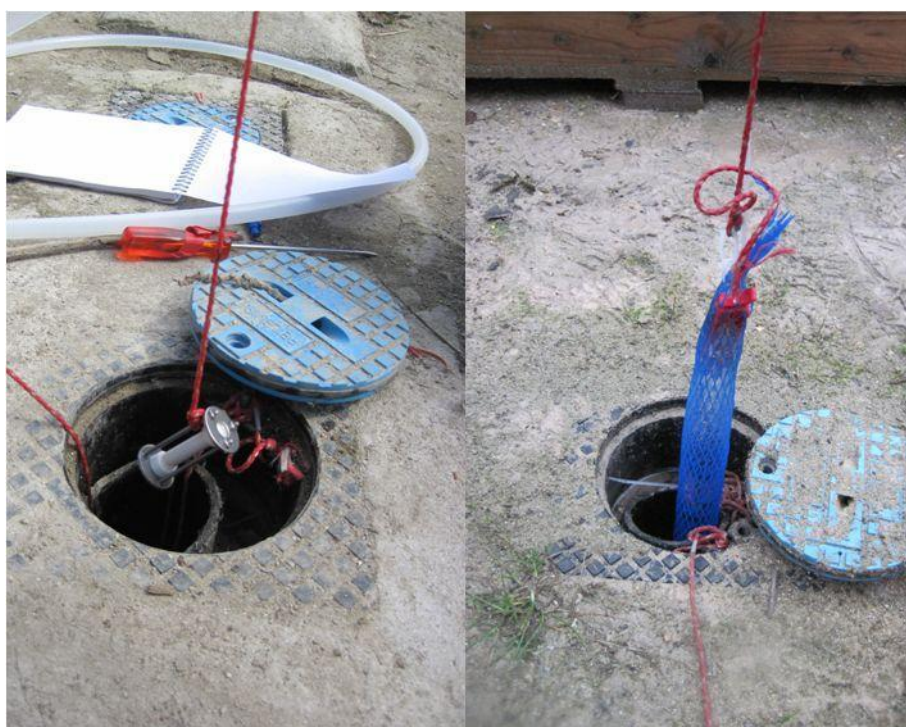


Groundwater quality measurement with passive samplers

Code of best practices





Summary

In Europe, passive sampling is an emerging way of measuring groundwater quality and therefore of characterizing and monitoring polluted sites. In the USA, the scientific literature is abundant on the subject and a lot of studies were conducted to assess their efficiency to measure groundwater quality. Nevertheless, in the frame of a previous project (the METROCAP project), a survey was conducted amongst French consultants and showed that passive samplers were not widely used in France because there was a need to provide feedback and guidelines to promote the use of passive samplers in a regulatory context. The situation seems quite similar in the other European countries.

In this context, after a general presentation of the different groundwater sampling techniques and particularly passive sampling, this report provides some feedback on the use of 4 passive samplers in the frame of the CityChlor project: PDBs (polyethylene diffusion bags), regenerated cellulose dialysis membranes, ceramic dosimeters and Gore sorber modules. In general, passive samplers seem technically and economically interesting to measure groundwater quality at contaminated sites because they showed a lot of advantages comparing to the conventional sampling technique: they were easy to install and retrieve, no external energy source or additional equipment was needed, no purge water was produced, no filtration was required on site and no cross contamination occurred. In addition they were generally more cost-effective than the conventional sampling technique. They could be seen as complementary tools to the conventional sampling technique, giving access to information that are not or hardly available with the conventional sampling technique, such as depth discrete samples or vertical contaminant profiling when deployed in series. Nevertheless, the use of passive samplers requires a good knowledge of the local hydrogeology and particularly natural vertical flows in long screened interval wells. In addition, passive samplers are generally contaminant-specific. Therefore, on sites contaminated by different contaminant classes, different kinds of passive samplers will have to be deployed. A summary of the tests done on the selected passive samplers is provided as well in this report but the reader is encouraged to refer to the corresponding reports of the pilot projects ("Ile de France" and "Utrecht") for further information.

Some general guidelines are given for an appropriate use of passive samplers for groundwater quality measurement concerning:

- passive sampler selection as regard to the aim of the study and the contaminants. Average concentrations over time or instantaneous representation of the conditions at the time of the sampling event as well as the contaminant type will condition the choice of passive sampler,
- passive sampler set up. Some information such as a good knowledge of the monitoring network and local hydrogeology (especially natural vertical flow measurement) should be available before passive sampler deployment. A successful installation will rely on an exposure time adapted to the selected sampler and an appropriate number and position of the passive sampler in the well,
- result interpretation. Generally, it is advised to compare the first results of passive sampling with the conventional sampling technique. Potential differences have to be

explained as regard to the different principles of operation of both methods and the local hydrogeology.

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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 sustainably 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.

1.2 CityChlor and technical innovations

The managing of knowledge and technical innovations are one of the key 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, 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. For the detailed outcomes, the reader is referred to the specific reports.

CityChlor - "new solutions for complex pollutions" http://www.citychlor.eu/
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2 Context and aim of this guideline

In Europe, passive sampling is an innovative way of measuring groundwater quality and therefore of characterizing and monitoring polluted sites. Passive samplers allow to sample pollutants in monitoring wells without creating active transport of groundwater and without any external energy sources. Identification and quantification of the pollutants is done by chemical analysis after retrieval of the sampler.

Passive samplers are presented as tools able to sample many contaminants such as Volatile Organochlorine Compounds (VOCs) in groundwater. This is generally done in a more cost effective and in a less inconvenient way for the population than conventional pumping methods (INERIS, 2011a). The scientific literature on the subject is abundant, showing that a lot of work related to their use and efficiency to sample groundwater has been performed, mainly in the USA. A lot of samplers are available on the market and some of them are still under development. 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 measure groundwater quality. Even though passive sampling is widely used for air monitoring in different industries and accepted by authorities for this purpose for many years, it seems that this level of acceptance is not reached for groundwater because of deficits in information, advertisement and reluctance for new and innovative tools.

In this context, the aim of this work on passive samplers in the frame of the CityChlor project was to improve practices in terms of polluted site characterization and monitoring in Europe. Several passive samplers were tested in order to provide feedback and recommendations on their selection and use for groundwater quality measurement in Europe in the context of polluted sites. This guideline was implemented not only by the results obtained in the frame of the CityChlor project but also by the results and feedback of previous projects on the subject, particularly the METROCAP (INERIS, 2011a, b, c, d) and ATTENA projects (ADEME, 2013). The aim of the METROCAP project (funded by ADEME and conducted by INERIS) was to test the technical and economical significance of passive samplers to characterize and monitor groundwater quality. This project confirmed their high potential for sampling in groundwater. The ATTENA project aimed at developing a procedure to implement monitored natural attenuation as a management tool for groundwater pollution. In this context, passive samplers were tested as innovative tools that could be useful to confirm monitored natural attenuation at a contaminated site.

This approach will allow disseminating passive samplers as an innovative and promising way of measuring groundwater quality in the frame of polluted sites by proposing harmonized recommendations and practices at the European scale.

In chapter 3 of this guideline, conventional and passive groundwater sampling techniques are presented. This chapter describes the advantages and limitations of each technique and provides a feedback on the use of these techniques for groundwater sampling by

consultants. Chapter 4 gives a more particular focus on passive sampling: definitions as well as principles of operation of the different types. Chapter 5 holds a summary of the tests carried out on 4 passive samplers in the frame of the CityChlor project: Polyethylene Diffusion Bags (PDBs), regenerated cellulose dialysis membranes, Gore sorber modules, and ceramic dosimeters. Chapter 6 provides a general feedback on passive sampling as well as details on design, principle of operation and installation and retrieval procedures of these 4 passive samplers. Advantages and limitations of the tested passive samplers are presented as well. Finally in chapter 7, the reader will find recommendations for the use of passive samplers for groundwater quality measurement. In annexes, operation fact sheets are provided for a practical use of passive samplers in the field.

3 Groundwater sampling strategies

3.1 Conventional sampling method

In general, 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. Wells are therefore installed on site in order to sample groundwater. They are made of a screened interval, consisting in a pipe with slots placed in the saturated zone of the soil. The length of this screened interval depends on the aquifer properties and on the goal of the study. In the unsaturated zone of the soil, a pipe is placed. A schematic view of a typical well is presented in Figure 1.

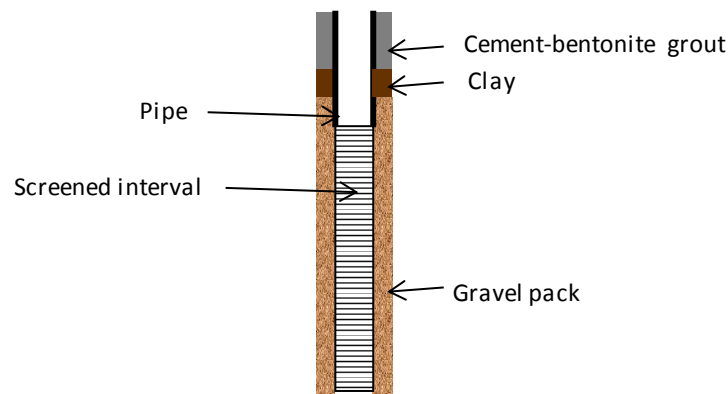


Figure 1: Typical design of a groundwater well

Several groundwater sampling strategies have been used in wells, especially what we are going to call the “conventional sampling method” in this report. This technique consists in purging the well; this could be done according to 2 different procedures:

- purging 3 to 5 times the well volume with a pump prior to sampling,
- purging the well until physicochemical parameter stabilization (Water Quality Indicator Parameters pH, Eh, conductivity, temperature, dissolved oxygen and turbidity),
- low flow purging (0.1 to 0.5 L/min) until physicochemical parameter stabilization.

The advantages of these conventional sampling methods rely on the ease of use and on a good practical knowledge of it all around the world. Nevertheless, these techniques could 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 could be a big issue when sampling groundwater in a well: it can alter the sample quality (because of aeration of 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 eliminated in a proper way which is quite expensive (Barcelona et al., 2005). The presence of turbidity may cause trace metal concentration overestimation because of colloid mobilization (Kaminski, 2006). In

addition, one of the main problems with this technique is to maintain a minimal draw down during pumping, which could be easily done in soils with a high transmissivity. The maximum flow and draw down for a given well depends on the hydrogeological context and on the design of the well (Barcelona et al., 2005). Nevertheless, low flow purging and sampling may solve these problems because it will induce a minimal hydraulic perturbation. This technique will as well reduce draw down in wells, the water volume to be treated as well as the mix with stagnant water above the screened interval.

Nevertheless, whatever the sampling method chosen and in order to delineate the vertical extension of a plume with the conventional sampling method, samples have to be taken from different wells with short screened intervals at different depths or from systems with different levels in the same borehole. These systems are more expensive than usual wells with long screened intervals. Samples coming from long screened interval wells and taken after purging the well will not give any information on the vertical distribution of the pollution in the aquifer. In the literature, experiments at the field scale and at the laboratory scale as well as numerical modeling showed that when low flow purging is applied to a well, samples are coming from all along the screened interval whatever the pump location. This observation means that with the conventional sampling method, the sample will be a mix of all the different levels of the watered screened interval, weighed by the flux coming in the well during the purge except if packers are used (but this is not easily done). Consequently, zones of high concentration might be diluted (McDonald and Smith, 2009).

In addition, these conventional methods will only give the contaminant concentration at the time of the sampling event ("snap shot sampling"). If contaminant concentrations show a lot of variations between 2 sampling events, the maximum concentration could be missed with the pump and consequently a potential risk for the Environment and human beings.

Finally, mass loss through volatilization, sorption on tubing and cross contamination have to be considered as well when sampling groundwater with a pump.

3.2 Passive sampling

Since about 10 years, sampling groundwater without purging the well has been extensively studied in a way to get a representative sample of the groundwater quality near the sampling point. Some field studies showed that the purge of a well was not necessary to obtain a representative sample. Water can migrate through the screened interval of a well and not be mixed with the upper stagnant water (Robin and Gillham, 1987; Kearl *et al.* 1992; Powells and Puls 1993; Vroblesky and Hyde, 1997). These studies showed that flow through the screened interval is generally horizontal and laminar and representative of the groundwater quality around the well.

But in some cases, natural vertical flow can be present, especially in wells with long screened intervals (> 3 m). In this way, zones with different concentrations can be connected and mixed. The pollutant concentrations are then homogenized all along the screened interval and the concentrations will be the same wherever the passive sampler will be placed. This

natural vertical flow can be measured with a “Heat-Pulse Flowmeter” specifically designed to measure flow ranging from 0.13 to 4.5 L/min.

Consequently, when no vertical flow occurs in the well (that is to say when the flow value is below the quantification limit of the measuring tool), passive samplers can be used to get quantitative data at a given depth of the aquifer. This is a real advantage comparing to the conventional method which leads to mean groundwater samples. Nevertheless, it seems that passive sampling will not totally substitute to conventional sampling methods: for example, sampling groundwater with a pump will be the appropriate method for further analyzing drinking water quality. The main differences between conventional and passive sampling are presented in Table 1.

Table 1: Main differences between conventional and passive sampling

Conventional sampling	Passive sampling
<ul style="list-style-type: none"> - Migration of water due to the purge - Drain water from above and below the screened interval - Mean concentration, weighed by the flux - Based on a fixed purged volume or on parameter stabilization - Gas exchange and mixing - Can lead to a high turbidity - Colloid mobilization - NAPL mobilization (the part which is normally immobile) 	<ul style="list-style-type: none"> - No forced migration of water - Depth discrete samples - Reduction of perturbations in the well - Turbidity reduction - Representative of “natural” conditions - Average concentrations over the exposure time possible

A lot of passive samplers were developed and improved at the laboratory scale. Some of them were implemented on site and tested on some pollutants but many of them were only tested at the laboratory scale (Gal et Roy, 2007; Vrana et al., 2005). The first passive sampling technique was used more than 20 years ago. Nevertheless, passive sampling systems are still under development and a lot of improvements were done recently for their building, calibration and quality insurance.

3.3 Feedback from consultants on these sampling techniques

In France, a survey was conducted among consultants in 2011 in order to have a feedback on their knowledge and use of passive samplers for groundwater quality measurement. A questionnaire was sent to 180 consultants among 145 consulting agencies (it was sent at most to 2 consultants in the same agency) and 55 answers were collected. The same procedure was followed in Germany and we collected 29 answers to the survey.

Results showed that passive sampling was not very well known among French consultants: only 42 % of the people knew this technique (thanks to a feedback from colleagues or to the scientific literature) and principles of operation were generally unknown. It seems that

passive samplers were more common in Germany since 79 % of the people knew this technique thanks to scientific literature and feedback from colleagues. Passive samplers are scarcely used in France (only 15 % of the people who answered the survey). It corresponds only to people coming from consulting agency with an R&D department and/or part of an international group. Traditional sampling techniques are often used in order to carry on the tests with the method previously used, because French consultants are reluctant to use them and fear that administrations will not accept it because it appears as a “non approved” method. This trend was not observed in Germany since 70 % of the consultants who answered the survey already used passive samplers. 30 % of people don’t use them in Germany because of the same reasons than in France. According to the feedback from the different partners of the CityChlor project, passive samplers are not widely used in Europe in general because no guidelines are available and therefore consultants may not be aware of this groundwater sampling technique.

Nevertheless, consultants who have already used passive samplers gave a positive feedback on them (both in France and in Germany). They applied passive samplers to a wide range of contaminants and cited as the main advantages that they allow depth discrete sampling, a good reproducibility of the sampling, a very easy principle of use and generally this is done at a lower cost than conventional sampling techniques. The hard result interpretation was pointed out as a limitation of these samplers as well as their calibration.

Consultants were very interesting in this emerging technique, because 81 % of the people who did not know passive samplers before the survey were keen to use them in the frame of site characterization and monitoring in France (resp. 85 % of people in Germany). Both in France and in Germany, consultants pointed out that a guideline was necessary for them to use passive samplers in appropriate conditions. According to them, the lack of such documents was a real limitation for them to use passive samplers for groundwater sampling. In addition, they need an acceptance of this technique by the administration in order to use passive samplers in a regulatory context. In this way, studies comparing results from conventional sampling techniques and passive sampling are needed to prove to the administrations that passive samplers are appropriate tools to characterize and monitor groundwater pollution.

3.4 Conclusion on the sampling techniques for groundwater

Conventional and passive sampling can be used for groundwater quality characterization and monitoring in the context of polluted sites. But whatever the method used, this has to be done after understanding the local hydrogeology as well as advantages and limitations of these two sampling techniques in order to well interpret the results.

As regard to the survey carried out amongst French and German consultants, this work was conducted in order to contribute to set harmonized guidelines for the use of passive samplers for groundwater quality measurement and to help for a wider use of them. It is quite understandable that consultants need comparisons between conventional and passive samplings in order to assess the effectiveness of this innovative sampling technique. Nevertheless, principles of operation of these two techniques are different and should be well

understood in order to well interpret the results. Basically, the conventional technique will provide a mean groundwater sample along the screened interval of the well after a purge whereas passive samplers will provide depth discrete samples (without any purge of the well). Therefore, each case study is a particular one and should be examined as regard to the principles of operation as well as advantages and limitations of both sampling strategies. In some cases, conventional and passive samplings are expected to provide comparable results (for example, when sampling in short screened interval wells or when packers are used with the conventional sampling technique in long screened interval wells). Nevertheless, in some cases, conventional and passive samplings are representative of different hydrogeological conditions, for example when no vertical flow occurs in a long screened interval well. Comparisons between pollutant concentrations given by conventional sampling technique and passive samplers should then be examined carefully when these two techniques sample “different” waters. It is very important to understand differences in principle of these 2 sampling techniques before interpreting the results.

4 Techniques for passive sampling

4.1 Definitions

Passive sampling is based on free flow of analyte molecules from the sampled medium to a collecting medium as a result of a difference in chemical potentials (Gorecki and Namiesnik, 2002). The flow of molecules will last until equilibrium is reached between the two media or until the sampler is retrieved. Therefore, this kind of sampling will not need any external energy sources but will depend on different driving forces and parameters such as concentration, pressure, temperature and electromotive force gradients which can be sum up as fundamental chemical potential gradients. The ITRC applied this general definition to groundwater sampling. They defined a passive sampler for groundwater as “one that is able to acquire a sample from a discrete location or interval in a well, without the active transport associated with a pump or purge technique”. Passive samplers can therefore be divided in 3 groups:

- grab samplers: they allow to recover a sample which is an instantaneous representation of conditions at the sampling point, at the moment of sample collection, without purging the well,
- diffusion samplers: compounds of interest reach and maintain equilibrium via diffusion through a membrane. Samples are time-weighted toward conditions at the sampling point during the latter portion of the deployment period. This time will depend on the analyte and on the sampling device. Typically, conditions during the last few days of deployment are represented and assuming that concentrations are not changing abruptly over these last few days, it can be assumed that the concentration is representative of the concentration in groundwater at the time of the sampling collection,
- integrative samplers: they rely on diffusion through a membrane or porous surface and sorption on an adsorbent to accumulate analytes in the sampler. Samples are a time-integrated representation of conditions at the sampling point over the exposure time. The result will be an average pollutant concentration over the entire deployment period.

4.2 Principles of operation

Generally speaking, a passive sampler is composed of a barrier and a receiving phase. The barrier could be a permeable or semipermeable membrane of specific material and thickness or only a static layer of water. The material and geometry of the receiving phase are chosen given the type of contamination and the objectives of the study. This could be a solvent, a chemical reagent or a porous adsorbent.

This receiving phase is designed to trap contaminants within the passive sampler which is running according to 2 different regimes:

- equilibrium regime: in this kind of sampling, the exposure time is long enough to obtain a thermodynamic equilibrium between the receiving phase and the water

surrounding the sampler. The sampler is therefore retrieved from the groundwater well when this equilibrium time is reached and concentration of the analyte is titrated in the receiving phase. The concentration of the analyte in groundwater corresponds to the concentration found in the receiving phase if the receiving phase is water or can be calculated based on the ratio of analyte distribution between the 2 media involved or experimental calibration if the receiving phase is not water. This kind of samplers are diffusion samplers such as PDBs (Polyethylene diffusion bags) or cellulose regenerated dialysis membranes,

- kinetic regime: in this case, it is assumed that the rate of mass transfer to the receiving phase is linearly proportional to the difference between the chemical activity of the contaminant in the water phase and that in the receiving phase. The amount of analyte collected by the sampler depends on the concentration in the sampled medium and the exposure time. When the sampling rate of the device is known, the time-weighted average concentration of the contaminant in water over the exposure time can be calculated as long as molecules trapped in the sampler are not released when the concentration in the sampling medium decreases and the sampling rate remain constant throughout the sampling time. The receiving phase should be resins or liquids allowing absorption and chemisorption phenomena. Samplers based on adsorption may be subjected to a competition between analytes. These kinds of samplers are integrative samplers such as ceramic dosimeters or Gore sorber modules.

Figure 2 shows the typical sampling procedure of a passive sampler. When the sampler is exposed to the sampled medium, the uptake of analyte will begin and will last until the chemical potentials of the analyte in the sampled medium and in/on the sorption material will be equal (thermodynamic equilibrium). As regard to his properties, a passive sampler will work in the kinetic region, in the equilibrium region or in both of them.

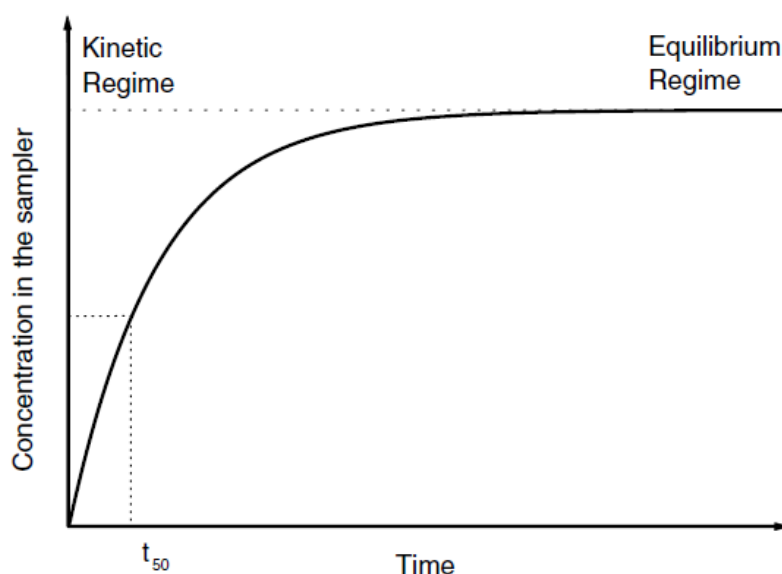


Figure 2: Operating regimes of passive samplers (after Vrana et al., 2005)

Within the barrier, convective transport is avoided and the transport occurs only due to molecular diffusion according to Fick's law. In aquatic environments, barriers are often made of polymers such as polyethylene, polydimethylsiloxane, polysulfone, regenerated cellulose, silicone-polycarbonate, cellulose acetate, PTFE, nylon, polypropylene, PVC... Porous materials can as well be used as barriers and in this case, the transfer is controlled by diffusion through the air or water trapped in the pores. The role of these barriers is to define the sampling rate of a contaminant for the passive sampler. Nevertheless, the barrier is not the only element to define the sampling rate because there is an aqueous boundary layer between the sampler and the sampled medium and a receiving phase boundary layer between the membrane and the receiving phase (Figure 3). These layers could play a significant role on analyte transfer, especially when the fluid flow across the sampler is low. The slower of these two processes (permeation through the membrane or diffusion through the static boundary layer) will mostly determine the sampling rate of the sampler. In Figure 3, the concentrations of analytes in each part of the diagram are a function of their diffusion coefficients and solubilities in all phases involved.

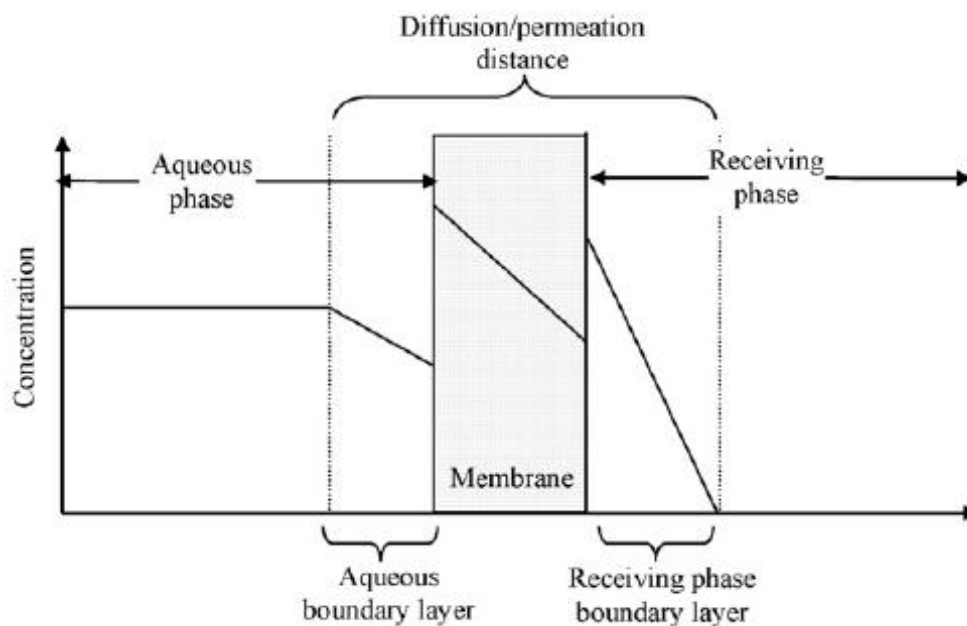


Figure 3: Concentration profile observed with permeation passive sampling from water (after Seethapathy and Gorecki, 2008)

The barrier is generally of 2 different types:

- diffusion-type barriers: analyte sampling rely on diffusion through a static layer of water neighboring the device,
- permeation-type barriers: analyte sampling rely on permeation through a membrane (porous or non porous). Permeation will include 3 steps: adsorption on the membrane, dissolution as well as diffusion in the membrane and desorption from the internal surface of the membrane.

Grab samplers are not included in this theory but can still be considered as passive samplers according to the definition of ITRC presented above because they are able to acquire a sample from a discrete location or interval in a well, without the active transport associated with a pump or purge technique.

4.2.1 Grab samplers

These samplers are designed to recover groundwater samples from monitoring wells without purging. The samples are representative of the conditions at the time and at the location of the sample collection. These samplers are moved down the well and left in the well for some time in order that hydrodynamic conditions of the well equilibrate. After this time, the sample is retrieved. The fact that the sampler is left in the well for an equilibration time will allow resettling the hydrodynamic regime of the well and will avoid a high turbidity in the sample. In addition, if contaminants can adsorb on the sampler material the equilibration time will nevertheless ensure a good estimation of the pollutant concentration in the aquifer.

4.2.2 Diffusion samplers

Diffusion samplers are filled with a liquid (deionised water in general). When the sampler is exposed to a contaminated groundwater, pollutants will diffuse through the membrane until concentrations inside the sampler are equal to the concentrations in groundwater. Therefore, diffusion samplers are recovered in equilibrium regime (Figure 2). These samplers are characterized by the time needed to achieve this equilibrium. The time needed is generally evaluated in the laboratory. These samplers should be designed to avoid the loss of compounds during their exposure and to quickly adapt and respond to the medium variations in concentrations. Different types of samplers can be found on the market. Some of them are equipped with a low density polyethylene membrane, which make them VOC specific and some of them can be equipped with other types of membranes, allowing them to sample a wide range of contaminants. Contaminants will migrate from the most concentrated zones to the less concentrated zones until equilibrium is reached (Figure 4).



Figure 4 : Concentration gradient before and after equilibrium for a diffusion sampler (after ITRC, 2007)

Concentration gradient from both sides of the membrane will drive the diffusion process. Diffusion rate will decrease when approaching the equilibrium. This diffusion rate will as well be highly affected by temperature. The equilibrium time will be affected by the type of membrane (thickness for example).

This process is reversible: when concentrations in groundwater decrease, pollutants will diffuse from the sampler to the groundwater until a new equilibrium is reached. Therefore, concentrations measured using diffusion samplers will be representative of the groundwater quality at the time of the retrieval of the samplers or of some days before, depending on the time needed to achieve this equilibrium.

4.2.3 Integrative samplers

Integrative samplers will not reach equilibrium with the sampled medium during their exposure time. Therefore, they are recovered in the kinetic regime (Figure 2). These samplers have often a low sampling rate combined with a high capacity to collect contaminants which allows them to continuously accumulate contaminants during their exposure time. The results will be a mean concentration of contaminant over the exposure time. Concentrations can be calculated when the sampling rate is known. In general the sampling phase and the sampled medium are separated with a “barrier”. This “barrier” will define the sampling rate for each compound at a given concentration as well as the sampler selectivity to limit the sampling to given contaminant classes. The sampling rate will as well depend on the sampler design, physicochemical properties of the contaminants and conditions of the sampled medium. These kinds of samplers are particularly interesting when contaminant concentration in groundwater is highly variable from a sampling campaign to another.

For integrative samplers it is necessary that the amount of sampled analyte is proportional to the amount of analytes in the investigated medium in order to make it possible to determine a mean concentration in time. The sampling rate should therefore be constant all along the sampling period. The receptor phase should correspond to resins or liquids allowing absorption and chemisorption phenomenon. In fact, samplers functioning on the basis of adsorption could be subjected to competition between analytes (this kind of device should not be used in case of high contamination). In addition, the exposure time have to be adapted to the concentration level in order not to saturate the adsorbent.

For further information on passive samplers, the reader is encouraged to refer to publications which give a general overview of passive samplers in water (e.g. Vrana et al., 2005; Huckins et al., 2006; Greenwood et al., 2007; Zabiegala et al., 2010).

5 Examples of use

Passive samplers were tested on 2 pilot sites (pilot project “Ile de France” and pilot project “Utrecht”). In this section, a summary of what was carried out on these pilot sites in the frame of the CityChlor project is presented. For more detailed information on the tests carried out on pilot sites, the reader will refer to the corresponding pilot project reports. In addition, fact sheets on the tested passive samplers are given in annexes.

Only diffusion and integrative samplers were used in the frame of the CityChlor project. Grab samplers were not tested. These tools were deployed in the specific context of chlorinated solvent concentration measurement in groundwater.

5.1 Pilot project “Ile de France”

This pilot project was an in-service facility located near Paris, France in an urban area. The site area was 6 700 m². Industrial activities started around 1926 and today the main activity is the production of door locks, metal fittings and their surface coatings. An aerial view of the site is presented in Figure 5 (the pilot site is circled in red and in blue is a wall separating different areas of the site). PCE and TCE were used and are still used. Soils and groundwater are polluted with chlorinated solvents (PCE, TCE, DCE and VC, source zones identified with red dots in Figure 5). On site, soils were composed of 50 cm to 1 m of embankments, then about 3 m of clay/sandy-clay and finally fine sand to 10 m deep. The alluvial aquifer was studied during the project: on site, the mean depth of the water table was 1.5 to 2 m below the ground surface and was about 10 m deep. The groundwater flow direction was monitored during the project and two main flow directions were identified: from north to south (during high water periods, flow direction 1) and from east to west (during low water periods, flow direction 2, see Figure 5).

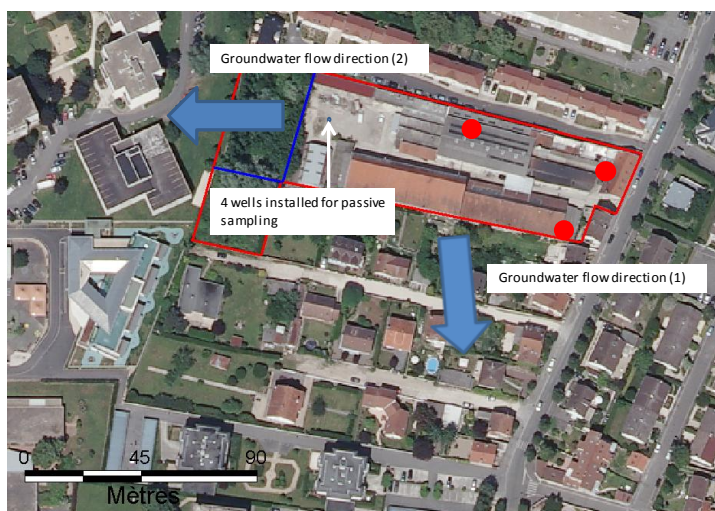


Figure 5 : Aerial view of pilot project “Ile de France”

The goal of this study on pilot project “Ile de France” was to assess the significance of passive samplers for groundwater quality measurement. Prior to the use of passive samplers, the groundwater contamination on site was characterized and 4 monitoring wells were installed at different depths. 4 passive samplers were tested in these wells: PDBs (Polyethylene Diffusion Bags), ceramic dosimeters, Gore sorber modules and regenerated cellulose dialysis membranes. 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. Passive samplers were tested on the following concentration ranges: PCE (17 – 5 900 µg/L), TCE (30 - 2 100 µg/L), cis-DCE (120 - 11 000 µg/L), trans-DCE (10 - 2 200 µg/L) and VC (10 - 7 100 µg/L).

In general, chlorinated solvent concentrations in groundwater given by the tested passive samplers were 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), cross-contamination was avoided, and no purge water was generated. They could as well offer complementary information compared to traditional sampling method because they allowed depth discrete and multi-level sampling in a well (although this was out of the scope of the CityChlor project).

5.2 Pilot project “Utrecht”

This study comprises the application of the Passive Flux Meter (PFM) for the measurement of chlorinated solvent mass fluxes and Darcy water fluxes in groundwater at a field site in Utrecht. It frames in the remediation project of the groundwater in the Utrecht central station area and is part of the CityChlor project (pilot project “Utrecht”: Monitoring of (bio)processes). In the city of Utrecht many different sources of VOC pollutions were found. It isn't possible to link all sources to a polluter and the plume is caused by different sources. The plumes are mixed as a result of years of groundwaterflow and extraction activities. It is a typical case of a large European city with many polluting activities like dry-cleaners and small metal-industry.

In the frame of this study 15 PFMs of 1.4 m length were constructed and installed in 6 different monitoring wells in the source and plume zone of 2 selected sites in the Utrecht study area: site Amsterdamsestraatweg and site Nachtegaalstraat. The PFMs were retrieved, sampled and analyzed after 3 weeks of exposure time (Sept-Oct 2012).

According to the analytical results groundwater velocities ranged from 0.8 to 3.3 cm/d at the site Amsterdamsestraatweg and from 0.2 to 4.7 cm/d at the site Nachtegaalstraat. Measured contaminant flux data at Amsterdamsestraatweg raised up to 4000 mg/m²/day for perchloroethylene (PCE), 1100 mg/m²/day for trichloroethylene (TCE), 1600 mg/m²/day for cis-1,2-dichloroethylene (DCE), 27 mg/m²/day for vinyl chloride (VC), and 12 mg/m²/day for cis-1,3-dichloropropylene (DCP) in monitoring well AF2.1. The latter indicated that this monitoring well could be located near a source zone. The other monitoring wells (AF1.1& AF3.1) were characterized by much lower mass fluxes (0-22 mg/m²/day for TCE and 0-7

mg/m²/day for DCP), indicating that they were located in the plume area. Measured mass fluxes at Nachtegaalstraat varied between 0 and respectively 7 mg/m²/day for perchloroethylene (PCE), 3 and 27 mg/m²/day for TCE and 0 and 28 mg/m²/day for DCE. At both sites increased contaminant fluxes were mostly related to increased groundwater fluxes.

Since hydraulic conductivities of the surrounding aquifer sands were not available, no corrections were made for the deviation of the groundwater flow field when passing the monitoring well and PFM.

The PFM has been successfully applied at two field locations in 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.

The PFM and the other passive samplers (Sorbiflux and SorbiCell) used in the pilot project "Utrecht" are not presented in the following sections of this report. For more information on these samplers, the reader is encouraged to refer to the pilot project "Utrecht" report entitled: "Integration of results, CSM Bio-washing machine".

6 Feedback on the tested passive samplers

6.1 General feedback on passive sampling

6.1.1 General advantages

In general, the tested passive samplers were very easy to use. Installation consists in lowering them into the groundwater well to the desired depth and retrieval of pulling them gently out of the well. They can be deployed in most wells, as long as the diameter is consistent with the dimensions of the samplers with minimal disturbance. The time needed to sample groundwater in the field is less than with the conventional sampling technique which may be more cost effective in some cases. Cross contamination is avoided because different samplers are used in different wells. They are disposable and no decontamination protocol is needed.

In addition, these samplers could be interesting in the case of low permeability aquifers when it is difficult to get groundwater samples thanks to other techniques (Parker et Clark, 2002). They can sample discrete intervals in the well and are a good alternative as well for measuring easily a vertical contaminant profile in wells when deployed in series and could be useful to locate zones with the highest concentrations. Nevertheless, natural vertical flows should be measured prior to multi level sampling.

By using passive samplers, there is no purge-water to be treated, which eliminates all or most disposal costs: there is no contaminated waste during sampling, instead of the passive sampler itself. No additional equipment is needed in the field and no external energy sources are required. Therefore, contrary to the pump which flow depends on the depth, passive samplers have no depth limit. They are practical for use where access is difficult or where discretion is desirable.

Due to the principle of operation of integrative samplers (accumulation of contaminant in the adsorbing phase), very low concentrations can be detected. These samplers could therefore be useful as warning points.

6.1.2 General limitations

When different contaminant classes have to be monitored, several passive samplers have to be used in general because most of them are contaminant-specific. Nevertheless, regenerated cellulose dialysis membranes are able to sample a wide range of contaminants as well as cations and anions. The only limitation in this case will be the water volume of the sample, given that laboratories need a quite large volume of water for each analysis.

For some passive samplers biological activity could be a problem which can result in lower concentrations detected by the sampler.

In addition hydrogeological conditions at the sampling point need to be well known, such as natural vertical flow, particularly when doing depth discrete and multi level sampling. For integrative samplers, concentration is derived thanks to an adsorbed mass. A calculation step is therefore necessary and some additional factors are often needed such as sampling time, water temperature, installation depth...

6.2 Diffusion samplers

6.2.1 Polyethylene diffusion bags

Sampler composition and principle of operation

Polyethylene diffusion bags (PDBs) are made of a tubular low density polyethylene membrane filled with deionized water. In general, this sampler is 50 cm in length and 4 cm in diameter and is contained in a polyethylene mesh in order to avoid damage to the sampler. Other dimensions are available on the market. A weight (bottle filled with sand) is attached to the end of the bag so that it stands at a given depth below groundwater surface and will not float. These samplers are specifically designed for VOC sampling.

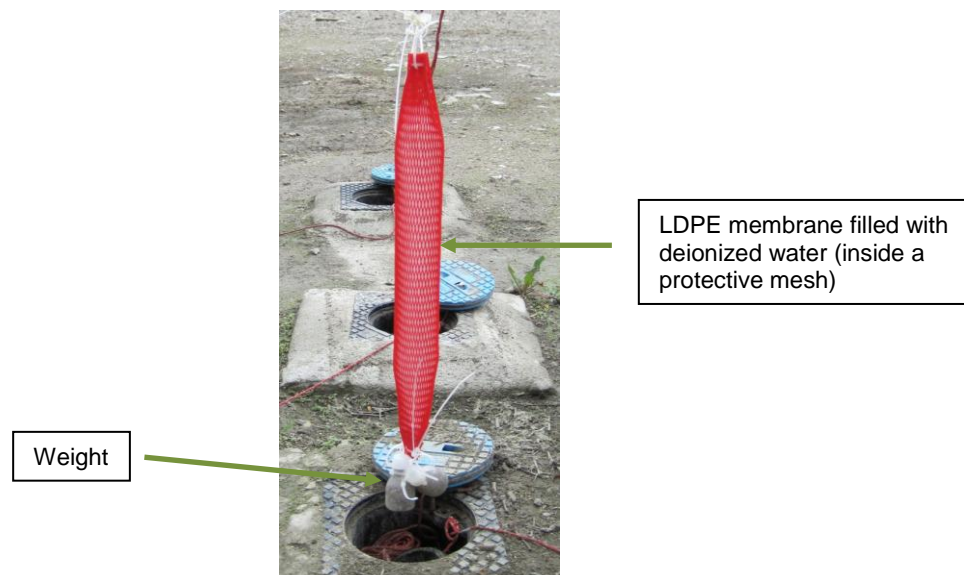


Figure 6: Polyethylene Diffusion Bag (PDB)

They are commercially available and delivered “ready-to-use” or can be easily hand-made. PDBs are specifically designed for volatile organic contaminant (VOC) sampling. Operation conditions of the PDB are based on molecular diffusion across the membrane. When the sampler is placed in water, VOCs will diffuse across the membrane from the contaminated

groundwater to the water in the sampler until concentrations are equal on both sides of the membrane. Therefore, when groundwater concentrations change, concentrations inside the PDB will change. VOC concentrations in the PDB are representative of the aquifer conditions between 1 to 4 days before the sampler retrieval.

Before installation, PDBs should be stored cool and dark. In order to avoid any contamination caused by polluted air, smoke, grease or oil of any kind, a prompt installation is recommended.

Sampler installation and retrieval

PDBs are attached to a cord that should be securely fixed to the wellhead or to a rod over the opening of the well. Then, they are lowered slowly down the well to avoid causing any damage to the polyethylene tubing on the casing. Note that any defects in liquid tightness caused during transport or installation will lead to impracticality of the PDB. The formation of gas bubbles inside the tubing is not relevant.

The exposure time of the sampler will depend on the time needed to achieve equilibrium with the sampled media after diffusion of the compounds across the membrane and on the time needed so that the system will go back to “normal” conditions after disturbances due to the installation of the sampler. A 2 week exposure is significant in most of the applications in soils of high to medium permeability, containing mainly sands and silts. Any longer exposure is possible as long as no bio-fouling of the membrane occurs. For low permeability soils, mainly made of clay and dense silts, a longer equilibrium time may be needed (Vroblecky and Campbell, 2001).

After an appropriate exposure time, PDBs are pulled carefully out of the well. Sampling should be done immediately in the field to avoid any effects due to sunlight and warmth. Transfer of the water contained inside the PDB is done thanks to a PTFE tubing. Sampling is therefore carried out under low-flow conditions to avoid volatilization of some compounds during this step. The water contained in the sampler is transferred to an appropriate sampling container thanks to the PTFE tubing. Leaky PDBs should not be considered during this step. Sampling containers should be stored cool and dark on the way to the laboratory.

Feedback on the sampler from tests in the frame of the CityChlor project

PDBs were very easy to install and retrieve (about 10 to 15 min per well) meaning that a lot of wells can be equipped in one day. In addition these samplers are not expensive (between 20 and 40 €) and the analysis can be done in any laboratory because it consists in analyzing VOC in water.

In general, the tests carried out in the frame of the CityChlor project showed that concentrations given by the PDBs were of the same order of magnitude than the ones measured in the groundwater samples taken with the conventional sampling technique (pump). They were most of the time comparable. In some cases, TCE and PCE concentrations were lower with the PDBs than with the pump but still in the same concentration ranges in general. This difference could be explained as regard to the lithology,

installation depths and physico-chemical properties of TCE and PCE (density comparing to water). A good reproducibility of the results was observed.

6.2.2 Regenerated cellulose dialysis membrane

Sampler composition and principle of operation

These samplers are very similar in structure and principle of operation to the PDBs. Nevertheless, they are not commercially available. Prior to on-site sampling, they should be built in the laboratory. They are made of a tubular membrane which in this case is of regenerated cellulose, filled with deionized water. For the tests carried out in the frame of the CityChlor project, clamps were attached to the upper and lower ends of the membrane. An other option is to attach a tap at the lower end of the membrane in order so that the transfer of water after exposure is easier and could be done under low flow conditions when VOCs have to be sampled. Nevertheless, in the frame of the tests described in this report, the transfer of water was carried out thanks to the same PTFE tubing than the one used for PDBs. The system should be contained in a polyethylene mesh in order to avoid damage to the sampler. A weight (bottle filled with sand for example) should be attached to the end of the bag so that it stands at a given depth below groundwater surface and will not float. For the membrane, different pore sizes and diameters are available. The length of the sampler is determined by the field technician but it is recommended by the ITRC (2004) that diffusion samplers should not represent more than 1.5 m of the screened interval of a well.

In the frame of this project, the sampler was 50 cm in length, 5 cm wide and the cutoff was 8 000 Da.

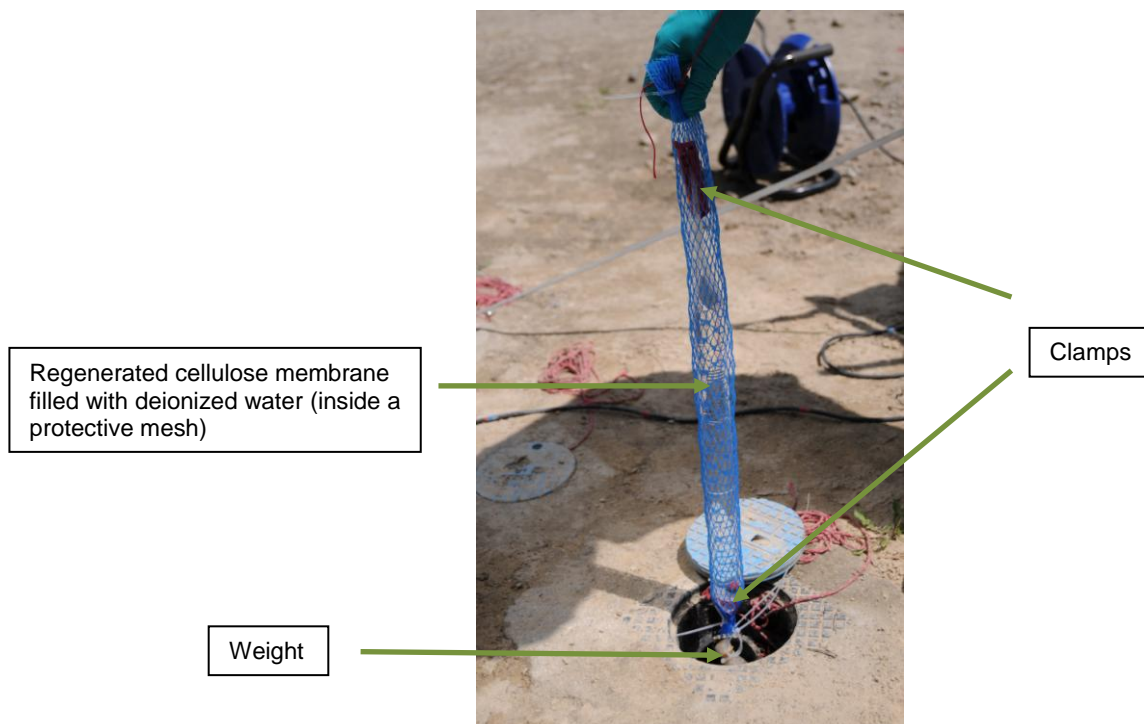


Figure 7: Regenerated cellulose dialysis membrane

Regenerated cellulose dialysis membrane samplers were developed for inorganic and organic compound sampling. They were successfully tested for sampling of a wide range of compounds (Vroblecky *et al.*, 2002; Vroblecky and Pravecek 2002; Imbrigiotta *et al.*, 2002). Principle of operation of this sampler is based on diffusion: compounds present in groundwater will diffuse across the membrane until equilibrium is reached on both sides of the membrane. Therefore, when groundwater concentrations change, concentrations inside the sampler will change.

These samplers should be built up during the week when their installation is planned and should be stored in water in order to keep the membrane permeable, flexible and strong.

Sampler installation and retrieval

Regenerated cellulose dialysis membranes are attached to a cord that should be securely fixed to the wellhead or to a rod over the opening of the well. Then, they are lowered slowly down the well to avoid causing any damage to the sampler tubing on the casing. Note that any defects in liquid tightness caused during transport or installation will lead to impracticality of the sampler.

The exposure time of the sampler will depend on the time needed to achieve equilibrium with the sampled media after diffusion of the compounds across the membrane and on the time needed so that the system will go back to “normal” conditions after disturbances due to the installation of the sampler. An up to 2 week exposure is significant in most of the applications. Any longer exposure is possible as long as no bio-fouling of the membrane occurs.

After an appropriate exposure time, regenerated cellulose dialysis membrane are pulled carefully out of the well. Sampling should be done immediately in the field to avoid any effects due to sunlight and warmth. Transfer of the water contained inside the sampler is done thanks to the tap attached at the lower end of it or to a PTFE tubing in the case of a clamp attached at the lower end of the membrane. Sampling is therefore carried out under low-flow conditions to avoid volatilization of some compounds during this step. The water contained in the sampler is transferred to an appropriate sampling container. Leaky dialysis membranes should not be considered during this step. Sampling containers should be stored cool and dark on the way to the laboratory.

Feedback on the sampler from tests in the frame of the CityChlor project

As PDBs, regenerated cellulose dialysis membranes were very easy to install and retrieve (about 10 to 15 min per well) meaning that a lot of wells can be equipped in one day. In addition these samplers were not expensive (the cost of a sampler was about 30 to 40 €) and the analysis could be done in any laboratory because it consisted in analyzing VOCs (or other compounds) in water. Given the size of the membrane pores, only the dissolved fraction of contamination is sampled so no filtration is required in the field when looking for inorganic compounds. Comparing to the PDBs, the main advantage of this sampler is that it is able to sample any type of compounds (organic and inorganic) in the same time. The only limitation will be the volume needed to analyze the water in the laboratory, meaning that if a

lot of different contaminant classes need to be analyzed, multiple samplers should be installed in the same time.

Nevertheless, these samplers are not commercially available. The time needed to build a sampler is about 15 min when people are used to. During our study, a loss in water volume (about 10 %) has been observed in some cases. This has been observed as well by ITRC (2007) and could be an issue when sampling VOC. Some tests were carried out with a tap instead of a clamp at the lower end of the sampler but the same problem was observed. An optimization of the sealing of the sampler should be done prior to carrying on further tests. In addition, they should be stored in water which could be not practical when a lot of samplers need to be installed in the same time in the field.

In general, the tests carried out in the frame of the CityChlor project showed that for cis-DCE, trans-DCE and TCE, concentrations obtained in groundwater sampled with dialysis membranes were of the same order of magnitude and comparable to the ones obtained from groundwater samples taken with a pump. This was not the case for VC: an over or under estimation was observed with the dialysis membranes which could be explained by volatilization of VC during sampling with both methods. Finally, an under estimation of PCE concentrations was observed with the dialysis membrane and this could be explained as for the PDBs, as regard to the lithology, installation depths and physico-chemical properties of PCE (density comparing to water).

6.3 Integrative samplers

6.3.1 Ceramic dosimeters

Sampler composition and principle of operation

Ceramic dosimeters are made of a porous ceramic tube of 1 cm in diameter, 5 cm in length and with 5 nm pores (Figure 8). A solid adsorbent is placed inside the tube. This adsorbent is selected as regard to the compounds of interest and the duration of the monitoring. It should have a high affinity for the contaminants and extraction should be carried out easily. A PTFE cap is placed at both end of the ceramic membrane. The diffusion coefficient of this cap is very low and the contaminant uptake is only controlled by the ceramic membrane. The ceramic tube is generally placed in a casing in order to avoid any damage during field installation and retrieval. Ceramic dosimeters can sample volatile organic compounds such as PAHs, BTEX or chlorinated solvents.



Figure 8: Ceramic dosimeter

Contaminants diffuse across the ceramic membrane, are adsorbed and accumulated in the adsorbent in a linear way during the exposure time.

Ceramic dosimeters should be stored in a humid environment before and after the installation.

After the sampling event, the adsorbent is removed from the dosimeter and contaminants are extracted (thermodesorption or with a solvent) and the adsorbed mass is determined (GC-MS). The mean concentration in groundwater over the exposure time is calculated thanks to a model. The parameters needed are the exposure time and the groundwater temperature.

Sampler installation and retrieval

Ceramic dosimeters are attached to a cord that should be securely fixed to the wellhead or to a rod over the opening of the well and lowered down the well. The exposure time of the sampler will depend on the concentration of the compounds of interest in groundwater. The sampler should be left enough time to reach the quantification limit of both the analytical method and extraction method and not too long in order not to saturate the adsorbent. Some typical minimum exposure times to reach the quantification limit for different concentrations are presented in Table 2.

Table 2: Minimum exposure time for ceramic dosimeter to reach the quantification limit of both the analytical method and the extraction method

	PAH		BTEX		VOC	
	Naphtalene	phenanthrene	Benzene	Toluene	TCE	PCE
Minimum mass (µg)	0.09	0.12	1.2	1.35	6	6.3
Concentration in solution	Required exposure time					
0.1 µg/L	330 d	1.4 y	9 y	11 y	61 y	73 y
1 µg/L	33 d	53 d	341 d	1.1 y	6.1 y	7.3 y
10 µg/L	3 d	5 d	34 d	41 d	224 d	267 d
100 µg/L	0.3 d	0.5 d	3.4 d	4.1 d	22.4 d	26.7 d

After an appropriate exposure time, ceramic dosimeters are pulled carefully out of the well and stored in a humid environment before analysis. Results will be a mean concentration of the contaminants in groundwater over the exposure time of the sampler.

Feedback on the sampler from tests in the frame of the CityChlor project

The main advantage of this sampler is that it provides time integrated concentrations over long periods (some tests have been made up to 1 year but not in the frame of this project). It is protected against contamination by micro organisms thanks to the low pore size of the membrane and no desorption occur when concentration in water decreases. Therefore it decreases the number of samples and analytical costs. Detection of punctual high concentrations can be possible in the frame of a long term monitoring. In addition, ceramic dosimeters are able to sample any kind of chemicals in aqueous environments (as long as the adsorbent is adapted). Sampling is not influenced by local hydrodynamic parameters; therefore, no calibration is required.

In general, the tests carried out in the frame of the CityChlor project showed that concentrations given by ceramic dosimeters were of the same order of magnitude than the ones calculated from groundwater samples taken with the pump during the sampler exposure time. Given the analytical uncertainty they were comparable for cis-DCE, in half of the cases for TCE and in only 20 % of the cases for PCE. For TCE and PCE, differences between the concentrations given by the two methods were observed in Pz F3 and Pz F4 which can be explained as for PDBs. Nevertheless, differences seemed less important than for PDBs.

These comparisons were made on 3 sampling campaigns concerning 4 wells that is to say 12 points of comparison are available at most for each analyzed compound. In order to further document the feedback on ceramic dosimeters, it would be interesting to assess them during longer exposure times and to compare the results to the conventional sampling technique, in the frame of a regulatory monitoring for example.

Nevertheless, a good knowledge of the concentration ranges is needed prior to the installation in order to assess the exposure time. In addition, as this sampler exhibit a low sampling rate it needs a long exposure time when compounds are present in low concentrations. They do not allow quantification of VC and trans-DCE.

6.3.2 Gore sorber modules

Sampler composition and principle of operation

The Gore sorber module is composed of hydrophobic adsorbents housed in a GORE-TEX® membrane. The hydrophobic adsorbent acts as a partitioning surface. Gore sorber modules can sample volatile and semi-volatile organic compounds.

Dissolved compounds with sufficient volatility partition to vapor across the membrane and are captured by the adsorbent in proportion to the concentration in the groundwater. As this is an integrative sampler, contaminants accumulate in the adsorbent.

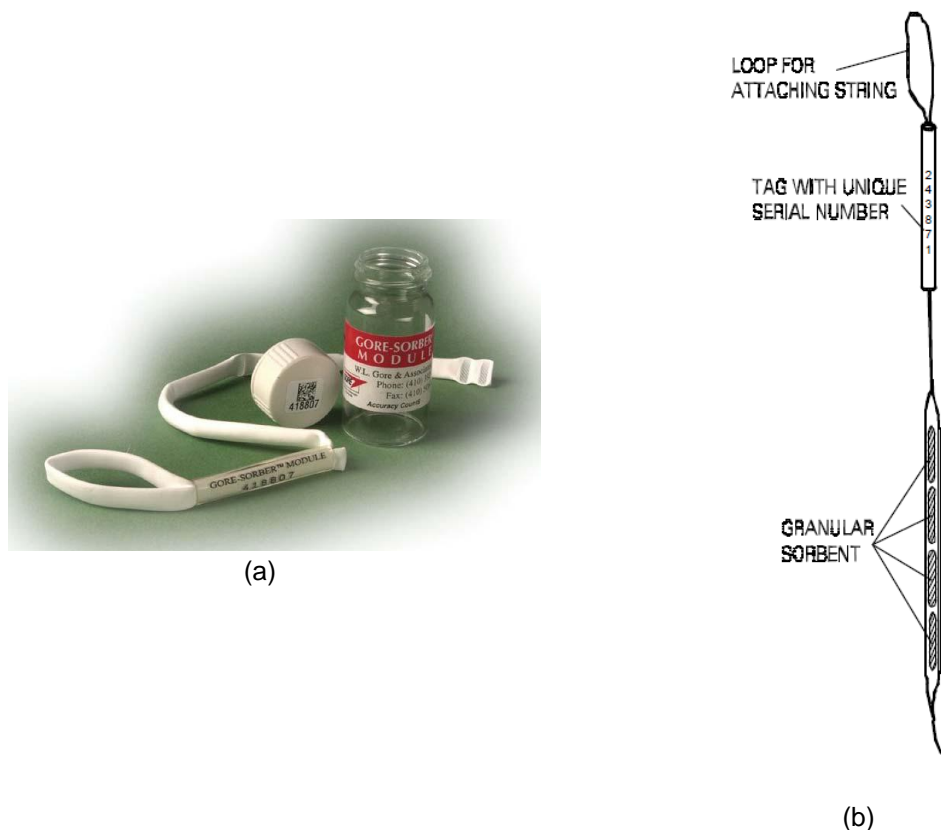


Figure 9: Gore sorber module (a) Picture of the module (from Gore)
(b) Schematic diagram of a module (from US EPA, 2000)

After retrieval of the sampler, the adsorbents are analyzed at Gore's laboratory using thermal desorption, gas chromatography and mass selective detection instrumentation, following US EPA 8260 analytical methods. Groundwater compound mass (μg) and concentrations (ppb) are then reported. Measured, compound-specific uptake rates for the module, exposure time, adsorption/desorption efficiencies, and masses desorbed are entered into an equation to determine the compound concentration. The uptake rates are corrected for water temperature, groundwater flow, and pressure (i.e., height of the water column above the module).

Sampler installation and retrieval

Gore sorber modules are attached to a cord that should be securely fixed to the wellhead or to a rod over the opening of the well. Stainless steel weights are tied to the lower end of the assembly and the sampler is lowered smoothly and quickly into the well. It should be avoided causing a splash at the water table. The fact that the module will float in water should be taken into account when determining the installation depth. The modules should be removed from their vials just moments before installing them in the well in order to avoid a possible contamination from air.

The exposure time of the sampler is generally between 30 min and 4 h in groundwater, depending on the concentration of the compounds of interest in groundwater.

Following the exposure period, the assembly is pulled to the surface. Using a clean paper towel, all excess liquid water is wiped away from the module, including under the serial number tag and from the insertion pocket that may be present. The module should then be returned to its unique vial and shipped to Gore's lab.

Feedback on the sampler from tests in the frame of the CityChlor project

Gore Sorber Modules are very practical to use: no refrigeration is needed (they only have to be transported in their glass vials) and they are very small, meaning that they can fit in every well and especially in small diameter wells where no other samplers can fit in.

Two types of Gore Modules were used: the Gore SPG008 for cis-DCE, TCE and PCE concentration measurement and the Gore type J for VC and trans-DCE concentration measurement. Concentrations measured by SPG008 were in the same order of magnitude than the ones obtained thanks to a groundwater sample taken with a pump after purging the well. They were comparable except for TCE in Pz F3 and PCE in Pz F3 and Pz F4 where concentrations were lower with the Gore module. This could be explained as for the PDBs. Type J module gave concentrations in the same range for both sampling techniques for trans-DCE but VC concentrations were under estimated with the Gore module. This type J module is in development; therefore we can expect a better estimation of VC concentration in groundwater with this type of passive sampler. Results obtained with the Gore modules showed a good reproducibility.

7 General guidelines for an appropriate use of passive samplers for groundwater quality measurement

7.1 Passive sampler selection

A lot of passive samplers are available on the market. In general, they are contaminant-specific and provide different information as regard to their principle of operation. Therefore, the selection should be done given:

- the aim of the study. This is important to choose the type of sampler (grab, diffusion or integrative samplers) as well as their number and installation depth,
- the compounds of interest. When the passive sampler type is defined, the compounds that need to be followed will define the final choice of the sampler among a few of them.

7.1.1 Aim of the study

As regard to the advantages and limitations of passive samplers identified in the frame of the CityChlor project and given the tests carried out, integrative and diffusion samplers seem particularly suited for a use on a site already characterized; they can therefore be used as part of groundwater quality monitoring. For site characterization (when it is the first time contaminant concentrations are measured in groundwater), it is more important to identify all contaminants than to measure exact concentrations. Passive samplers could fail in this task because most of them are designed for a specific contaminant type and a lot of passive samplers would be needed to cover a wide range of contaminant classes which could be more expensive than conventional sampling techniques. DNAPL and NAPL will in addition be more likely detected with an active than with a passive method. Grab samplers could be applied for characterization but they were outside the scope of the CityChlor project.

As for groundwater monitoring with conventional sampling techniques, the aim of the study should first be known before using passive samplers because the monitoring network (number and types of wells investigated, monitoring period, number of samples needed) will be designed to achieve this goal. Therefore, the number and type of passive samplers as well as their installation depth will depend on this.

In the frame of groundwater quality monitoring, concentration evolution of contaminants over space and time are needed. In order to select the passive sampler type (grab, diffusion or integrative sampler) the goal of the monitoring as regard to the way contaminant concentrations should be interpreted over time needs to be defined. Two main types of information could be needed:

- average concentrations of contaminants over time: in this case, integrative samplers should be used. They could be especially significant in the frame of a long term monitoring, when high concentration variations occur between different sampling campaigns, leading to a difficult interpretation of the results (this is often the case for chlorinated solvents for example). Mean concentrations over time could lead to a better overview of the contamination evolution over the monitoring period. In the same vein contaminant mass going through a well over time (contaminant mass flow rate) will be available thanks to integrative samplers. Having this information along several transects will give the opportunity to conclude on a concentration and flow evolution in space and time,
- instantaneous concentrations at the time of sample collection: in this case, grab or diffusion samplers should be used.

The possibility of having different types of information regarding to the contaminant concentrations (mean or instantaneous concentrations) is one of the specificities of passive samplers comparing to conventional sampling. With a pump, only instantaneous concentrations can be determined.

In the same time, the aim of the monitoring in space should be defined (Table 3).

Table 3 : examples of monitoring aims

Aim of the study	Verifications before installing passive samplers and type of passive samplers needed
Determination of the contaminant vertical distribution	No natural vertical flow in the well (flowmeter measurements) ➡ Grab, diffusion or integrative samplers depending on the type of information needed over time
Determination of the contaminant concentration at the surface of the water table	Static water level should be in the screened interval of the well (whatever the seasonal variations of the water table level and the pumping that may occur) ➡ Grab, diffusion or integrative samplers depending on the type of information needed over time
Monitoring of a plume migration	In wells installed at the limit of a plume, zones with higher permeabilities will be the preferential pathways for contamination migration. It's interesting to install samplers in front of these zones (evaluated by horizontal flow measurements, no natural vertical flow should occur in the well) ➡ Integrative samplers in general
Use passive samplers as warning points	Contamination will often migrate in a zone where the hydraulic conductivity is the highest (this zone will have a more important contribution to the groundwater sample when sampled with a pump). This zone should be evaluated by horizontal flow measurements, and no natural vertical flow should occur in the well). Passive samplers are interesting because they could detect a contamination that could be diluted at concentrations below quantitation limit after conventional sampling with a pump. ➡ Integrative samplers in general

The type of passive sampler is in anyway selected given the information on the concentration needed (mean concentration or instantaneous concentration). The possibility of vertical distribution determination and of depth discrete samples is an other specificity of passive samplers, comparing to conventional sampling.

7.1.2 Compounds to monitor

When the type of passive sampler has been selected, the contaminant classes to monitor should be considered because most of passive samplers are contaminant specific. Among the different passive sampler types (grab, diffusion and integrative samplers), different samplers are designed for different contaminant classes. For a site with different contaminant classes, there will not be a broad range of passive samplers available. A solution could be to install different samplers in the same time, corresponding to the different contaminant classes present on site.

Table 4 presents an overview of the main passive samplers that were identified for groundwater quality measurement.

Table 4: Overview of the main passive samplers for groundwater quality measurement (after INERIS, 2011d)

Type	Technology	Construction	Environment	Exposure duration	Volume of the sample	Implementation specificities	Adsorbent / receiving phase	Compounds	Detection limit	Advantages	Limits	Application	References	Supplier/Vendor	Price
Integrative samplers	Semi-permeable membrane device (SPMD)	polyethylene strip (91.4 cm x 2.5 cm x 50 microns) filled with triolein, closed by hydrophobic ends	groundwater (except in case of low permeability), surface water , ambient air , soil for PAHs and PCB)	ambient air : about 24 hours / water : 10-30 days	depending on sampling rate (ex: 30 days of exposure, 5 litres sampled per day: 150 litres)	dark environment / submerged by water / transport in a airtight container/ vandalism risk	Trioleine	hydrophobic organic compounds (PAHs, PCB, pesticides, dioxins, most of the hydrophobic SVOCs , some VOCs)	-	accurate / reproducible / cheap / easy to use / applicable to air and water	only sample organic compounds / difficult cleaning protocol / sensitive to biofilm formation / difficult transport conditions	sources delineation / estimation of organisms exposure	IRTC (2006), Esteve-Turillas, F.A. (2008), Vrana B. et al. (2005), Verreydt B. et al. (2010)	commercially available from EST (Environmental Sampling Technology) Inc. (St Joseph, MO)	\$50 per SPMD system (with trioleine-membrane) / \$250 per SPMD suspension system / \$5 liquid for preliminary extraction
	Polar Chemical Integrative Sampler (POCIS)	sorbent material (solid) contained between two polyethersulfone porous membranes	groundwater , surface water	from 2 weeks until 1 month	a set of 4 POCIS disks (4,7 cm diameter) sample from 1,5 to 10 liters of water during 30 days of exposure	light ray exposition should be limited / vandalism risk / A set of 4 POCIS can be installed in a container of 3.85 litres	different adsorbent (receiving phase) available	VOCs at low concentration (µg/L), few polar SVOCs, herbicides, pharmaceuticals and veterinary products, bodycare with log K _{ow} <3	-	easy-to-use / installation and removal easy and rapid / the adsorbent can be adapted depending on the targeted compounds / qualitative data	membrane sensitive to biofilm formation / field samples require a specific process prior to laboratory	contamination monitoring / toxicity estimation	ITRC (2006), Vrana et al. (2005), Alvarez et al., (2005).	US patent published in november 2002 (U.S. Patent 6,478,961), commercially available from EST (Environmental Sampling Technology) Inc. (St Joseph, MO) and USGS Columbia Environmental Research Center	\$65 per POCIS disk / \$300 per POCIS suspension system / \$75 per analysis (processing and extraction)
	Ceramic dosimeter	Ceramic tube (5 cm x 1 cm) filled with a solid adsorbent material, closed by PTFE caps	groundwater , surface water	from 2 weeks until 1 year	-	the minimal exposure time should be reached in order to be able to detect and quantify the targeted compounds	various ion-exchange resins (Amberlite® IRA-743), Dowex® Optipore-493, Tenax®	PAHs, BTEX, HVOCs, alkylnaphtalenes	µg/L	thickness and stability of the ceramic membrane / no additional calibration / long-term monitoring	low accuracy	groundwater monitoring in the frame of MNA or other techniques of remediation / control of contaminants discharges	Martin et al. (2001, 2003), Vrana et al. (2005), Bopp et al. (2005), Weiss et al. (2007), Kot-Wasik et al (2007), Verreydt et al. (2010), Seethapathy et al. (2008)	German patent published in 1999 (German Patent DE 198 30 413 A1) par Grathwohl	160€ per Ceramic Dosimeter
	Chemcatcher® (Universal passive sampler using Empore disk)	Inert plastic housing (eg PTFE), containing a solid phase disk attached to a porous receiving polymer as well as a diffusion disk controlling membrane	surface water	from 2 weeks until 1 month	-	-	non-polar sampler: chromatographic adsorbent / polar sampler: mix of several adsorbents	polar and non-polar organic compounds, Cd, Cu, Ni, Pb and Zn	ng/l	high sampling rate / rapid equilibration	low sampling volume capacity / sensitive to turbulences / Sampling rate influenced by the presence of biofilm	<i>in situ</i> integrative measurement of organic compounds / integrative and speciation measurement of inorganic compounds	Vrana et al. (2005), Vrana et al. (2006b), Gunold et al. (2008), Shawn et al. (2009), Shaw and Mueller (2009), Greenwood et al. (2007).	-	-
	MESCO (Membrane Enclosed Sorptive Coating)	Bag or tube (of regenerated cellulose membrane or LDPE), filled with distilled water and containing a stir bar, coated by polydimethylsiloxane (PDMS silicone) as receptor phase	groundwater , surface water	from few hours to 1 week	-	sampler small-size /no complex materials and equipments necessary for installation	Polydiméthylsiloxane (PDMS) coating a bar	PAHs, PCB, pesticides organochlorinated compounds	ng/l to pg/l	small-size sampler / no purge / no need of important volume of solvents / polar and non-polar compounds sampled by MESCO in case of regenerated cellulose membrane	low stability of the cellulose membrane / quantitative data only accessible using PRC	groundwater monitoring in the frame of MNA or other techniques of remediation / control of contaminants discharges	Vrana et al. (2001, 2006a, 2006b)	no published patent, no official supplier but could be easily built (Paschke 2005)	-
	GORE® Sorber Module	different adsorbent materials (depending on the targeted compounds), filling a flat tube (Gore-Tex membrane)	groundwater , surface water , ambient air , soil gas	from 2 to 14 days	depends on the sampling rate of each targeted compound as well as the exposure duration	can be used in most of the formations (clay to sand) whatever the humidity level (dry soils to saturated soils)	carbonaceous or polymeric resins	BTEX, MTBE, PAHs,VOCs et SVOCs.	µg/L	minimal flow disruption / no minimal sample volume / suitable for duplicate samples / detects low concentrations / can be used with short water columns	not suitable for long-term monitoring / limited by the vapor pressure of the compounds collected / do not monitor neither sampling parameters (field conditions) nor inorganic compounds	groundwater quality monitoring	Einfeld and Koglin, (2000), Vrana et al. (2005), ITRC (2005)Verreydt et al. (2010)	commercially available from W. L. Gore & Associates, Inc., et breveté (USA)	from \$185 to \$285 per GORE™ Sampler (analysis included), depending on the targeted compounds, the set of samplers is delivered with trip blank, field blank and investigation equipments)
	Sorbicells	polypropylene cartridges, filled with an adsorbent and a tracer, placed on a medium containing a supply pipe air, a reservoir and a HDPE suspension wire	groundwater , surface water	from 1 or two weeks until 6 months	from 0,1 to 0,5 litre	should be installed perpendicular to the water flow direction / the detection limit depends on the volume of water sampled / sampling exposure duration should be linked to sorption capacity and dissolution properties of the tracer used	silica gel, carbonaceous resins, zeolites and/or active charcoal	nitrate, phosphates, pesticides, VOCs, heavy metals, etc (depending on the receiving phase)	µg/L	not affected by most environmental parameters / sampler robustness / long-term monitoring / integration of hydraulic flow dynamics and concentrations / no biodegradation or diffusion of compound outside sampler	Detection limit depends on the volume of water / water level variations can influence the sampling flow	pollution alert monitoring / in situ remediation monitoring and evaluation / Environmental studies / Risk Assessment	De Jonge & Rothenberg (2005), Gran, C. (2009), Rozemeijer, J. (2010), Verreydt et al. (2010)	commercially available from Sorbisen	50€ per Sorbicell cartridge / 218€ per reusable Sorbisen Groundwater system



Type	Technology	Construction	Environment	Exposure duration	Volume of the sample	Implementation specificities	Adsorbent / receiving phase	Compounds	Detection limit	Advantages	Limits	Application	References	Supplier/Vendor	Price
Diffusion samplers	PDB (Polyethylene Diffusion Bag Sampler)	bag or tube (dialysis membrane or LDPE) filled with deionized water	groundwater	from 2 weeks to 1 year	from 250 to 300 mL (but other volumes can also be reached depending on the sampler dimensions)	easy-to-use / installation and removal easy and rapid	-	non-polar VOCs (< 10 Å)	-	easy to set up and retrieve / disposable / samples taken on discrete intervals or on a longer interval (vertical integration) / vertical profile of contamination / avoids turbidity	cannot be used for all the compounds / sensitive to biofilm formation	VOCs long-term monitoring / characterization of VOCs profiles versus depth coupled with flow data	Vroblesky, D.A. (2001), Vroblesky & Campbell (2001), ITRC (2004), Vrana et al. (2005), ITRC (2006), Verreydt et al. (2010)	commercially available from Columbia Analytical Services Inc. (Rochester, NY.) and d'EON Products, Inc. (Snellville GA)	\$25 per PDB sampler / other equipments could be also provided if necessary (weight, polyester material, fasteners , labeling...) for additional \$60
	Regenerated Cellulose Dialysis Membrane Sampler	hydrophilic membrane made of regenerated cellulose, filled with deionized water (available in 2 sizes: 6.4 cm x 61 cm long or 3.2 cm long x 61 cm)	groundwater	2 weeks	6,4 cm x 61 cm long = 969 mL et 3,2 cm x 61 cm long = 155 mL	avoid turbidity problems during sampling (no filtration) / sampler construction requires technical training / installation and removal easy and rapid	regenerated cellulose	VOCs, cations/anions, most trace metals, explosive compounds, silica, ethene, CO ₂ , CH ₄ , total dissolved solids (TDS), Dissolved Organic Carbon (DOC)	ng/l	cost of groundwater monitoring reduced / avoid turbidity / disposable device: no cleaning required and no cross contamination / rapid equilibration for most compounds	sampler must be kept under water from its construction until its implementation in situ / membrane can be biodegraded in 4-6 weeks / sampler lose a small amount of water (<3% per week)	groundwater monitoring in the frame of MNA / groundwater sources localization and delineation	ITRC (2006), ITRC (2007), Vroblesky et al. (2002), Voblesky and Pravecek (2002), Imbriogiotta (2002)	sampler not commercially available (must be built by the operator) / regenerated cellulose membrane commercially available from Filtration Products, Inc (/Sequin, TX) and Spectrum Laboratories Inc. (Laguna Hills, CA)	\$187 /10 m of pre-cleaned regenerated cellulose membrane (50 mm diameter)
	Rigid Porous Polyethylene Sampler (RPP)	polyethylene rigid container (pore 6-15 microns) with a thickness of 2 mm (3.8 x 12.7 cm ID) filled with deionized water	groundwater	14 days for most compounds but depends on compound solubility	from 90 to 100mL	sampler pores should not contain air before its establishment	deionized water	inorganic and organic compounds, VOCs and SVOCs, anions/cations, perchlorate and Cr	-	easy to use / costs of monitoring reduced/ commercially available / disposable / inorganic and few organic compounds	low volume / may be damaged if exposed to ambient air / less reliable for VOCs / has not been tested for all compounds / well diameter should be > 5.1 cm	long-term monitoring / vertical profiles in case of deep wells	IRTC (2006), IRTC (2007),	commercially available from Columbia Analytical Services (Kelso, WA)	\$40 à \$50 per RPP
	Nylon-Screen Passive Diffusion Sampler (NSPDS)	polypropylene bottle with large openings,(about 175 mL, diameter 62 mm at the top, and 58 mm below, height of 58 mm) filled with deionized water, with a grid of nylon (mesh of 125 microns) placed over the opening and covered with a ring opening of 58 mm l	groundwater	few weeks	until 1 liter (if the total volume of the samplers set reaches 200 mL)	critical orientation of the membrane	-	most VOCs, metals, anions	-	most contaminants sampled / no purge / disposable	Well minimum diameter 10 cm/ratio of the area of the membrane on the volume or height of the sample bottle	groundwater monitoring in case of metals sensitive to oxido-reduction	ITRC (2006), Verreydt et al., (2010), Vroblesky et al., (2002).	commercially available from Columbia Analytical Services, Inc (www.caslab.com) (not for large distribution), US patent in process (USGS)	\$40 à \$50 per NSPDS
	Passive Vapor Diffusion Samplers (PVD)	glass bottle with threaded end, empty and not closed of 20 or 40 mL or vial VOA, closed in an envelope of two layers of LDPE or two zip bags	groundwater	from 1 to 3 weeks	20 or 40 mL of gas	pay attention in the case of stream beds with rapid cinetic of erosion: the sampler can be taken away during its implementation	gas (air)	VOCs	from 6 to 100 ppb per volume	determine the heterogeneities of releases concentrations / protected from sediment and potential contamination during its exposition / easy to set up and retrieve	if VOCs concentrations should be determined with accuracy, then, preliminary studies using other sampling methods are necessary	characterization and monitoring (localization of VOCs hot spots under streams and lakes)	Vroblesky and Campbell, 2001; Church et al., 2002; ITRC, 2005; Vroblesky et al., 1992; 1996; Verreydt et al., 2010	non patented sampler, easy-to-built using VOA vials, bag of polyethylene, or a flat tube and a polyethylene heat seal machine. (Church et al. (2002) have provided instructions on the construction and installation of sensors PVD); Vapor Diffusion sampler a	\$10 per PVD sampler
	«Peeper» Sampler	rigid containers that can contain volumes of water separated from their environment by porous membranes	groundwater, surface water	from 1 to 2 weeks	usually from 1 to 20 mL	should be installed perpendicular to the water flow direction / easy-to-use / installation and removal easy and rapid	-	most VOCs, metals, anions	-	poral water concentration measurement / no purge / in situ monitoring of trace elements	well diameter should be > 10 cm / small volumes of water sampled but with an accurate sampling depth	accurate concentration measurement of the pore water, which can be compared to "Risk-Based standards" (soit RBCA) or to "Federal/State Cleanup Criteria"	ITRC, 2005; Parsons, 2005; Verreydt et al., 2010.	commercially available from specialist suppliers as well as constructed by researchers.	flat Peeper sampler (\$312)
Grab samplers	Hydrasleeve®	polyethylene bag closed at the top by a valve. Weight stainless steel clip. Drain tube	groundwater, surface water	at least 24 hours	from 650 mL to 1250 mL	sample volume required for analysis / diameter of the piezometer / screened interval length	-	all	-	most contaminants sampled / cost efficient / disposable	Sample volume required / Do not sample at the bottom of the well	short-term monitoring / multi-depth sampling	IRTC (2006), IRTC (2007)	Geolnsight (Las Cruces, NM), EON products (Snellville, GA), EnviroEquip (Australia)	\$20 per Hydrasleeve (3.8 cm) / \$25 per reusable weight
	Snap sampler	glass or polyethylene bottles closed by "Snaps"caps at each end. The sampler body is suspended with a device consisting of a polyethylene tube in which there is a cable	groundwater, surface water	2 weeks	40 mL or 125 mL or 350 mL	sample volume required for analysis / sampling depth	-	almost all the compounds, but mostly VOCs, explosive compounds, anions, metals and 1,4-dioxane	-	most contaminants sampled / cost efficient / sample not exposed to ambient air (volatilization avoided) / accurate sampling depth / no influence of meteorological conditions / no influence of operator technical training / easy to set up and retrieve / no	small sample volume / Implementation in wells> 5 cm in diameter / the suspension system should be dedicated to a single well / the use of a reel mechanism is strongly recommended	wells with low yields and short water column / piezometers with short screened intervals	ITRC (2006), ITRC (2007), ProHydro SOP (2008)	ProHydro (Fairport, NY)	\$165 per Snap Sampler



7.2 Passive sampler set up

7.2.1 General installation and retrieval: knowledge of the monitoring network

Characteristics of the wells in which passive samplers have to be installed need to be precisely known:

- **well diameter:** passive samplers should be selected as regard to this parameter,
- **screened interval position and depth:** passive samplers should be installed in front of the screened interval,
- **variation of the groundwater level:** passive samplers should totally remain in water during their exposure time.

As for conventional sampling of groundwater, installation and retrieval procedures should be the same from one campaign to an other. Rubber gloves should be worn when manipulating the samplers. In addition, the installation and retrieval times should be recorded as well as any other information (e.g., visible evidence of free product).

7.2.2 Type of samples to collect: knowledge of the local hydrogeology

The use of passive samplers relies on the presence of horizontal flow through the screened interval of the well. Therefore, comparing to conventional sampling techniques, some additional parameters need to be measured depending on the aim of the study:

- **natural vertical flow** in the well. The assessment of this parameter is crucial when depth discrete samples or multi level sampling are needed. Passive samplers can provide these kinds of samples if there are no natural vertical flows in the well. Vertical flows can be measured thanks to a heat pulse flowmeter. They can be due to a difference in lithology along the screened interval of the well.
- **water production of soil horizons** in the screened interval of the well. Some information can be obtained thanks to a vertical logging of physico-chemical parameters or with horizontal flow measurement of different horizons in the well when pumping. This will give information on the origin of water when pumping. This is an important measurement if passive samplers have to be installed in front of such horizons when monitoring a plume migration for example. This parameter can be measured with a heat pulse flowmeter.

7.2.3 Exposure time: passive sampler type and concentration ranges

The exposure time of the sampler will depend on the type of sampler selected. For diffusion sampler, the exposure time should be long enough so that the equilibrium with the sampled media is achieved after diffusion of the compounds across the membrane and the system is back to “normal” conditions after disturbances due to the installation of the sampler. This exposure time is generally given by the manufacturer or can be easily found in literature. For integrative samplers, the exposure time will depend on the concentration of the compounds in groundwater. The sampler should be left enough time to reach the quantification limit of both the analytical method and extraction method and not too long in order not to saturate the adsorbent. This information is often given by the manufacturer as well and can be found in literature.

7.2.4 Number and position of passive samplers

In wells with screened intervals shorter than 1.5 m, the sampler will generally be installed in the middle of the screened interval whatever the presence or not of natural vertical flow in the well. Samples will be considered as depth discrete samples.

For wells with longer screened interval, natural vertical flow should be measured¹. The number and position of passive samplers will depend on the presence or absence of natural vertical flow and of the objectives of the study:

- when there are natural vertical flows in a long screened interval well, contaminant concentrations are homogenized all along the screened interval and therefore depth discrete samples cannot be obtained. Passive samplers will give a mean concentration along the screened interval and will provide the same kind of information provided by a sample taken with the conventional sampling technique,
- when no vertical flow occurs in the well, passive samplers can be used for quantitative concentration data at different depths. If a vertical profile of contamination is expected, several passive samplers can be deployed in the same time, in the same well. Then the most contaminated part of the aquifer can be monitored for example.

7.3 Data interpretation

When groundwater is currently monitored thanks to conventional methods (well volume purge sampling or low-flow sampling), using passive samplers instead of it could require a side by side comparison test of these two methods to determine if passive samplers are appropriate tools at a particular well. Tests have shown that contaminant concentrations from passive samplers adequately represent local ambient conditions within the screened interval even if the contaminant concentrations are different than the conventional method. This may be due to pumping incorporating water from zones above or below the screened interval with higher

¹ It should be noted that in some countries (for example in Flanders) the use of screened intervals longer than 2 m have to be motivated by the expert.

or lower concentrations (Vroblesky and Petkewich, 2000) or from mixing of chemically stratified zones (Vroblesky and Peters, 2000). For this comparison, it is recommended that passive sampling is done prior to conventional sampling with the pump because difference could arise from well disturbance during equipment removal and deployment at the time of sampling if the pump is introduced in the well before passive sampling. Nevertheless, active and passive samplings rely on different approaches and mechanism that is why a one-to-one correlation between the results may not occur. When results are not the same, this will not necessarily invalidate either sampling method.

8 Conclusions and further work

In this work, passive samplers were identified as an innovative and promising way of sampling groundwater. They seemed very interesting to measure groundwater quality at contaminated sites because they showed a lot of advantages comparing to the conventional sampling technique: they were easy to install and retrieve, no external energy source or additional equipment was needed and they were generally more cost-effective than the conventional sampling technique. In addition, cross contaminations were avoided.

Passive samplers can be considered as complementary tools to the conventional sampling technique and can be installed in cases where the other techniques seem less appropriate. For example, these samplers could be interesting in the case of low permeability aquifers when it is difficult to get groundwater samples thanks to other techniques. They can sample discrete intervals in the well and are a good alternative as well for measuring easily a vertical contaminant profile in wells when deployed in series. Therefore they could be useful to locate zones with the highest concentrations. They are appropriate when access is difficult or discretion is desirable. They have no depth limit and can be easily used in deep wells.

Nevertheless, the main limitation of passive samplers relies in the fact that a very good knowledge of the local hydrogeology is mandatory (especially a characterization of natural vertical flows in wells) in order to well interpret the results, particularly when long screened interval wells are used to measure groundwater quality. In addition, passive samplers are generally contaminant-specific, meaning that several of them will be needed on sites with different contaminant classes.

As regard to these advantages and limitations and given the tests carried out in the frame of the CityChlor project, integrative and diffusion samplers were identified in this project for a use on a site already characterized; they can therefore be used as part of groundwater quality monitoring. Nevertheless, knowledge of the hydrogeology of the site is essential when applying passive methods. This knowledge will often not be available in an early phase. A 'blind' application of results of passive methods can lead to wrong conclusions.

The significance of passive samplers for groundwater quality measurement was confirmed in this project. For a better proof of application of this sampling method in Europe in the frame of polluted site management some additional tests could be carried out:

- passive samplers have to be tested for other contaminant types. In the frame of previous French research projects (METROCAP and ATTENA projects) and the CityChlor project, mainly VOC sampling was assessed. Some preliminary tests were as well available on PAHs. Therefore tests have to be carried out for PAHs and BTEX since they belong to contaminant classes that are most often met on polluted sites. Tests on trace metals could be the following step,
- as passive samplers were assessed in relatively well designed and “controlled” conditions, they now have to be tested in the frame of a “real” regulatory monitoring (at least for chlorinated solvents) and the results have to be compared to the

conventional sampling technique. Diffusion and integrative samplers have therefore to be tested for longer exposure times, especially those which seemed promising in this work. This should allow to know if integrative samplers could help to give a better interpretation of the contaminant concentration variation in groundwater from a sampling campaign to an other,

- passive samplers could be compared to low-flow sampling,
- passive samplers have to be tested in other situations and particularly multi-level sampling have to be assessed in the field.

In order to encourage consultants to use passive samplers for groundwater characterization and monitoring, the standard ISO 5667-11:2009 should be amended to consider passive samplers and give general guidelines concerning their use in groundwater. This could be a good follow up of the standard ISO 5667-23:2011 on passive samplers for surface waters. A suggestion for authorities would be to approve the use of passive sampling technologies on a well-by-well basis: to consider passive sampling, a sampling plan and comparison between new and conventional sampling techniques could be required. If sampling data do not match up, they could request additional work for the proposed sampling technology to be considered or justification on why the results are different or what passive samplers can offer to the monitoring that is not easily done with the technique currently used.

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10 Operation fact sheets

PDBs – POLYETHYLENE DIFFUSION BAG SAMPLER

disposable diffusion passive sampler

MODULE COMPOSITION

- ◆ Low density polyethylene tubular membrane filled with deionized water (*thickness: 4 mm, pore diameter: 10 Å*)
- ◆ Protective polyethylene mesh cover
- ◆ Weight

➔ standard dimensions: 50 cm in length, 4 cm in diameter (*other dimensions are available depending on the supplier*)



SAMPLED COMPOUNDS

VOLATILE ORGANIC COMPOUNDS

- ◆ Some PAHs
- ◆ BTEX
- ◆ VOC
- ◆ Dissolved gases (e.g. He, Ne, H₂, O₂, N₂)



SAMPLE

- ◆ **Snap-shot sample**, representative of groundwater composition 1 to 4 days before retrieval
- ◆ Water sample volume: 350 mL (*if standard dimensions*)
- ◆ Quantification limit: depends on the laboratory dealing with the analysis (water sample to be analyzed)

ON-SITE PROTOCOL OF USE

1. **PDB transport and storage:** cool, dark and sealed environment
2. **Installation** (10 min/PDB):
 - ➔ wear nitrile rubber gloves and handle PDB carefully, open the shipping/storage bag containing the PDB and check if PDB is in good condition (*no leakage, no air inside the tubular membrane*)
 - ➔ fix the weight to the bottom of the PDB using cable clips (*most often provided by the supplier and already fixed on*)
 - ➔ open the groundwater well, attach the other end of the PDB to a cord that is securely fixed to the wellhead or to a rod over the opening of the well (*string length depends on PDB installation depth*)
 - ➔ lower slowly the PDB at the correct depth (in order to avoid damage), and close the groundwater well

3. **Exposure time:** a 2 week exposure time is significant in most of the applications in soils of high to medium permeability, containing mainly sands and silts. Any longer exposure is possible as long as no bio-fouling of the membrane occurs. For low permeability soils, mainly made of clay and dense silts, a longer equilibrium time may be needed.
4. **Retrieval and on-site water sampling (10 min/PDB):**
 - wear nitrile rubber gloves and prepare a pointed Teflon tubing for low-flow sampling (*most often provided by the supplier*) and the sampling containers
 - open the groundwater well, pull carefully the PDB out of the well
 - tap the LDPE membrane using the pointed Teflon tubing. Make the sample flow slowly into the sampling container, avoid spluttering and bubbling
 - close the sampling containers carefully (*without any air bubbles in the bottle*)
 - close the groundwater well
5. **Sampling container transport and storage:** cool and dark on the way to the laboratory



ADVANTAGES

- ◆ Very easy to install and retrieve
- ◆ Fast sampling method
- ◆ Inexpensive
- ◆ Routine analysis for the laboratory
- ◆ Very well validated in the lab and in the field



LIMITATIONS

- ◆ Long-span exposition makes biofilm and may disturb compounds transfer through the LDPE tubular membrane
- ◆ Contaminant-specific
- ◆ Short term fluctuation in concentration (hours) will not be detected
- ◆ Finite sample volume

EXAMPLE OF SALES REFERENCES (AMONG OTHERS)

- ◆ ALS Environmental (<http://www.caslab.com>)
- ◆ Innovative Messtechnik Dr. Weiss (IMW)
- ◆ PLM équipements (<http://www.plm-equipements.info/presentation>)

From 20 to 40 € per PDB (*standard dimensions, without groundwater analysis*)

REGENERATED CELLULOSE DIALYSIS MEMBRANE

disposable diffusion passive sampler

MODULE COMPOSITION

- ◆ Porous tubular membrane made of regenerated cellulose and filled with deionized water (*thickness: 4 mm, pore diameter <28 Å*)
- ◆ Protective polyethylene mesh cover
- ◆ Weight
- ◆ Clamp and tap for the sampling

➡ between 50 and 60 cm in length, between 3 et 6 cm in diameter (*depending on the selected membrane*)



SAMPLED COMPOUNDS

- ◆ Organic compounds (VOC, BTEX, PCB...)
- ◆ Inorganic compounds (trace metals, cations, anions...)
- ◆ Dissolved organic carbon, dissolved gases (e.g. methane)

SAMPLE

- ◆ Snap-shot sample, representative of groundwater composition 1 to 4 days before retrieval
- ◆ Water sample volume: 350 mL (*depending on the module dimensions*)
- ◆ Quantification limit: depends on the laboratory dealing with the analysis (water sample to be analyzed)

ON-SITE PROTOCOL OF USE

1. Module assembly:

- ➡ wear nitrile rubber gloves, prepare the desired membrane length and a protective mesh
- ➡ moisturize the membrane in a deionized water bath during 5 to 10 min
- ➡ attach the lower end clamp or the tap with cable clips
- ➡ fill the membrane with deionized water and close the membrane with a clamp at the upper end of it (*no air bubble should be present inside the membrane*)
- ➡ check the sealing of the assembly
- ➡ put the assembly inside a protective mesh

2. Transport and storage of the sampler: deionized water bath

3. Installation (10 min/sampler):

- ➔ wear nitrile rubber gloves and handle the sampler carefully
- ➔ remove the sampler from the deionized water bath
- ➔ fix a weight to the bottom of the sampler using cable clips
- ➔ open the groundwater well, attach the other end of the sampler to a cord that is securely fixed to the wellhead or to a rod over the opening of the well (*string length depends on sampler installation depth*)
- ➔ lower slowly the sampler at the correct depth (in order to avoid damage), and close the groundwater well

4. **Exposure time:** a 2 week exposure time is significant in most of the applications in soils of high to medium permeability, containing mainly sands and silts. Any longer exposure is possible as long as no bio-fouling of the membrane occurs. For low permeability soils, mainly made of clay and dense silts, a longer equilibrium time may be needed.

5. Retrieval and on-site water sampling (10 min/sampler):

- ➔ wear nitrile rubber gloves and prepare the pointed Teflon tubings for low-flow sampling (*if no tap at the lower end of the sampler*) and the sampling containers
- ➔ open the groundwater well, pull carefully the sampler out of the well
- ➔ tap the membrane using the pointed Teflon tubing or open gently the tap fixed at the lower end of the sampler. Make the sample flow slowly into the sampling container, avoid spluttering and bubbling
- ➔ Close the sampling containers carefully (*without any air bubbles in the bottle*)
- ➔ Close the groundwater well

6. **Sampling container transport and storage:** cool and dark on the way to the laboratory



AVANTAGES

- ◆ Very easy to install and retrieve
- ◆ Fast sampling method
- ◆ Inexpensive
- ◆ Routine analysis for the laboratory
- ◆ No filtration required in the field when looking for inorganic compounds
- ◆ Able to sample any type of compounds in the same time
- ◆ Very well validated in the lab and in the field



LIMITATIONS

- ◆ Non commercially available: should be built in the laboratory
- ◆ Long-span exposition makes biofilm and may disturb compounds transfer through the LDPE tubular membrane
- ◆ Low water volume
- ◆ Sometimes loss of water volume during sampling (could be an issue for volatile contaminant sampling)
- ◆ Short term fluctuation in concentration (hours) will not be detected
- ◆ For some substances a precleaned membrane is necessary

EXAMPLE OF SALES REFERENCES (AMONG OTHERS)

- ◆ Suppliers of membranes and clamps: Cellu-SEP, Spectra/Por....
 - ◆ Suppliers of tap: Fisher Scientific...
 - ◆ Supplier of protective mesh: Raja, Cylex...
- From 30 to 50 € per sampler

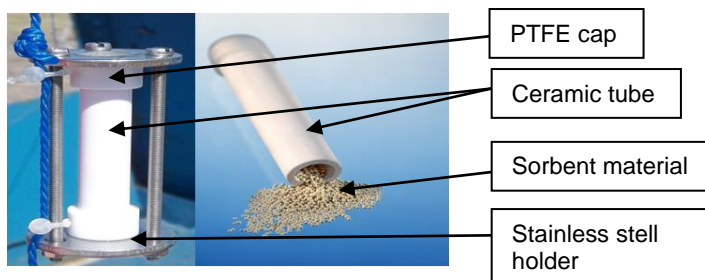
CERAMIC DOSIMETER

Reusable integrative passive sampler

MODULE COMPOSITION

- ◆ Porous ceramic tube (5 cm in length, 1 cm in diameter, pore size 5 nm)
- ◆ Adsorbent inside the tube
- ◆ Stainless steel holder

Dimensions: 4 - 5 cm in length, 1 cm in diameter



SAMPLED COMPOUNDS

- ◆ VOC
- ◆ PAH
- ◆ BTEX
- ◆ Heterocyclic compounds

SAMPLE

- ◆ Time integrated sample, the result is an average concentration of the compound in groundwater over the exposure time (compounds are continuously adsorbed on the adsorbent)
- ◆ Contaminant are thermodesorbed or chemically extracted from the adsorbent in the lab and then analyzed by GC/MS

ON-SITE PROTOCOL OF USE

- 1. Sampler transport and storage:** in humid environment (wrap in a wet paper towel), in a clean zip plastic bag and cool
- 2. Installation (5 min/ceramic dosimeter):**
 - ➔ wear nitrile rubber gloves and handle the sampler carefully
 - ➔ check the good condition of the sampler
 - ➔ open the groundwater well, attach the sampler to a cord that is securely fixed to the wellhead or to a rod over the opening of the well (*string length depends on sampler installation depth*)
 - ➔ lower slowly the sampler at the correct depth (in order to avoid damage), and close the groundwater well

3. **Exposure time:** exposure time should be long enough in order to reach the quantification limit and not too long in order not to saturate the adsorbent. This depends on the concentrations in groundwater
4. **Retrieval of the sampler** (5 min/ceramic dosimeter):
 - ➔ wear nitrile rubber gloves and prepare a jar of deionized water, paper towels and a zip plastic bag
 - ➔ open the groundwater well, pull carefully the sampler out of the well
 - ➔ wrap the ceramic dosimeter in a humid paper towel and place it in a zip plastic bag
 - ➔ close the groundwater well
5. **Transport and storage after sampling:** the sampler is sent back to the supplier for analysis. It should be in a humid environment (humid paper towel) and cool during shipment



ADVANTAGES

- ◆ Very easy to install and retrieve
- ◆ Time integrated concentrations over long periods
- ◆ Protected against biodegradation by micro-organisms thanks to the low pore size of the membrane



LIMITATIONS

- ◆ Contaminant-specific
- ◆ Good knowledge of the concentration before installation needed (in order to optimize the exposure time)
- ◆ For low concentrations (1 µg/L) exposure time can be long (1 year)
- ◆ No quantification of VC and trans-DCE
- ◆ Measurement of groundwater temperature and calculation step necessary to have access to the concentrations

EXAMPLE OF SALES REFERENCES (AMONG OTHERS)

- ◆ Tübingen University, Geological Institute, Applied Geology Group
- ◆ Innovative Messtechnik Dr. Weiss (IMW)

About 150 - 200 € (*ceramic dosimeter and analysis*)

GORE SORBER MODULE

disposable integrative passive sampler

MODULE COMPOSITION

- ◆ Gore Tex® membrane
- ◆ Hydrophobic adsorbents

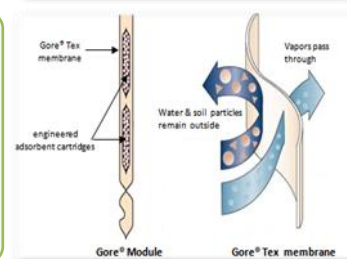
➡ **dimensions: 28 cm in length, 0.5 cm in diameter**



SAMPLED COMPOUNDS

VOLATILE ORGANIC COMPOUNDS

- ◆ Some PAHs
- ◆ BTEX
- ◆ VOC



SAMPLE

- ◆ Time integrated sample, the result is an average concentration of the compound in groundwater over the exposure time (compounds are continuously adsorbed on the adsorbent)
- ◆ Contaminant are thermodesorbed from the adsorbent in the lab and then analyzed by GC/MS

ON-SITE PROTOCOL OF USE

- Gore module transport and storage:** in its unique closed glass vial
- Installation** (10 min/Gore sorber module):
 - ➡ wear nitrile rubber gloves and handle the module carefully
 - ➡ open the vial and take the module out of its glass vial thanks to the loop
 - ➡ open the groundwater well, attach the loop of the module to a cord that is securely fixed to the wellhead or to a rod over the opening of the well (*string length depends on module installation depth*)
 - ➡ for the installation depth, take into account the fact that the module will float
 - ➡ lower slowly the module at the correct depth (in order to avoid damage), and close the groundwater well
- Exposure time:** exposure time should be long enough in order to reach the quantification limit and not too long in order not to saturate the adsorbent. This depends on the concentrations in groundwater (generally 30 min to 4 h)

4. Retrieval of the module (10 min/module):

- wear nitrile rubber gloves and prepare a paper towel and the glass vial
- open the groundwater well, pull carefully the PDB out of the well
- wipe with the paper towel any liquid that may be present on the module
- put the module in its unique glass vial and seal it carefully
- close the groundwater well

5. Transport and storage after sampling: the module is shipped back to the supplier in its vial for analysis. Nothing in particular is required for the return shipment.



ADVANTAGES

- ◆ Very easy to install and retrieve
- ◆ Small: can fit in any groundwater well
- ◆ No refrigeration needed: easy transport
- ◆ Short exposure time: sampling carried out in 1 day
- ◆ Can be used as well for soil gas and indoor air concentration measurement



LIMITATIONS

- ◆ No supplier in Europe
- ◆ Contaminant-specific
- ◆ Calculation step to have access to the concentrations

SALES REFERENCES (PATENTED)

- ◆ W. L. Gore & Associates, Inc

200\$/module (pack module+analyse, frais de port non compris)



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