An integrated approach for the effective management of the risks of water contamination by emerging contaminants

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# 3D modelling for assessing and forecasting PFAS distribution and evolution in a groundwater at a catchment scale

Action B.4.1 *Production and validation of the flow and transport numerical model*

*Vicenza 03.03.2021*

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ENTE COORDINATORE

REGIONE DEL VENETO

LIFE PHOENIX Project

lifephoenix.eu

PARTNER ASSOCIATI

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# *Presentation Overview*

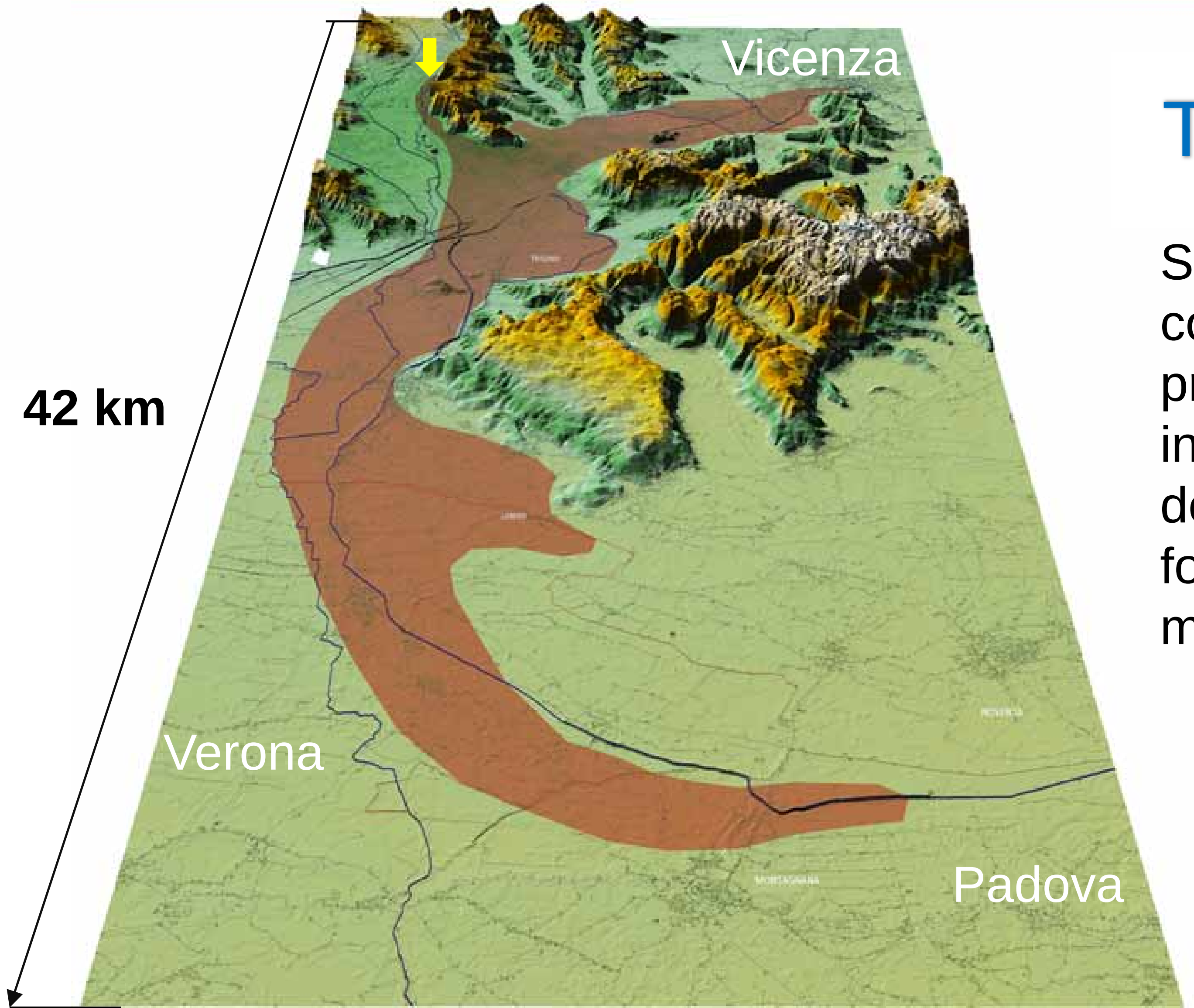
1. PFAS pollution in Veneto Region and LIFE PHOENIX Project
2. Goals of the action B4.1: the assessing and forecasting model
3. The Hydro-geological flow and trasport model and its implementation
4. Run simulations and conclusions

# PFAS pollution in Veneto Region

In 2013, the CNR / National Research Council detected the presence of a new class of contaminants (PFAS) in surface waters and in water public supply points in the Veneto Region, province of Vicenza and neighboring municipalities.

The reconstruction of the pollution carried out by ARPAV in 2013 allowed the identification of the origin of the pollution - fluorochemical plant - and the first delimitation of the contaminated territory. The extensive environmental surveys highlighted that the fluorochemical plant had an important impact on the water of large areas of the Veneto region, more than 200 square kilometers between the provinces of Vicenza, Padua and Verona.

The concentration value in the groundwater, out of polluted site, up to maximum values of 70.000 nanogram per liter.




# The issue

Since the first studies, the extension and complexity of the chemical-physical processes of pollution suggested the introduction of new analysis tools to decision-making support. This especially for the groundwater, the environmental matrix most polluted.

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# Need for knowledge to support decision-making

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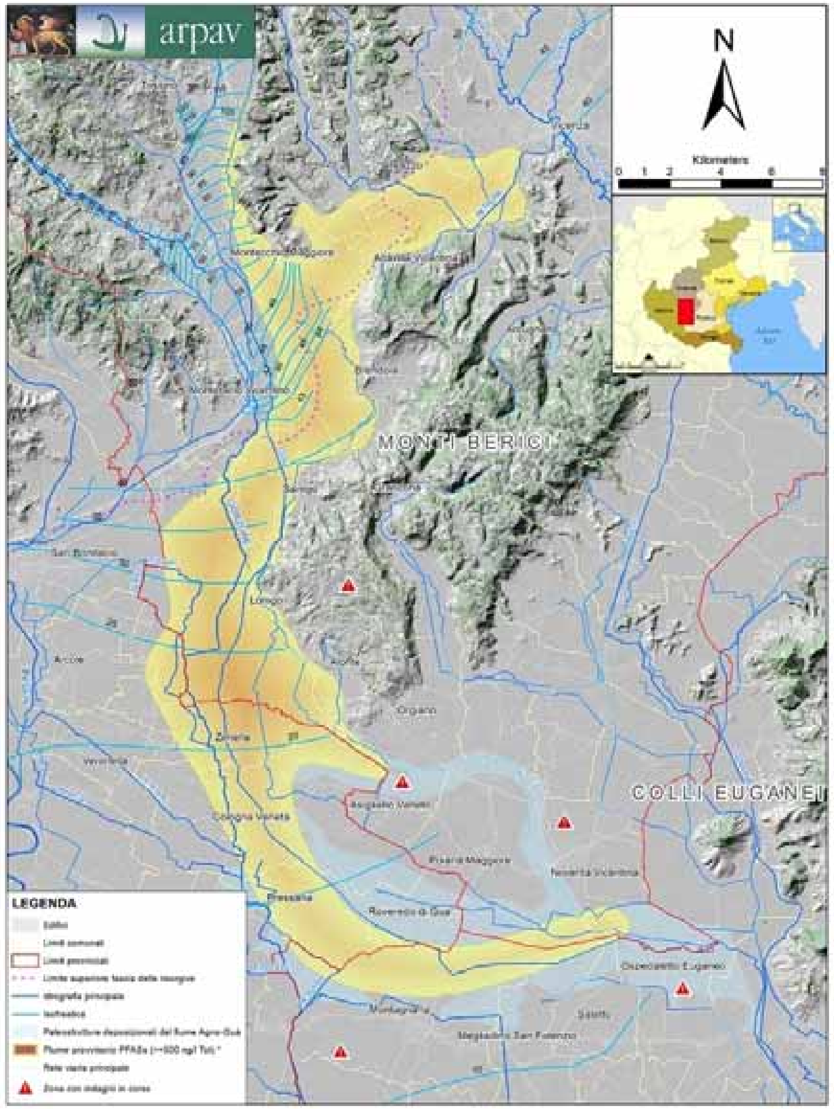



- When did the pollution start?
- How much contaminant has been spreading in the environment?
- Why do exist different contamination plumes (one for each PFAS species) and what are the consequences?
- How long the pollution will be present?
- How long had the pollutants taken to reach the public supply wells present in the area?
- What will be the evolution of contamination?

The key words are **interpret, quantify and predict**

# EU LIFE PHOENIX PROJECT

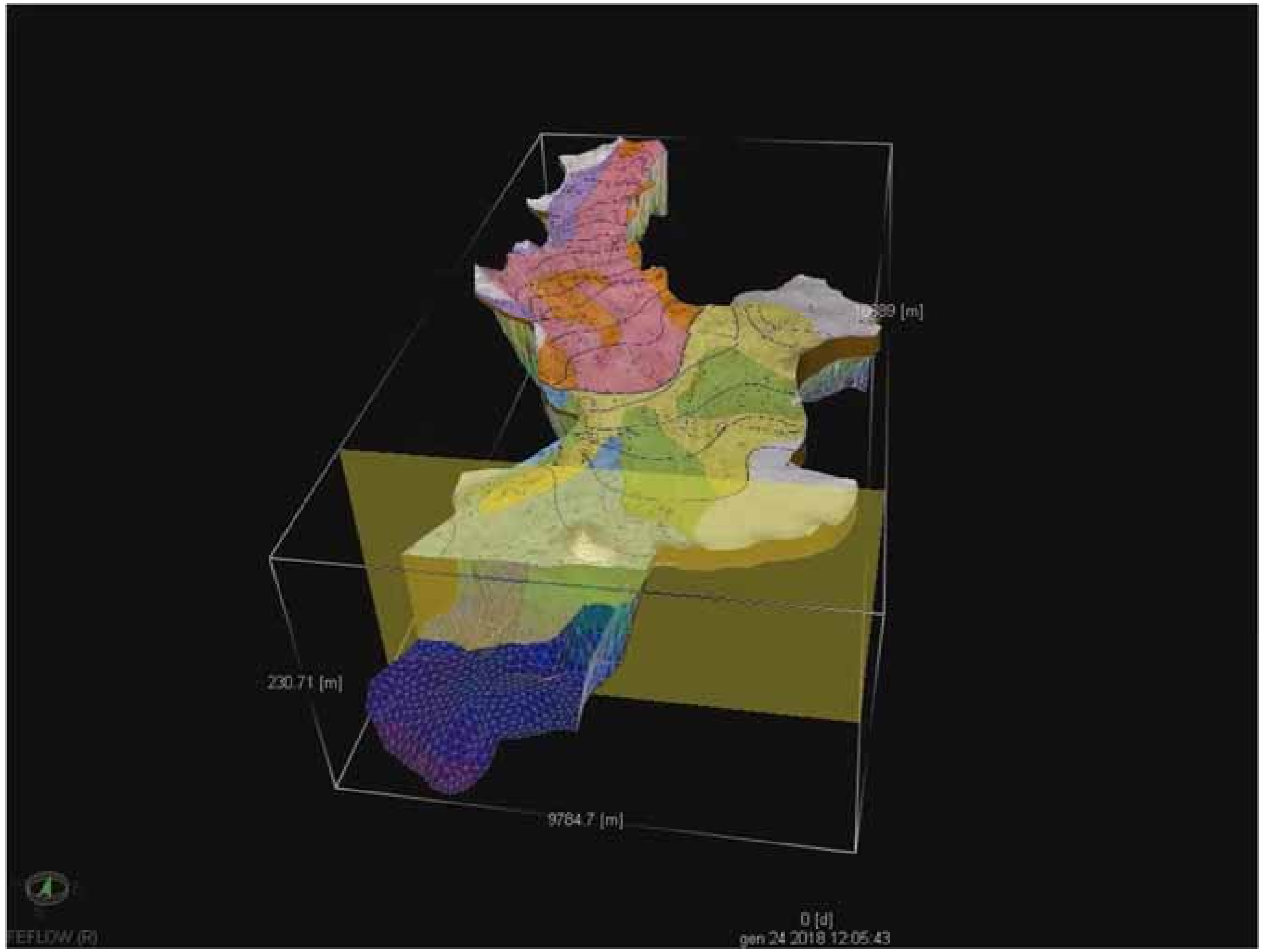
As part of the European LIFE PHOENIX project, the advanced decision-support prediction tool introduced by ARPAV is numerical modelling applied to groundwater and surface waters. This mathematical model provides the ability to **interpret**, **quantify** and **predict** the many aspects about the PFAS contamination.

In other words, with numerical modelling, the **TIME** is inserted in the environmental data analysis, with the ability to simulate the present, past and future spatial evolution of pollutants.

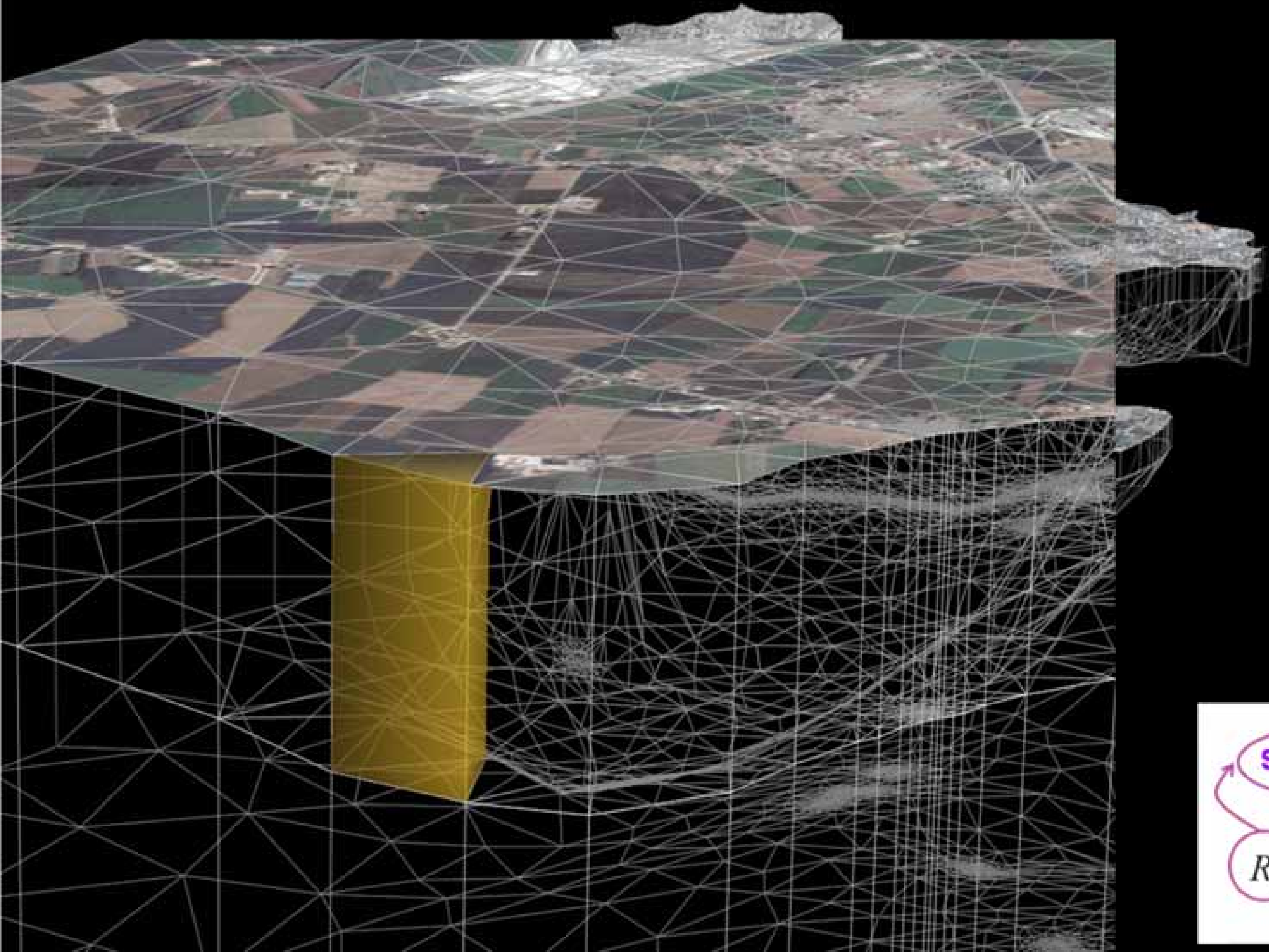
# NUMERICAL MODEL

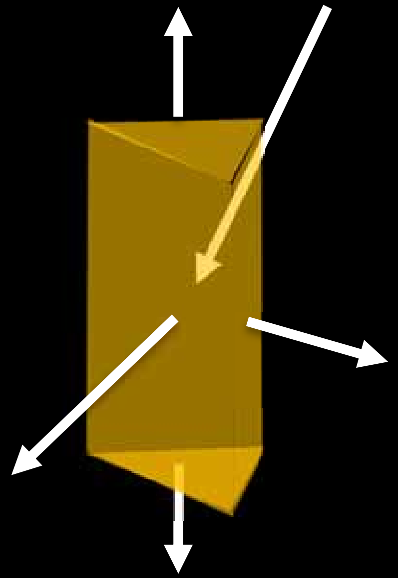
What is a numerical model? A numerical model is a mathematical model where the physical-chemical processes of the real world are simulated through mathematical equations (flow and transport equations).

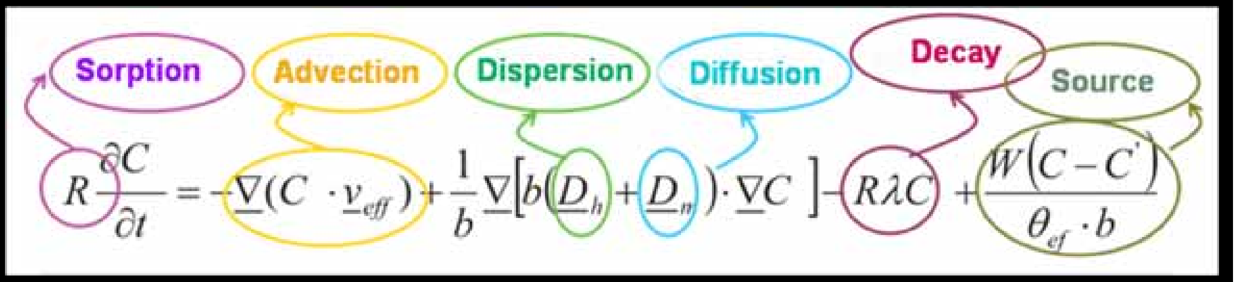
The numerical models, through the **discretization** of real space (simulation domain), allow the best (and most complex too) reproduction of the physical-chemical processes of the real world.



***HOW IT WORKS: The discretization introduces the concept of Representative Elementary Volume (REV), defined as a volume in which the microscopic properties are averaged to obtain approximately constant macroscopic values, independent of the dimensions of the REV (Bear, 1972).***








$$R\frac{\partial C}{\partial t} = -\underline{\nabla}(C \cdot \underline{v}_{eff}) + \frac{1}{b}\underline{\nabla}\left[b(\underline{D}_h + \underline{D}_n)\cdot\underline{\nabla}C\right] - R\lambda C + \frac{W(C - C')}{\theta_{ef} \cdot b}$$

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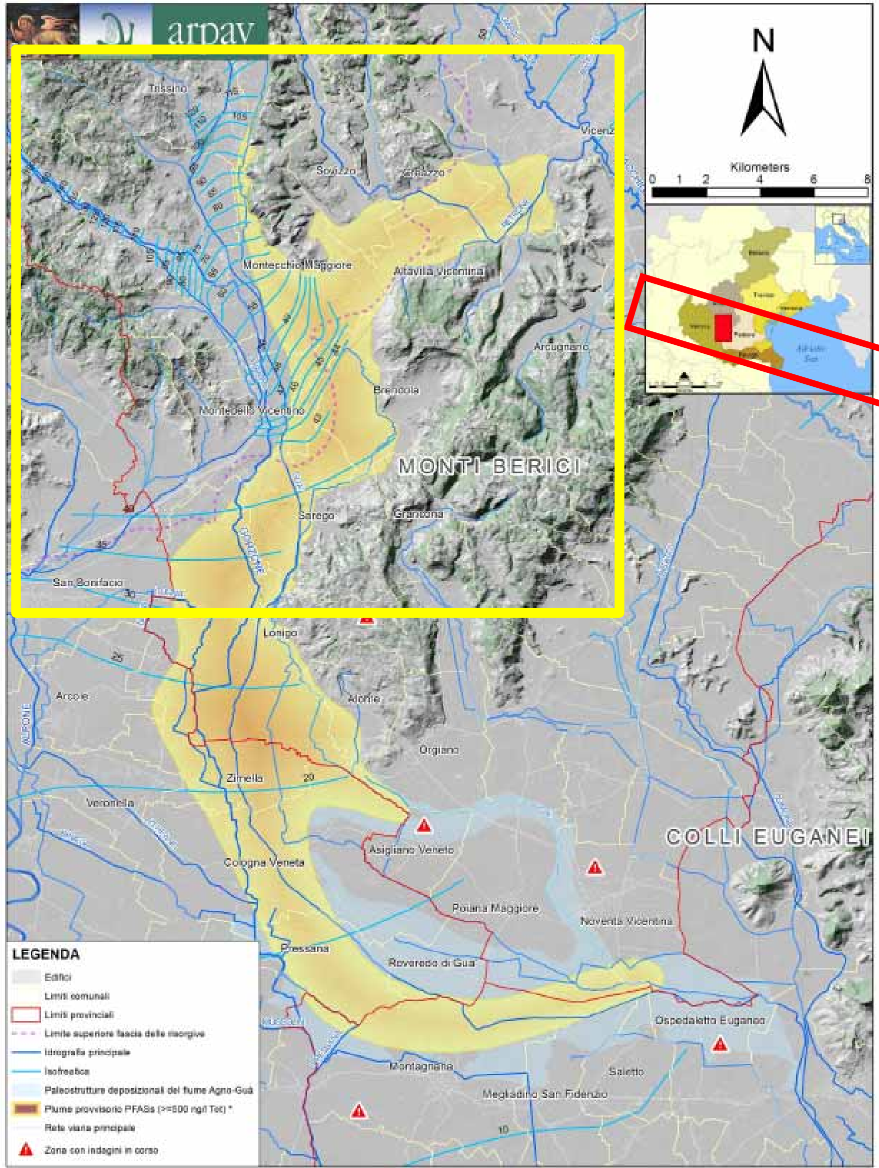
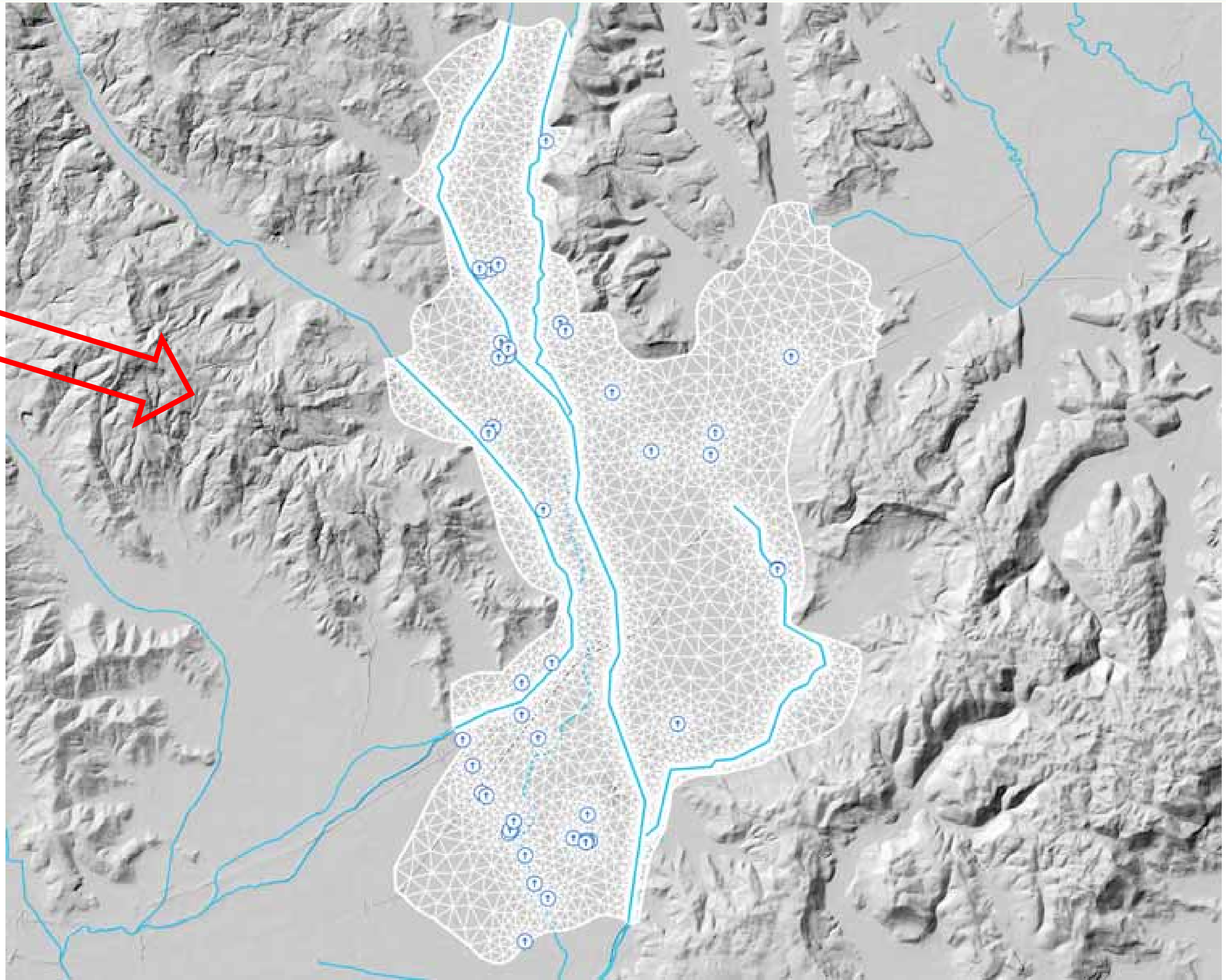
# Where:

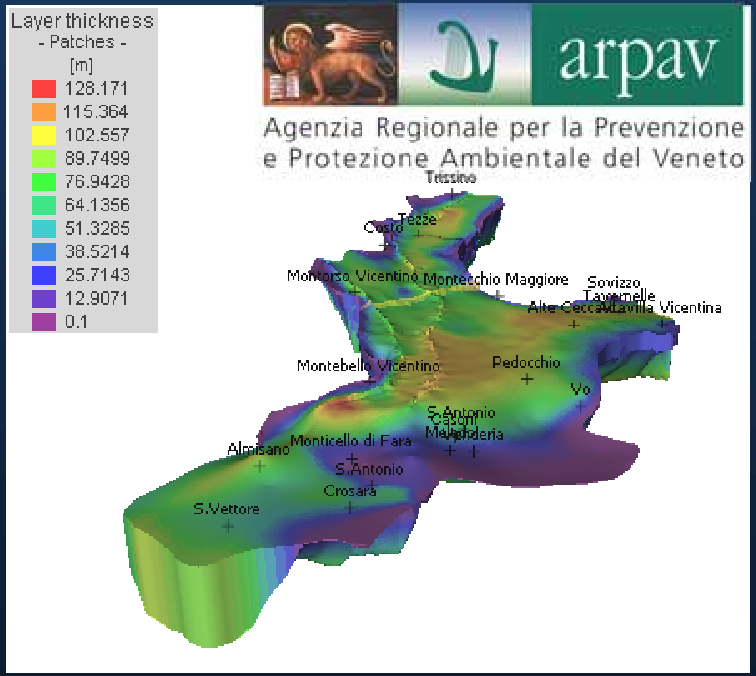


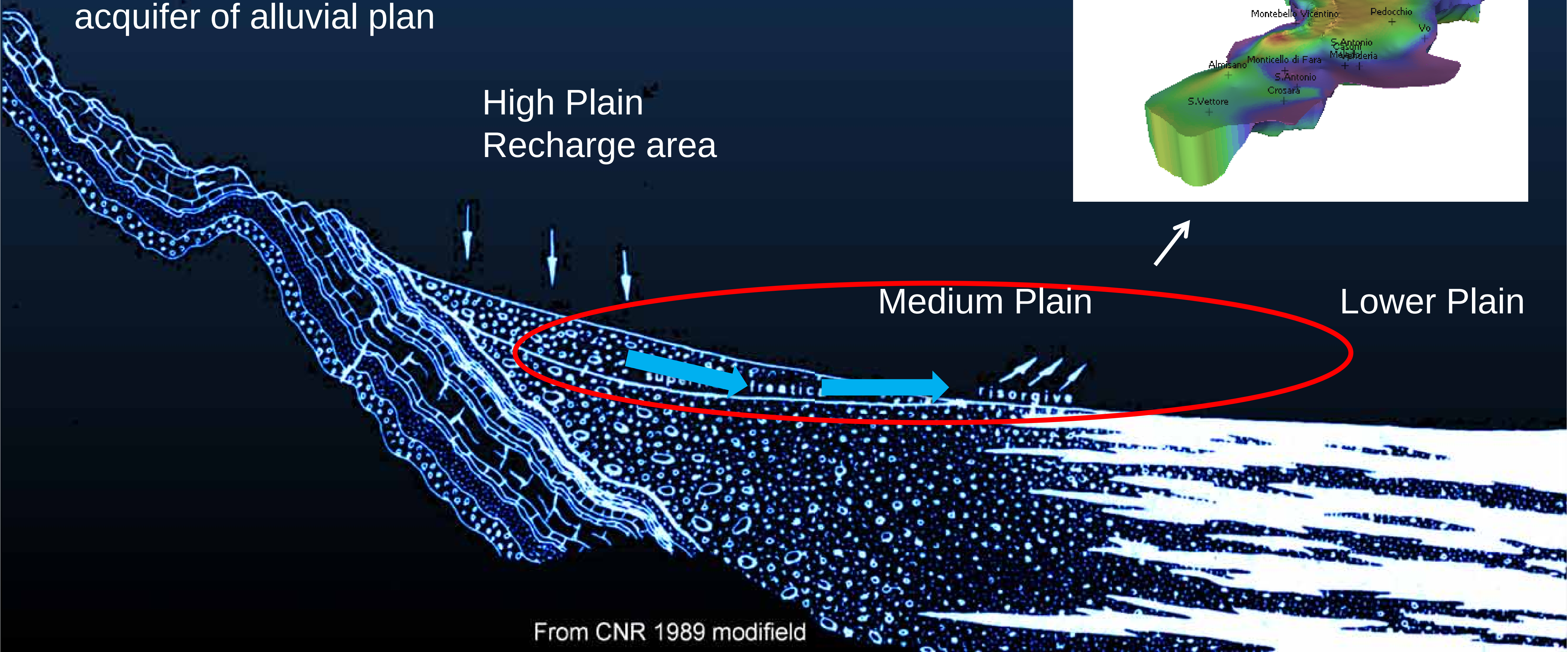



# Hydrogeological asset

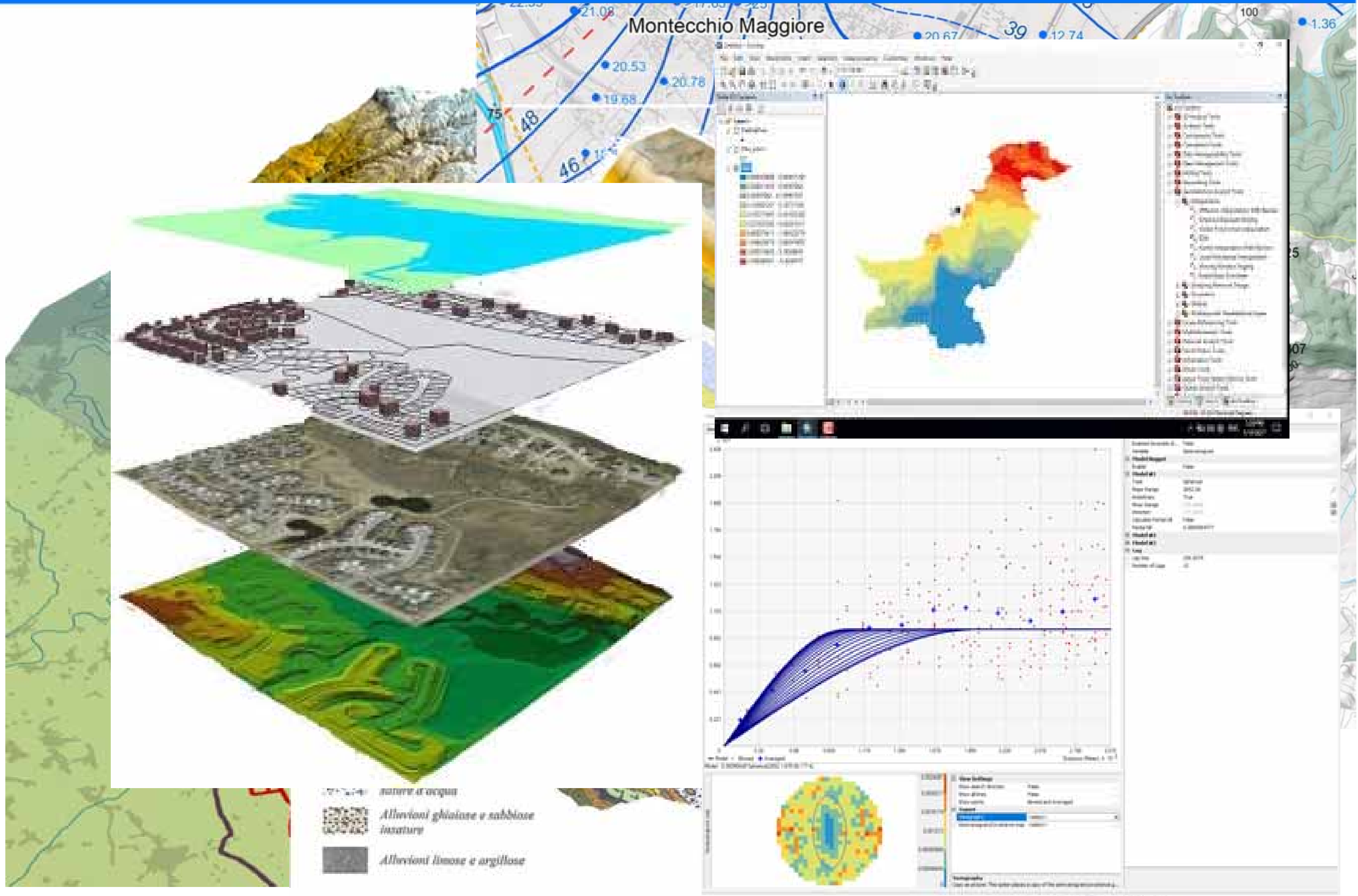
2 large hydrogeologic domains: rock aquifers of the mountains, porous acquifer of alluvial plan

Full 3 D MODEL



Implementing numerical modeling requires a lot of data and information. A lot of scientific knowledge is integrated such as hydrogeology, mathematics, chemistry, geostatistics, geographic information systems (GIS). All these scientific subjects are necessary to simulate the spread of pollution in the environment.



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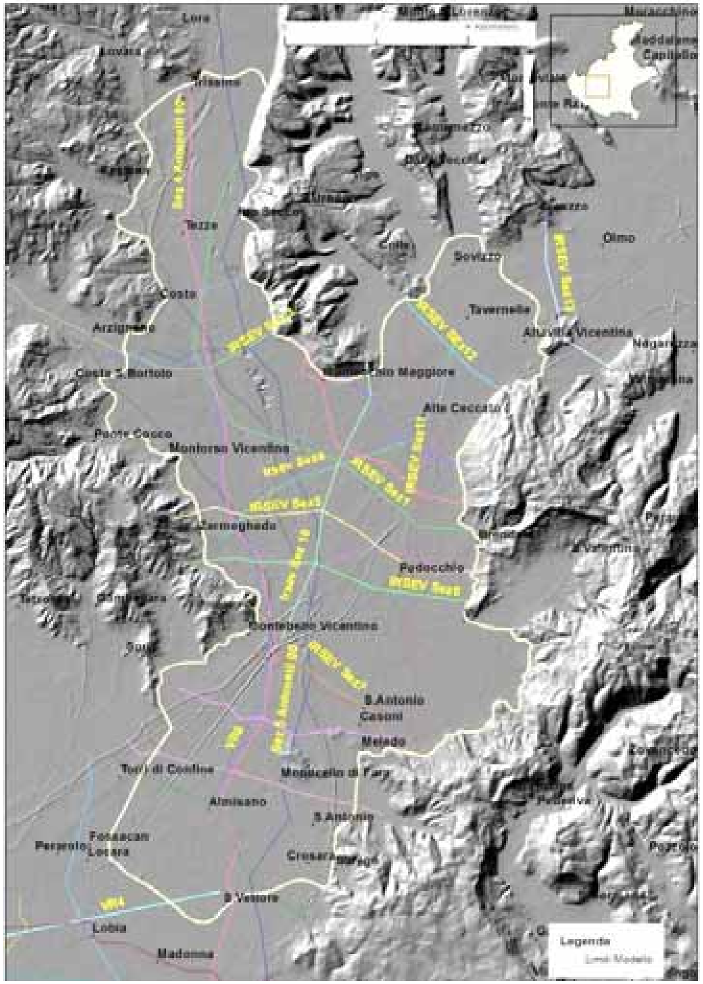
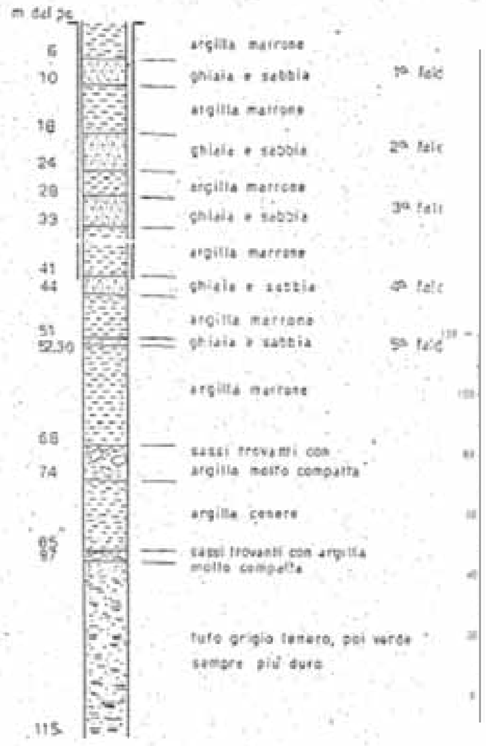
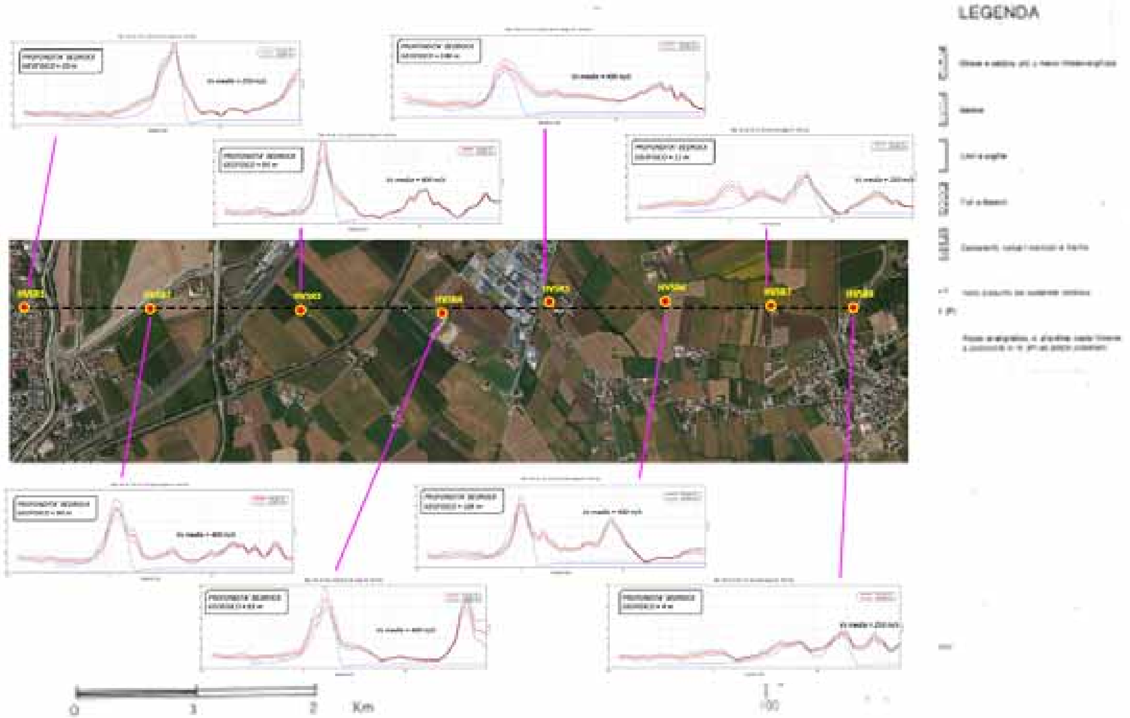
# GEOLOGICAL DATA




A very extensive data collection from different databases and studies (Antonelli 1993; IRSEV 1979, GIADA project 2005-2010, etc.) allowed the definition of a three-dimension geological model. In addition, a geophysical survey has been performed. When the geological data was not available, the sequence stratigraphies were interpolated or interpreted.



# GEOCHEMICAL DATA (Kd)

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An important step of data acquisition was the experimental determination of the partition coefficients.

This activity was carried out through 3 steps:

- Core drilling
- Sampling
- Experimental laboratory determinations

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## PFAS: A DIFFERENT CHAIN LENGTH DETERMINES A DIFFERENT SOLUBILITY AND SORPTION AND SO A DIFFERENT TRANSPORT AND FATE IN WATER

**Kd is important for retardation.**

***"the process by which a solute travels at a slower rate than the average linear velocity because of partitioning onto the solid phase of the porous medium"***

| CATEGORIA | FAMIGLIA | SOTTO-FAMIGLIA | COMPOSTO | ACRONIMO | FORMULA | SOLUBILITÀ TEORICA (25°C) mg/L | SOLUBILITÀ SPERIM. mg/L | Koc TEORICA | Koc SPERIM. | DENSITÀ g/mL | PESO MOL. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Sostanze perfluoroalchiliche (PFAS) | Acidi perfluoroalchilici (PFAA) | Acidi carbossilici perfluoroalchilici (PFCA) | Acido perfluoro butanoico | PFBA | $C_4HF_7O_2$ | 765,7[1] | nd | 58.43 | 76[9] | 1.645 | 214,038 |
| | | | Acido perfluoro pentanoico | PFPeA | $C_5HF_9O_2$ | 61.11[1] | nd | 269.9 | 23[8] | 1.713 | 264,046 |
| | | | Acido perfluoro esanoico | PFHxA | $C_6HF_{11}O_2$ | 4.703[1] | nd | 1247 | nd | 1.762 | 314,053 |
| | | | Acido perfluoro eptanoico | PFHpA | $C_7HF_{13}O_2$ | 0.3527[1] | nd | 5761 | nd | 1.792 | 364,061 |
| | | | Acido perfluoro ottanoico | PFOA | $C_8HF_{15}O_2$ | 0.02595[1] | 3400 mg/L (24°C)[5] [7] 9500 mg/L (25°C)[4] | 26620 | 79[10] 115[8] | 1,7 | 414,068 |
| | | | Acido perfluoro nonanoico | PFNA | $C_9HF_{17}O_2$ | 0.001882[1] | nd | 12300[1] | 251[10] 251[8] | 1.8[2] | 464,076 |
| | | | Acido perfluoro decanoico | PFDeA | $C_{10}HF_{19}O_2$ | Bassa[3] | nd | nd | 631[8] 3981[10] | 1.8[2] | 514,083 |
| | | | Acido perfluoro undecanoico | PFUna | $C_{11}HF_{21}O_2$ | Bassa[3] | nd | nd | 1995[8] 63096[10] | 1.8[2] | 564,091 |
| | | | Acido perfluoro dodecanoico | PFDoA | $C_{12}HF_{23}O_2$ | Bassa[3] | nd | nd | nd | 1.8[2] | 614,098 |
| | | Acidi solfonici perfluoroalchilici (PFSA) | Acido perfluoro butansolfonico | PFBS | $C_4HF_9O_3S$ | 107[1] | 4620 mg/l (24°C)[7] | 221.6 | | 1.811 | 300,100 |
| | | | Acido perfluoro esansolfonico | PFHxS | $C_6HF_{13}O_3S$ | 0.5971[1] | nd | 4729 | 3981[10] | 1.8[2] | 400,115 |
| | | | Acido perfluoro ottansolfonico | PFOS | $C_8HF_{17}O_3S$ | Bassa[3] | 370 - 680 mg/L[6] 5700 mg/l(24°C)[7] | nd | 372[8] 6310[10] | 1,25 | 500,130 |

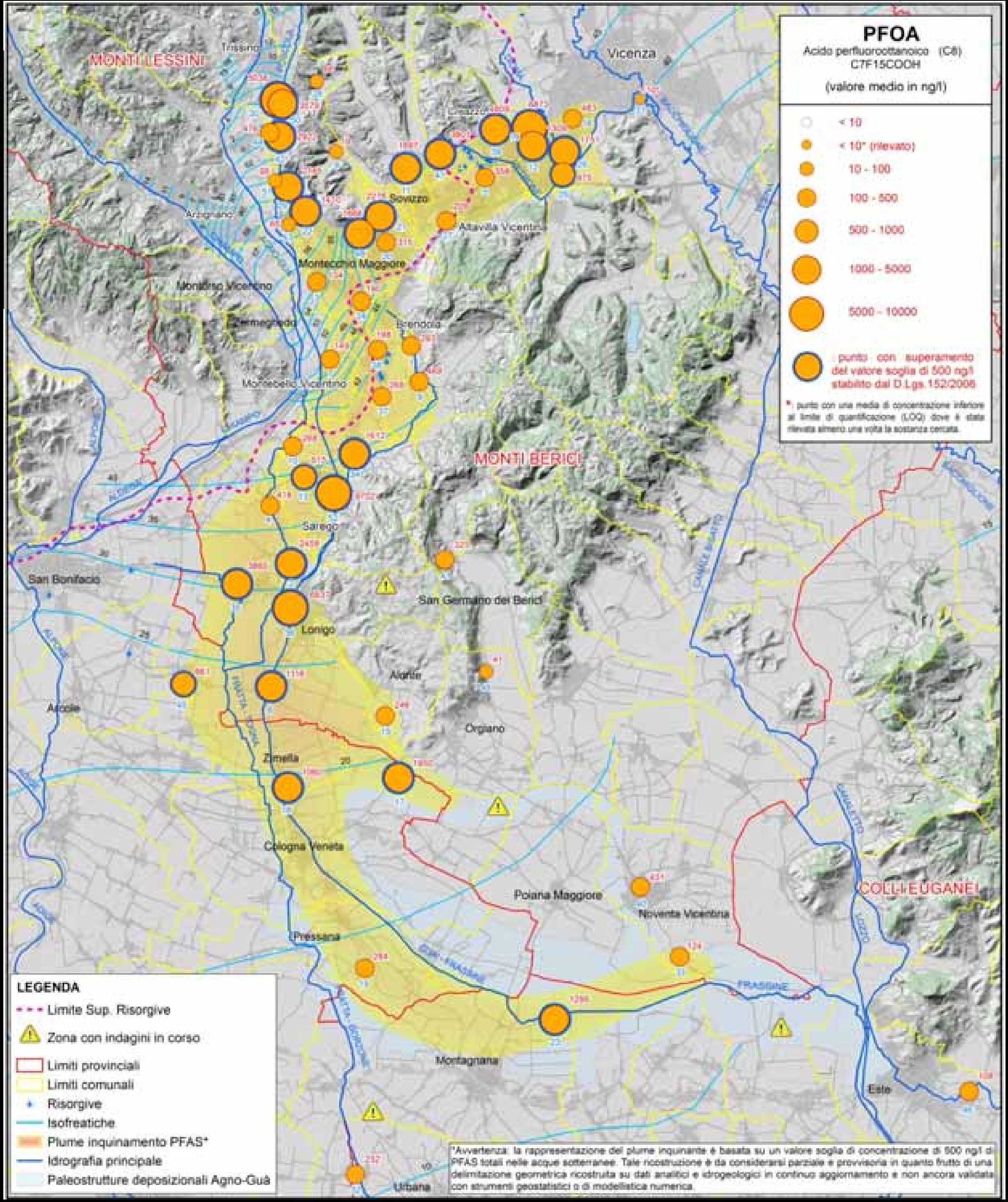

PEAT

# Groundwater monitoring

PFAS

DISTRIBUTIONS IN

GROUNDWATER

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*http://www.arpa.veneto.it/arpav/pagine-generiche/sostanze-perfluoro-alchiliche-pfas*

# RESULTS OF GROUNDWATER MONITORING

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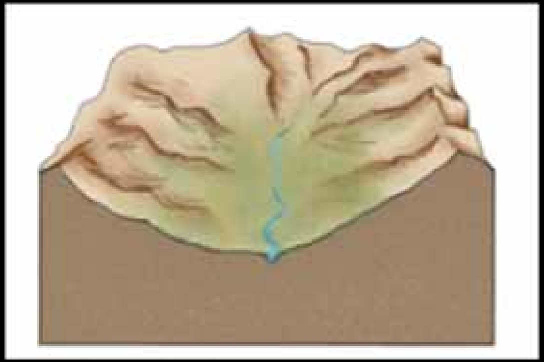
***PFOA** (perfluorooctanoic acid) **is the most important congener for quantity and distribution.***


| | PFBA | PFBS | PFDeA | PFDoA | PFHpA | PFHxA | PFHxS | PFNA | PFOA | PFOS | PFPeA | PFUnA |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| COMP. MEDIA % PFAS | 20.57 | 12.88 | 0.79 | 0.16 | 3.86 | 10.29 | 1.18 | 0.23 | 39.77 | 3.94 | 10.49 | 0.16 |
| Presenza | 51 | 51 | 12 | 2 | 46 | 51 | 32 | 7 | 52 | 38 | 50 | 2 |
| Lungh. Catena | 4 | 4 | 10 | 12 | 7 | 6 | 6 | 9 | 8 | 8 | 5 | 11 |

Action B.4.1 Production and validation of the flow and transport Numerical Model

# FROM THE REAL TERRITORY TO THE MATHEMATICAL MODEL



Glacier Valley formation
https://en.wikipedia.org/

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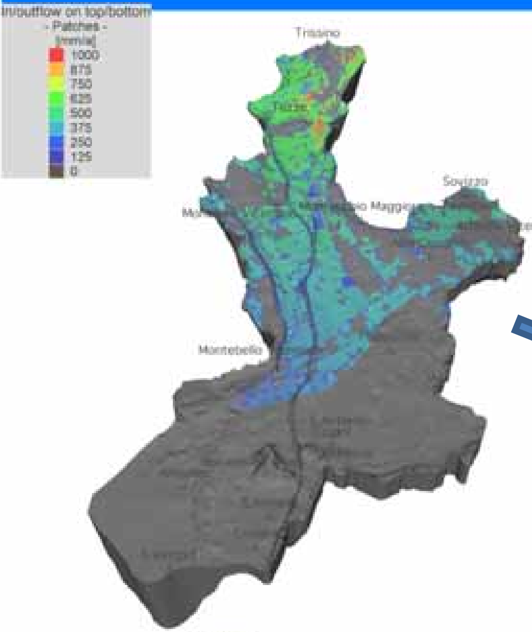
# BOUNDARY CONDITIONS

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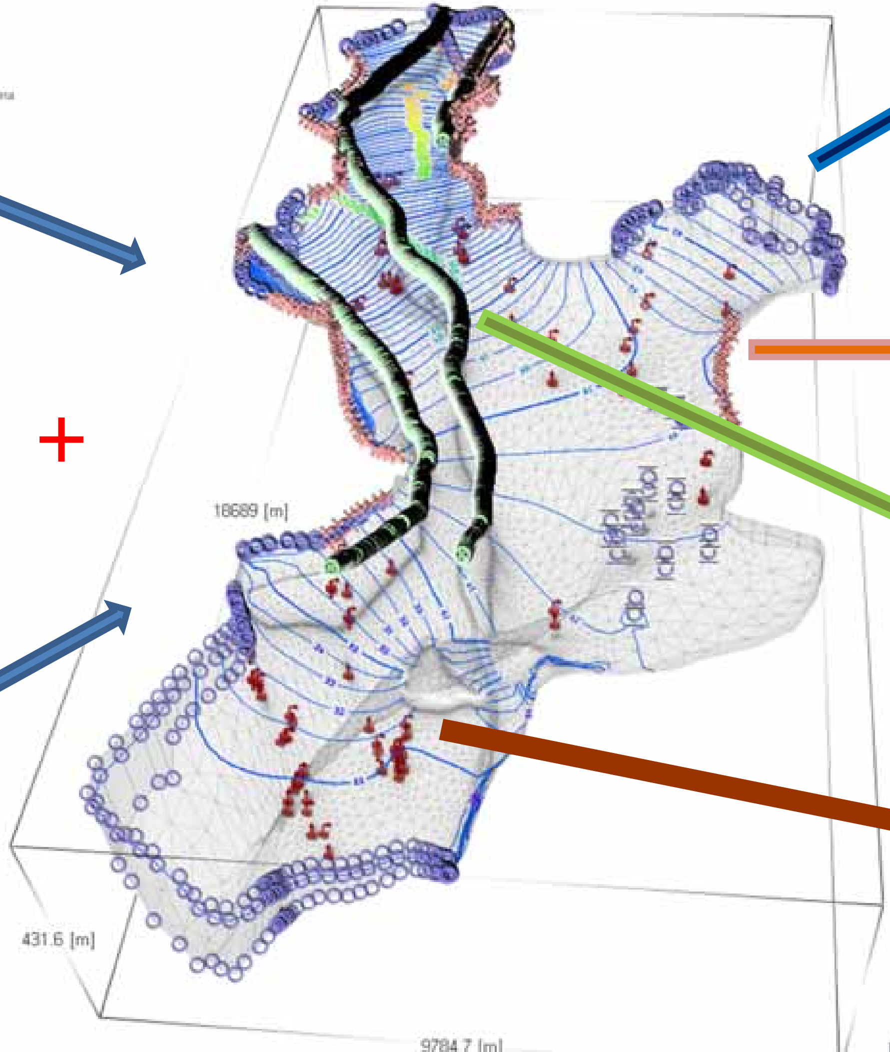


***1° kind conditions (Dirichlet)***: *Hydraulyc head boundary condition.*

***2° kind conditions (Neumann)***: *Fluid flux BC , a special case of the Neuman boundary condition where the gradient or flux is zero.*

***3° kind conditions (Cauchy)***: mixed condition, It is typical of river (for this it is also called River boundary c.)

***Multilayer Well BC***: water flow of punctual withdrawals (pumping wells, etc)

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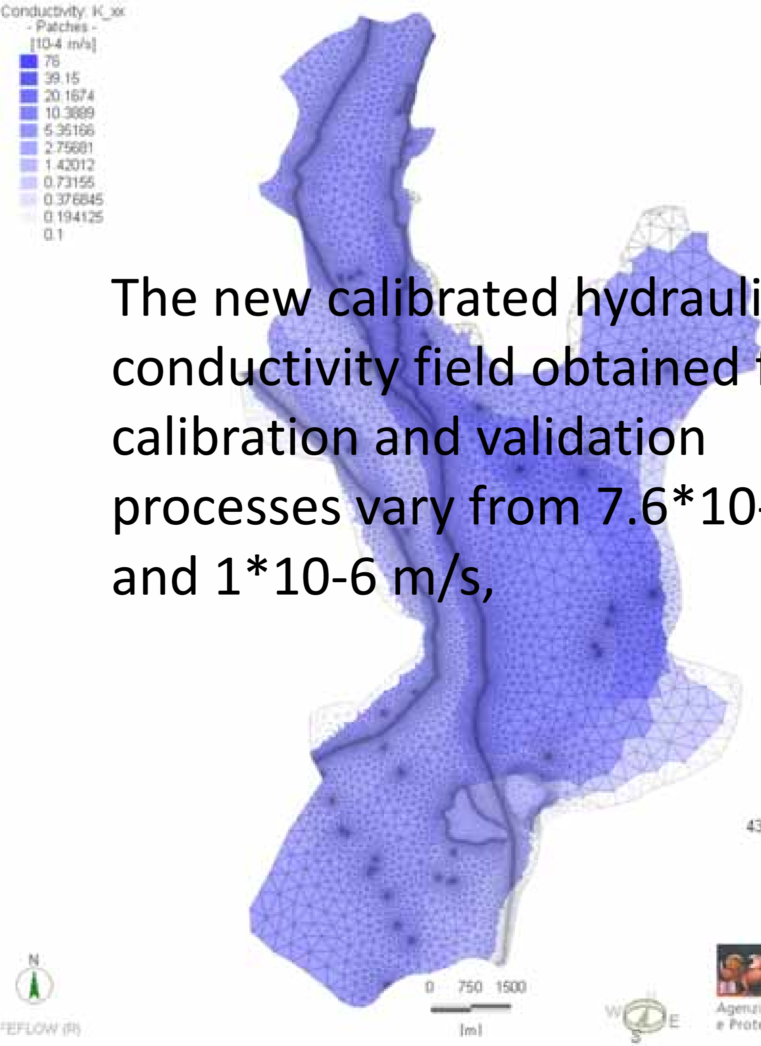
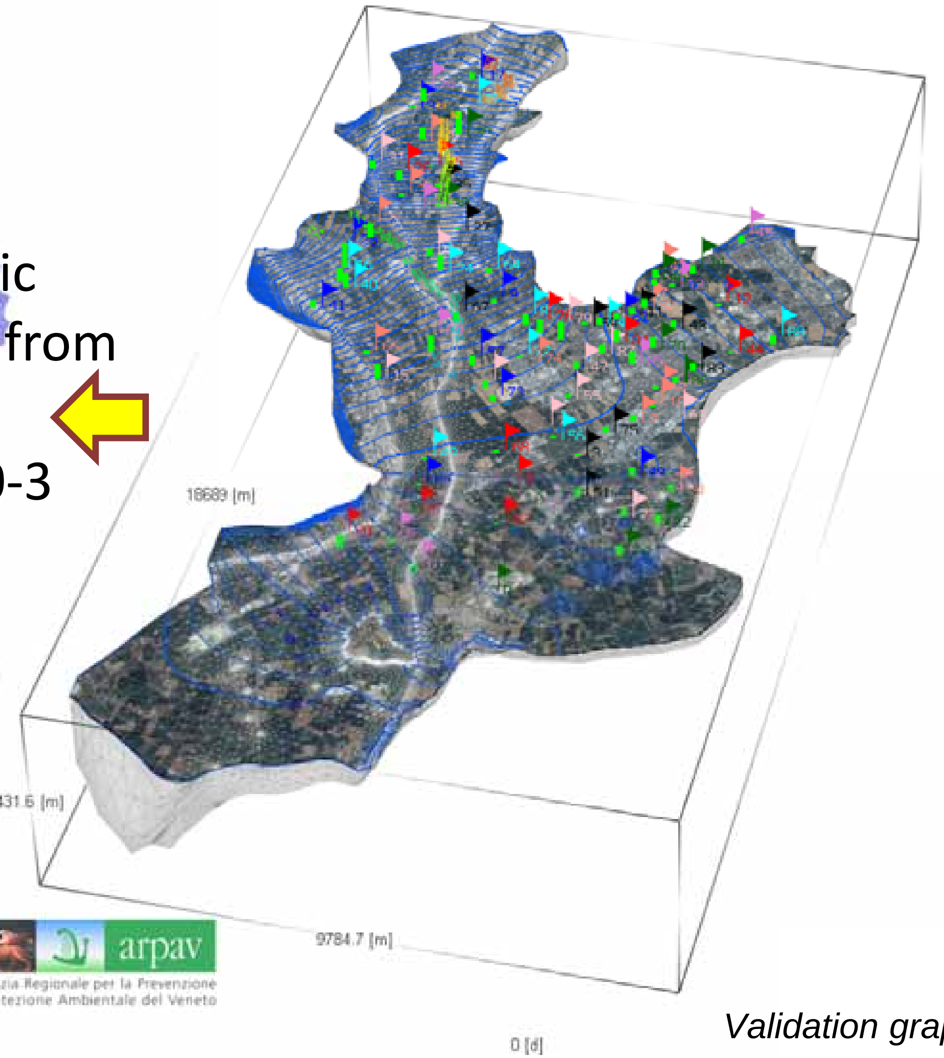
# CALIBRATION AND VALIDATION




The new calibrated hydraulic conductivity field obtained from calibration and validation processes vary from 7.6*10-3 and 1*10-6 m/s,

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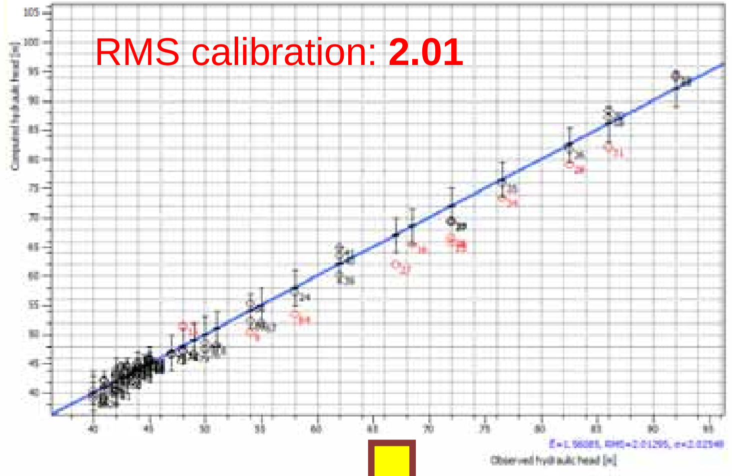
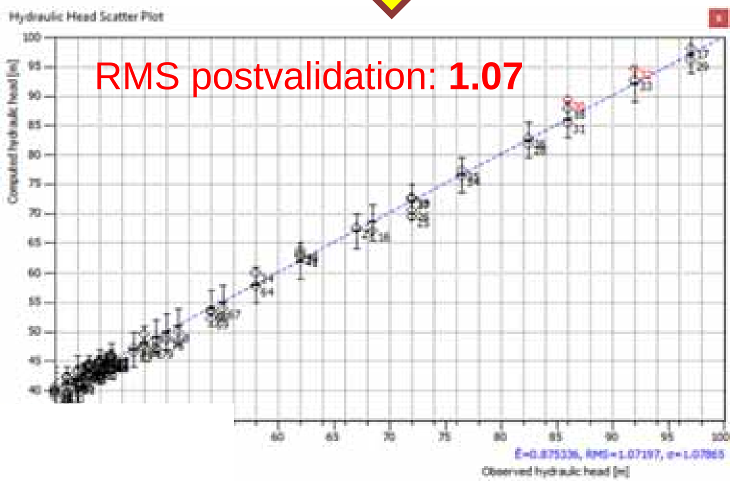
RMS precalibration: **3.12**

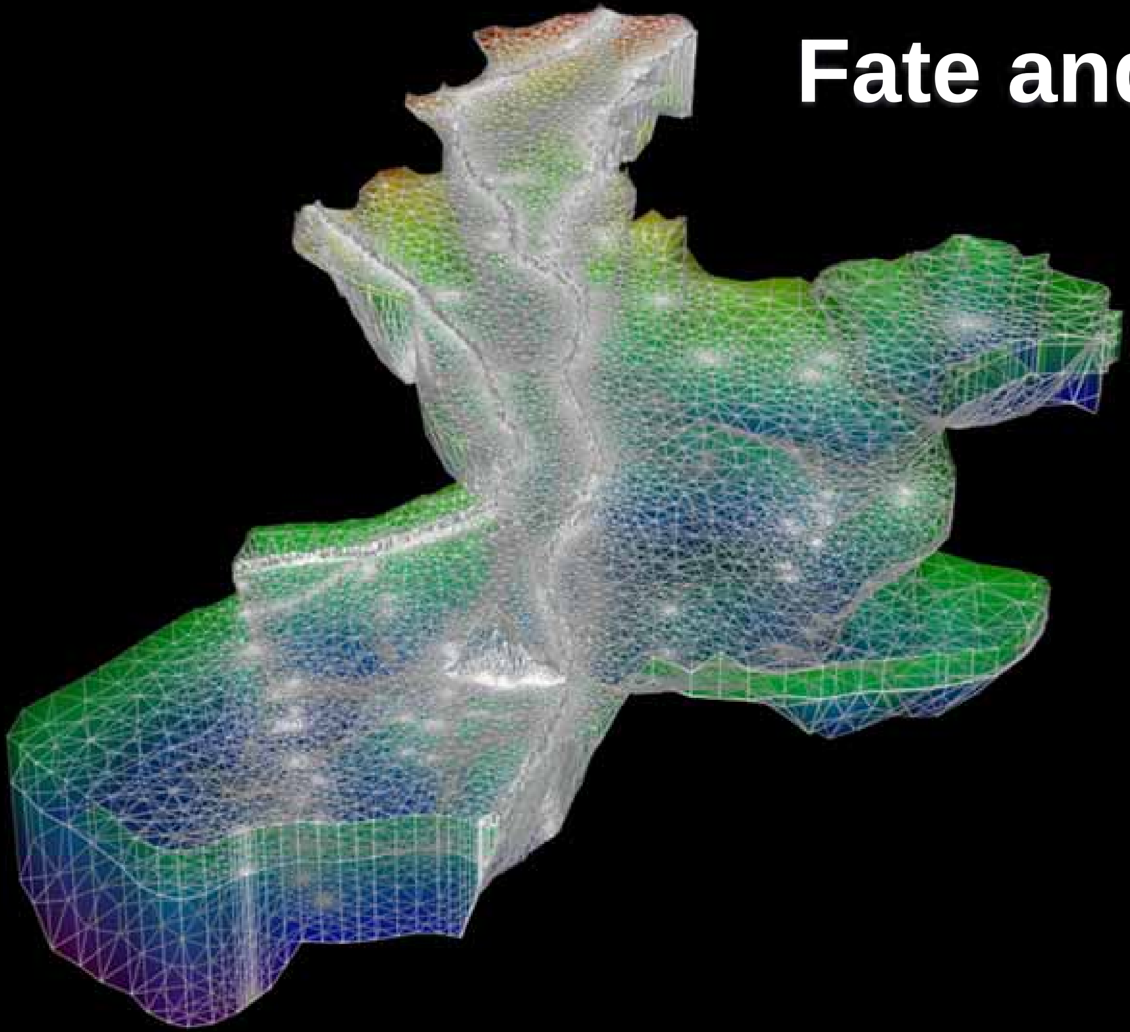
RMS calibration: **2.01**




RMS postvalidation: **1.07**




*Validation graph and regression formula obtained after validation.*



# Fate and transport numerical model

AREA: **93.8** km2 (catchment scale)
MUNICIPALITIES: **15**
RIVERS: **50** KM
DISCRETIZATION AQUIFER: **498.440** ELEMENTS
AQUIFER VOLUME : **6.626.500.000** MC

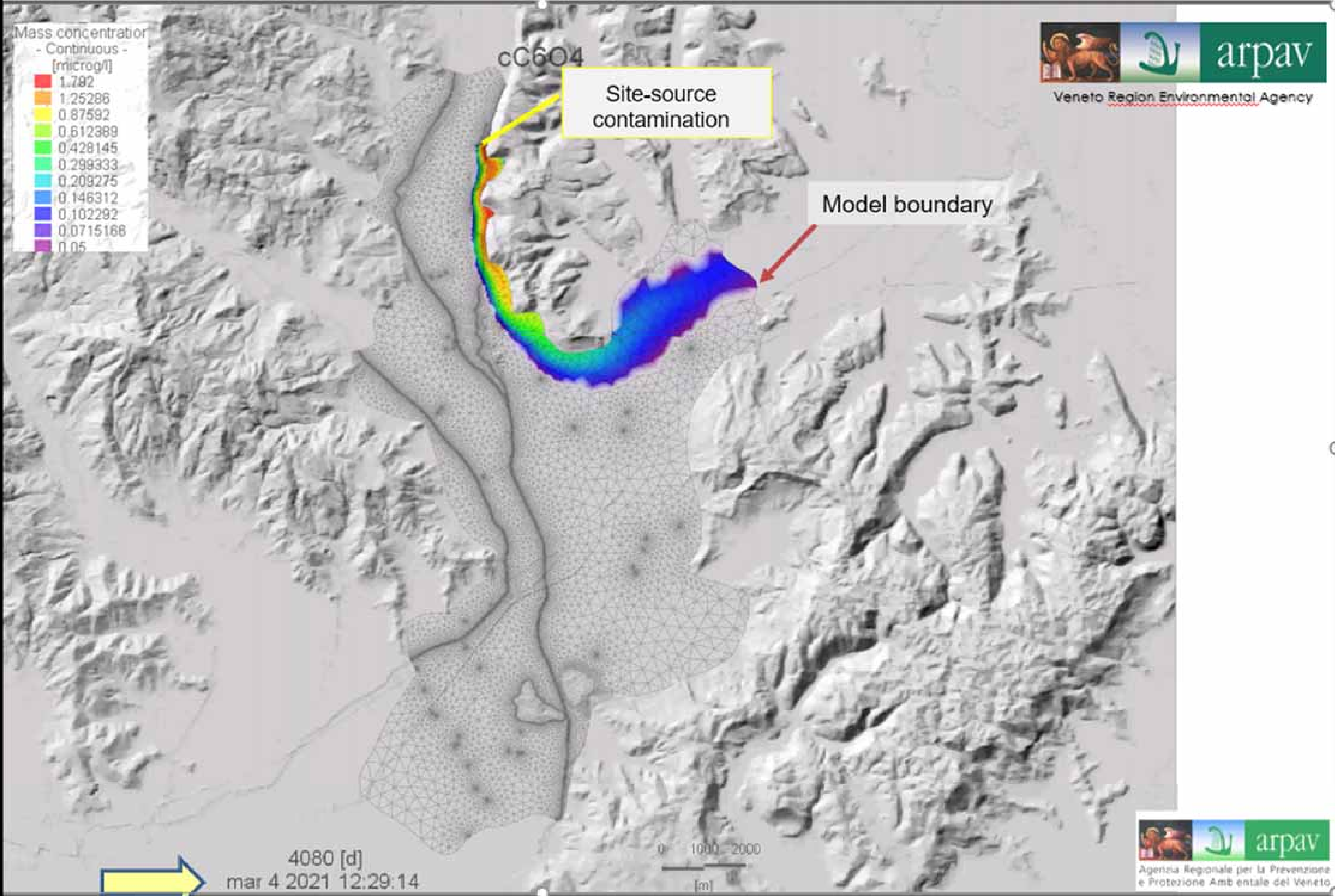
# Fate and transport model simulations

# cC6O4

Simulation run of the transport of cC6O4 in groundwater.

## Interpret quantify

PLEASE NOTE: This scenario uses LOQ 50 ng L. With different LOQ the simulation evolution plume will be different.



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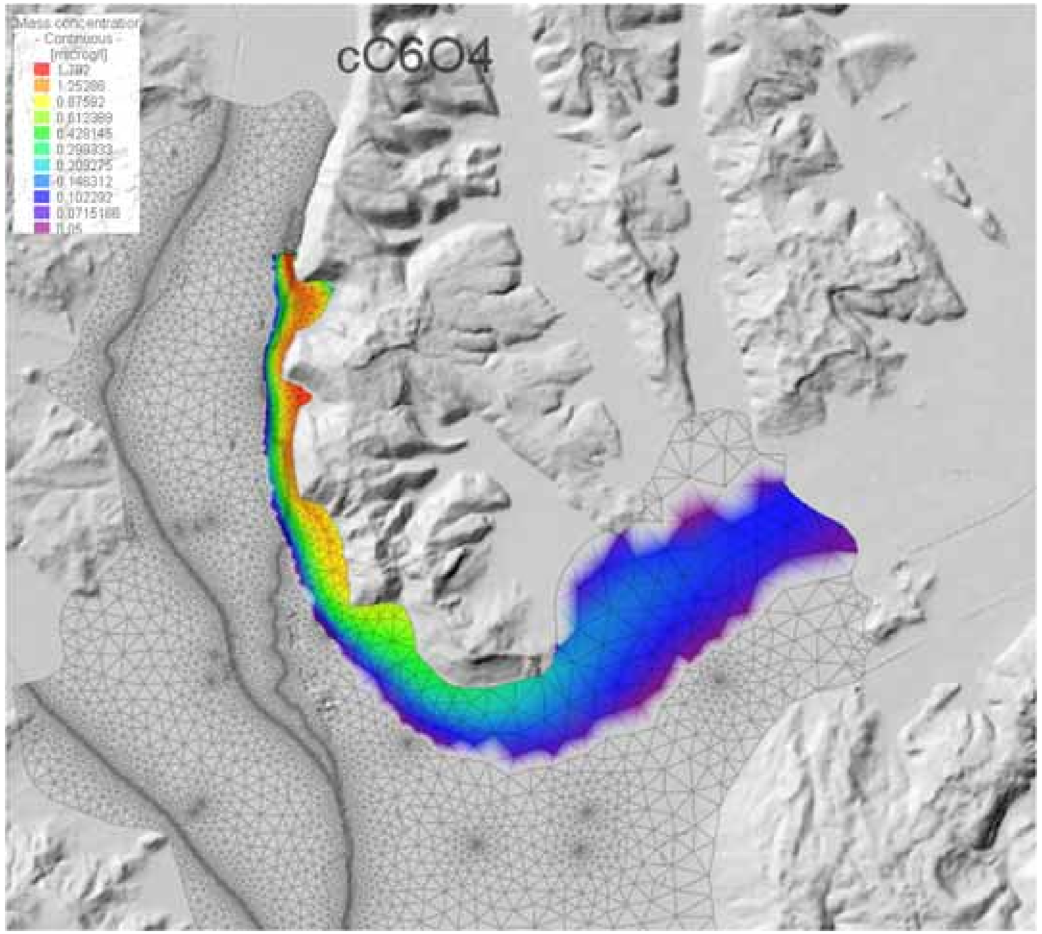
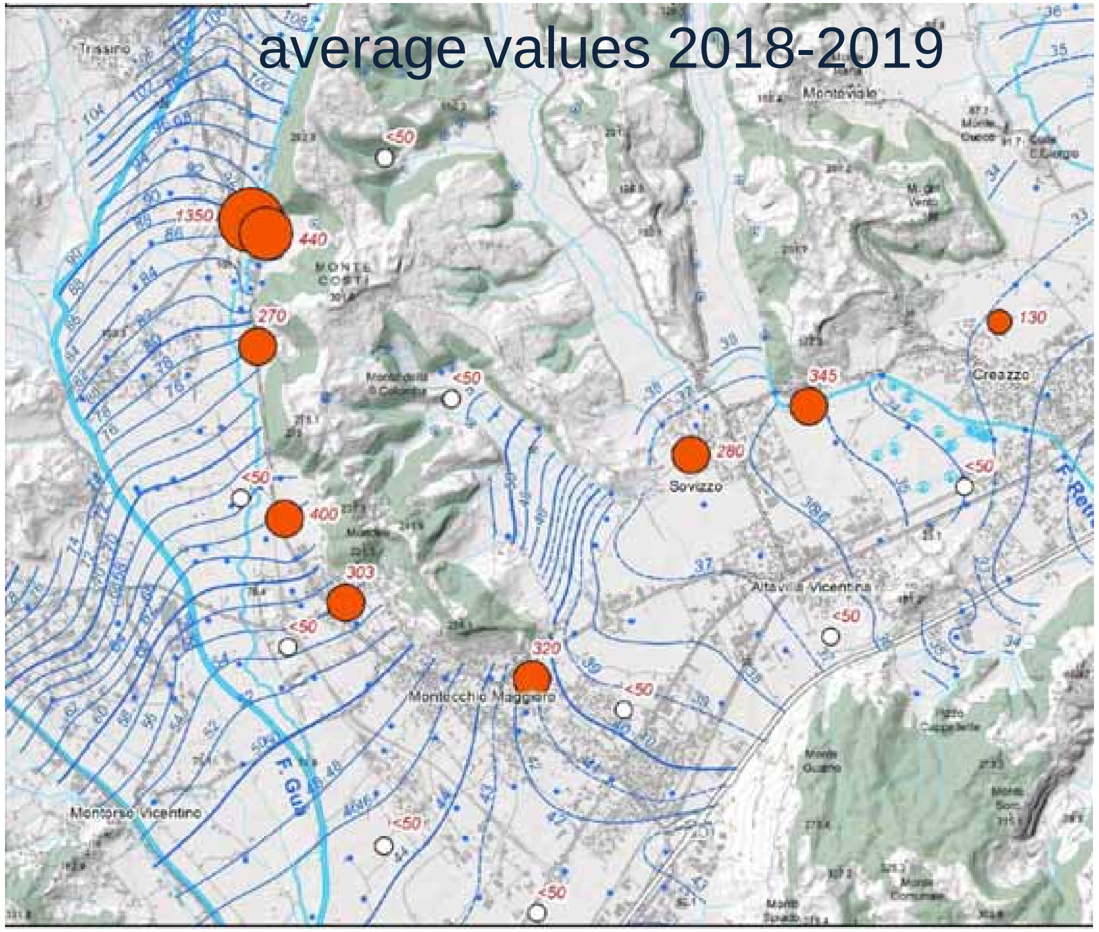
## cC6O4 SIMULATED LOQ 50 ng L




## cC6O4 OBSERVED LOQ 50 ng L




PLEASE NOTE: 50 nanograms per liter is the old laboratory limit of quantification (LOQ). With the new current LOQ (40 nanograms per liter), the detected pollution, and so the plume shape, may be different.

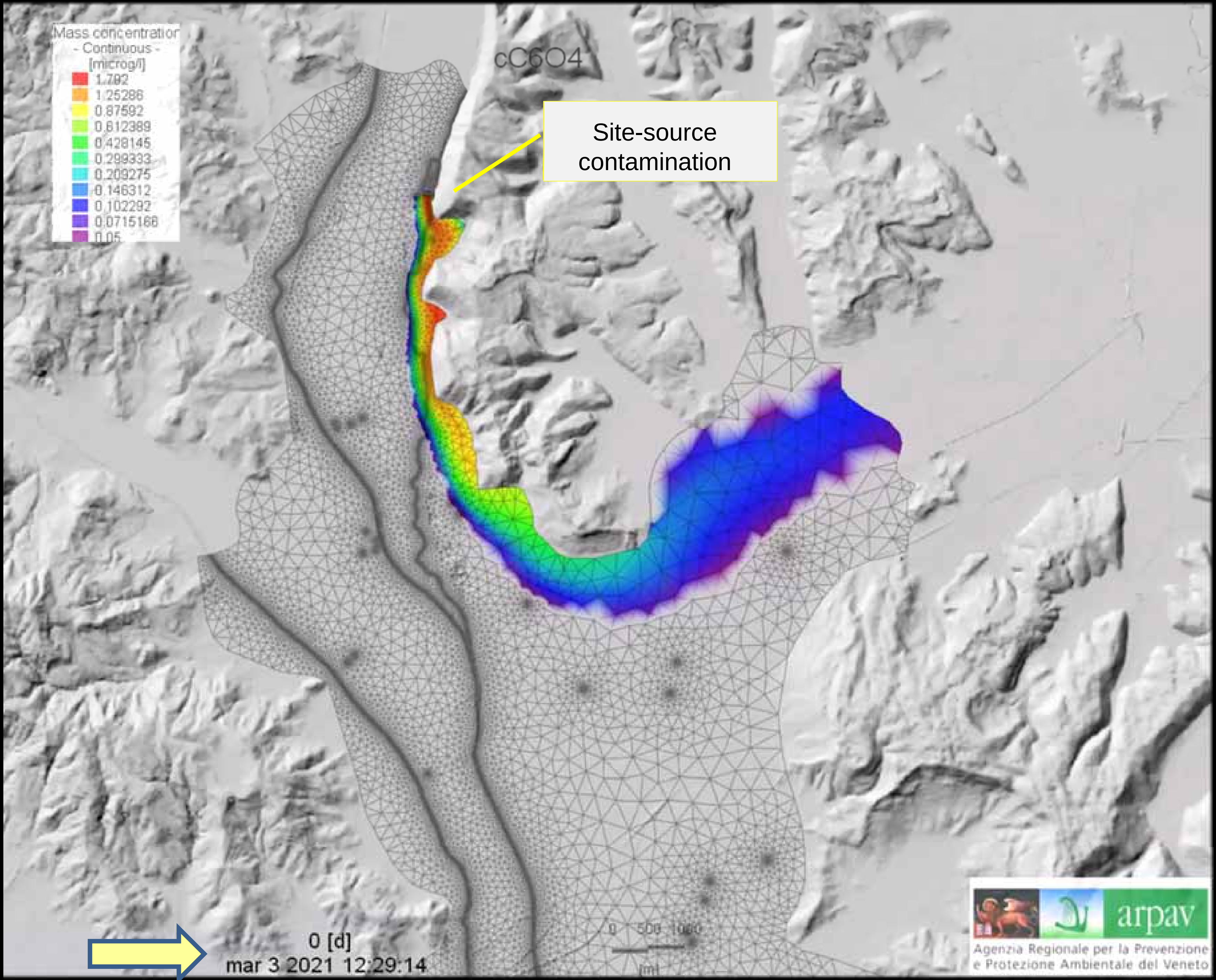
# cC6O4

## FORECASTING SCENARIO

## predict

Simulation run of the fate of cC6O4 in groundwater.

PLEASE NOTE: This scenario uses current LOQ 40 ng L. With different LOQ the simulation evolution plume will be different.

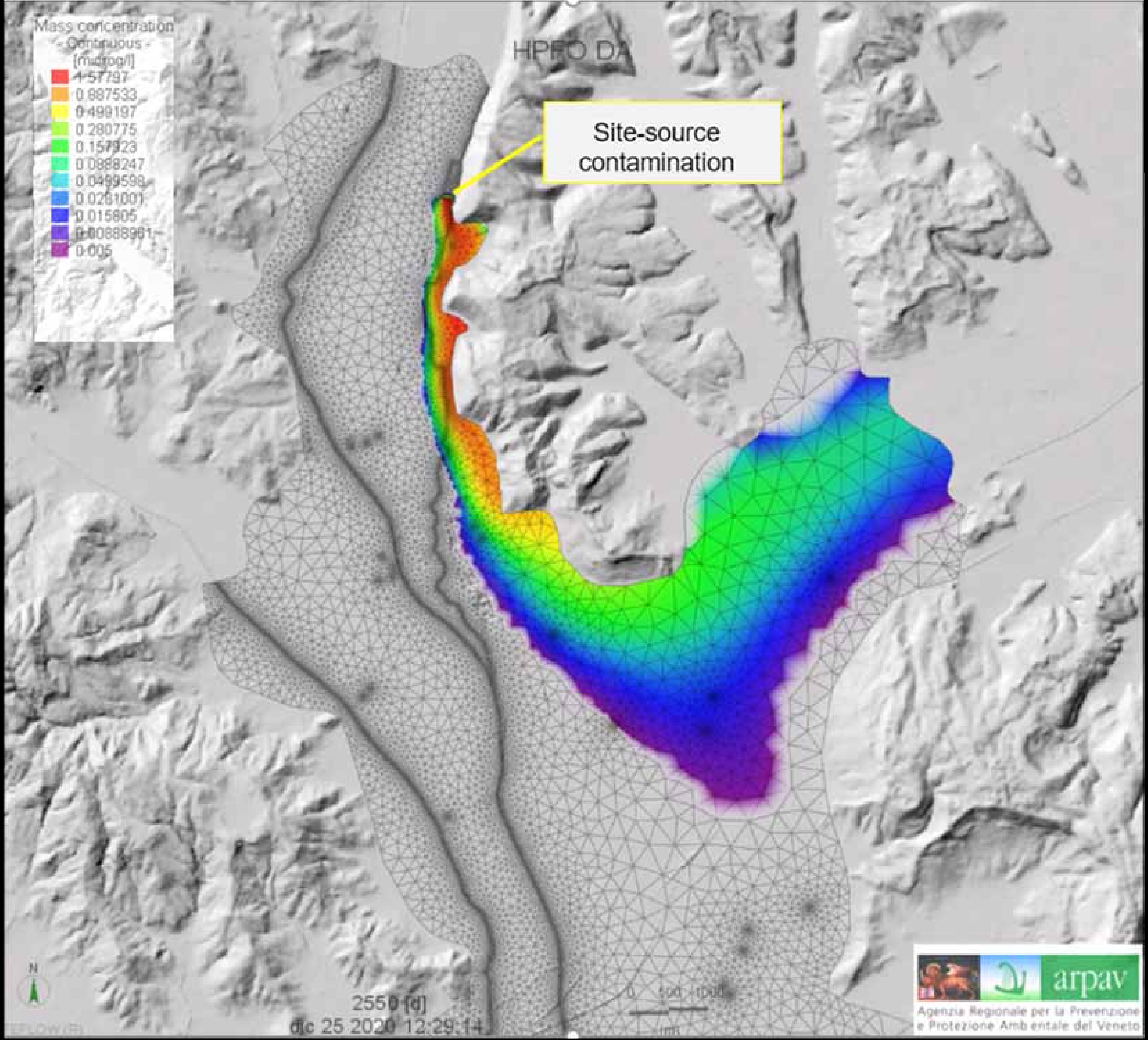


# HFPO-DA

## Interpret quantify

Simulation run of the fate of HFPO-DA in groundwater.

PLEASE NOTE: This scenario uses current LOQ 5 ng L. With different LOQ the simulation evolution plume will be different.

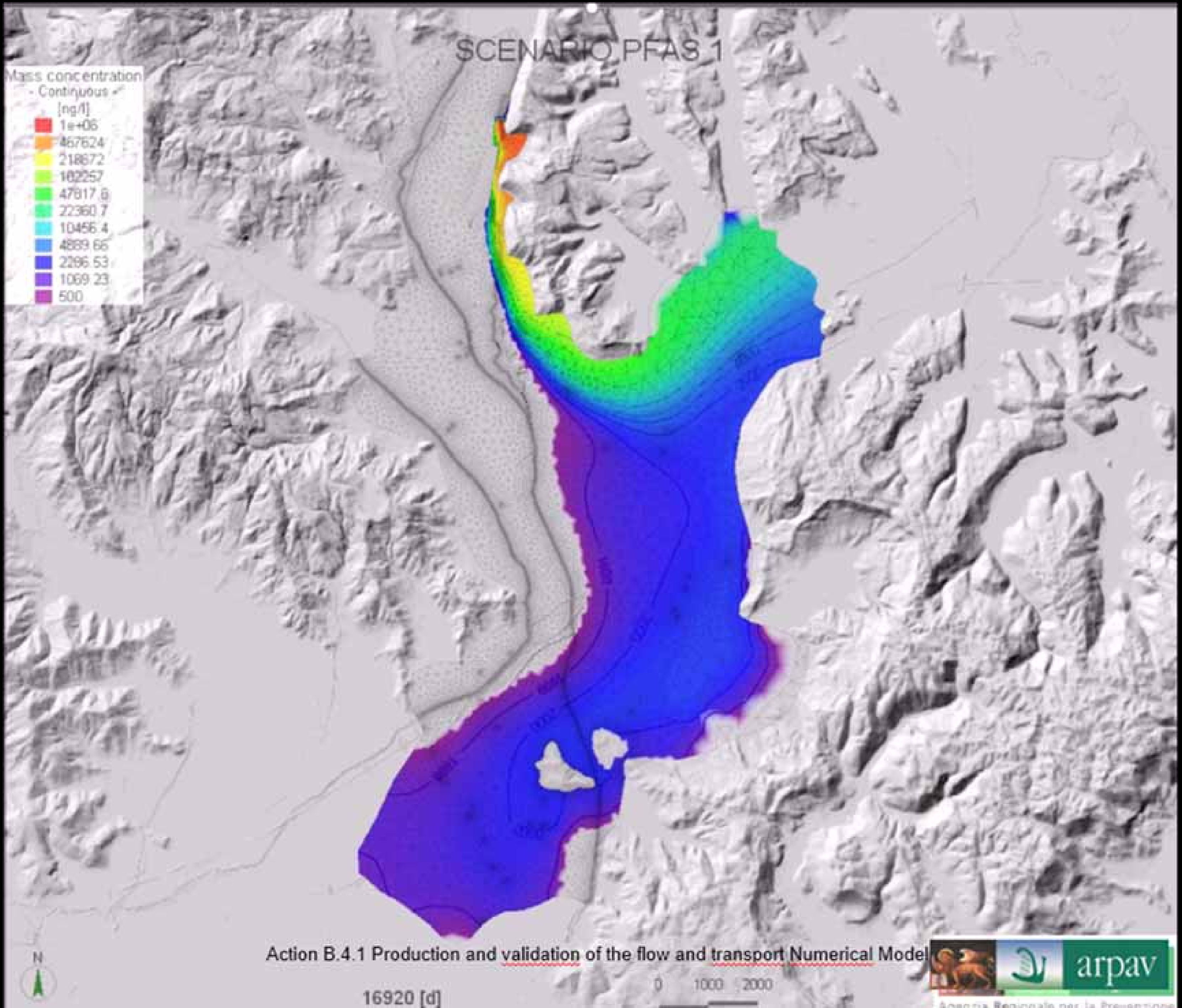


# **PFAS**
# Representation of contamination evolution by reconstructed emission scenario

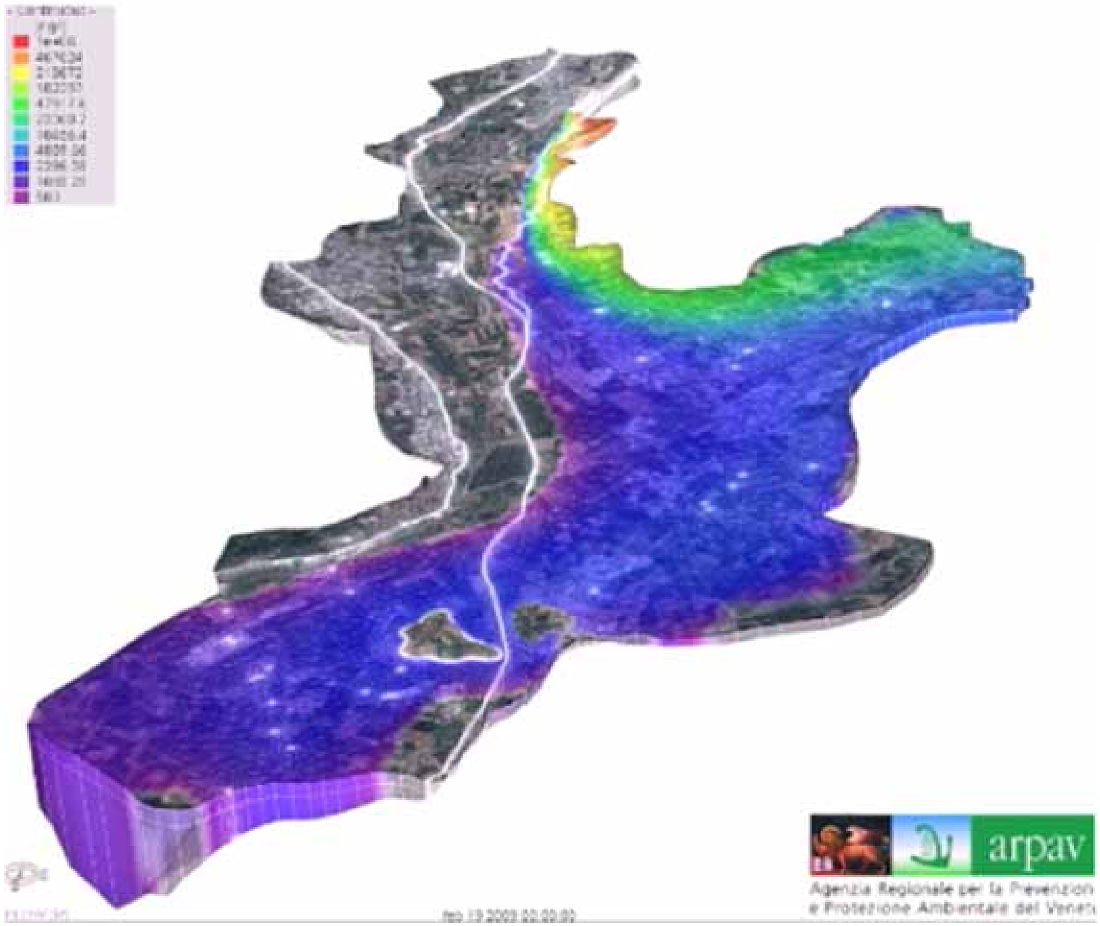
# PFOA (scenario)

Simulation run of the transport of PFOA in groundwater.

**Interpret quantify**



# CONCLUSION

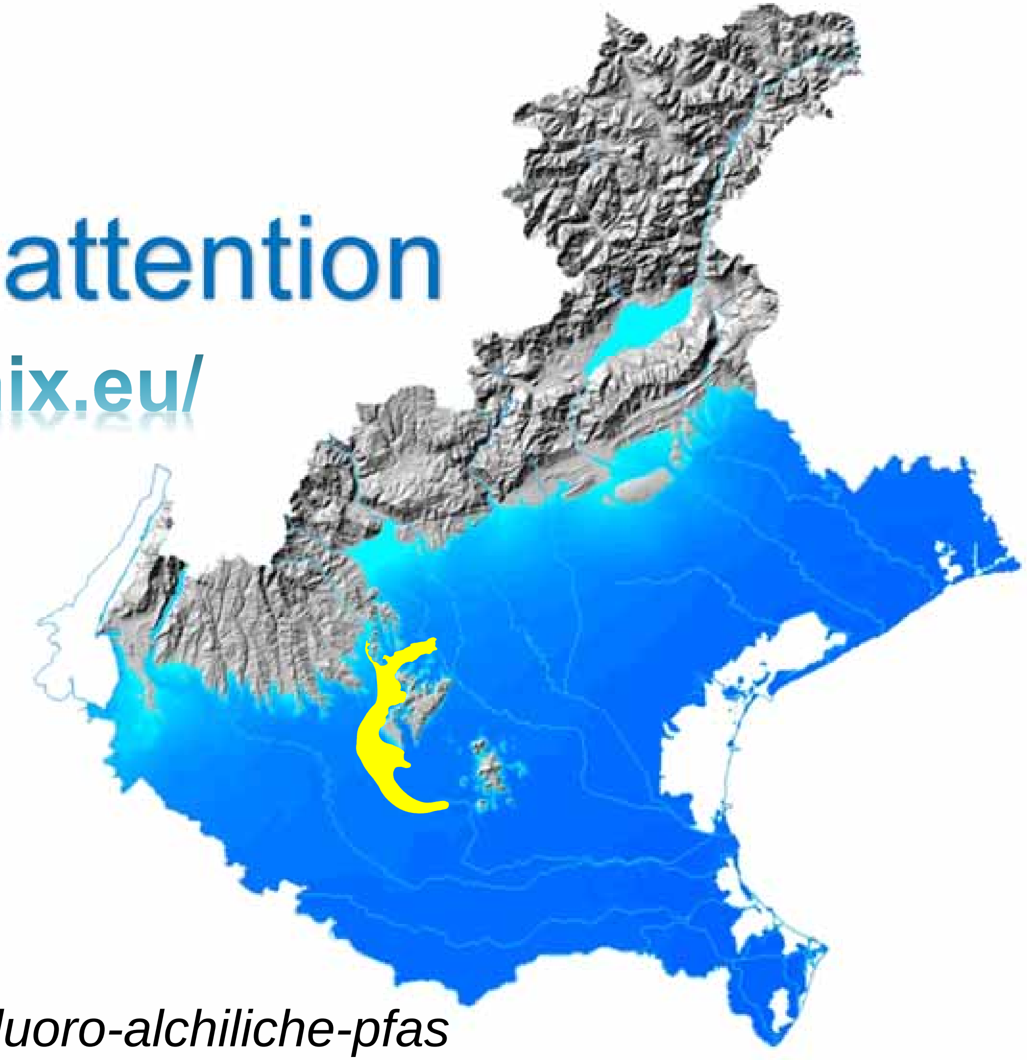



- A 3D finite elements model (FEM) of the aquifer sedimentary basin was developed and tested. Advection, diffusion, hydrodynamic dispersion, adsorption have been simulated;
- The numerical modeling implemented through the LIFE PHOENIX project is proving to be a important **tool for interpreting and predicting the propagation of pollutions** in groundwater;
- **Fate and transport model** represents an advanced analysis tool **for decision making** in order to respond to real problems in different type of scenarios (eg. Accident with release of a new contaminant).

# Thank you for your attention

**https://www.lifephoenix.eu/**

PFAS



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*http://www.arpa.veneto.it/arpav/pagine-generiche/sostanze-perfluoro-alchiliche-pfas*