Groundwater, soil, soil gas and indoor air characterization

Technical book

Investing in Opportunities

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INTERREG IVB

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1 Introduction

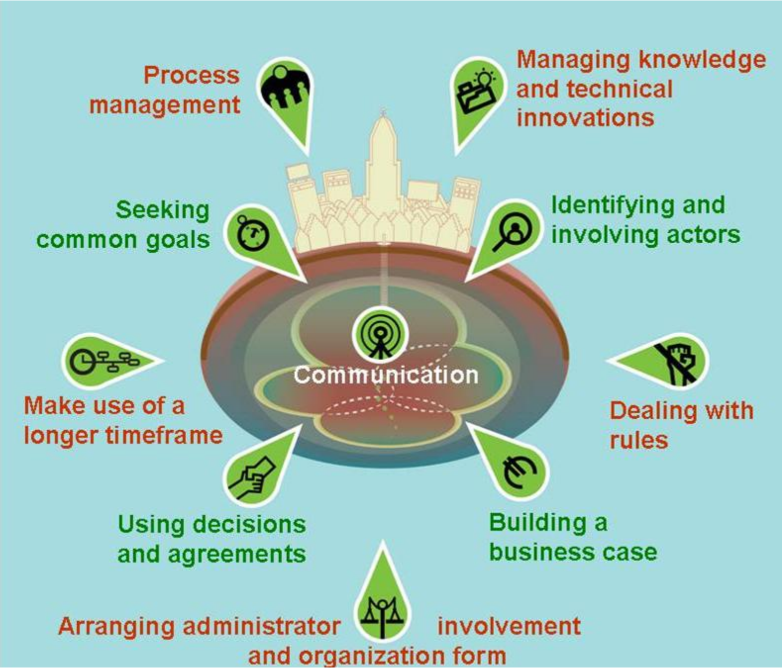
1.1 CityChlor and the integrated approach

Space is scarce in Europe. Even in the subsurface it is getting busier. Large-scale soil and groundwater contamination with chlorinated solvents are often an obstruction for urban developments. The traditional way of dealing with polluted soil and groundwater does not work in all cases and is not economically and sustainable feasible. In urban environments multiple contaminations with chlorinated solvents are often mixed with each other and spread underneath buildings. This not only leads to technical problems for remediation, but also to liability and financial discussions and hence has an impact on society. An integrated approach and area-oriented approach is needed to tackle the problems. The CityChlor project has demonstrated that remediation and sustainable development can evolve on a parallel timescale.

An integrated approach combines all aspects that are relevant to tackle the problems that pollution with VOC in urban environment causes. Depending on area, site and context different aspects together or parallel to each other can be used. Not only technical solutions are included, but also socio-economical aspects as urban development, communication, financial and legal aspects, time, space, environment and actors (active & passive) have to be handled.

CityChlor did not remain at single case remediation, but looked at the area as a whole in a bigger context: the area-oriented approach. A technical approach that makes it possible to remediate, monitor and control multiple groundwater sources and plumes within a fixed area.

CityChlor provides building blocks for an integrated approach. Off course there is no fixed path towards 'the' best solution. Every case has its own actors and context and will demand a different strategy. The project identified 10 success factors that are essential for the integrated approach that will lead to sustainable city development.



These success factors can be used as a guideline and checklist to increase the chances for a successful integrated approach. Each individual success factor leads the user through all the elements necessary for that specific success factor. The success factor also provides links to useful tools for the user.

1.2 CityChlor and technical innovations

The managing of knowledge and technical innovations are one of the success factors to achieve a sustainable city development. A development project has to cope with loads of information coming from different disciplines in different (technical) languages and with different uncertainties. With chlorinated solvents in particular, the knowledge about the pollution will always have a certain uncertainty that can have an impact on the course and the costs of the remediation. An efficient 'managing of knowledge' will try to decrease this degree of uncertainty.

CityChlor therefore also worked on the technical aspects of characterization and remediation. The conventional techniques that are applied for investigation and remediation have their limitations dealing with chlorinated solvents. Promising innovative techniques exist, but do not easily find their way to current application. This barrier is often caused by lack of knowledge on different levels. Experts and contractors do not always have the means to invest in experiments with new techniques, authorities are reluctant to accept techniques of which the results may be uncertain and clients aren't eager to pay for experimental techniques.

Dissemination of knowledge can break this deadlock. CityChlor therefore collected experiences from field application of innovative techniques and implemented itself a number of techniques in pilot projects. The technical books give a brief overview of the main findings and results. For the detailed outcomes, the reader is referred to the specific reports.

2 Characterization tools for a better remediation

The first step of the remediation process of a polluted site is the characterization of the pollution: source zone detection and plume delineation with the main goal of evaluating the possible effects of the pollution on the environment and on human health. This is the only way to understand the fate of the pollution on site and as a consequence to define the urgency and the extent of the remediation process. Enough time and efforts has to be invested at this stage and several techniques have to be combined for a full characterization of the pollution because characterization is a critical step. This is the baseline to build a conceptual site model, necessary to understand the possible route of exposure to the contaminants and to design one (or more) efficient remediation process(es). An other issue in urban areas is related to the high density of possible sources of chlorinated solvents, making the search for responsibilities a difficult process. This needs sometimes other characterization tools. Pollution is spread unevenly over the soil matrix, making it very difficult to detect and characterize the source zones. Therefore, reliable characterization tools need to be used. This characterization must still be going on during and after the remediation process through a monitoring network to show the efficiency of the remediation on the source and the absence of residual impacts on the environment. In addition, a combination between several techniques tested and developed in the frame of the CityChlor project makes them suitable for an approach considering large areas with multiple plumes and sources.

Soil and Groundwater characterization

Groundwater contamination endangers the quality of underlying water bearing layers and hence the supply of drinking water. In general, groundwater sampling requires the drilling and installation of permanent groundwater monitoring wells. This installation is often carried out without knowing exactly the location of the pollution source and the delineation of the pollution plume which makes it quite difficult to install them in the most appropriate locations at first glance. That is why Direct Push Technology (DPT) was tested. This technology was supposed to provide a quick and efficient localization of the source zones and pollution plumes. It was selected because it appeared as a group of good screening techniques for groundwater, soil and soil gas contamination characterization prior to the installation of monitoring wells for groundwater and soil gas.

Then, when groundwater monitoring wells are installed at the appropriate locations, groundwater is generally sampled thanks to a pump after purging the well. Purging a large volume of water can be a big issue when sampling groundwater in a well because it can alter the sample. In addition, a large contaminated water volume will have to be stored and eliminated in a proper way which is quite expensive and can be an issue in urban areas. Depending on the volume of the well, this sampling technique may be time consuming. In order to avoid some of these issues, some countries use “low-flow” sampling: the well is purged at a low flow (between 0.1 to 0.5 l/min) and the groundwater is sampled when physico chemical parameters are stable. Nevertheless, when sampling with a pump in long screened interval wells (even during low-flow sampling), the determination of the vertical distribution of the pollution is not possible; an average concentration is obtained. That is why passive sampling was investigated in the frame of the CityChlor project. This technique is able to provide groundwater samples without purging the well and depth discrete samples under some circumstances.

An other parameter to take into account when dealing with groundwater monitoring is the design of the monitoring phase itself. Some methods were therefore tested in order to define rules to decide when to stop the monitoring or how to adapt it (long term monitoring optimization, LTMO)

Soil gas and indoor air characterization for a better risk assessment

The main health risk when dealing with chlorinated solvent contamination is vapor intrusion into indoor air. Soil gas monitoring is therefore particularly important for chlorinated solvent pollution in urban areas: sampling techniques have to be properly defined as well as the wells in which the sampling collection occurs. The classic wells designed for groundwater sampling are not suitable for this purpose. The advantages and limitations of different well designs were studied to come to harmonized recommendations at the European scale. In addition, volatile organochlorine compounds (VOC) concentrations in indoor air have to be measured properly. The combination of efficient modeling and correct measuring is essential for a proper estimation of the impact of pollution on indoor air quality. The three models that are used to this effect in Europe (Johnson & Ettinger, VOLASOIL and Modflow-Surfact) still need verification, especially for groundwater contamination. The accuracy of these models was verified and developed with a specific focus on the transfer from groundwater to indoor air. How the results from models were based on characterization of the vadose zone and/or the groundwater was as well examined.

Fate and transport modelling of chlorinated organic compounds from groundwater to indoor air reveals a specific knowledge gap concerning the fate of vinyl chloride (VC) and dichlororethylene (DCE) in unsaturated soils. VC is almost never detected in soil gas which may be due to its biodegradation during vapor migration in the vadose zone. Degradation of VC and DCE was therefore studied at several scales in the frame of the CityChlor project: at the scale of the plume in soil gas, at the scale of the multilevel gas probe and at the laboratory scale.

Human health risk assessment

Risk assessment tools, concepts and choices are not specific to urban contexts or to chlorinated solvents. The single-site risk assessment was studied by means of advantages and limitations of the different tools. Points of interest in the evaluation of the results given by a tool were as well studied. This information is necessary for a comprehensive understanding of site characterization, remediation as well as management, risk perception and community involvement.

Area oriented investigation approach for groundwater management

Finally, in order to go from the single site approach to considering larger areas, the characterization of groundwater pollution in a large area was evaluated with the risk assessment aspects that are related to this groundwater pollution.

Characterization tools in the frame of the CityChlor project

All these specificities of chlorinated solvents in urban areas make it essential to investigate all environmental media. Therefore, there is a need for reliable, fast and cost-effective techniques that allow to detect, characterize and delineate chlorinated solvent pollution in groundwater, soil, soil gas and indoor air. Several recent technologies try to respond to those challenges. At present, these techniques are seldom used and there is a need for guidelines to use them in an appropriate way. In the frame of the CityChlor project, some existing characterization techniques were selected because they were suitable for chlorinated solvents and seemed to be promising for a use in cities in an economically advantageous way. All the existing characterization techniques were not tested. Characterization tools tested in the frame of the CityChlor project for groundwater, soil gas and indoor air characterization are presented briefly in the following sections of this technical book. As far as possible only commercially available tools were tested. Figure 1 is a summary of characterization tools and concepts tested in the frame of the CityChlor project.

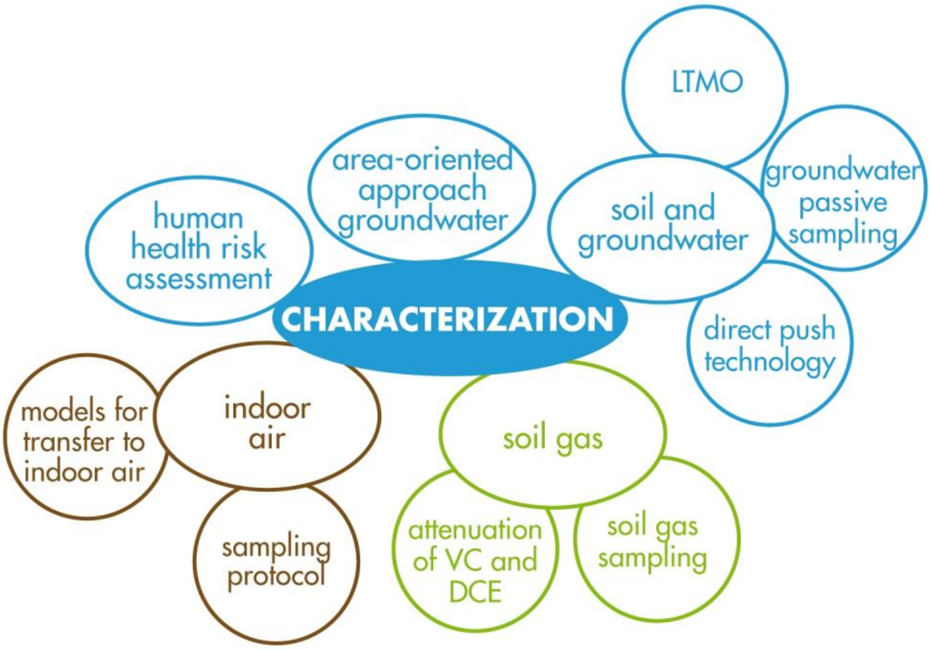


Figure 1: Content of this report and associated reports

For more information on a specific characterization technique the reader is encouraged to refer to the corresponding technical and pilot project reports.

Detailed information and lessons learned can be found in the technical and pilot project reports (**http://www.citychlor.eu/**)

2.1 Groundwater characterization

2.1.1 Groundwater passive sampling

The overall goal of groundwater sampling in the frame of polluted site characterization and monitoring is to get a representative sample of the groundwater quality near the sampling point. Therefore, wells are generally installed on site in order to sample groundwater. The **conventional groundwater sampling technique** consists in purging the well with a pump prior to take a groundwater sample. This technique is **easy** to implement, **very well known** and **widely used** all around the world. Nevertheless, this technique **can have some limitations** that need to be known at the time of the sampling event and when interpreting the results. Purging a large volume of water can be a big issue when sampling groundwater in a well because it can alter the sample, it can dewater the screened interval, produce turbidity or mix the groundwater with zones above or below the screened interval. In addition, a large contaminated water volume will have to be stored and eliminated in a proper way which is quite expensive and can be an issue in urban areas. Depending on the volume of the well, this sampling technique may be time consuming. In order to solve these problems, some countries use low-flow sampling which consists in purging the well at a low flow (between 0.1 to 0.5 l/min in general) and sampling groundwater when physico-chemical parameters are stable. Nevertheless, when sampling with a pump in long screened interval wells (even with low-flow sampling), the determination of the vertical distribution of the pollution is not possible; a mean concentration is obtained. That is why passive sampling was investigated in the frame of the CityChlor project.

In Europe, passive sampling is an innovative way of sampling groundwater and therefore of characterizing and monitoring polluted sites. They are able to sample many contaminants such as VOC in a more cost-efficient way and are less disturbing for the population than conventional pumping/active methods. Nevertheless, **the feedback on this technique is limited** in Europe though some of these samplers are routinely used in some countries and by some consultants. In addition it's highly probable that this technique will be used more widely in the near future. Therefore, **there is a need for a code of best practices at the European level** in order to create a frame for the use of passive samplers to characterize and monitor groundwater quality. **The CityChlor project has met this need by producing guidelines on the use of passive samplers for groundwater quality measurement in the frame of polluted sites.**

Prior to the use of passive samplers on a pilot site (see report of pilot project Ile de France), the groundwater contamination on this site was characterized and 4 monitoring wells were installed at different depths (Figure 2).

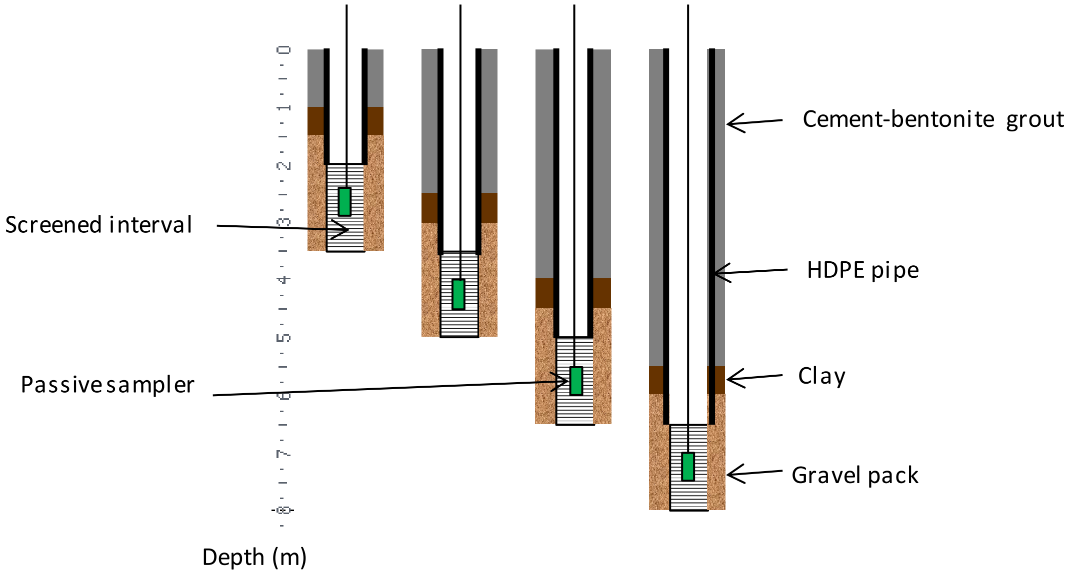


Figure 2: Groundwater wells designed for passive sampler assessment

On the pilot project “Ile de France”, 4 passive samplers were tested in these wells: PDBs (Polyethylene Diffusion Bags), Ceramic Dosimeters, Gore® Sorber Modules and Dialysis Membranes (Figure 3). Passive samplers were installed in the middle of each screened interval and in some cases several passive samplers were installed in the same time. **The tests consisted in comparing the concentrations in groundwater given by these passive samplers to those obtained with the conventional sampling method**, that is to say well purging prior to groundwater sampling with a pump. When interpreting the results, it should be kept in mind that these 2 techniques rely on different physical principles and may sample different waters. Nevertheless, comparisons are needed to promote the use of them: consultants want to know the significance of the results coming from passive samplers comparing to the sampling technique they are used to which is understandable. In addition, in some cases, comparisons are possible with some assumptions. For example, this is the case when small screened interval wells are used.

On the pilot project “Utrecht”, the Passive Flux Meter (PFM) for the measurement of chlorinated solvent mass fluxes and Darcy water fluxes in groundwater was tested (Figure 3). These PFM were installed in 6 different monitoring wells in the source and plume zone of 2 selected sites in the Utrecht study area.

<u>Figure 3</u>: Passive samplers tested in the frame of the CityChlor project

(a) PDB; (b) Regenerated cellulose dialysis membrane; (c) Ceramic dosimeter
(d) Gore® sorber module; (e) PFM

On the pilot project “Ile de France”, chlorinated solvent concentrations in groundwater given by the tested passive samplers were generally consistent with the ones obtained from the conventional sampling method. Our results showed that **passive samplers were very interesting to monitor groundwater at a contaminated site**. In addition, they were very easy to use, generally more cost effective than the conventional sampling method (particularly the PDBs) and cross-contamination was avoided. They could as well offer complementary information compared with traditional sampling method because they allowed depth discrete and multi-level sampling in a well. In this way, the most contaminated part of the aquifer could be monitored. In addition integrative passive samplers will give a pollutant mass flow rate or an average concentration in groundwater over the exposure time which can be very interesting for long term monitoring of polluted sites where groundwater concentrations are highly variable. Consequently, **they seem to be very promising tools for the long term monitoring of groundwater on characterized contaminated sites**.

The PFM has been successfully applied at two field locations in the pilot project “Utrecht”. The acquired flux data could be used in combination with traditional soil and groundwater sampling methods in order to get a broader view of the groundwater contamination at the Utrecht study site.

Detailed information and lessons learned can be found in the technical report
"Passive samplers for groundwater quality measurement – Code of best practices"

and in the pilot project reports (in French with an English summary and in English)
"Caractérisation des eaux souterraines, des sols, des gaz du sol et de l'air intérieur : site pilote Ile de France"
"Integration of results, CSM Bio-washing machine"

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2.1.2 Direct Push Technology

Direct Push Technology (DPT) refers to a group of techniques used for subsurface investigation by driving, pushing and/or vibrating small-diameter rods into the ground. By attaching tools to the end of the rods, they can be used for in-situ measurements or for the collection of samples from soil, groundwater or soil air. DPT holds a group of versatile techniques that aid in cost-efficient and flexible soil investigation. DPT is based on the use of probes that are advanced into the ground by a static, hammer, vibration drive source or a combination of these. With DPT, depth profiles of physical or chemical parameters can be measured (for example conductivity or chlorinated solvent concentrations, samples can be taken and equipment for sampling or measurements can be installed. DPT can be used in non-consolidated underground for the investigation of soil, groundwater and/or soil air. For unconsolidated material, depths of more than 50 m can be reached in favorable conditions. Typical depths of application lie in the range of 15 to 35 m.

A large number of probes is available for the measurement of physical and hydro-geological parameters and for the sampling of the underground under well defined conditions (e.g. in-situ sampling on specific depths). Several of these probes can be combined leading to an optimization of the research. The **high flexibility** also allows a **fast and efficient installation** of measurement and sampling equipment in the underground for continuous observations. Depending on the diameter of the probing equipment, also classical borehole measurements can be carried out with DPT (e.g. measurements of gamma radiation for the detection of clayey soil layers). Several techniques however require calibration by other techniques or by soil sampling and analysis.

Measurements and samplings are point measurements in space and time. Reproductive measurements at the same spot are not possible. For the understanding of the spatial distribution of parameters, several probings are required, e.g. along transects.

DPT probings are faster and more flexible than conventional drilling techniques. Due to the smaller diameter of DPT probes (generally between 38 and 100 mm), the technique is less invasive. This reduces the time needed for sampling or measurements and increases the density of collected data. The number of sampling points can be higher than with conventional techniques within the same time and budget. As soil material is only pushed sidewards with the propulsion of the probe, there is no drilled out material. This reduces costs as there is no need for removal of (polluted) material. The limited diameter of the probe will restrict the impact of the probings themselves on the underground. The equipment is also more easily cleaned than conventional drilling equipment, limiting the risks of cross-contamination.

Some DPT allows on-site reading of results and therefore enables to react in a flexible way on results and to adapt the programme of the investigation on the basis of intermediate findings. This approach has the advantage that results are available faster, with lesser costs and with higher quality and that the location of sample points can be optimized.

DPT is applied in environmental soil investigation since 20 years, but there is a difference in the status of these techniques between the different regions involved in CityChlor. The project offered an opportunity to exchange experiences with DPT and to eliminate these dissimilarities. Three DPT techniques that are relevant for chlorinated solvent pollution were evaluated in more detail (see Figure 4 for examples): the MIP (Membrane Interface Probe) and BAT sampler (pilot project “Ile de France”), as well as the EnISSA MIP (Enhanced In Situ Soil Analysis Membrane Interface Probe) and the NAPL FLUTe (NAPL Flexible Liner Underground Technologies) sampler (pilot project Kortrijk).

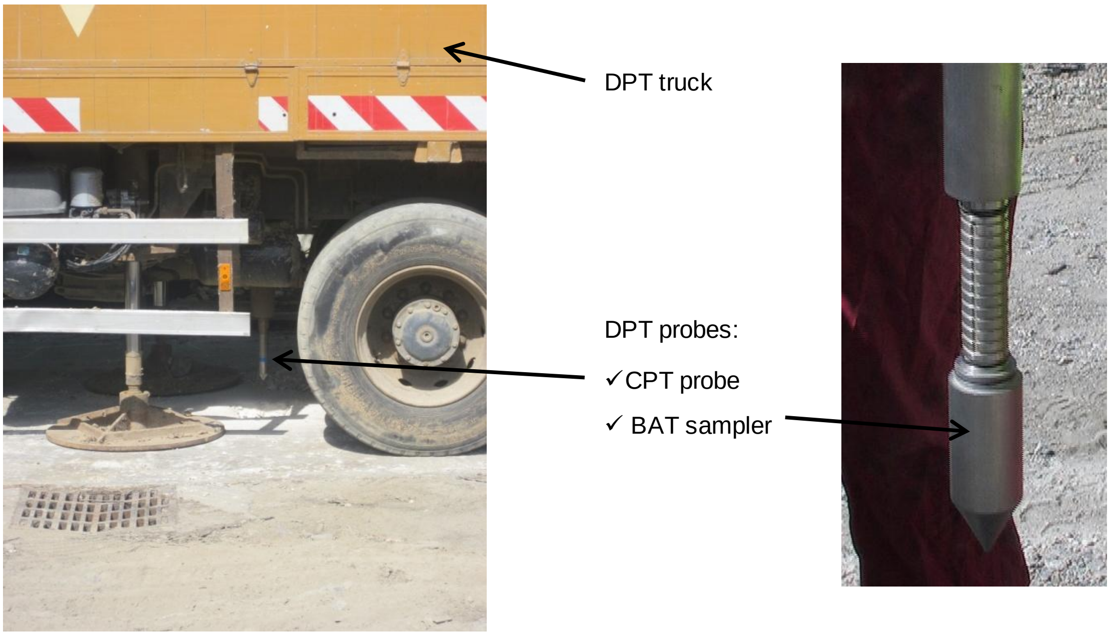

Figure 4: Example of DPT probes (CPT: cone penetration test for information on the lithology and BAT sampler for groundwater sampling)

Detailed information and lessons learned can be found in the technical report
“Direct-Push Technology”

and in the pilot project reports (in French and in Dutch, with an English summary)
“Caractérisation des eaux souterraines, des sols, des gaz du sol et de l’air intérieur : site pilote Ile de France "
“CityChlor Pilootonderzoek EnISSA MIP – Spinnerijkaai Kortrijk”
“CityChlor Pilootonderzoek NAPL FLUTe sampler – Spinnerijkaai Kortrijk”

http://www.citychlor.eu/

2.1.3 Long term monitoring

Monitoring groundwater quality and its evolution over time is necessary to assess the remediation efficiency and ensure the protection of human health and the environment on polluted sites.

Nevertheless, **groundwater well network set up during the site characterization may not be perfectly suited for long term monitoring**, because this is generally carried out with a different purpose to define the nature and extent of the problem, when the site is not very well known (characterization potentially based on groundwater passive sampling and DPT). In addition, monitoring programs are not always well designed: incomplete information or in some cases more information than needed is provided.

In this context, in the USA, work is carried out on **Long Term Monitoring and its Optimization** (LTMO), to offer an opportunity to improve the cost-effectiveness of long term monitoring. Optimization techniques have initially been tested and applied to the design of monitoring networks for site characterization, detection monitoring and compliance monitoring on polluted sites but they are now most often applied to groundwater monitoring programs after remediation. LTMO is based on a **two-step approach** (two steps successively implemented):

- a **qualitative approach**, based on a technical approach. A hydrogeologist will evaluate the effectiveness of the monitoring program in its current configuration,
- a **quantitative approach**, based on statistical and digital analysis to assess the effectiveness of the monitoring program in its current configuration. This quantitative approach must be coupled with a qualitative review.

These methods are mostly used in the USA on large sites, with large monitoring networks. In the frame of the CityChlor project, **the main methods for LTMO were analyzed and tests were carried out to adapt these methods to smaller sites**, similar to those involved in the CityChlor project with a chlorinated solvent pollution in urban area.

The work carried out during the CityChlor project showed that **the “qualitative approach” was the most relevant one** because it was leading to a framed and reproducible approach when analyzing all the collected data from the beginning of the monitoring. This approach is based in any case (whatever the design of the monitoring network) on the same qualitative indicators (the same questions that people need to ask themselves) which are presented in the technical report “Long term monitoring optimization”. This “qualitative approach” will use the collected data in order to improve the conceptual model, and in particular to better understand groundwater and contaminant flow paths (present and future). For example, this approach can lead to decreasing sampling frequency if groundwater velocity is lower than its initial definition.

Detailed information and lessons learned can be found in the technical report
“Long term monitoring optimization”

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2.2 Soil gas characterization

2.2.1 Soil gas sampling

As chlorinated solvents are volatile compounds, gas transfer from the source to the atmosphere is significant and has to be characterized and monitored. Therefore, soil gas sampling is an important aspect in the frame of polluted site characterization and monitoring as well as in risk assessment. To do so, a 3D soil gas plume characterization and delineation will be necessary. That is why soil gas wells and soil gas sampling techniques have to be designed and well mastered to give reliable results.

Various soil gas installation designs, sampling techniques and analysis methods are currently used in Europe. Most of them are **complementary** tools and most of the time the choice is lead by the site specificities as well as the objectives of the study and its costs. Many studies were carried out on soil gas sampling and some official reports expressed practical recommendations. **Few codes of best practices** dedicated to soil gas well installations and soil gas sampling methods have been published. Among them, some have not been updated since several years. Then, actual practices do not fit in with the best measurement protocols. Moreover, these different measurement methods are characterized by some limits that may cause problems of representativeness (humidity, depression influence, sampling duration). That is why writing a guide within the frame of the CityChlor project was relevant, especially in the context of chlorinated solvent pollution in urban areas. **The objectives were to review each type of soil gas well designs and sampling methods, to compare some of them thanks to field measurements and then using this feedback to provide guidance to consultants on their own choice.**

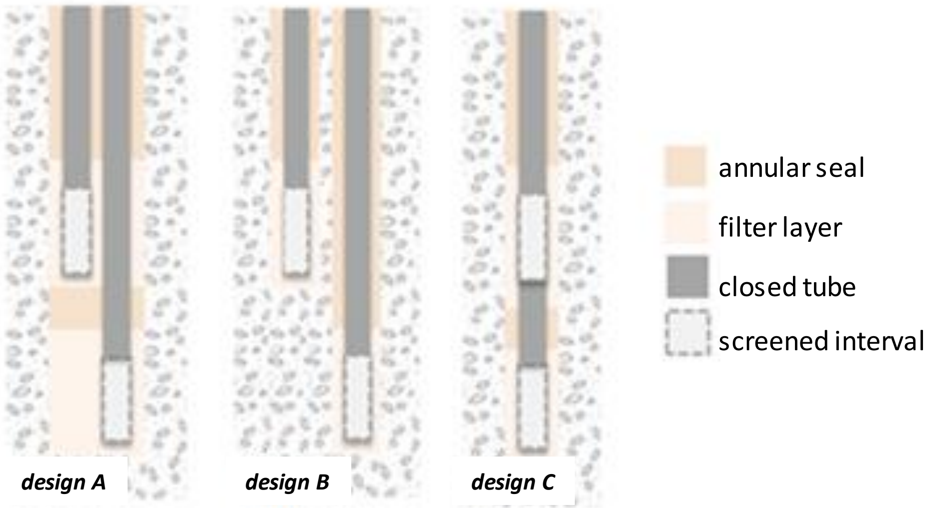
Two different sampling strategies are used in European countries: surface flux sampling and soil gas sampling. It is essential to make a difference between them because they do not provide the same information.

Surface flux measurement, using surface flux chambers, quantifies gas transfer from soil to ambient air. This type of sampling does not measure soil gas but value the gas diffusion and convection at the interface soil/ambient air. Surface flux chambers can be used with instantaneous, active and passive sampling techniques. Flux measurements can be used and provide access to the dynamic component of gas transfer from soil to indoor air. They are particularly helpful for screening (delineation of sources and plumes) as well as determining the optimum monitoring wells location. They are also usually used for gas transfer modeling in order to settle parameters.

On the contrary, soil gas sampling provides information about soil gas composition located in the vadose zone (at the sampling location and depth). It is carried out with temporary or permanent installations. Temporary installations are gas vapor probes (rod methods) or direct push technologies (geoprobe). Permanent installations are micro-soil gas wells and soil gas wells. Whatever the installation used, soil gas sampling can be carried out with instantaneous, active or passive techniques. Soil gas measurements enable source and plume characterization and delineation (screening and diagnosis). It is also possible, using multi-level installations to value gas transfer deep down. These data are particularly relevant for risk assessment, settling source parameters in models or simply calculating risk. Soil gas measurements can also perform soil gas characterization and monitoring, especially in the context of contaminated site management or remediation (oxidation, venting, bio-monitored natural attenuation, etc).

In the frame of the CityChlor project, **three soil gas well designs have been implemented in pilot project "Ile de France"**, in order to give recommendations on soil gas multi-level sampling (see report on pilot project "Ile de France" and Figure 5):

- 2 soil gas wells implemented in the same borehole (design A),
- 2 soil gas wells implemented in different boreholes (design B),
- 2 screened intervals at 2 different depths in the same well (design C).



***design A*:** two soil gas wells implemented in the same borehole
design B: two soil gas wells implemented in two different boreholes
design C: two screened intervals at two different depths in the same well

Figure 5: soil gas wells implemented on CityChlor pilot project "Ile de France"

In the frame of the CityChlor **project, two sampling methods have been used for soil gas sampling: active** measurements (sorbent tube, canister, sampling bag) and **on-line measurements** (PID) were carried out on pilot project "Ile de France" within the soil gas permanent wells presented previously. PCE, TCE, cis and trans-DCE were analyzed. Six soil gas sampling campaigns were conducted.

For active measurements, c**oncentrations were of the same order of magnitude when sampling was carried out at the same location and the same depth whatever the soil air well design** (for a wide concentration range). The main observations of active sampling carried out in different soil gas well designs were:

- concentrations measured in design C using packers to separate two sampling depths in the same monitoring well were nevertheless different than concentrations measured in designs A and B especially for the upper sampling level,
- concentrations measured in design A and B were quite similar (for the same location and same depth).

On-line measurements consisted in purging the well and then in soil gas recirculation within the well with carbon dioxide and pressure monitoring. The three different designs tested gave roughly the same behavior concerning the parameters of the purge (pressure, CO_2) and the results of the soil gas monitoring (PID, Ecoprobe). PID results lead to the same results as active sampling. When PID measurements were carried out in design A and B, concentrations measured at the two different depths were not in the same order of magnitude. Design B tends to reduce the differences between the chlorinated compounds soil gas concentrations of the two levels investigated comparing to design A. In the specific case of large lithology variations at low distance (for variable backfill under concrete slab), design B can be preferred if the sealing between the levels can be achieved and controlled.

Based on these results, **soil gas well designs and soil gas sampling methods were compared** in order to improve our knowledge in soil gas behavior in depth as well as in permanent installations. The feedback presented in the code of best practices is not limited to the results relevance of the various installations and sampling techniques but includes also their practicability and cost.

Detailed information and lessons learned can be found in the technical report
"Soil gas characterization and monitoring: designs of soil gas wells and soil gas sampling tools"

and in the pilot project report (in French, with an English summary)
"Caractérisation des eaux souterraines, des sols, des gaz du sol et de l'air intérieur : site pilote Ile de France "

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2.2.2 Attenuation of VC and DCE in the vadose zone

Fate and transport modelling of chlorinated organic compounds from groundwater to indoor air reveals a specific knowledge gap concerning the fate of vinyl chloride (VC) and dichlororethylene (DCE) in unsaturated soils. VC is the most toxic and mobile degradation compound of the chlorinated solvents. It is often the limiting compound in a remediation based on risk. But surprisingly enough, **VC is almost never detected in soil gas**, even when measured at high concentrations in groundwater. Current models do not take into account this particularity. **One main explanation is that VC biodegrades during vapor migration in the vadose zone**.

Different bacterial populations are involved in the biodegradation of chlorinated ethenes. These can be classified into four groups according to their metabolism: anaerobic reductive dechlorination, anaerobic oxidation, aerobic oxidation and aerobic cometabolism and assimilation. **In the frame of the CityChlor project, a specific focus was done on the aerobic oxidation**.

Degradation of VC and DCE was studied at several scales: at the scale of the plume in soil gas, at the scale of the multilevel gas probe and at the laboratory microcosm scale. Field data coming from two soil gas sampling surveys of a network of 29 gas probes on pilot project “Ile de France” was used. Vinyl chloride soil gas concentrations were monitored with 3 different designs of gas probe.

These first results, which were observed with samples of soil coming from one level of the vadose zone, prove the **degradation potential of the vadose zone and the natural attenuation of the level of VC concentration during the migration to the soil surface.** These first results concerning aerobic degradation in the vadose zone need to be refined in the future.

Degradation of VC in unsaturated zone gives hope to the possible inclusion of this biodegradation term in the flux balances of chlorine solvent and metabolites reaching the soil surface. A better determination of the conditions of the degradation and of the conditions of gas migration is necessary to enable effective control of VC and DCE vapor flow.

Detailed information and lessons learned can be found in the technical report
“Attenuation of VC in the vadose zone”

http://www.citychlor.eu/

2.3 Indoor air characterization

2.3.1 Protocol for indoor air sampling

At sites contaminated with chlorinated solvents, **the transfer of vapors into houses and buildings is often a major concern in terms of risk assessment**. In cases where evaporation is expected, direct measurement of the indoor air quality is preferred over a value predicted by a transfer model. However, **in order to obtain reliable and representative measurements of indoor air quality, guidelines are needed**.

Based on a review on literature, most relevant and most recent document was the study report from INERIS N° DRC-10-109454-02386B – 'The management of contaminated sites and soils: Characterization of indoor ambient air quality in relation to potential soil pollution by volatile and semi-volatile components'. **Methods presented in this report relate exclusively to the characterisation of gaseous chemicals in indoor air for general populations**, excluding populations concerned with occupational health regulations. This excludes particles (dust from the soil) and radioactive (radon and decay products) chemicals, bio-contaminants, allergens, mites and microorganisms (moulds, etc.). This document does not cover the preceding stages such as soil and/or groundwater and/or soil gas investigations or the document review (site history, conceptual site model, etc.) for which there are other guides and tools available. The premises covered by this document are homes and offices open to the public including educational and early childhood facilities (nurseries, nursery schools, primary schools, high schools and colleges, leisure centres, etc.) and offices. **Methods presented in this document were followed on pilot project "Ile de France"**.

Detailed information and lessons learned can be found in the technical report
"The management of contaminated sites and soils: characterization of indoor ambient air quality in relation to potential soil pollution by volatile and semi-volatile chemicals"

and in the pilot project report (in French, with an English summary)
"Caractérisation des eaux souterraines, des sols, des gaz du sol et de l'air intérieur : site pilote Ile de France "

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2.3.2 Models for predicting transfers to indoor air

Soil vapor migration of chlorinated solvents into house, with subsequent inhalation, is often the main exposure pathway to humans at sites contaminated with VOCs. **Two approaches** are commonly used for quantification of indoor concentrations: **indoor gas measurement** or **transfer modeling** from the source. Analytical 1-D models (Johnson and Ettinger and VOLASOIL) development is relatively well advanced but **measurements for model calibration and "validation" hardly exist in the literature**. Furthermore, **predictions** of indoor gas concentrations **from different models may vary by several orders of magnitude**, depending on the application. With Figure 6, we can say that to be realistic, the phenomenon will have to be modeled in 3-D or at least in 2-D if there is a symmetry.

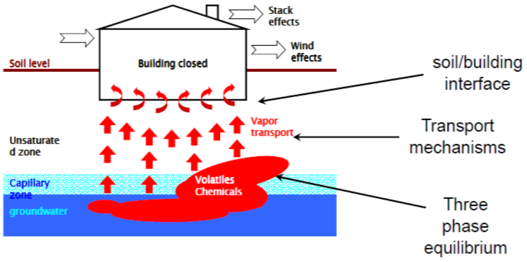

Figure 6: Example of vapor transfer to indoor air

The work carried out in the frame of the CityChlor project consisted in building a numerical 2-D model for vapour intrusion. Specifically, the influence of the lithology (multilayer, thickness and soil properties) as well as the influence of concrete properties on vapor intrusion into dwellings were studied for several scenarios. In addition, our model takes into account the indoor air phenomena; therefore it can overlap with indoor air measurement. Numerical modeling was performed with COMSOL Multiphysics. COMSOL is a finite element analysis for various physics and engineering applications, especially coupled phenomena or multiphysics. Our model takes into account the phenomena in soil, indoor air and outdoor air (strong coupling).

Many scenarios were studied considering the soil: monolayer, multilayer (with slightly permeable layer), various thicknesses, various water content profiles and several source locations. Concerning the concrete, various thicknesses and permeabilities were examined. For each scenario, indoor air concentration was followed in three points, as well as the concentration profiles in the soil.

Comparison of the chlorinated solvent concentration shows how much thickness was important on vapor intrusion. The impact of concrete permeability was highlighted, as well as the influence of water content. This study showed two things:

- our model can depict the phenomena involved in vapor intrusion model, in a coupled way (subsurface and indoor air) with the possibility to have soil and indoor air concentrations for comparison with fields measurements,
- parameters such as soil and slab characteristics impact the results, showing that field measurements are of great importance.

One important conclusion is that the characterization of numerous input parameters for soils and slab is a critical step to perform a relevant modeling.

Detailed information and lessons learned can be found in the technical report
“Models for predicting transfers to indoor air”

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2.4 Human health risk assessment

Human health risk assessment (HHRA) can be conducted in **different ways** and in order to meet **different objectives**. This approach can be used for:

- derivation of Soil Quality Standards: soil screening value (trigger values, target values, etc),
- site-specific risk assessment,
- development of remediation objectives,
- ranking of contaminated sites.

Soil Screening Values (SVs) are generic quality standards adopted in many countries to regulate the management of contaminated land. The actions to be conducted when exceeding the soil SVs vary according to national regulatory frameworks. They range from the need for further investigations to the need for remedial actions. These soil screening values are called differently according to the different European regions/countries: trigger values, reference values, target values, intervention values, clean-up values, cut-off values and many others names can be found.

Each country developed its own system, i.e. methodology or software package to quantify the risk posed by a contaminant in evaluating a source-pathway-receptor linkage: ‘Risc Human’ for The Netherland, ‘UMS’ for Germany and ‘Vlier Humaan’ for Flanders. In France commercial software packages, like RBCA Toolkit or RISC are usually used. A project is currently running to develop a risk assessment tool which will be compulsory used. In Flanders, 'Vlier-humaan' has been revised. In 2013 a new model, named S-Risk, will be introduced.

That is why, in the frame of the CityChlor project, we proposed an overview of concepts and tools used by the different European regions/countries involved in this project for human health risk assessment (Flanders, France, Germany and the Netherlands).

General concept on HHRA is given. For each country, the contaminated site management and the tools used in HHRA and more specifically in the case of chlorinated solvent in urban areas are presented.

In general, it was observed that **a consensus on the methodology was found between the different partner countries**; indeed the management of contaminated sites is based on the same HHRA concept following the current or future use of the site. The human health risk characterization is preceded by two steps: exposure assessment (‘probability’ in Risk Assessment terms) and the hazard assessment (‘effect’ in risk assessment terms). HHRA is all about linking exposure to effects, oral, inhalation and dermal exposures, relevant timeframes for exposure as regards to the occurrence of effects, and the compatibility of estimated Exposure and critical exposure (Toxicological Reference Value). It leads to quantify the risk of a contaminated site on human health.

In the specific case of chlorinated solvents in urban areas, the conceptual model allows identifying the primary contamination sources and the potential exposure pathways as usual (e.g., ingestion of contaminated water, inhalation of chemical in air, etc). In this context, **the**

different exposure pathways and transfer models that are taking into account in the HHRA tools used by the different partners to quantify the specific risk of a site contaminated by chlorinated solvent were compared in the frame of this project. Large differences in the predicted exposure doses given by the models were pointed out when models default exposure parameters were used. When parameters are unknown, the use of default data can impact significantly the conclusions in a site's risk management. A reliable characterization of the site is necessary.

Detailed information and lessons learned can be found in the technical report
"State of the art of contaminated site management – Policy framework and human health risk assessment tools"

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2.5 Area oriented investigation approach for groundwater management

In the CityChlor project the area oriented approach for groundwater management is defined as a technical approach, which makes possible to remediate, monitor and control multiple groundwater sources and plumes in a defined area. Areas polluted by commercial or industrial activities can be both (i) complex single site locations with various sources of pollution and (ii) larger areas such as city quarters, brownfields or even natural areas (former landfills). Furthermore, the term area includes also all compartments (soil and groundwater) and has to be extended to the border around the plumes.

The area oriented approach is particularly suitable for areas with various sources of pollution, which form distinctive plumes of pollution. This means that this approach considers the pollution coming from several sources that might merge or overlay. The basic concept of this approach is to investigate the impact and effect of pollution on different subjects of protection (e.g. groundwater, intake of drinking water, etc.) and thus, to assess contaminant plumes and their relationship to potential contaminant sources. The main task is to trace the pollution plume along the transport pathways back to the source. In this way, polluting area can be (i) identified, (ii) ranked according to its impact on groundwater, and finally (iii) prioritized in the way that remediation measures shall be concentrated only on the relevant sources of pollution.

The first step of the area oriented approach is a historical investigation as well as the typical single site characterization. Further investigation may include an integral pumping test and conceptual hydrogeological model, which enables to identify and localize the plumes of pollution with their contaminant loads. The plumes interactions can be qualified by using backtracking techniques such as fingerprints or numerical modelling. Consequently, the area oriented approach might be at the first step more extensive than the typical single case approach. However, in complex situations only an area oriented approach can ensure effective and well targeted activities, which are confirmed by experience collected over many years in Stuttgart.

In the report of this action, **the presented case study “Stuttgart-Feuerbach” reveals important methodological aspects and provides important recommendations for the possible general application of the area oriented approach**.

Additionally, this report includes legal aspects of the implementation of the area oriented approach for each participating country of this project: Germany, the Netherland, Flanders and France. The applications and corresponding limitations of the area oriented approach regarding national laws are presented as well.

Detailed information and lessons learned can be found in the technical report
“Area oriented investigation approach for groundwater management”

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3 Conclusions

Chlorinated solvents are amongst the most common soil and groundwater contaminants due to their widespread use as dry-cleaning solvents and degreasing agents. Due to their physicochemical properties they produce large scale plumes of pollution in the groundwater. Pollution by chlorinated solvents is in many cases caused by small-scale activities such as dry-cleaners, garages and metal-using industry, which generated multiple contaminant sources for widespread groundwater pollution in urban areas. In the densely populated Northwestern-Europe, these pollution plumes are situated under residential and urban development areas and are therefore difficultly accessible. Vapors can migrate through building slabs and affect the quality of indoor air. But pollution does not only pose a direct risk by exposure to contaminants, it also indirectly restrains economic development and harms the quality of life due to the slow processes of investigation and remediation and the resulting long period of uncertainty. Therefore, there was a need for cost-effective, reliable and fast tools for characterization of pollution, tools for measurements as well as models for risk-evaluation. Extensive documentation about European research is available, but this innovation is scarcely considered in daily work and integration of these innovations in routine procedures is required.

The work carried out in the frame of the CityChlor project concerning the characterization of sites polluted with chlorinated solvents supported the Water Framework Directive (WFD)/Groundwater Directive (GWD) implementation by testing, verification and developing best practices for monitoring and characterization technologies. This should help to meet the requirements set by the “prevent and limit” objective of WFD Art. 4 and GWD Art. 6 for industrial pollution at local and regional level. A correct characterization allows taking the necessary measures to prevent and to limit further damages to the environment.

The CityChlor project offers codes of best practices of useful tools for characterization of the different environmental media concerned by the threats caused by chlorinated solvent pollution: groundwater, soil gas and indoor air in urban areas. Risk models that allow the evaluation of the impact of pollution on human health were studied and the integration of these characterization tools in an area oriented investigation approach for groundwater management was evaluated. Some of the tests on characterization techniques were carried out in order to look for an application in the case of chlorinated solvent contamination in urban area from existing tools. They were assessed and this came to recommendations (passive samplers, DPT, long term monitoring optimization and soil gas characterization). Other actions did not come to operational recommendations but were carried out in a research purpose which confirmed the interest of their study in the frame of other R&D projects (attenuation of VC and DCE in the vadose zone and models for predicting transfers to indoor air). All actions related to characterization were linked to field investigations (except for human health risk assessment). Detailed results are presented in the corresponding pilot project reports. All these reports should convince end users such as consultants of the capacity of the tested techniques. In addition, it should enable authorities to accept the implementation of these innovative techniques. For example, these codes of best practices could form the nucleus for further European standardization processes steered via CEN (European Committee for Standardization).

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