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Innovative tools for the site characterization: Compound Specific Isotope Analysis (CSIA), Background Fluorescence Analysis (BFA), Compositional Fingerprint (CF) and Electrical Resistivity Tomography (ERT). A case study

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INNOVATIVE CHARACTERIZATION TECHNOLOGIES

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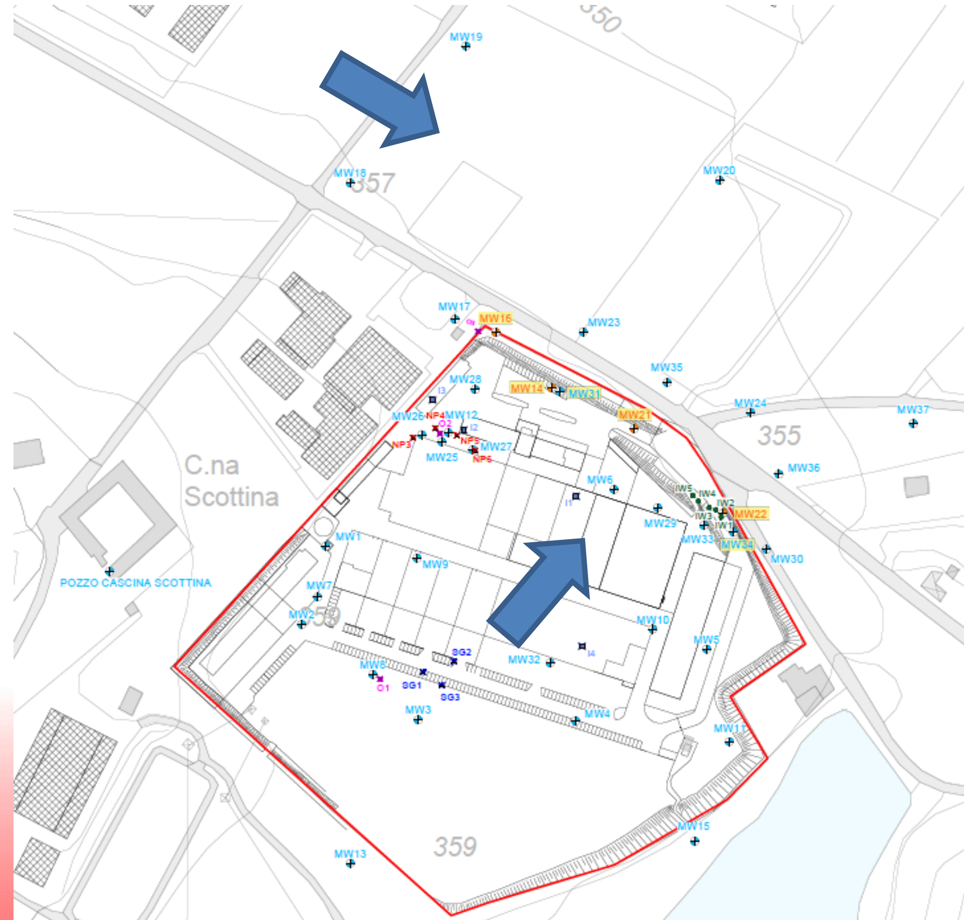
The Site

- Former Automotive Manufacturing site located in Northern Italy
- Groundwater is impacted by chlorinated solvents (mostly PCE, TCE and 1,1-DCE) and hexavalent chromium



The Site

- Complex hydrogeological conditions due to heterogeneous morainic hill
  - Inconsistent depth-to-water values prevent the elaboration of reliable groundwater contour maps
  - Several installed wells resulted dry
  - Ground water flow pathway not fully understood
  - Not possible to use direct-push technologies
- Different technologies were used in fall/winter 2017 and spring 2018 in order to collect additional data for the update of the site conceptual model, focused on the identification of (potential) different sources of contaminants in groundwater and the downgradient floWe pathway
  - Compound Specific Isotope background Analysis (CSIA)
  - Background Fluorescence Analysis (BFA)
  - Compositional Fingerprint (CF)
  - Electrical Resistivity Tomography (ERT)

CSIA Main Principles

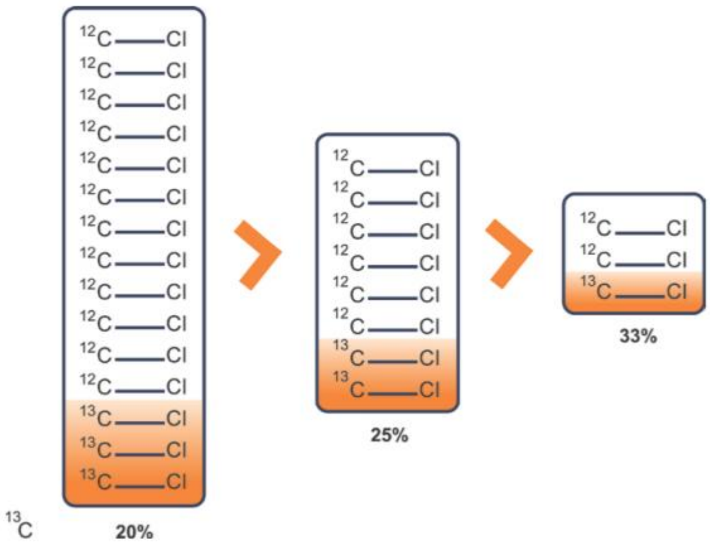
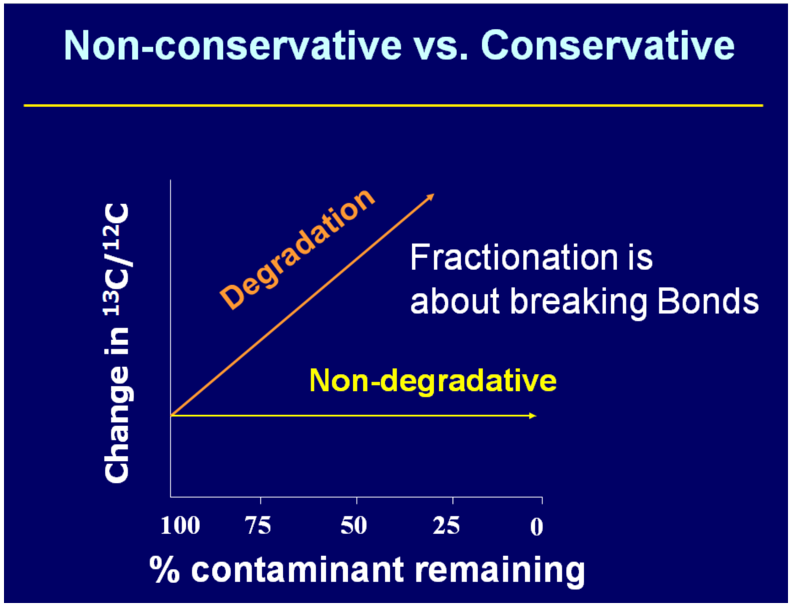


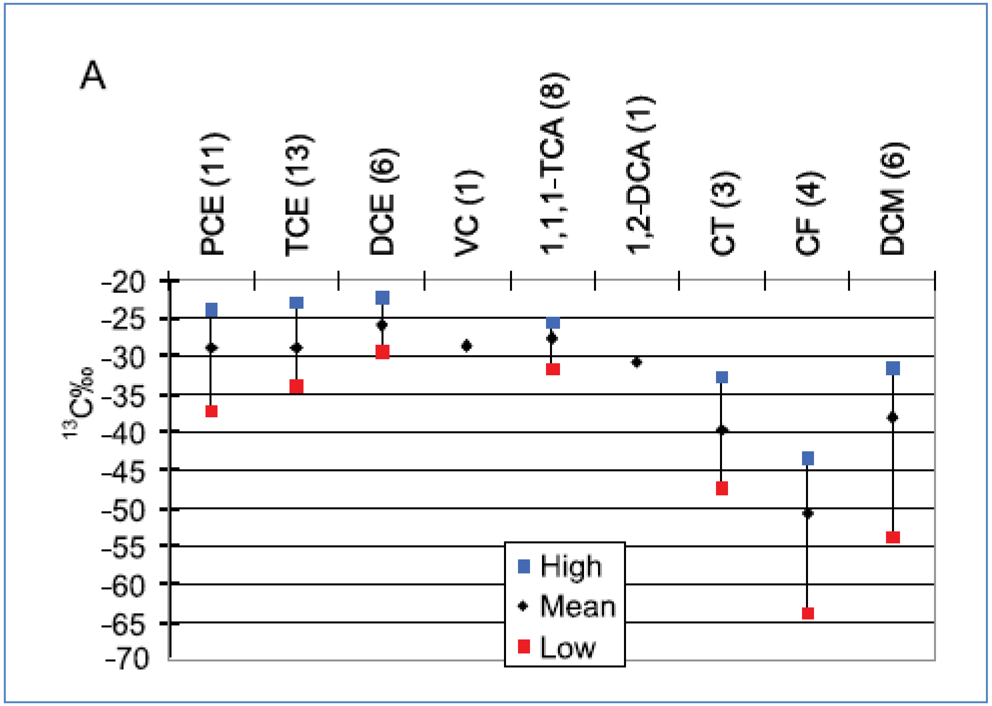
Figure 2. Illustration of ^{13}C enrichment during degradation of a contaminant with a C-Cl bond.



- According to the behaviour of the carbon isotopes of a chlorinated compound (CHC) moving in groundwater from point A to point B, $\delta^{13}C$ of the a CHC (measuring the overall ratio of isotope ^{13}C to isotope ^{12}C in the CHC molecules of the analyzed GW aliquot) should increase from point A to point B if the CHC has been biodegraded. If not biodegraded, $\delta^{13}C$ should remain the same.

- If $\delta^{13}C$ decreases from point A to point B, this clearly suggests that the CHC in point B has not been originated in point A.

CSIA Main Principles



- Similar $\delta^{13}C$ values of the same CHC in different monitoring wells may indicate the presence of the same source or different sources with similar isotopic fingerprint (low value information).

- Instead, different $\delta^{13}C$ values of the same CHC in different monitoring wells indicate the presence of different sources (unless downgradient $\delta^{13}C$ values are less negative than upgradient ones).

Minimum, maximum and mean carbon (A) isotope ratio of chlorinated hydrocarbons from different manufacturers and production batches measured to date. The number in parentheses following each compound name indicates the number of samples analyzed for that compound. PCE is tetrachloroethylene, TCE is trichloroethylene, DCE is dichloroethylene, 1,1,1-TCA is 1,1,1-trichloroethane, 1,2-DCA is 1,2-dichloroethane, CT is carbon tetrachloride (tetrachloromethane), CF is chloroform (trichloromethane) and DCM is dichloromethane. Data compiled from (Beneteau et al., 1999; Holt et al., 1997; Hunkeler and Aravena, 2000c; Jendrzejewski et al., 1997; Jendrzejewski et al., 2001; Shouakar-Stash et al., 2003; van Warmerdam et al., 1995; Zwank et al., 2003).

CSIA 2017 Main Results – Case Study

MW19:
$\delta^{13}C$ TCE:
-24.1 ‰

MW18:
$\delta^{13}C$ TCE:
-22.6 ‰

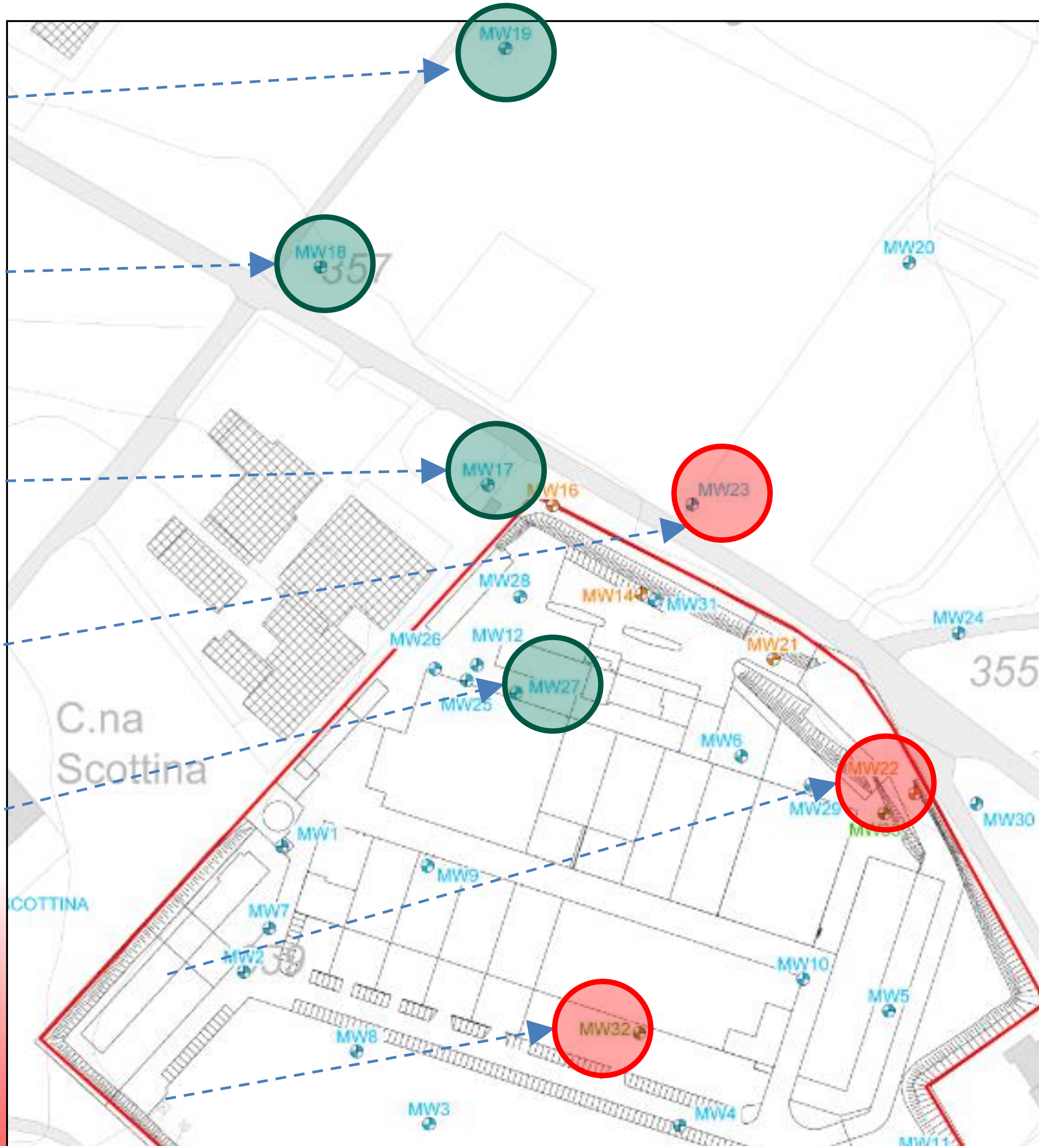
MW17:
$\delta^{13}C$ TCE:
-26.7 ‰

MW23:
$\delta^{13}C$ TCE:
-44.3 ‰

MW27:
$\delta^{13}C$ TCE:
-27.2 ‰

MW22:
$\delta^{13}C$ TCE:
-41.0 ‰

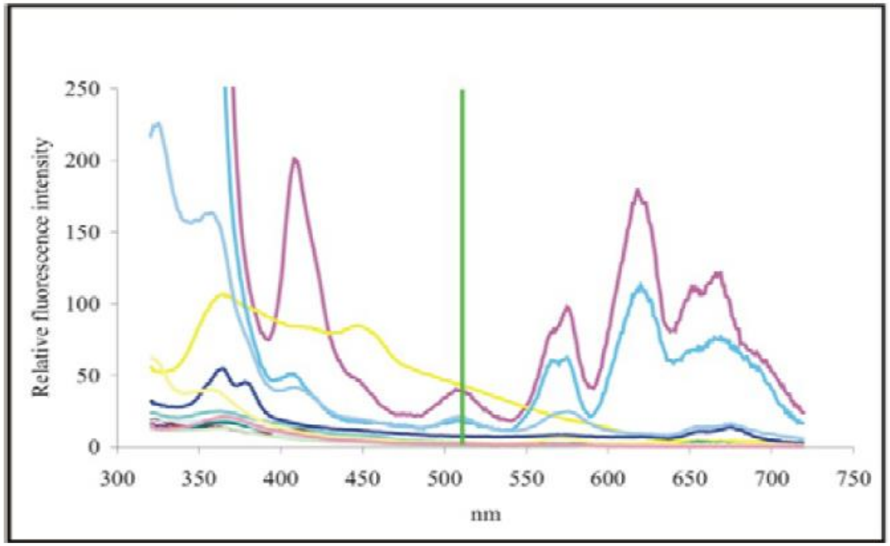
MW32:
$\delta^{13}C$ TCE:
-39.1 ‰

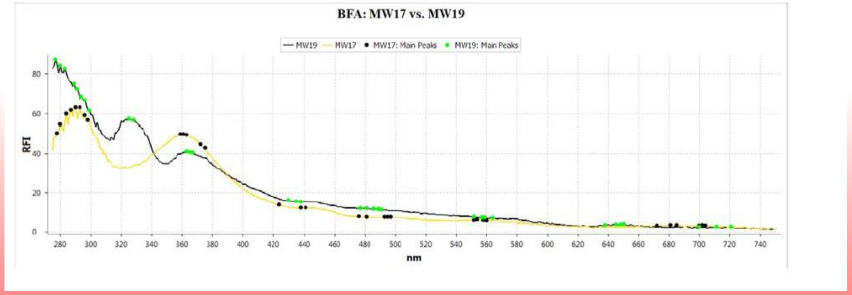


Main Results:

- **At least two different sources of TCE** are present, one impacting the Eastern area (red circles group), one impacting the Western area (green circles group). Inside any group, the presence of different sources with similar isotopic signatures cannot be excluded.
- TCE detected in the main source area of CHCs (MW12 area, represented by MW27) cannot be the origin of the TCE detected in MW23, since $\delta^{13}C$ values in MW23 are far lower than those detected in MW27
- 1,2-DCE data (not shown) confirm TCE results
- PCE and 1,1-DCE data (not shown) do not allow to understand if one or more sources are present (similar values were detected in all monitoring wells)

BFA Main Principles





Background fluorescence analysis (BFA) uses the intrinsic fluorescence properties of the dissolved organic carbon (DOC) content of a water sample. It can be used as a fingerprinting tool.

BFA is based on the fact that most organic compounds (both natural and anthropogenic) emit a characteristic fluorescence. These compounds emit a characteristic light if they absorb specific electromagnetic radiation.

Using a spectro-fluorometer, all fluorescent organic substances in a single water sample are detected.

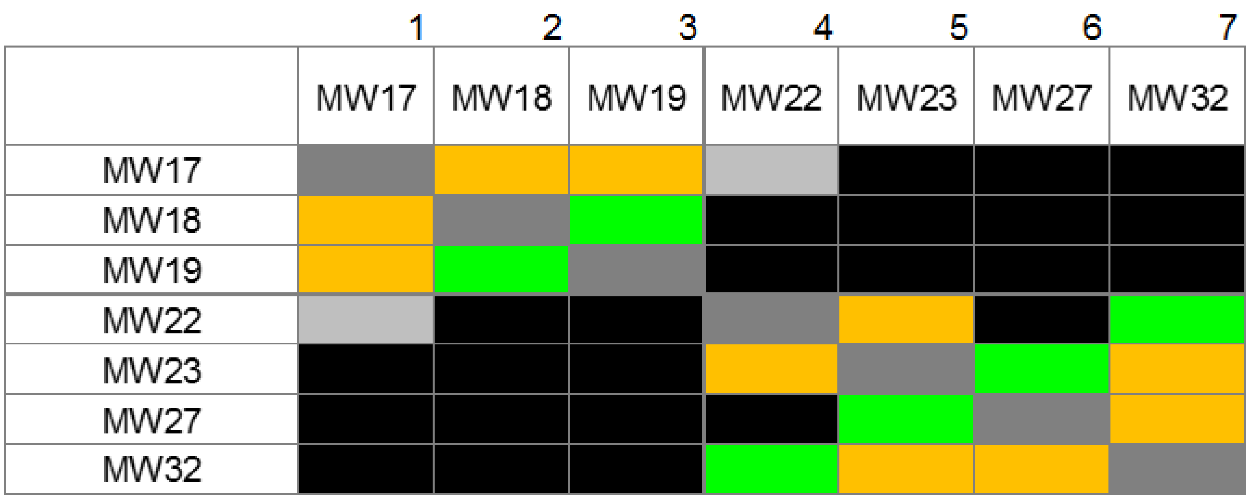
The fluorescence fingerprints are also called **synchroscans**. Each synchroscan contains a graphical 2D representation of all dissolved organic fluorescent compounds in the water sample. If all synchroscans from a site are compared, an expert can recognize hydraulic connections between sample locations, and
information about contaminants, their degradation products, migration, and natural attenuation processes.

In fluorescence fingerprints each line represents a water sample. If the fluorescence fingerprints show a similar pattern (e.g. slopes and peaks) then one can conclude that the organic freight must be similar as well.

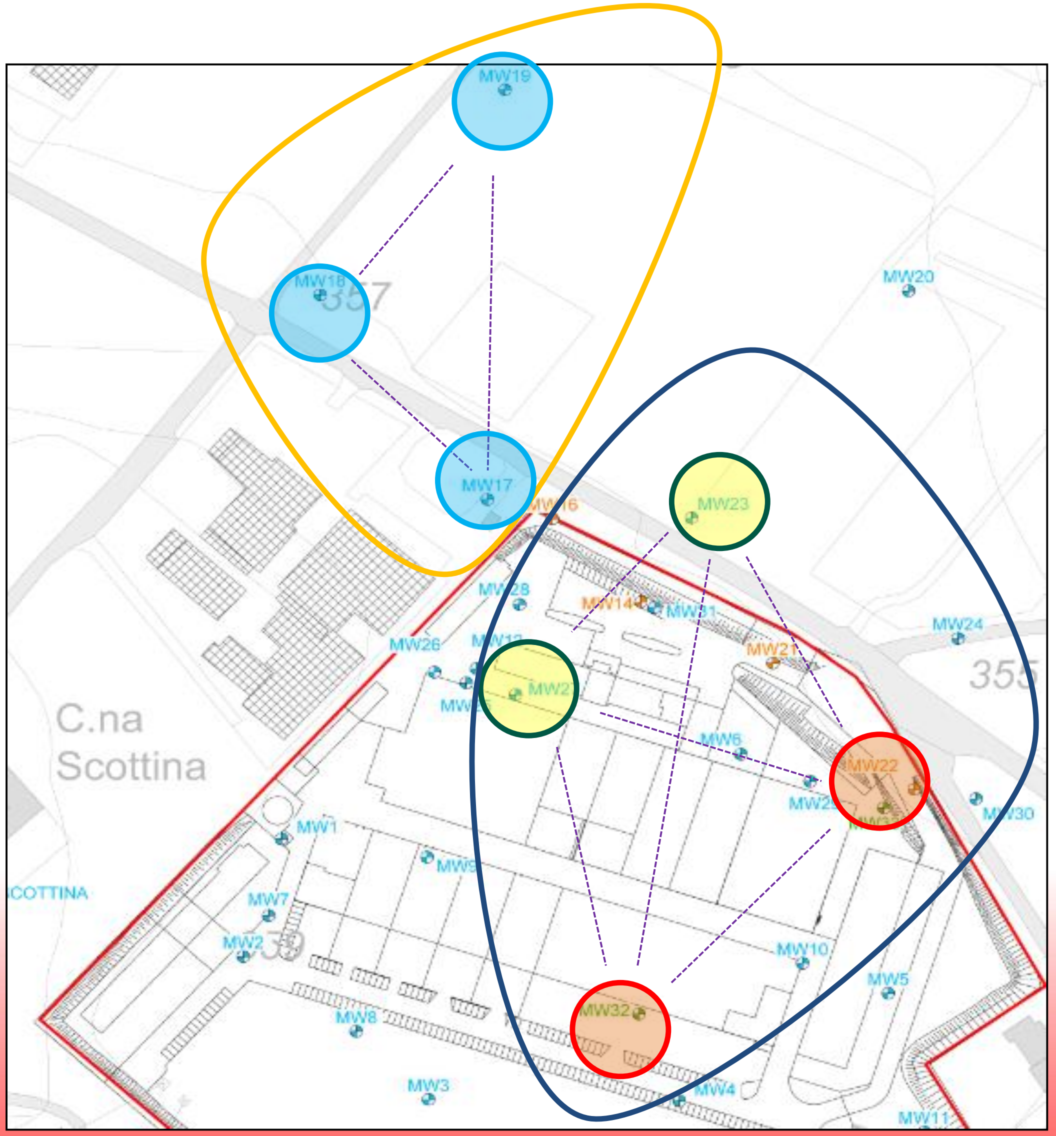
Instead, if different patterns are present, this indicates the absence of hydraulic connections.

BFA 2017: Similarities in Synchroscans

most major peaks match	→	considered for the flow path evaluation	→	potential preferential ground water flow
some major peaks match				
some fingerprint segments match			→	potential matrix ground water flow
some minor peaks match	→	not considered		
barely any peaks/segments match				



BFA 2017 Results – Case Study



Main results:

- No similarity was detected between monitoring wells in the western area (MW17, MW18 and MW19 – inside orange line) and those in the Eastern area (MW22, MW23, MW27, MW32 – inside blue line). Then hydraulic connections between these groups of wells should be excluded. Potential connections are shown in dashed purple lines.

- Three different couples of wells (light blue, yellow and orange circles) are characterized by very similar syncroscans: MW17-MW18, MW27-MW23 and MW32-MW22. This suggests that, using BFA as an independent line of evidence, potential hydraulic connections among these wells are likely. Considering also **isotopes results**, the connection between MW23 and MW27 can be excluded.

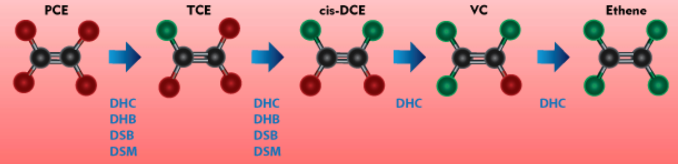
CF Main Principle

Compositional fingerprinting can be used, in favourable cases, to differentiate among sources of contamination.

It consists of the calculation of the percentage abundances of chemicals in a given groundwater sample and in the comparison among percentage abundances in different samples.

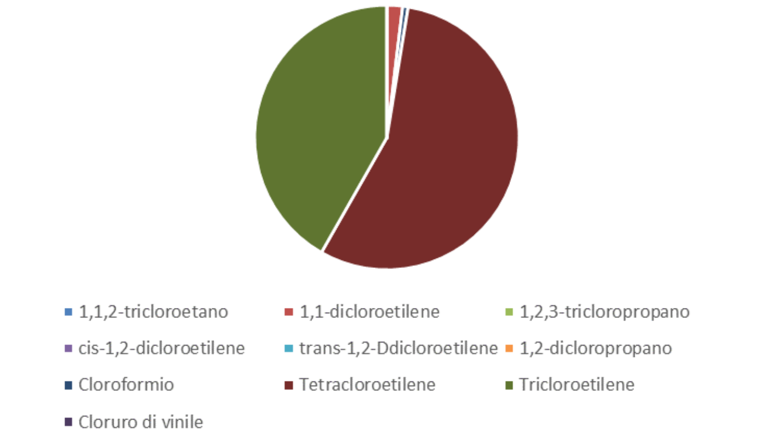
Groundwater samples with similar percentage abundances of chemicals may be indicative of a common contamination source and suggest potential hydraulic connections among wells.

Downgradient samples may be enriched of degradation products.



Analyte	Concentration (µg/l)	Percentage abundance (%)
1,1,2-tricloroetano	<0,017	-
1,1-dicloroetilene	0,11	2
1,2,3-tricloropropano	< 0.094	-
cis-1,2-dicloroetilene	<0,07	-
trans-1,2-Ddicloroetilene	<0,084	-
1,2-dicloropropano	<0,015	-
Cloroformio	0,038	1
Tetracloroetilene	3,2	56
Tricloroetilene	2,4	42
Cloruro di vinile	< 0.017	-

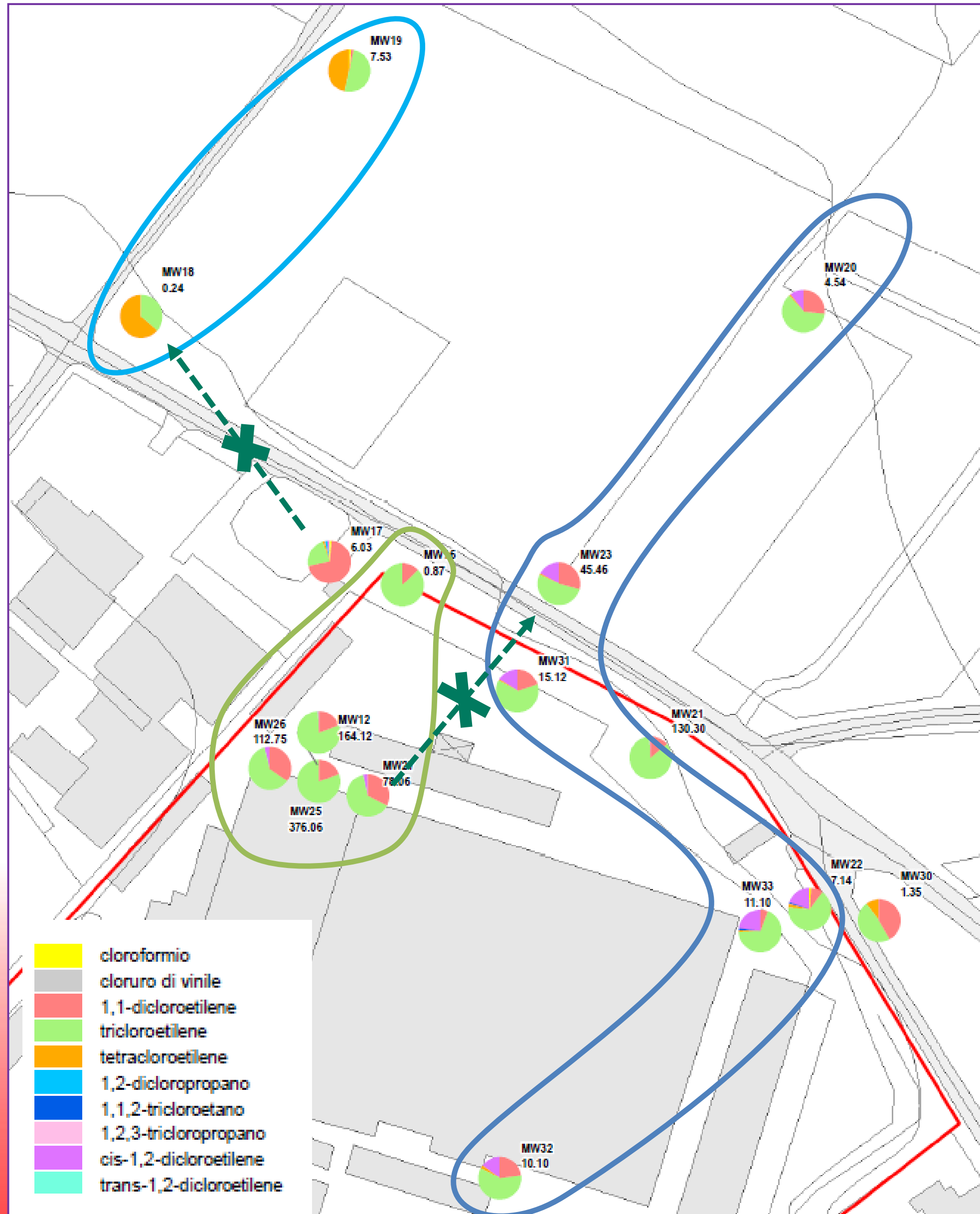
Sum 5,748



CF Main Results – Case study

Figure based on October 2017 groundwater monitoring campaigns

<u>Results were verified also with available historical average compositional data</u>

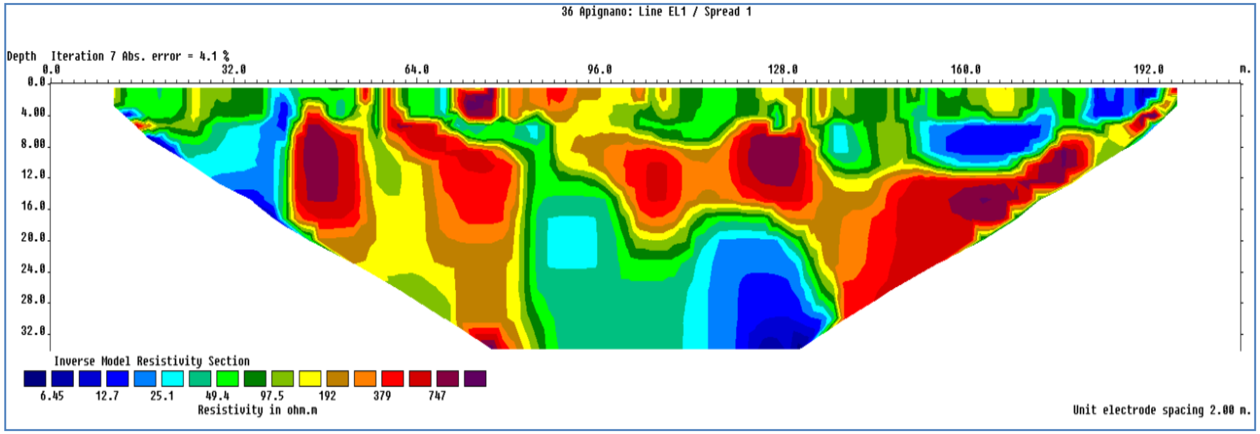


<u>Results:</u>

- Three different groups of wells (inside light blue, orange and green lines) with similar CHC compositions were identified, suggesting the presence of (at least) three different sources

ERT – Main Principles

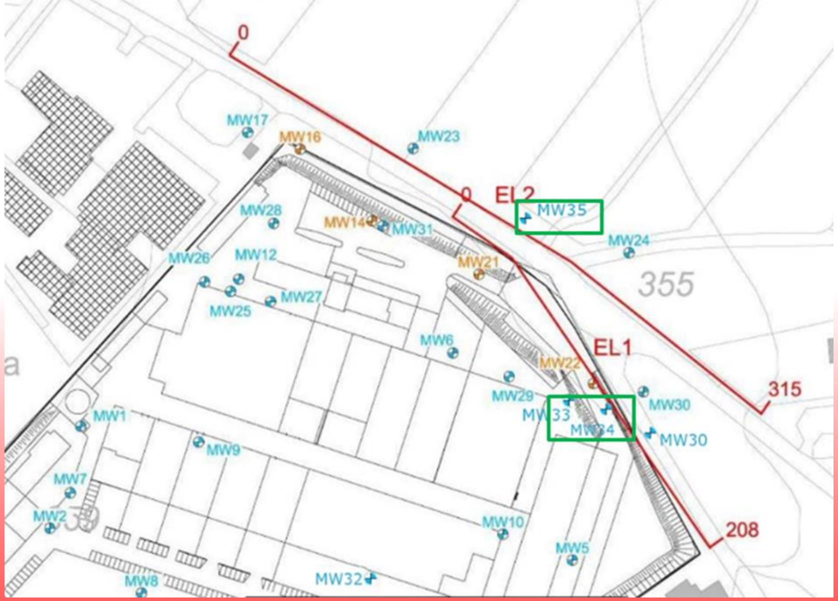
- Electrical Resistivity tomography is a geophysical survey technique that allows subsoil investigation and may provide information about the presence of water-bearing subsoil volumes (**potentially useful for the location of monitoring wells to be installed**).
- This technology characterizes the subsoil in terms of apparent resistivity.

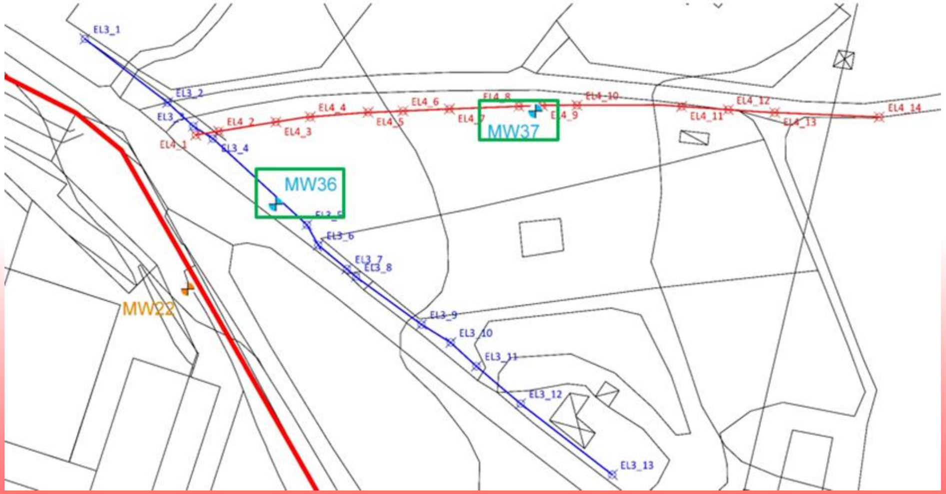


- Low-resistivity zones (green and blue areas in the section, with resistivity values < approx. 100 ohm m) represent potentially saturated subsoil volumes.
- The lowest values (in blue) may also be related to fine materials (silt and/or clay).
- Based on the above, at a first analysis **installing the new monitoring well in «green» areas (approx. 50 – 100 ohm m) maximizes the chances to intercept a productive water-bearing subsoil portion.**

ERT Main Results

- A geophysical test through two electrodes' arrays (EL1 and EL2) was conducted in March 2018 and, on the basis of these results, other two electrodes' arrays (EL3 and EL4) were conducted in October 2018 for the installation of additional monitoring wells in the area N-NE of MW22





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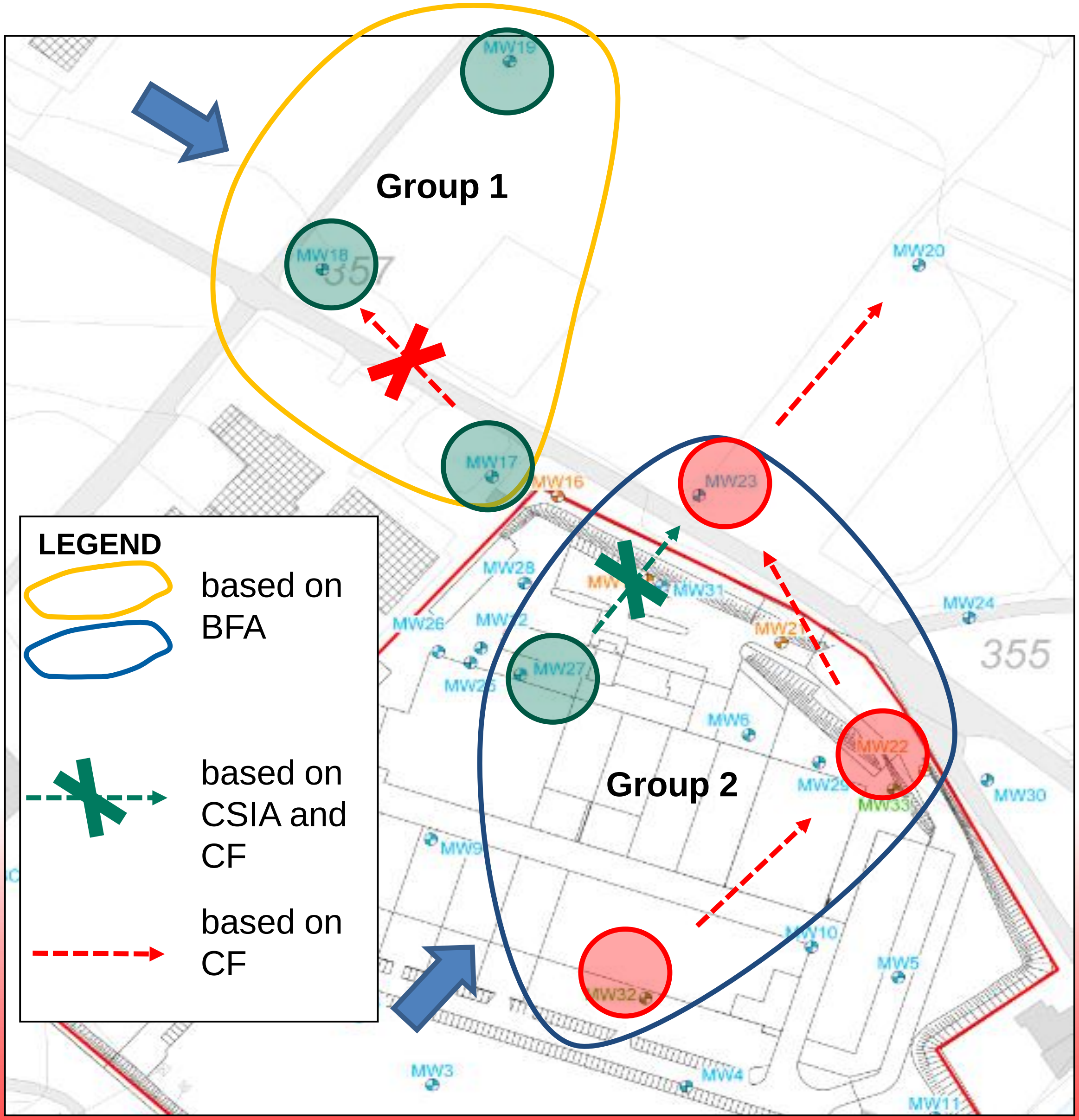
Updated Site Conceptual Model



Results, based on all lines of evidence (in monitoring wells were all of them were applied – MW17, MW18, MW19, MW22, MW23, MW27, MW32) :

- Hydraulic connections between MW17, MW18 and MW19 (Group 1) and MW22, MW23, MW27, MW32 (Group 2) should be excluded, based on **BFA** and **CF**.
- Inside Group 2, MW27 cannot be the origin of the TCE and 1,2-DCE detected in MW23, based on **CSIA**.
- Based on the above, at least **three sources** of CHCs are present, one impacting MW18 and MW19, one impacting MW27 and one impacting MW22, MW23 and MW32. This is supported also by compositional data.
- Characteristics of external impacts (MW23) are compatible with those identified in on site wells (MW22, MW32).

Lessons Learned

- In complex low permeability hydrogeology, the reconstruction of groundwater flow basing upon depth to water measurements in monitoring wells can be misleading
- Particularly in cases where High Resolution Site Characterization technologies (i.e. MIP) are not applicable, additional lines of evidence with different technologies like ERT, CF, BFA, CSIA are very useful for source recognition and reconstruction of migration pathways

Thank you

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The business of sustainability