On-Site Component-Specific Detection of Volatile Organic Components with the EnISSA-MIP

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ABSTRACT: Chlorinated solvents have affected soil and groundwater quality in many European cities. Besides environmental and health effects, this contamination also has a large socioeconomic impact. Because it is a common problem, nine partners from Flanders (Belgium), the Netherlands, France, and Germany are working together to develop an integrated approach in the CityChlor project. Within the CityChlor project, an innovative soil characterisation technique, EnISSA-MIP, was validated by comparing the results with classic techniques on a site in the city of Kortrijk (Belgium). The EnISSA technique combines the best of both the on-site "screening" and off-site "analytical" worlds by generating detailed on-site soil profile data with low detection levels (µg/l level) and a broad analysis spectrum. This report presents the results of the EnISSA measurements and their comparison with traditional sampling methods within the CityChlor pilot site in the city of Kortrijk, Belgium. Taken into account the different sampling methods, the EnISSA results correspond well with the analyzed soil and groundwater samples. Moreover, this demonstration project illustrates that EnISSA allows the development of an enhanced conceptual site model, providing accurate spatial data, which the soil expert will never obtain using only traditional sampling strategies.

INTRODUCTION

Chlorinated solvents have affected soil and groundwater quality in many European cities. Besides environmental and health effects, this contamination also has large socio-economic impacts. Because it is a common problem, nine partners from Flanders, the Netherlands, France, and Germany are working together to develop an integrated approach in the CityChlor project. With a research budget of 5.2 million euro, of which 50% is financed by the INTERREG IV B programme, the partners have set up seven demonstration sites to support the studies and workshops. More information can be found on www.CityChlor.eu. In Flanders (Belgium), the EnISSA (Enhanced In Situ Soil Analysis) technique was validated by comparing the results with traditional techniques on a site at the city of Kortrijk (Belgium). Secondly it was demonstrated how EnISSA can contribute to the development of a better conceptual site model (CSM).

When setting up a conceptual site model, different sampling strategies and sampling techniques could be used to generate information. The selection of which strategy or technique is used depends upon the ability for the data to decrease the overall uncertainty of the conceptual site model.

Regulatory-approved laboratory analytical methods, "classical methods", are commonly assumed to be almost free of uncertainty. Screening data, such as the Membrane Interface Probe, are assumed to be relatively uncertain, and therefore, less able to support decision making or regulatory actions. However, the effective capability of data to support decisions does not only rely on the analytical quality of the data (Van Ree and C. Carlos, 2003). Both analytical and spatial uncertainty contribute to the overall uncertainty of a sampling method. The aim of the EnISSA technology is to find the optimal balance between analytical uncertainty and spatial uncertainty.

"On site" soil screening technologies such as the membrane interface probe (MIP) are already frequently used in addition to traditional sampling methods. They are used to provide detailed screening of (semi)volatiles and make on-site, real-time characterisation possible. However, conventional MIP has a high analytical uncertainty: it has relatively high detection limits compared to typical risk or clean-up values and does not differentiate between individual chemical compounds, limiting accurate decision making.

EnISSA-MIP. The EnISSA-MIP is a thorough extension of the conventional membrane interface probe (MIP) application. It makes it possible to detect individual compounds at low levels using the conventional MIP-probe. The conventional MIP is a screening tool with semi-quantitative capabilities to measure volatile organic contaminants (VOCs) in the subsurface, developed by Geoprobe®. Using different push technologies, the MIP is pushed into the soil.

The membrane is semi-permeable and is comprised of a thin film polymer impregnated into a stainless steel screen for support (T.M. Christy, 1996). The membrane is placed in a heated block attached to the probe. This block is heated to 120° C. Heating the block helps accelerate diffusion of the contaminants through the membrane. Diffusion occurs because of a concentration gradient between the contaminated soil and the clean carrier gas behind the membrane. A constant gas flow carries the contaminants to the gas phase detector at the surface. For the detection of volatile organic compounds, typically a combination of detectors is used (PID, DELCD, XSD, FID).

Quantification with the conventional MIP is difficult due to the use of sum-detectors. Since the detectors have a different response for different compounds, one cannot correlate the detector signal with concentration since conventional MIP is non-discriminable. Therefore the conventional MIP system can only give an indication of the order of magnitude of the contaminant concentrations.

Generally, the detection limits are much higher compared to for example the cleanup or norm values which are typically risk based (Bronders, 2008). Therefore, conventional MIP is only applicable in the higher concentration zones and not readily applicable for plume investigations. Moreover, for the plume zone, a survey using sampling wells is still needed. This means that for the plume zone, only limited spatial information is obtained. New developments on the detector technology (e.g., XSD) are directed towards lowering detection limits, but intrinsically the detectors remain sum-detectors.

The EnISSA technology comprises a MIP coupled to a transportable GCMS system. The advantages of using a GCMS as detector, are the low intrinsic detection limit of the detector and the capabilities to measure individual compounds, hence bringing the lab into the field. However the typical cycle times between GCMS measurements are 15-30 min limiting the practical and economical suitability on the field. As a result such

measurements can't be applied for commercial site investigations. For example, the (un)homogeneity in contaminant distribution in the soil/groundwater can necessitate the determination of the contamination each 30 cm going downwards. Therefore using a conventional GCMS measurement, each 30 cm the operator should wait for at least 15 min. This means that only 8-9 m could be screened in one day, which is not economically viable.

Within the EnISSA technology, the GCMS system has been modified in order to allow very short analysis times. By using a combination of an innovative GCMS configuration and a smart method optimisation, it was possible to develop analysis methods with a very short cycle time (typically 1 min). As stated before, these short cycle times are crucial for the practical implementation of a MIP-GCMS in the field. Field evaluations indicated that the EnISSA MIP is capable of measuring soil profiles for individual compounds with detection limits near 10-20 µg/l.

FIELD WORK

Site Description. The pilot project is carried out on the site of a former spinning and weaving mill. A pollution with chlorinated solvents originating from three sources has spread over a distance of more than 100 m. In vertical direction, the pollution has spread to a clay layer at 20 m-bgl. Groundwater samples indicated that zones with DNAPL may be present on the site. The geology is fine to medium coarse sand with narrow loamy/clayey layers. At 20 m-bgl an impermeable clay layer occurs. The groundwater table is expected at 1,50-2,00 m-bgl.

Sampling Strategy. Within the CityChlor project, EnISSA MIPs were carried out in the source as well as in the plume zone and compared with traditional soil and groundwater samples to validate the EnISSA results.

Three EnISSA MIPs were conducted in the source area. These were validated by classic sampling wells (1 m filter) and soil samples, which were taken each 50 cm by dual tube sampling. In the plume zone, groundwater samples were taken for confirmation of three EnISSA MIPs. Samples were sent to an off-site laboratory for analysis.

RESULTS AND DISCUSSION

EnISSA Results. Figure 1 gives an example log for EnISSA MIP 10004. Only the logs for PCE, TCE, DCE and VC are given in Figure 1. The logs for TCA, DCA and BTEX are not shown for clarity. As is demonstrated by MIP 10004, a different distribution of individual compounds is observed. The possibility of measuring the individual contaminant distribution is the main advantage of EnISSA, since no other screening technique or traditional approach can obtain these data.

Source Zone. Since the EnISSA results give concentration levels for individual compounds they can be directly compared with groundwater analyses. However, such an evaluation is not straightforward due to the difference in sampling matrix. As the EnISSA MIP and in general MIP heats up the whole matrix around the probe, EnISSA MIP measures both the contaminants dissolved in the groundwater and the contaminants ad-

sorbed at the soil matrix. Secondly the sampling volume is different between the MIP and the groundwater well. While a groundwater well typically integrates over 1 m filter length, the MIP gives point measurements.

Results were obtained for PCE, TCE, DCE, VC and BTEX. Figure 2 gives a comparison between the EnISSA results and groundwater results for DCE. Figure 3 compares the soil samples with the EnISSA results. The correlation between both data sets is good, taken in account the above mentioned remarks.
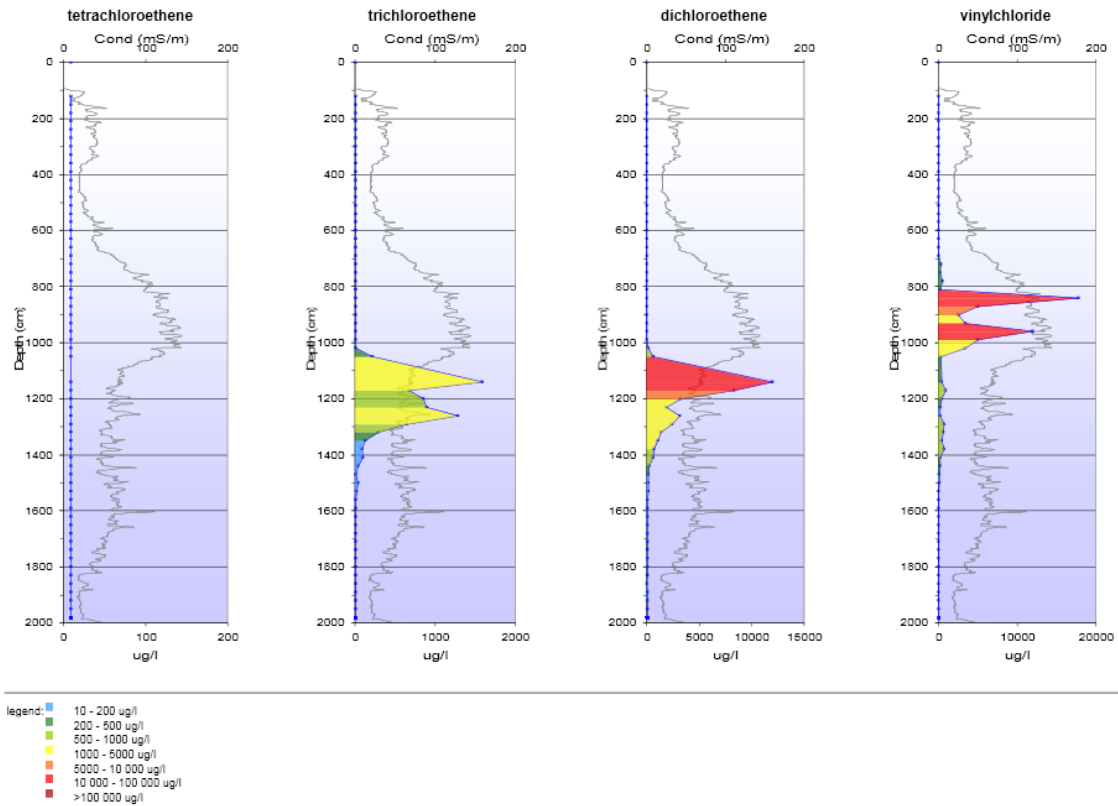
FIGURE 1. EnISSA MIP 10004.

For EnISSA MIP10001 and EnISSA MIP10003, pure product was visually observed during sampling of the sampling well at 7,50 and 9 m-bgl. The presence of pure product gives a huge discrepancy between the EnISSA results and the groundwater samples. The difference is due to the fact that EnISSA measures both dissolved phase and the pure product. For the groundwater sample, only the dissolved phase is analysed in the off-site laboratory after pure product removal.
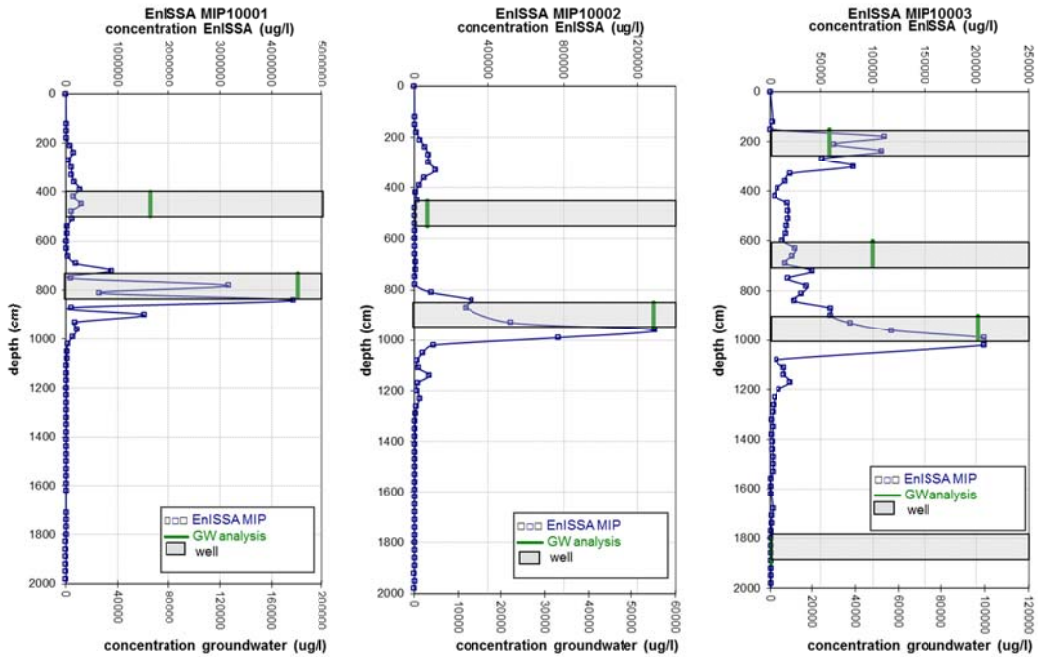
FIGURE 2.comparison between the EnISSA results and the groundwater samples for DCE. Remark that the scales are different.
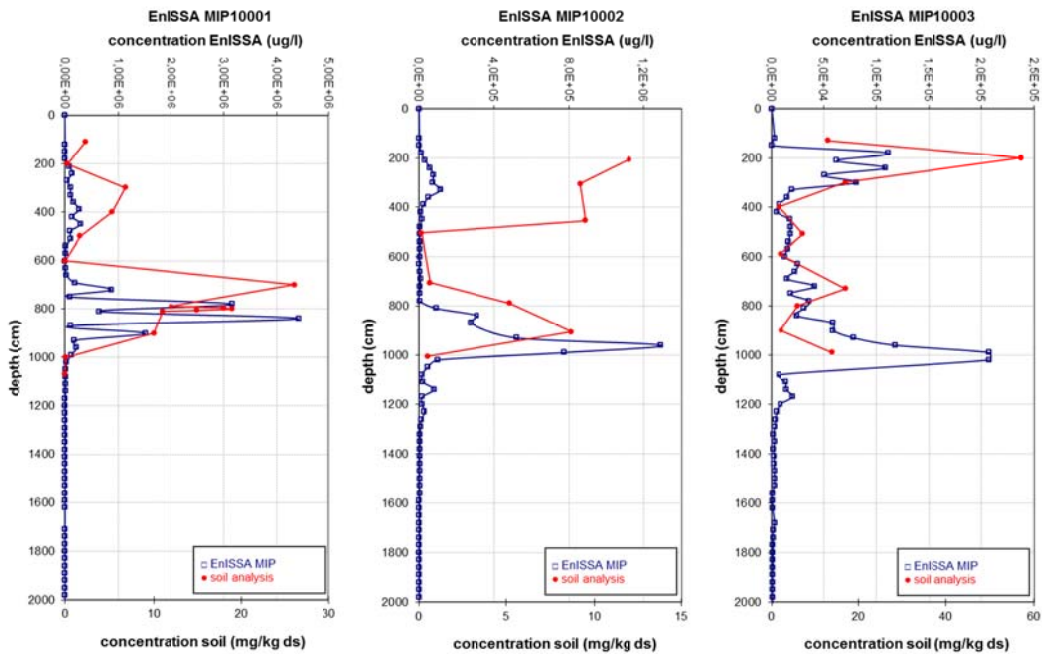
FIGURE 3. Comparison between the EnISSA results and the soil samples for DCE. Remark that the scales are different.

Plume Zone. Results were obtained for PCE, TCE, DCE and VC. Figure 4 gives the EnISSA results in the plume zone compared with groundwater samples for DCE. Taking into account the different sampling volume, the results of EnISSA MIP 10004 compare well with the groundwater samples. For EnISSA MIP 10005 a lower concentration level is observed with EnISSA, which could not be explained based on geology. Finally, EnISSA MIP 10006 confirms the detection limit of the EnISSA method. Note that due to an inaccurate filter location, the DCE concentration is highly underestimated by the traditional sampling well at EnISSA MIP 10006.

Figure 5 gives the correlation between the EnISSA results and the groundwater samples. The majority of the results show that the EnISSA results are within a factor 3 compared to the groundwater results. As the concentration increases, figure 5 shows that the discrepancy between the data sets is higher. This is due to the contribution of the adsorbed contaminants which will be measured by EnISSA, but less by the groundwater samples.
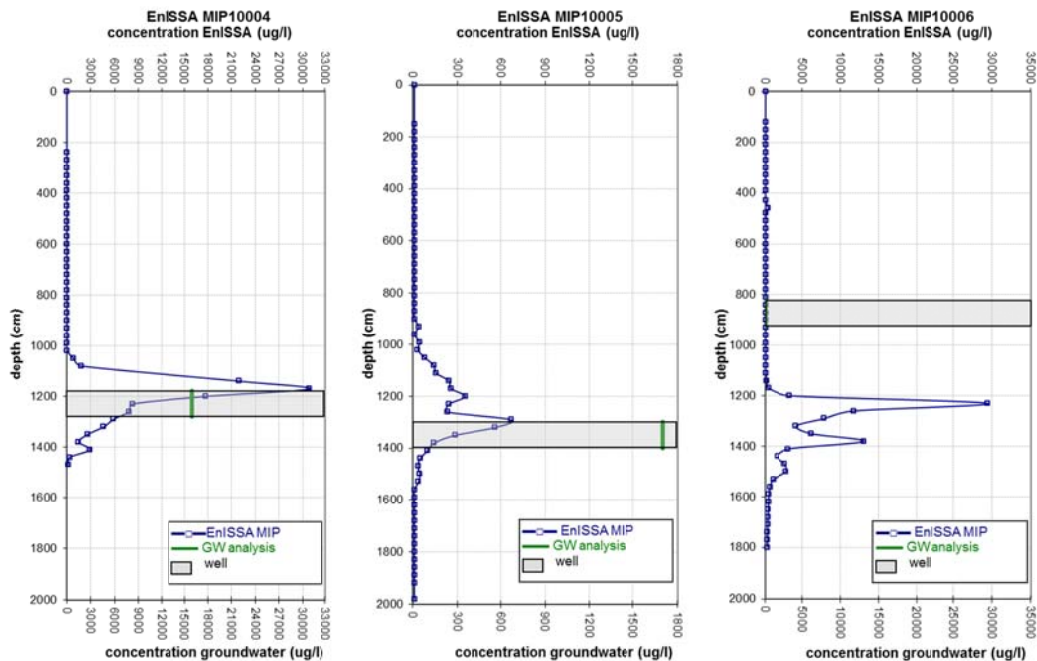
**FIGURE 4. Comparison between the EnISSA results
and the groundwater samples for DCE.**

This indicates that the EnISSA method generates at least semi-quantitative data which gives concentration ranges in the same order of magnitude as groundwater samples. Secondly since the spatial uncertainty of the EnISSA results is much lower compared to the traditional sampling methods, one can state that EnISSA is capable of delivering data with very high spatial certainty and which approach a quantitative technique.
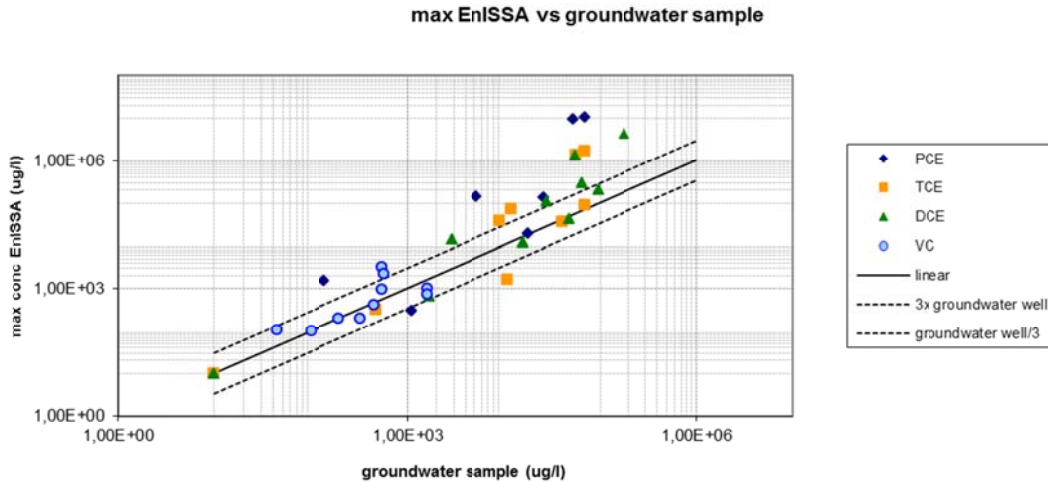
FIGURE 5. correlation between EnISSA results and groundwater samples.

Cost Comparison. Figure 6 gives a cost comparison between an EnISSA campaign and a traditional campaign. For the EnISSA campaign the cost for two confirmation sampling wells is included. Using EnISSA during site characterization leads to a cost saving of approximately 30% compared to traditional approaches. Secondly, the cost per screened meter ("information meter") is much higher for a traditional survey. For a survey based on the EnISSA MIP, the cost per information meter is about 4 times lower compared to a traditional survey.
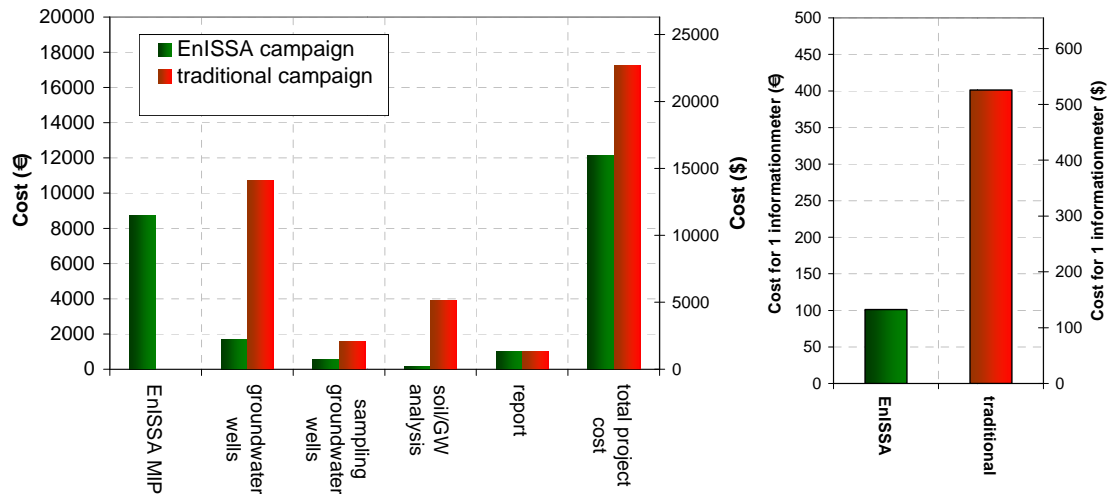
FIGURE 6. Cost comparison between an EnISSA campaign and a traditional approach.

CONCLUSIONS

On a pilot site at the Spinnerijkaai Kortrijk (Belgium), the EnISSA MIP was demonstrated and validated. The demonstration was performed in the framework of the CityChlor project, which aims to develop an integrated approach for soil and groundwater contaminations with chlorinated solvents.

The main advantages of the EnISSA MIP are:

- The EnISSA MIP improves the conceptual site model. As was demonstrated by the comparison between EnISSA and traditional sampling strategies, the EnISSA MIP gives an optimal balance between a low spatial uncertainty and a low analytical uncertainty yielding a high resolution CSM.
- The EnISSA MIP uses an innovative GCMS system which is adapted to connect with the Membrane Interface Probe (MIP). This connection generates a MIP application with component specific detection at much lower detection limits compared to conventional MIP. This is a major advantage compared to other on site technologies, which in most cases measure sum-parameters.
- As was demonstrated on the pilot site, the comparison between the EnISSA MIP and traditional sampling strategies, both in source and plume zone, showed that the results were in the same order of magnitude (factor 3) as the groundwater samples. This indicates that the EnISSA MIP can be seen as a quasi quantitative technique for characterization of volatile subsurface compounds.
- The use of EnISSA during site characterization leads to a cost saving of approximately % compared to traditional approaches. Secondly, the cost per screened meter ("information meter") is much higher for a traditional survey. For a survey based on the EnISSA MIP, the costs per information meter is about 4 times lower compared to a traditional survey.

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Bronders, J., I. Van Keer, I., J. Bronders, K. Touchant, and D. Wilczek, 2008. "Application of the Membrane Interphase Probe: An evaluation." *Journal of Soils and Sediments. 9*(1): 74-82.

Christy, T.M., 1996, A driveable permeable membrane sensor for the detection of volatile compounds in soil, *In Proceedings of the 1996 National Outdoor Action Conference, Las Vegas, Nevada.* NGWA, Columbus Ohio.

Van Ree, D., and C. Carlon. 2003. "New technologies and future developments – how much truth is there in site characterisation and monitoring?" *Land Contamination & Reclamation*. 11(1): 37-46.

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On-site component-specific detection of volatile organic components with the EnISSA-MIP

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City Chlor

Tackling urban soil and groundwater contamination caused by chlorinated solvents

improve the quality and minimize the pollution of soil and groundwater by developing an **integrated approach** to tackle the threats caused by contamination with chlorinated solvents in urban areas.

9 partners from Flanders, Netherlands, France, Germany

Lead partner: OVAM

The Public Waste Agency of Flanders, Belgium

TOGETHER WE MAKE TOMORROW MORE BEAUTIFUL
OVAM
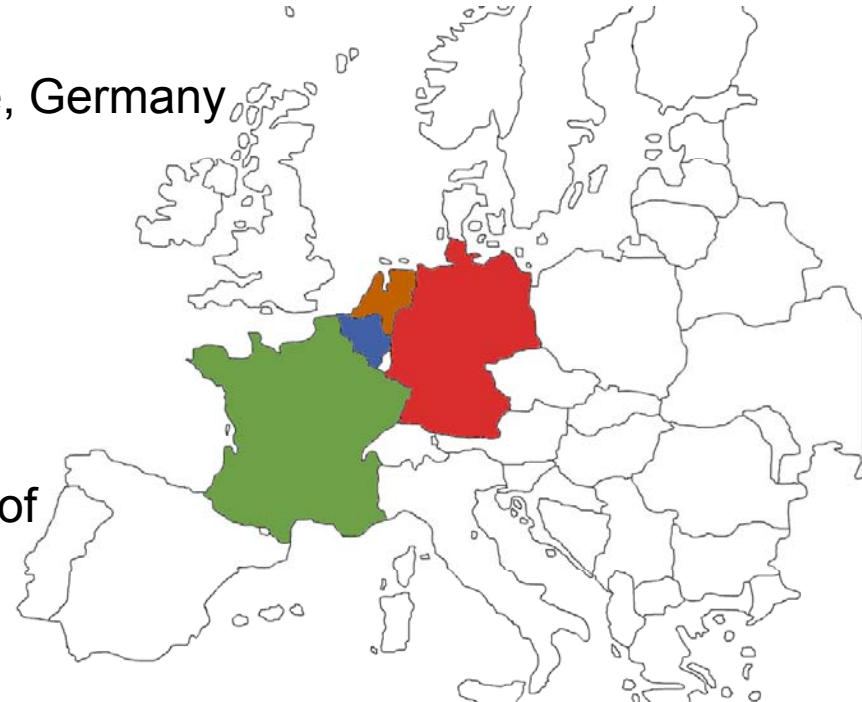
Research budget 5.2 M€ (50% funded by Interreg IV NWE project)

The aspects – depending on area, site and context – are:

- socio-economy
-techniques, ⟶ **Pilot project 2:**

Validation & demonstration of an innovative site characterisation tool

-time,
-space,
-environment and
-actors (active & passive).

EnISSA
enhanced in-situ soil analysis
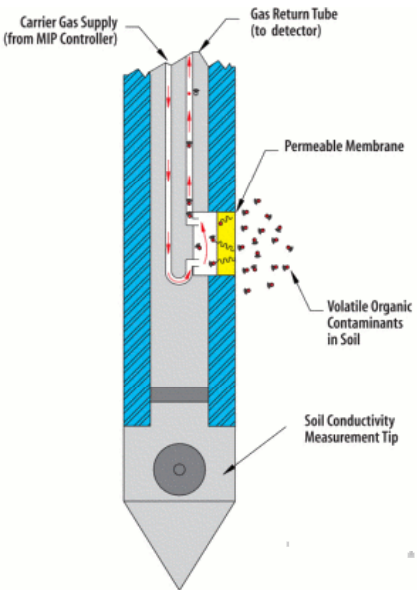
Membrane Interface Probe

- Direct push

- Local heating of soil

- Hydrophobic semi permeable membrane

- Inert carrier gas & transport to detector

Typical setup: Combination of three detectors:

* Dry electrolytic detector (DELCD) or

Halogen specific detector (XSD)

* Photo ionisation detector (PID)

* Flame ionisation detector (FID)
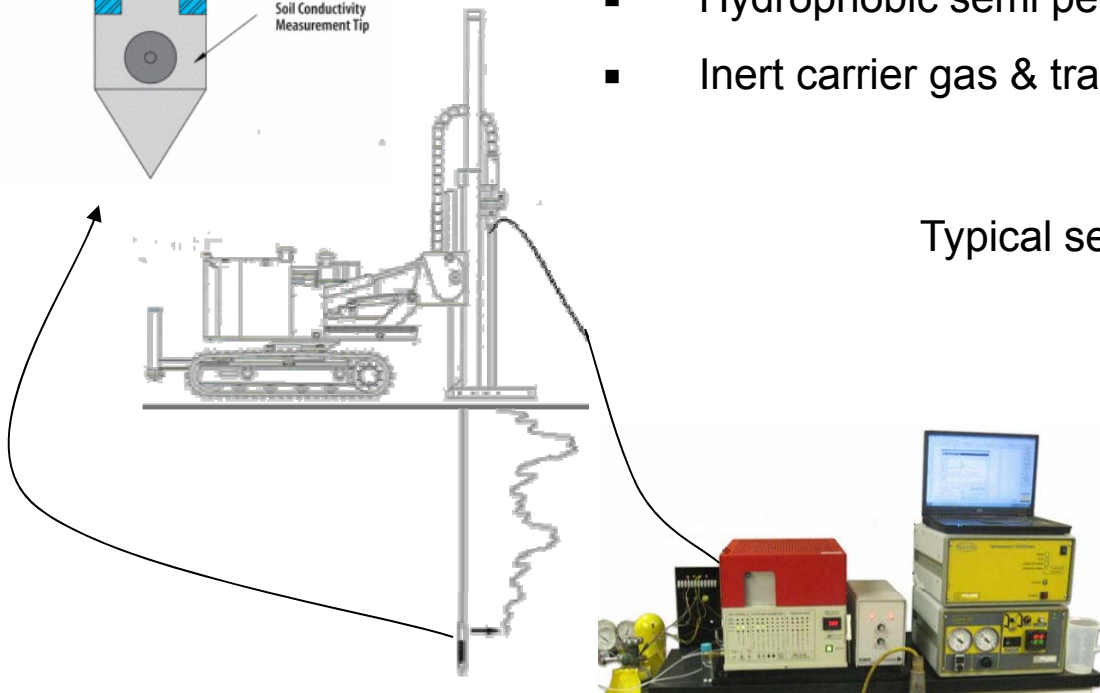
PID, FID, DELCD & XSD

→ Summation-detectors: no information on individual contaminants: polluent cocktails!

→ detectionlimit > groundwater clean-up values in Flanders : µg/l

EnISSA MIP

MIP with dedicated **GC-MS detection** combined with proprietary contaminant sampling technology

Highly detailed profiles for individual compounds on ppb level

GCMS: Optimized for field measurements:

* ruggedized

* cycle/analysis time: 1 min

→ 1 measurement per 30 cm at probing speed of 30 cm/min

* up to 12 compounds
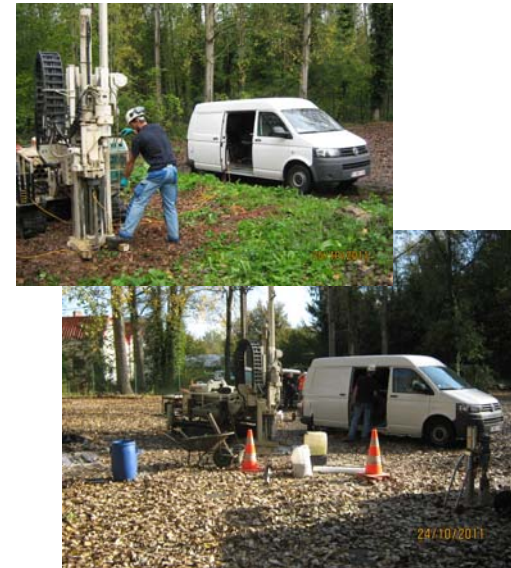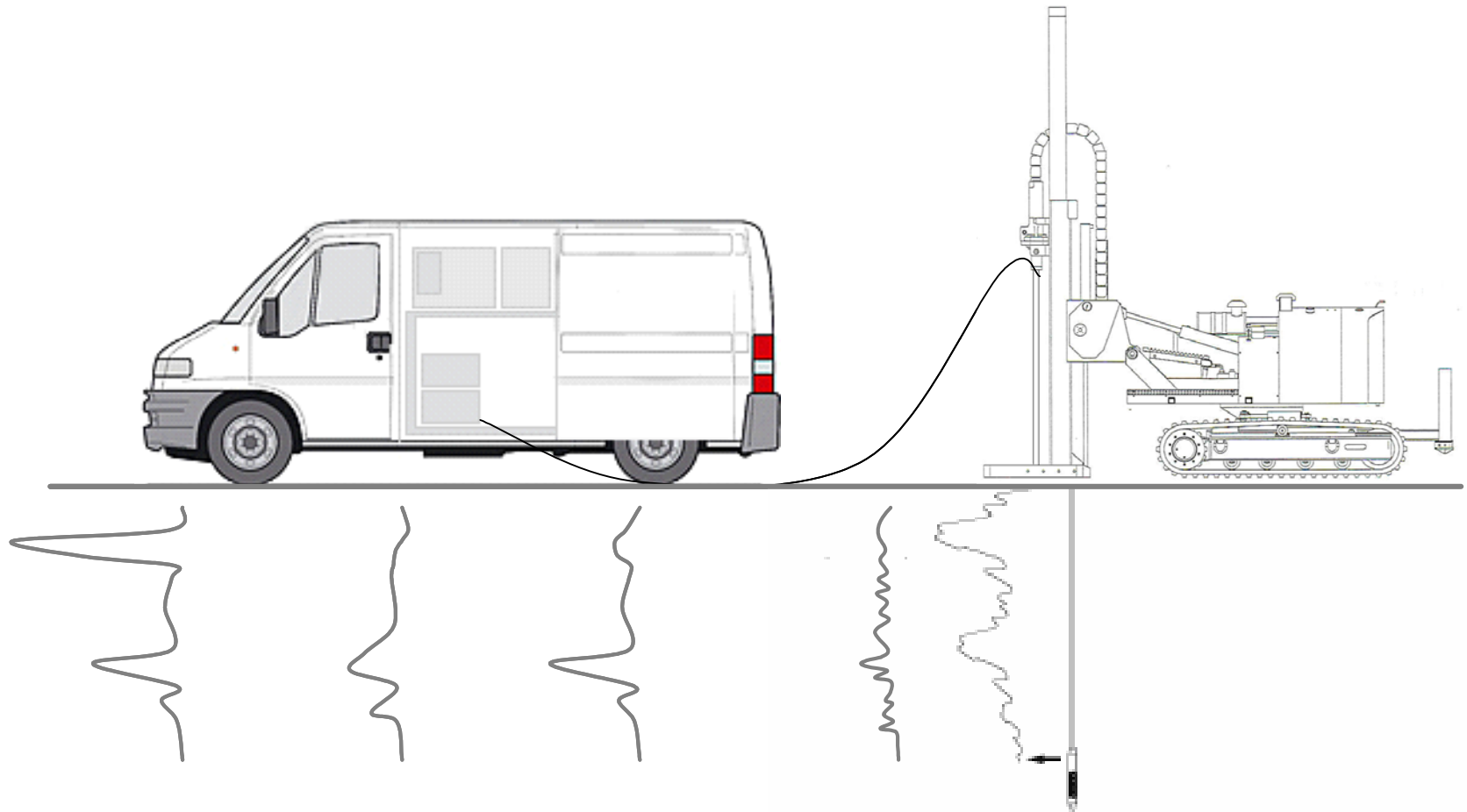
Tetrachloroethylene	Vinylchloride	1,2 dichloroethylene	PID	Soil Conductivity
Measurement of individual components			Measurement of sum parameters	Measurement of soil parameters

Site description:

* Location: Kortrijk (Belgium)
* Former spinning and weaving mill
* Contaminants: CVOC & BTEX
* Three sources, possible DNAPL

Purpose: Validation of the EnISSA MIP by traditional sampling

MIP configuration:

MIP Controller Model MP6505 / Field Instrument Model FI6000

40 m unheated Teflon-Peek trunkline

35 ml/min N2 flow
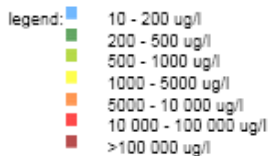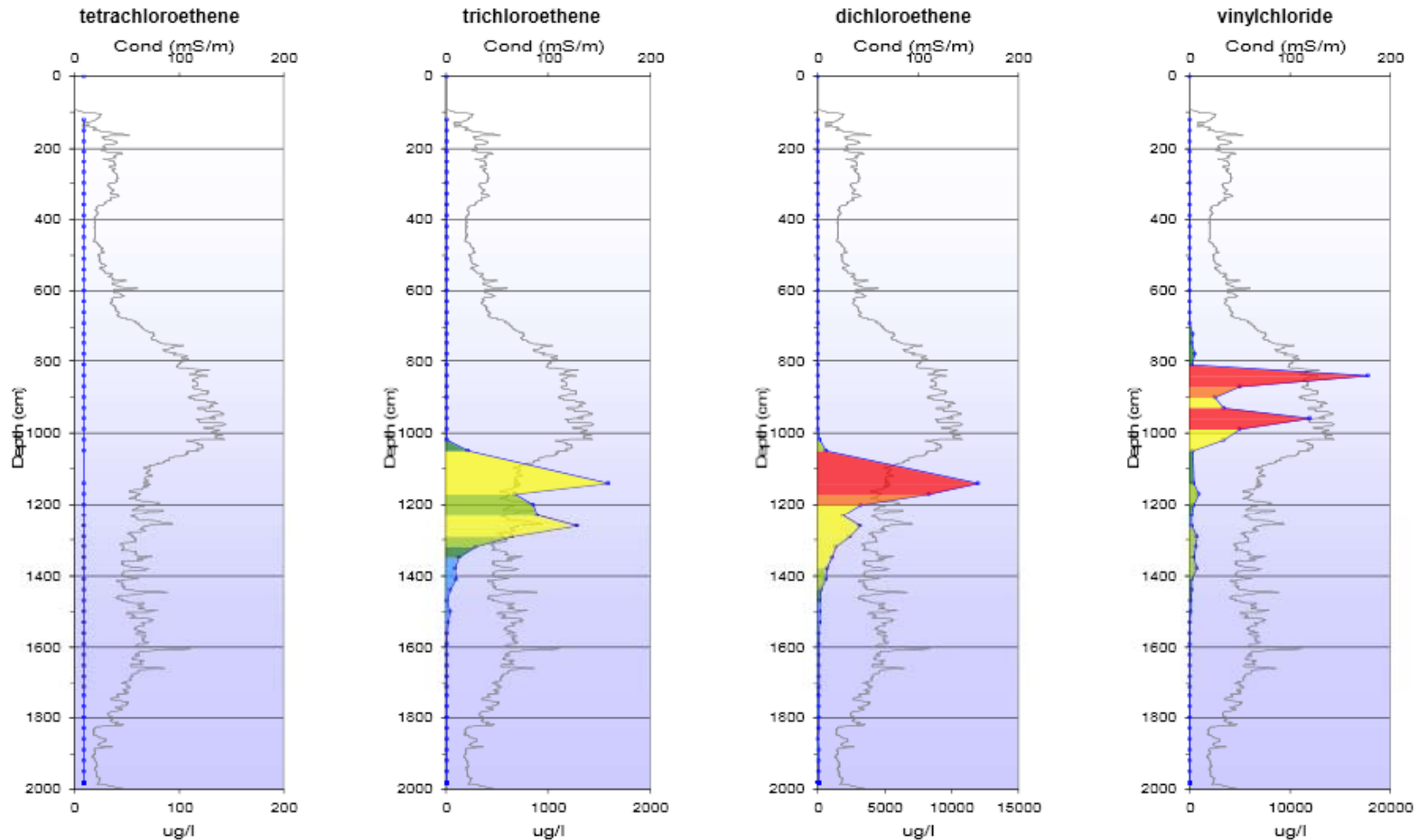
EnISSA → detailed soil profiles for individual compounds

    * low detection limit

    * each 30 cm or less: characterization of up to 12 compounds
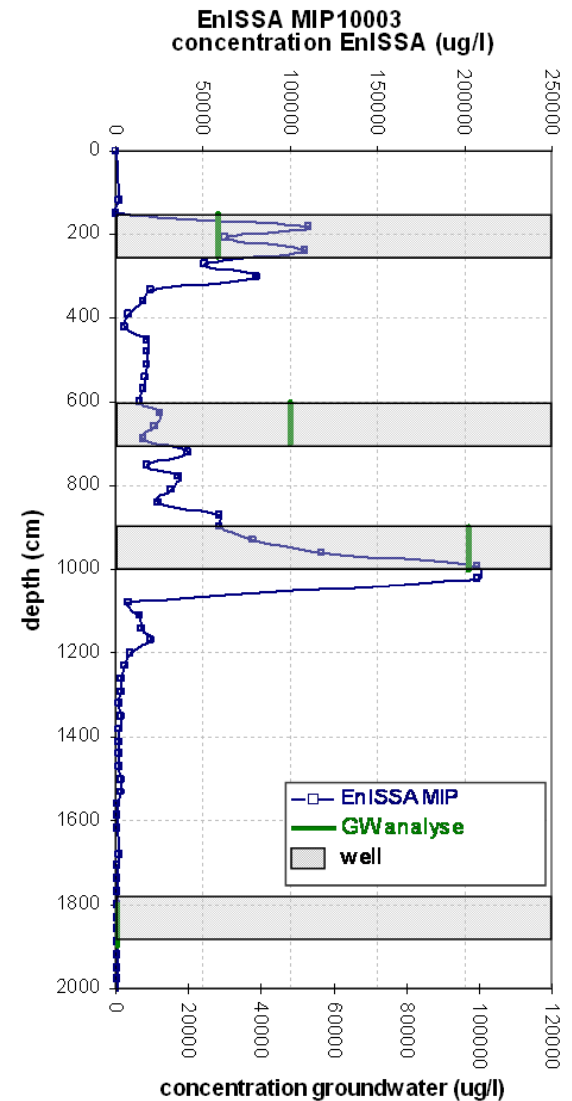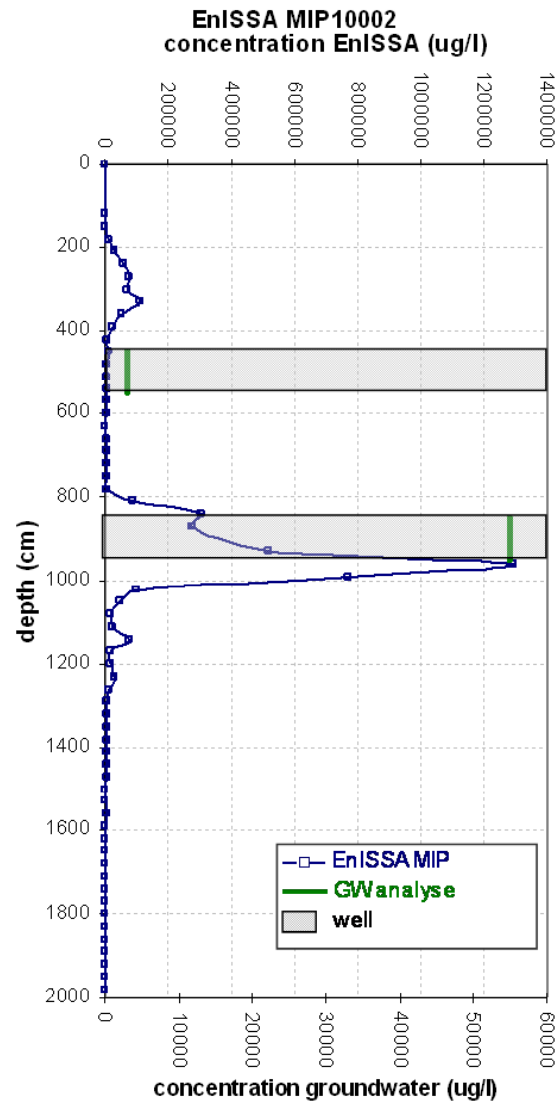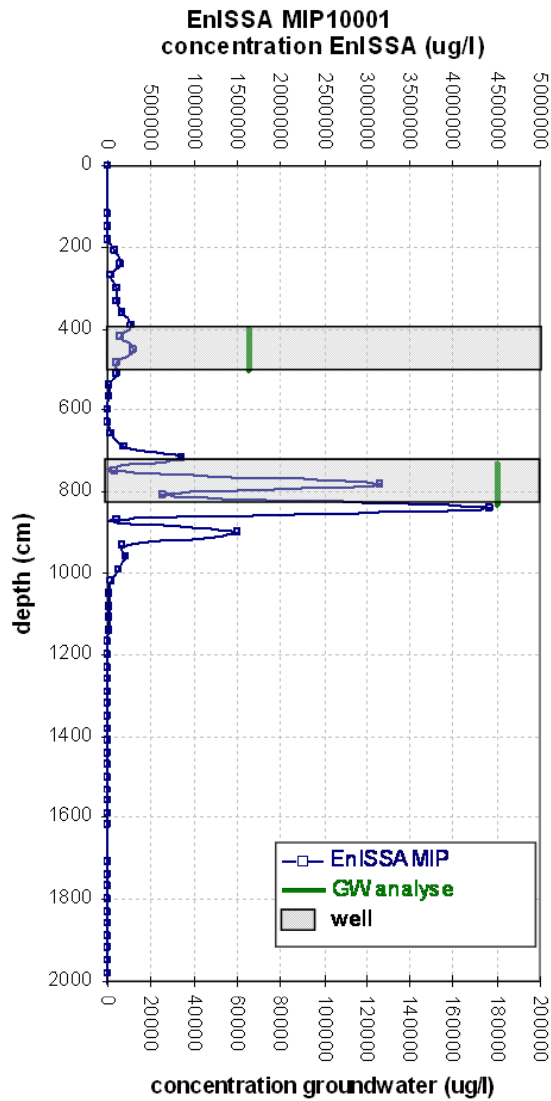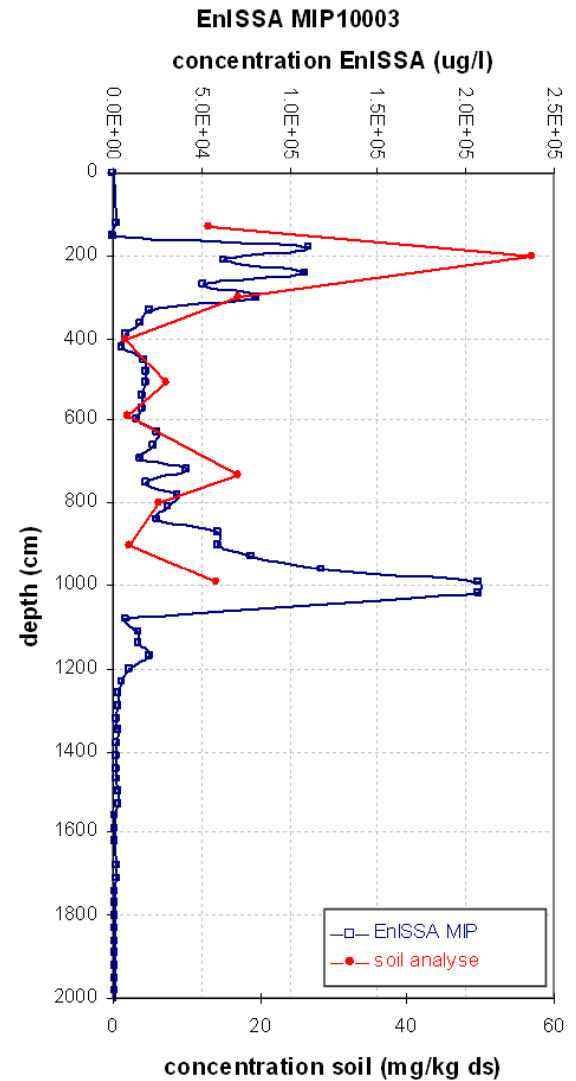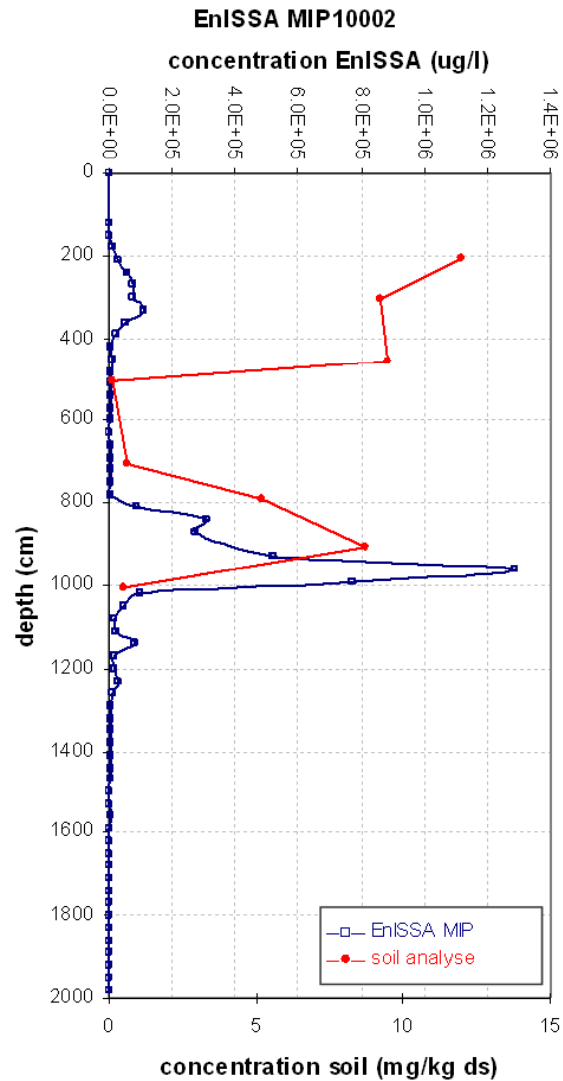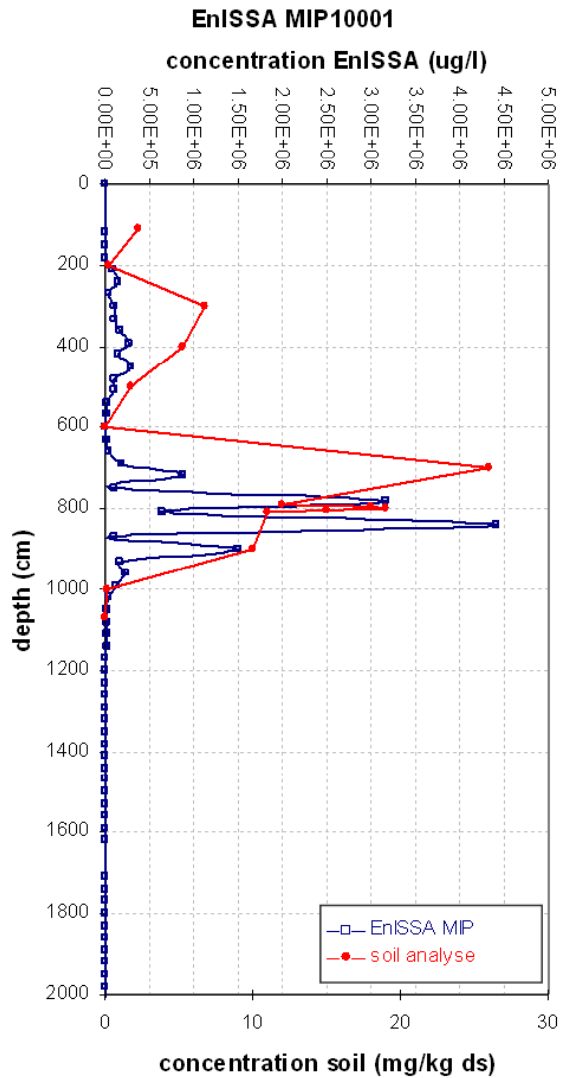
EnISSA gives a soil/ground water profile for each component:

▶ profile confirmed by soil & groundwater samples
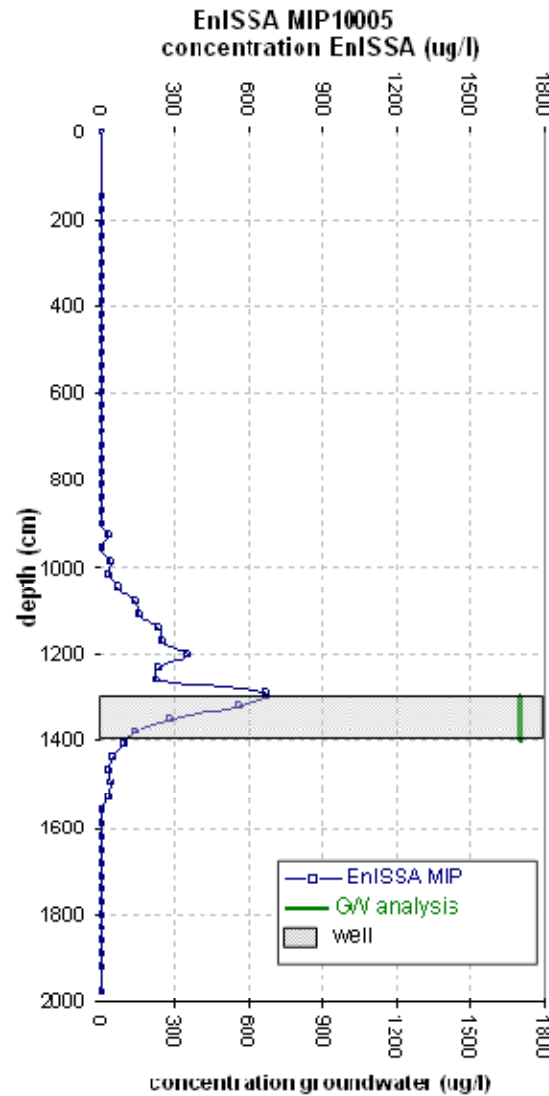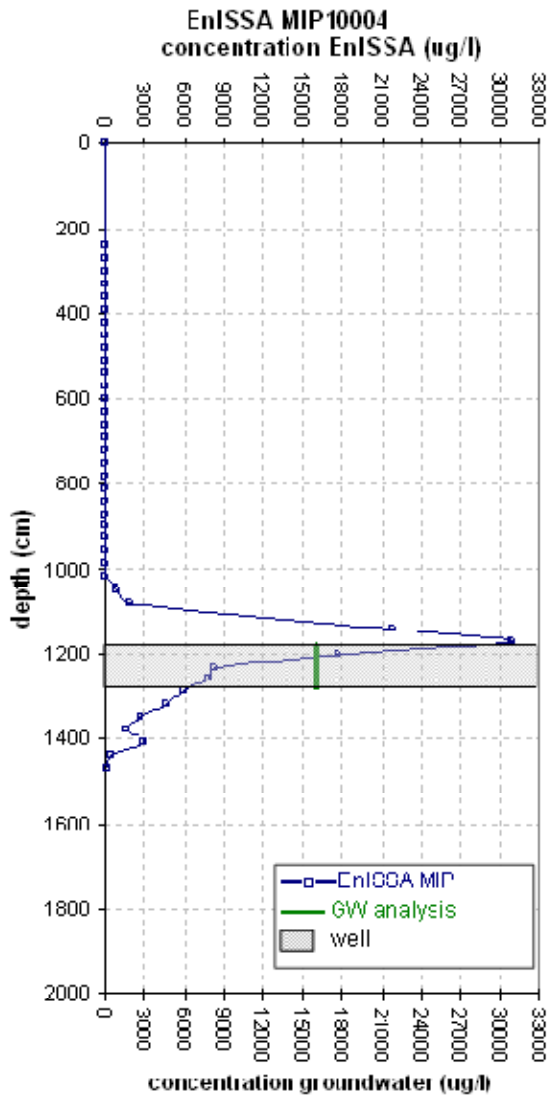
EnISSA gives indication for presence of DNAPL:

▶ visualy determined during ground water sampling
▶ soil & groundwater samples also indicate presence of DNAPL

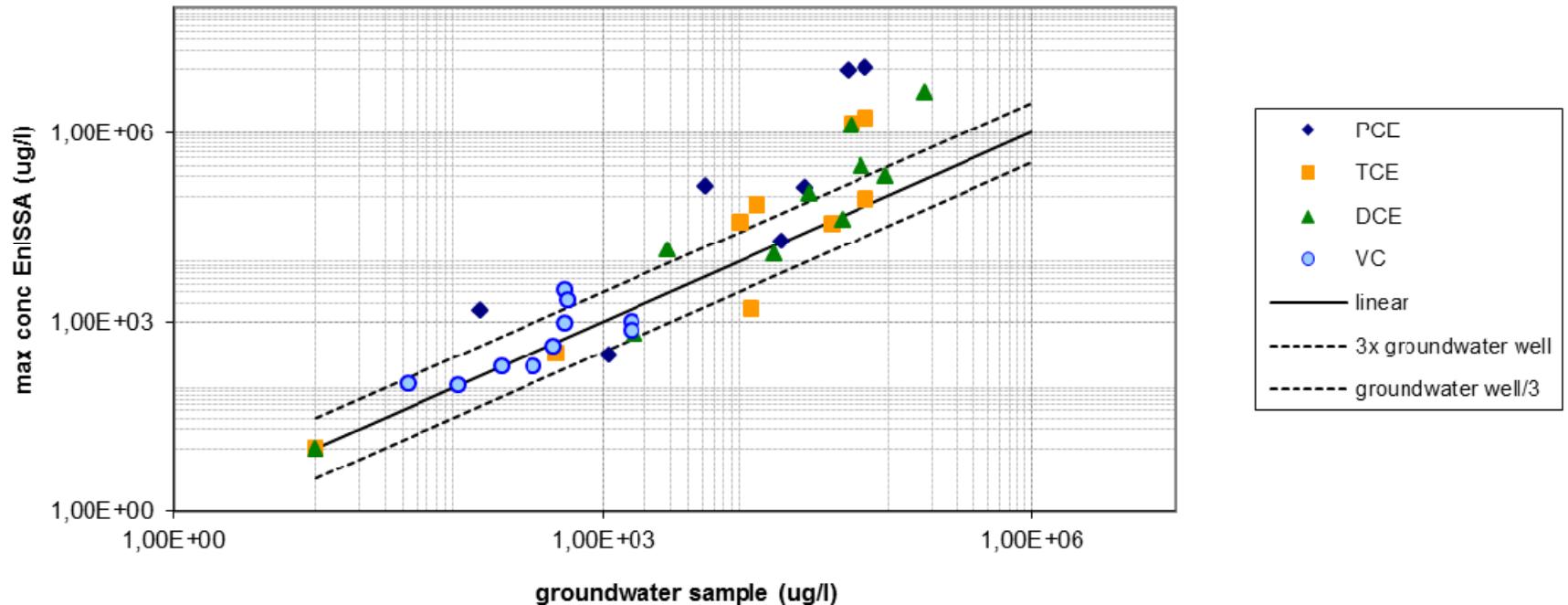**EnISSA concentrations vs. groundwater concentraties:**

▶ correlate BUT:

! EnISSA measures soil- , groundwater- & pure product phase
! Calibration EnISSA with aqueous solution
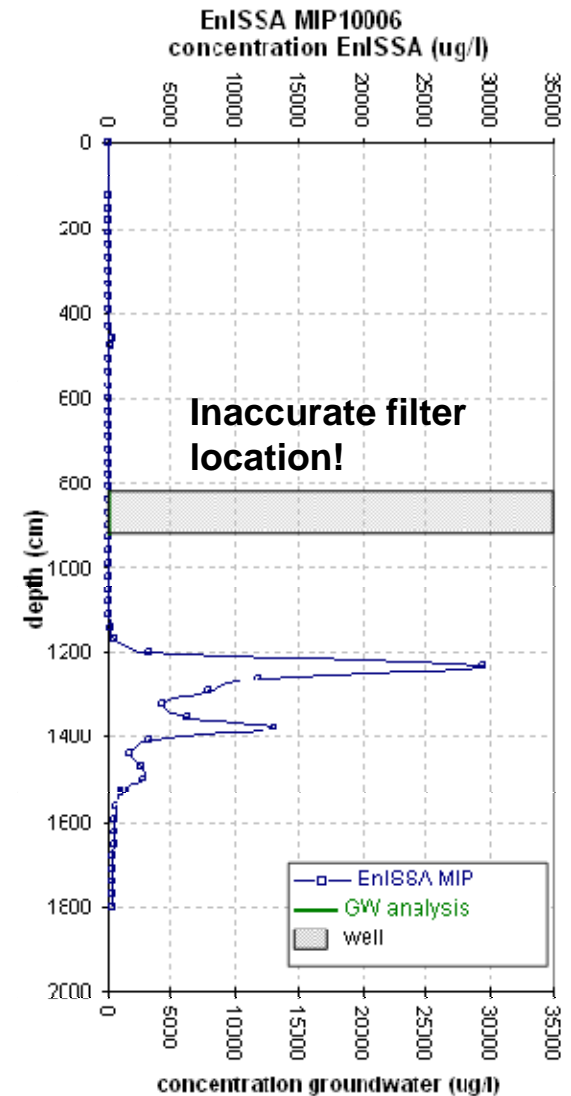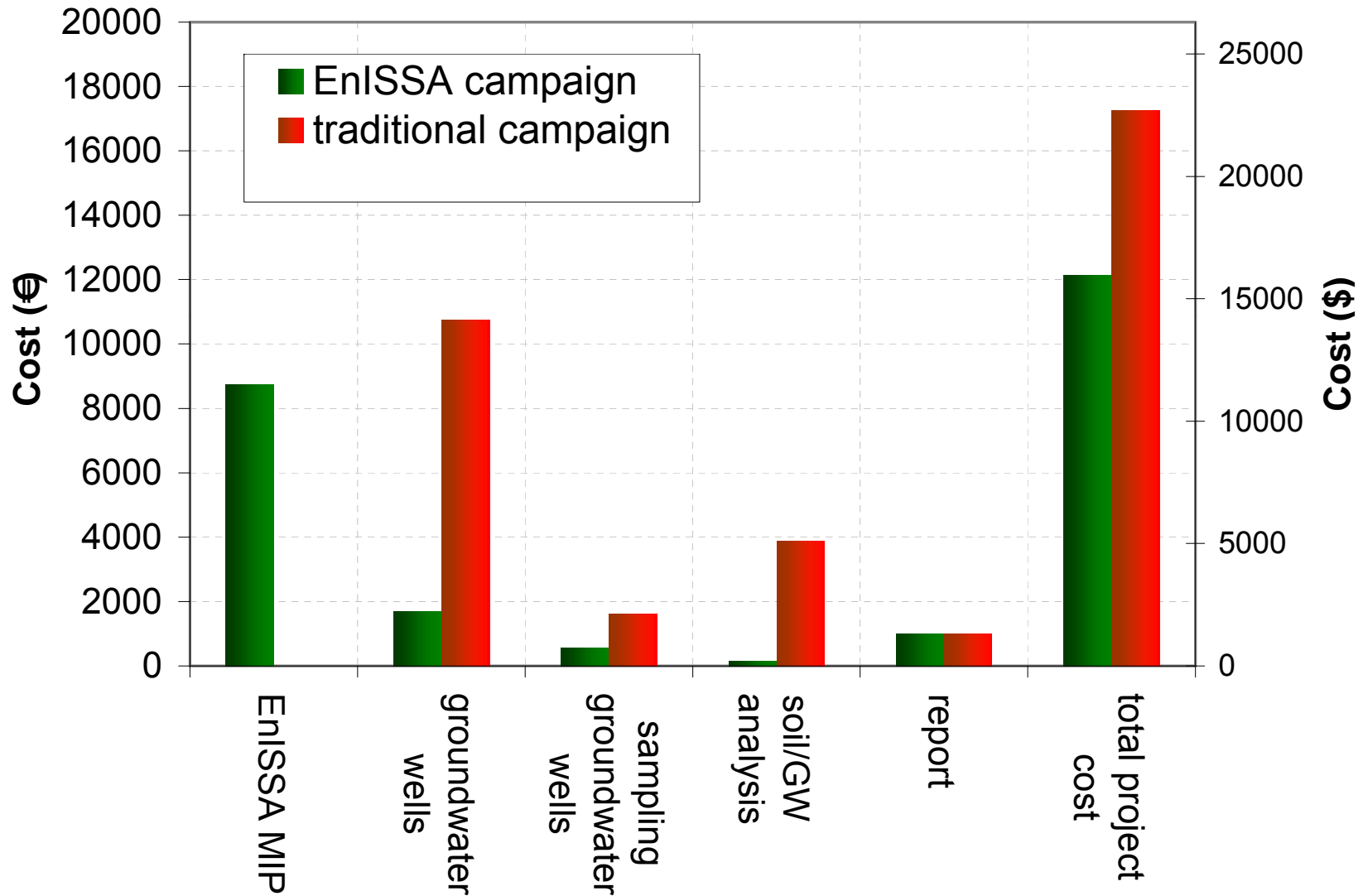
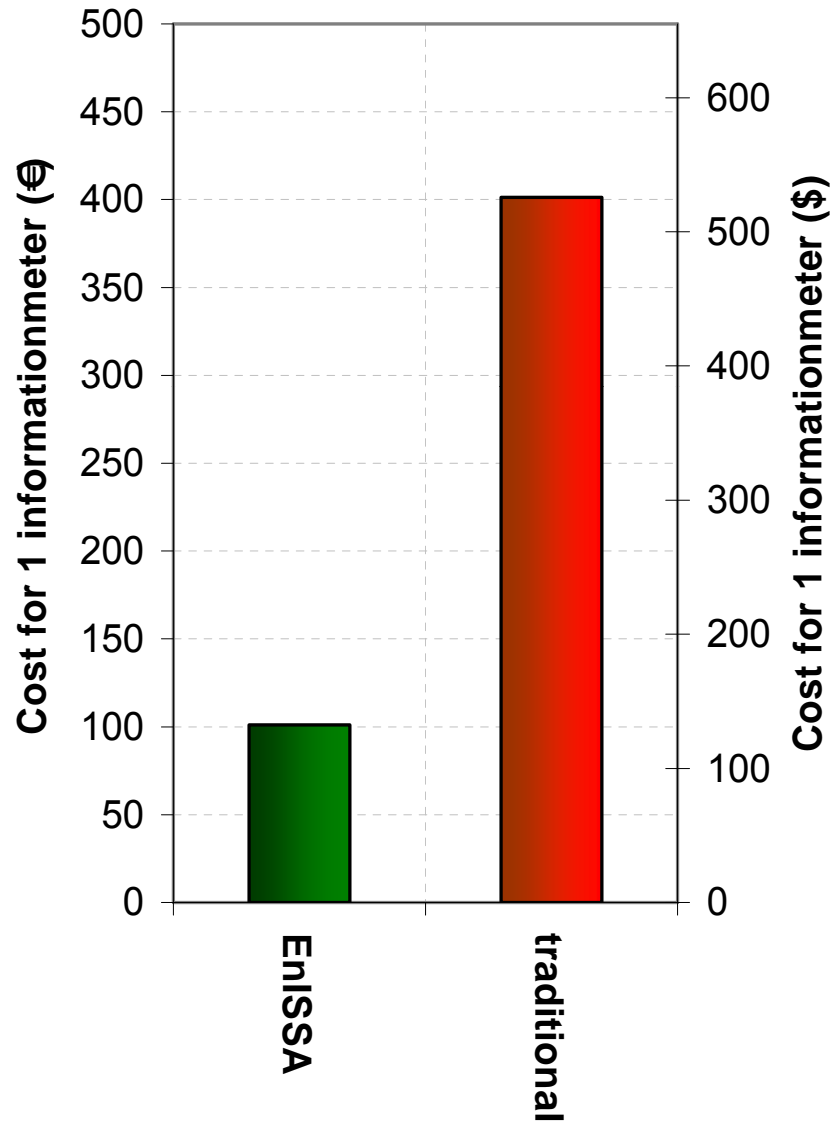# 3. Field results

max EnISSA vs groundwater sample

* contribution of the adsorbed contaminants which will be measured by EnISSA but not by the groundwater samples

* EnISSA results vs. groundwater results: order of magnitude is comparable → semi-quantitative or better?
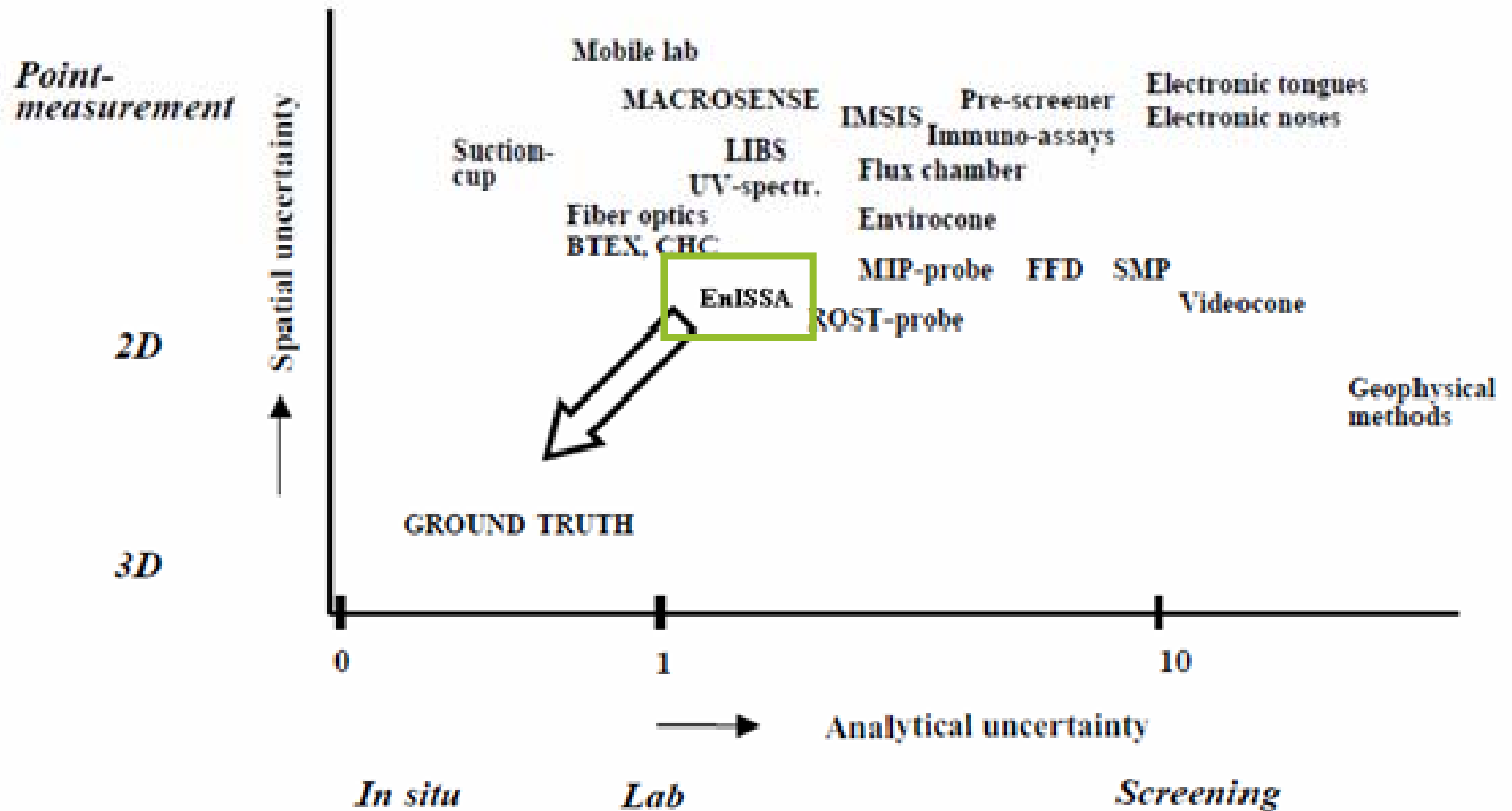
4. Cost comparison

4. Cost comparison

ARE WE THERE YET?

4. Conclusions

entire delineation of contamination: source + plume

  EnISSA MIP measures on ppb level

  → source and plume

  (Conventional MIP measures on sub-ppm level)

- Order of magnitude = groundwater sample → high quality screening tool -

"On site" information on pollution cocktails:

  EnISSA MIP measures individual compounds in contrast to the sum-detectors used in conventional MIP

- Each 30 cm up to 12 compounds can be distinguished -

strategic sampling well locations:

  The entire delineation of source and plume obtained by EnISSA MIP makes it possible to place sampling wells at strategic locations reducing sampling costs and time.

More information:

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