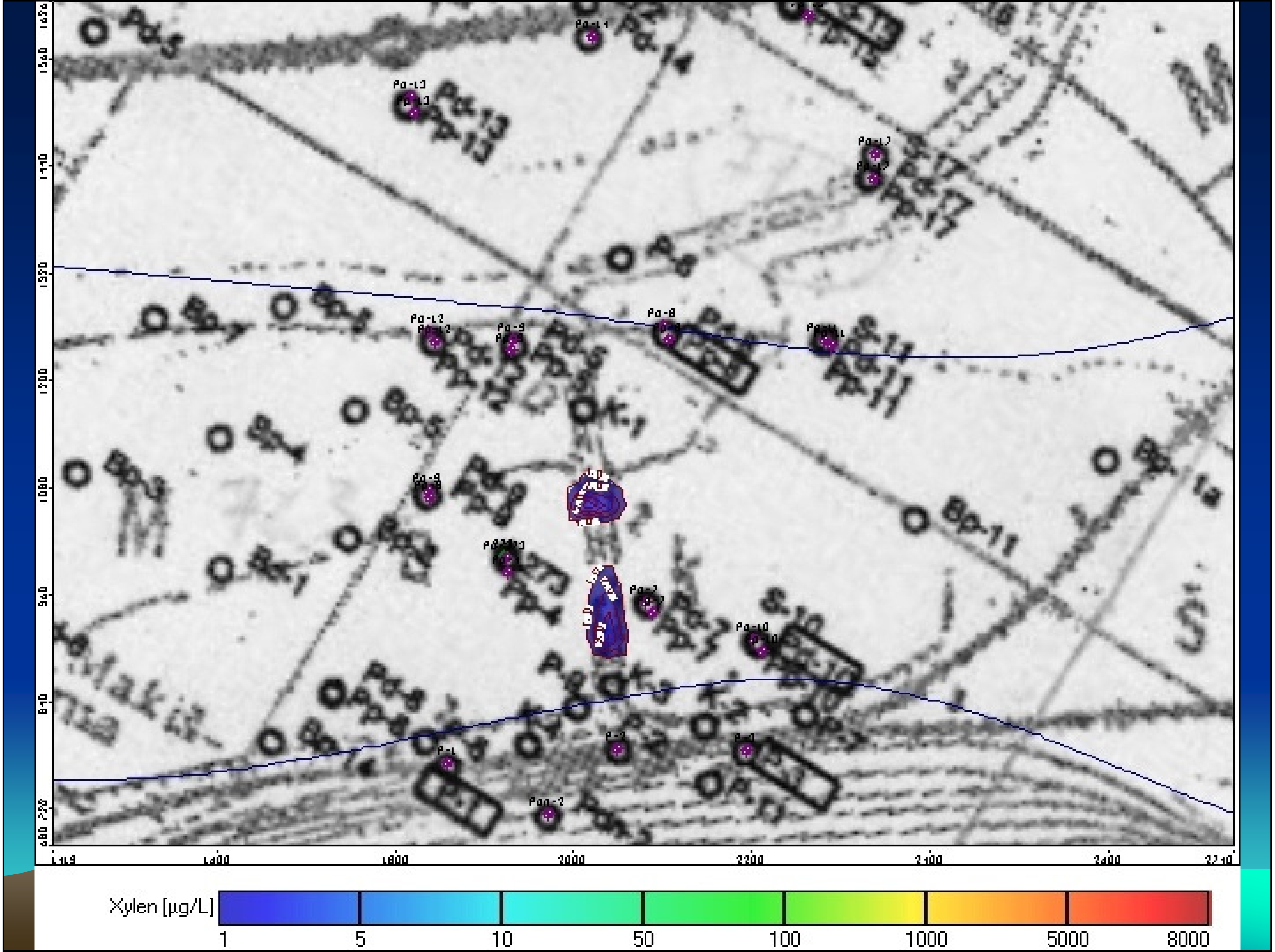
Movement of dissolved xylene with advection, dispersion, adsorption and microbial biodegradation – low Kd (calibrated case)

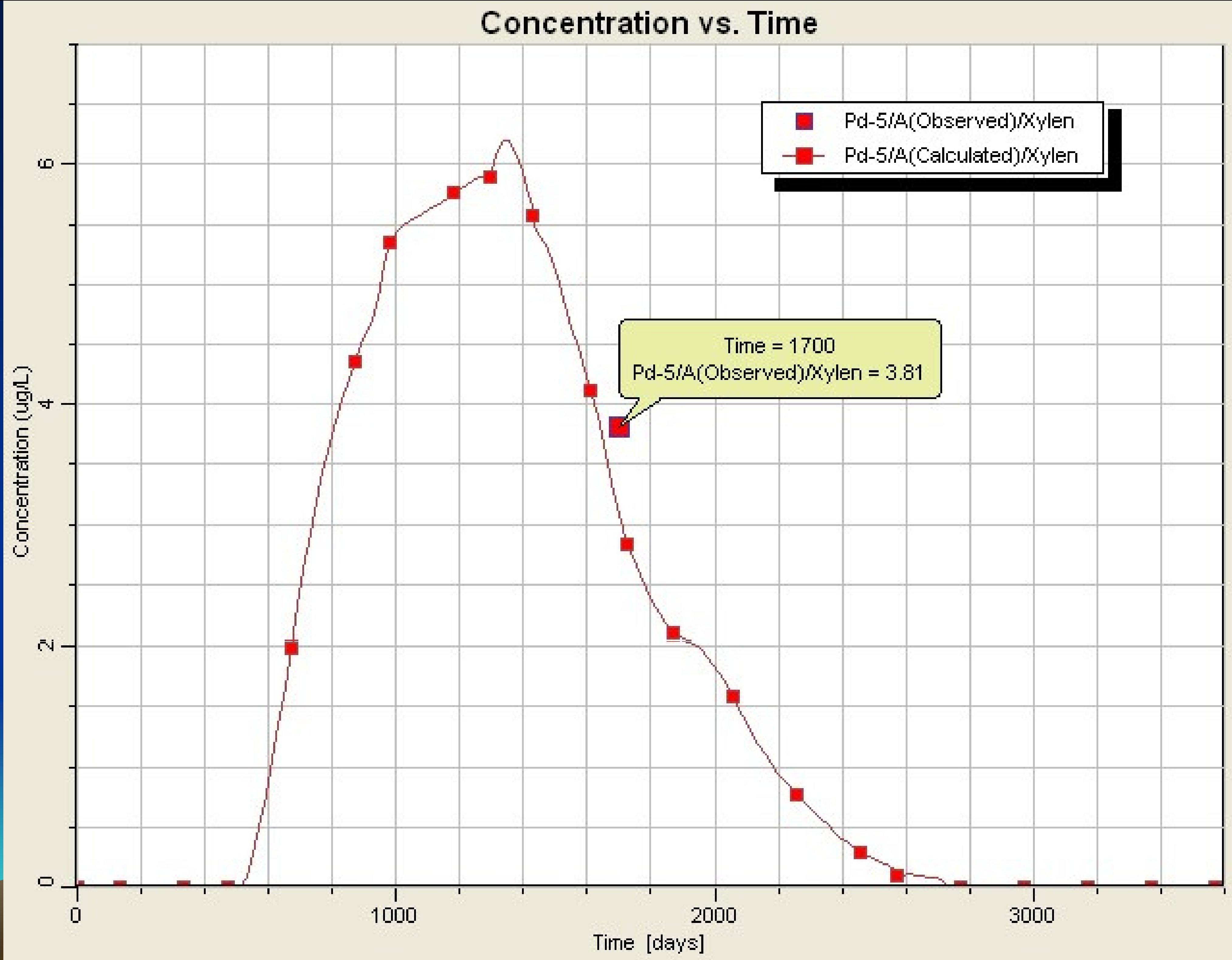

Xylen [µg/L]
1
5
10
50
100
1000
5000
8000
0
600
1200
1800
2400
3000
3600
4044
2629
2400
2000
1600
1200
800
400
0


Xylen [µg/L]
1
5
10
50
100
1000
5000
8000

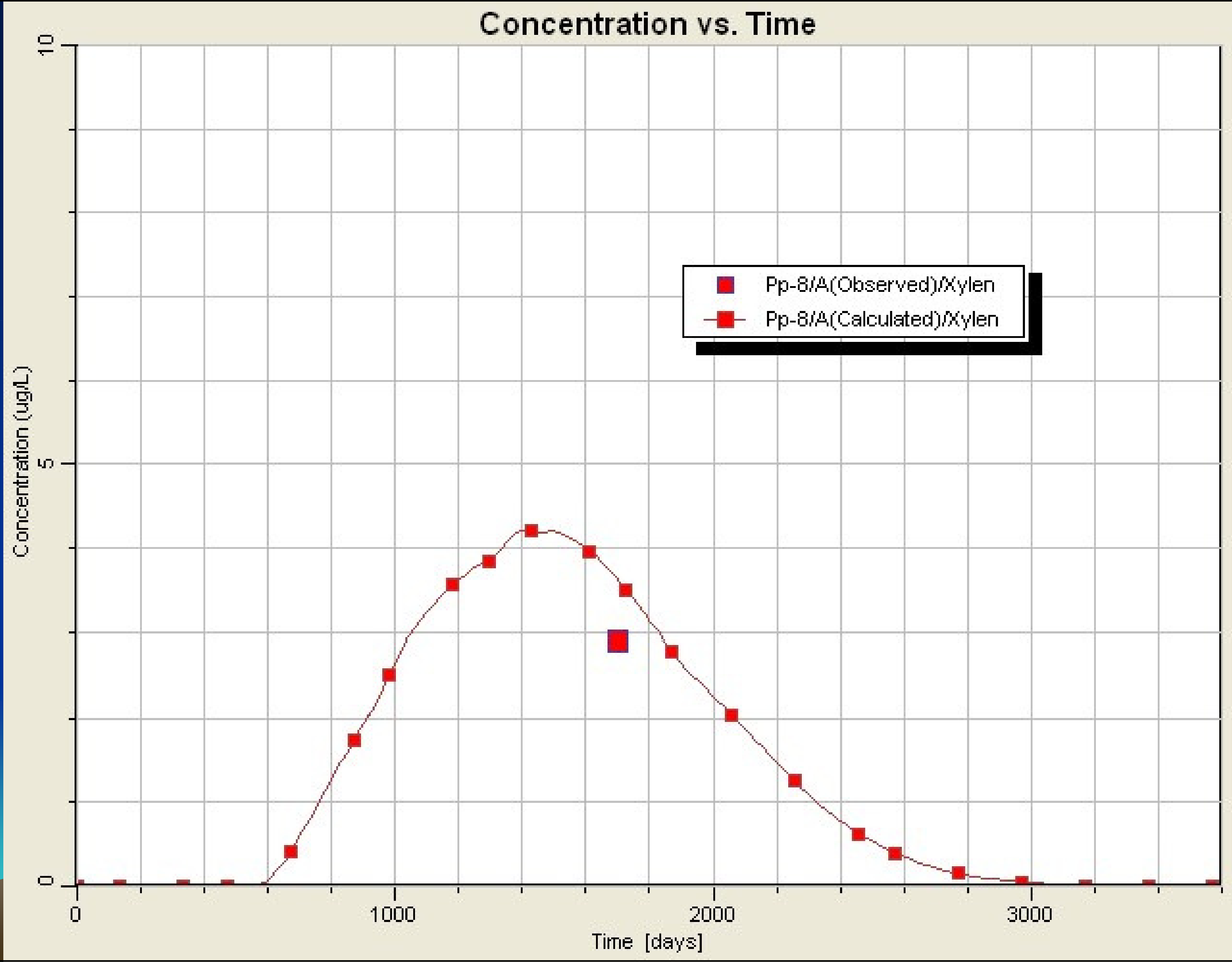

Xylen [µg/L]
1
5
10
50
100
1000
5000
8000


Xylen [µg/L]
1
5
10
50
100
1000
5000
8000

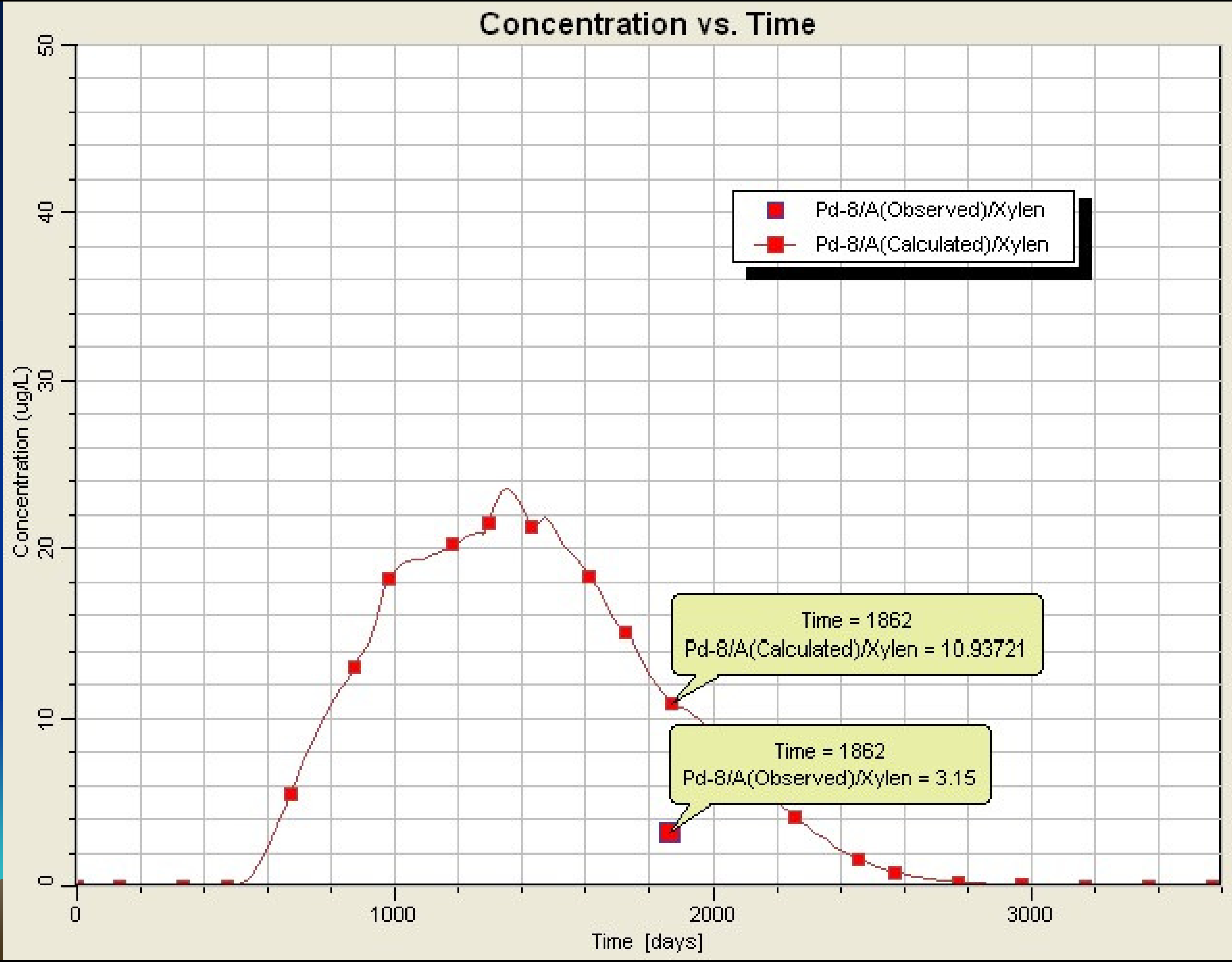

Xylen [µg/L]
1
5
10
50
100
1000
5000
8000



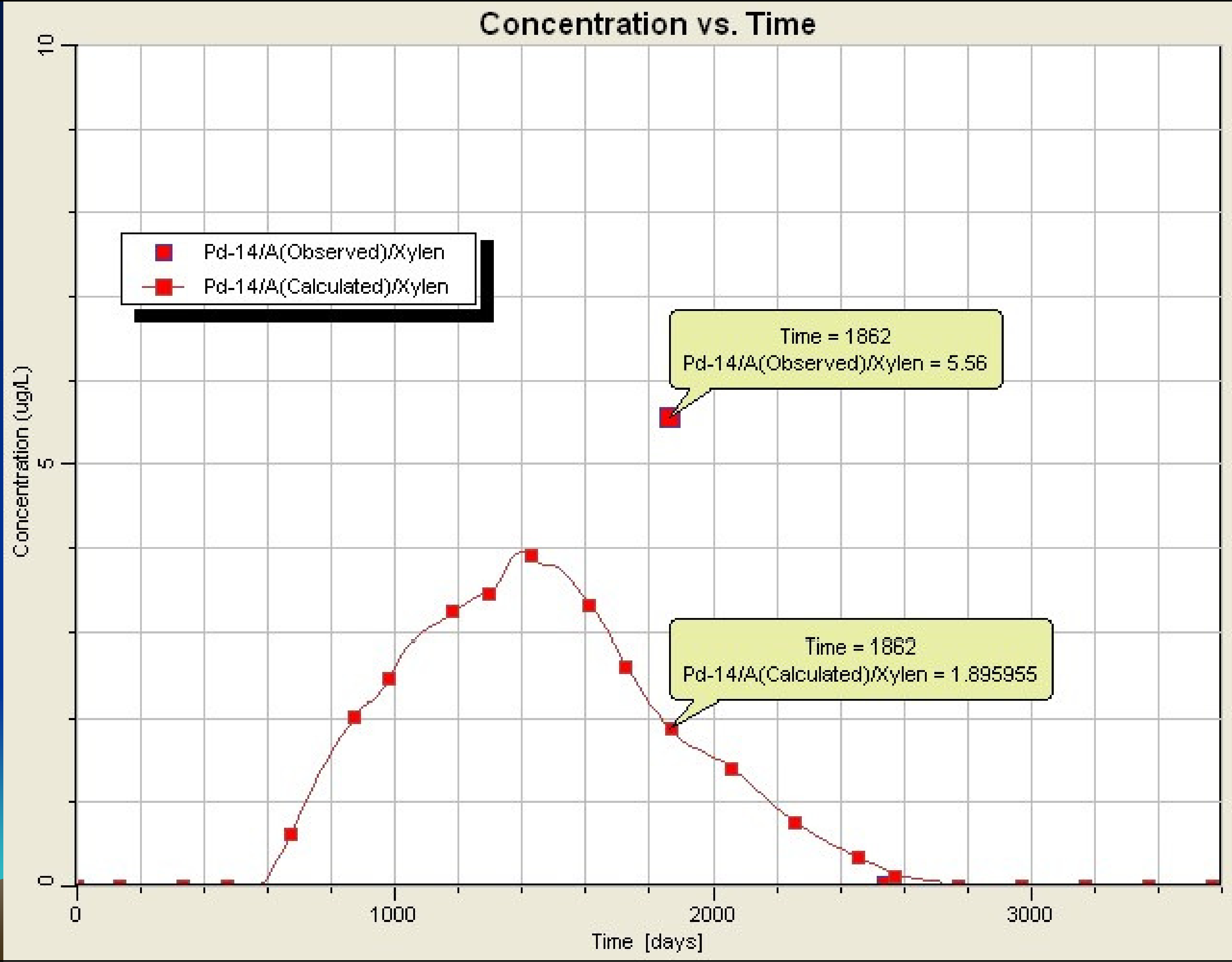
Concentration vs. Time
Pd-5/A(Observed)/Xylen
Pd-5/A(Calculated)/Xylen
Time = 1700
Pd-5/A(Observed)/Xylen = 3.81
Concentration (ug/L)
0
2
4
6
0
1000
2000
3000
Time [days]



Concentration vs. Time
Concentration (ug/L)
10
5
0
0
1000
2000
3000
Time [days]
Pp-8/A(Observed)/Xylen
Pp-8/A(Calculated)/Xylen



Concentration vs. Time
Pd-8/A(Observed)/Xylen
Pd-8/A(Calculated)/Xylen
Time = 1862
Pd-8/A(Calculated)/Xylen = 10.93721
Time = 1862
Pd-8/A(Observed)/Xylen = 3.15
Concentration (ug/L)
0
10
20
30
40
50
0
1000
2000
3000
Time [days]



Concentration vs. Time
Pd-14/A(Observed)/Xylen
Pd-14/A(Calculated)/Xylen
Time = 1862
Pd-14/A(Observed)/Xylen = 5.56
Time = 1862
Pd-14/A(Calculated)/Xylen = 1.895955
Concentration (ug/L)
10
5
0
1000
2000
3000
Time [days]

Conclusion

- In this case it is not necessarily to introduce active method of groundwater remediation since it is shown that plume will not move toward well field
- Monitoring is necessarily