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# PASSIVE SAMPLING TECHNOLOGIES: Current State and Future Challenges

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#### Abstract

Over the recent years, more and more attention is paid to the protection of the environmental compartments such as air, water, sediments and soil. However, such action targeted at a protection cannot be effectively implemented without continuous and reliable data monitoring. In this respect, qualitative information is needed to bring such programs into effect. For that reason, this study was conducted as a theoretical foundation for VIM project designed by the Mikkeli University of Applied Sciences.

There are several reasons why exactly passive devices were considered for evaluation: first they provide more reliable and qualitative results than any other sampling devices in the field; utilization of samplers is quite easy and convenient for users; they allowed researchers to estimate time averaged concentration which is a critical part for statistical measurement; devices are relatively cheaper than other samplers.

In this bachelor's thesis such characteristics of most popular passive samplers were considered as design, working structure, exploitation procedure of the devices, sampling medias, factors affecting measurements, quality assurance options in the field and laboratory analysis and limitations for wide acceptance. Approximate costs of different devices were estimated as well.

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#### Foreword and background of this work

Over the recent years, more and more attention is paid to the protection of the environmental compartments such as air, water, sediments and soil. To ensure continuous and consistent improvement of the surrounding area development of legislation was very dynamic. A number of countries have been farsighted in making international agreements and establishing national legislation to improve the environment. Now when relevant acts and laws entering into force, targeted programs are either being evolved or are already implemented, more companies and organizations trying to identify possible pollution trends and quality of environmental media. However, these programs cannot be effectively implemented without continuous and reliable monitoring data. For example, it is particularly difficult to assess the quality of water basins where the number of pollutants are changing through time and effect spatial dependence from the nature. Such uncertainty also holds for sediments, air and soil can pose a significant risk of pollutants transformation through different environmental pathways. In this respect, qualitative information is needed to bring programs into effect. For that reason, this study was conducted as a theoretical foundation for VIM project designed by the Mikkeli University of Applied Sciences.

#### 1. INTRODUCTION

With drastic development all around the globe and expansion of human influence on the environment, the quality of the surroundings nowadays is among highest priority across the world. As a result many international monitoring networks are in progress, gathering information for e.g. air quality mapping. However much less attention has been paid to water monitoring and there is still a similar need for comparable, representative data on pollutants loads and trends. In order to succeed, exclusively reliable information is needed that is comparable and will force risk assessment and penitentiary actions. In this regards, sampling as a way to conduct environmental monitoring may be very beneficial.

The number of sampling methods are very high and only expanding with time, adapting for each type of environment, methodology being used and materials being sampled. Given such broad areas to be monitored, there are certain ongoing problems that developers and managers could face. For example, when examine surface and groundwater, all sources of impact should be considered whereas wastewater samplings are carried out only after detailed description of the enterprise, its technologies, operations and interactions of individual elements engaged into the process are considered. [6] This confirms the need for paying attention to the huge number of details and connections involved in the sophisticated, complex processes.

Much emphasize has been placed on spot or grab monitoring methods at given time and place with subsequent storage and laboratory analysis. However, without additional data it would be problematic to extrapolate water quality on the other river spots or time using this methods thus measurements may be less representative and inaccurate. [2] Taking into account the cost of improper information is rather high and once mistake occurred, they are too difficult to correct, an integrated measuring approach is required to improve existing conventional methods. This approach also has to be relatively low-cost, effective, that would allow measuring of not only fate and concentrations of substances but will be able to assess potential hazards these chemicals might pose to the environment and to human health. Passive sampling techniques are quite promising in that way as many of named requirements are fulfilled. Most of them are under development, however with high probability may be included in permanent set of tools of those responsible for monitoring. [2] To describe suitability of the various passive sampling techniques for pollution monitoring and their effectiveness this study was

implemented. Different samplers are considered with application to various contaminated media including groundwater, surface waters, sediments and soil.

#### 2. THEORETICAL FUNDAMENTS

As mentioned before, widely used grab or bottle sampling proven rather efficient, however they associated with a number of drawbacks in the monitoring. These methods cannot properly estimate constantly changing number of pollutants over time and may miss out episodic pollution events. Even though periodicity for the measurements may raise, method still will be unpractical and the reliability of the results will be of concern. Various passive sampling devices has several drawbacks and benefits (table 1).

TABLE 1. Drawbacks and benefits of sampling devices [4, p.16]

	Passive sampler	Grab sampler	Automated grab
			sampler
Need secure location	No (+)	No (+)	Yes (-)
Need infrastructure	No (+)	No (+)	Yes (-)
Analyte loss during	No (+)	Yes (-)	Yes (-)
transport and storage			
Detection of episodic	Yes (+)	No (-)	Yes (+)
pollution event			
Identifies short term	No (-)	No (-)	Yes (+)
patterns in pollution			
concentration			
Determination of	Sometimes (-)	Yes (+)	Yes (+)
total concentrations			

Estimation of pollutant concentrations in water can also be made by measuring concentrations in benthic sediments and then using equilibrium distribution coefficients to derive levels of dissolved analytes. This approach is limited by the assumption of equilibrium between the sediments and the water column, and the potential effects of organic carbon quality differences among sediments or the formation of non-extractable, sediment-bound residues that are not accounted in current equilibrium-partition models. [1]

Another way are *in situ* analysis methods that have been improved significantly in recent decades due to a certain number of advantages. First, these methods in comparison with traditional sampling, process the information faster, which in turn eliminate risk of sample division, especially for labile compounds. In addition, when samples taken at significant depths, results can be modified during transport to the surface and these can be associated with large changes in temperature and pressure. Another important advantage is that most of the devices with the potential to use *in situ* 

monitoring were developed for use in the laboratory what makes them less expensive and more sensitive replacement for conventional analytical methods.

In situ techniques can be divided into three distinct groups, one of which is continuous in situ sampling. This group of techniques comprises electrodes that provide a continuous response to analyte concentrations in the water; examples include pH and ion selective electrodes. The second group contains techniques that provide series of *in situ* discrete measurements, including voltammetric and flow injection analysis techniques. [9] In the last group, fractionation and accumulation of the analyts occurs *in situ*, but post analysis is performed later in a next stage at the laboratory. Last one contains passive samplers that are the subject of this thesis.

#### 2.1 Working principle

Sampling process based on the techniques of free flow of analyte molecules from the sampled medium to a receiving phase, as a result of a differences between the chemical potentials of the analyte in the media. This net flow continues until equilibrium is established in the system or until the sampling period is stopped. The most passive sampling devices follow the equilibrium kinetics (figure 1). [2]

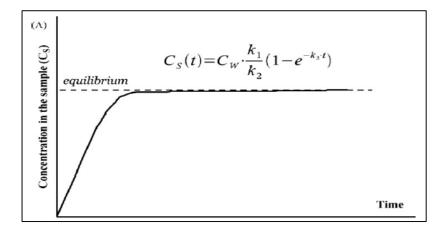


FIGURE 1. Exchange kinetics between the sampler and the water [8]

Here Cs(t) is the concentration of the contaminant with time, Cw – contaminant concentration in the aqueous environment, t –time and k1 and k2 - are the uptake rate and the offload rate constants respectively. [8]

Two main accumulation regimes, either kinetic or equilibrium, can be distinguished in the operation of a sampler during field deployment. In this respect, these passive devices sometimes, can for practical reasons, be divided into equilibrium and non-equilibrium samplers.

In equilibrium sampling, the exposure time is sufficiently long to permit the thermodynamic equilibrium between the water and the reference phase. Here above equation reduces to:

$$Cs\left(\frac{k1}{k2}\right) = C_w K(1)$$

With kinetic or integrative sampling the rate of mass transfer assumed to be linearly proportional to the difference between the chemical activity of the contaminant in the water phase and that in the reference phase. [1] This regime is represented by the following equation:

$$Cs(t) = C_w K_1 t (2)$$

The advantages of kinetic or integrative sampling are the ability to sequester contaminants from episodic events which commonly not detected with spot sampling, moreover they can be used where water concentrations are variable. They permit measurement of ultra-trace, yet toxicologically relevant, contaminant concentrations over extended time periods. Worth mentioning, that for both operational modes, knowing of phase-water partition coefficient (K) allows estimation of dissolved analyte concentration. [3]

#### 2.2. Passive sampling devices

For proper understanding of working mechanisms and potential applications of passive samplers, composite materials used in different samplers have to be discussed. Three most commonly used types of passive samplers are those using polyethylene (PE), polyoxymethylene (POM), and solid phase micro-extraction (SPME) materials (picture 1).



PICTURE 1. Selected passive samplers [1]

Another type of passive sampler called semi-permeable membrane devices (SPMDs) have been used primarily in the water column as surrogates for biota such as fish and have not been so widely used. Several novel passive sampling devices suitable for monitoring a range of non-polar and polar organic chemicals, including pesticides, pharmaceutical/veterinary drugs and other emerging pollutants of concern have recently been developed. Among them are ceramic dosimeters, MESCO, SPATT, Chemcatcher, and POCIS sampling devices. [2]

Passive samplers are simply pieces of plastic sheeting that range from about 15  $\mu m$  to 100  $\mu m$  in thickness and can be easily cut with scissors to be as large or small as needed. The PE plastic drop cloth available from hardware stores is frequently used as passive sampler material. The POM passive sampler uses a more specialized type of polymer, but it also can be purchased in large sheets. The solid phase microextraction (SPME) passive sampler is actually fiber-optic cable. The inner fiber core consists of glass that does not readily absorb hydrophobic contaminants but the insulating polymer, polydimethylsiloxane (PDMS), coating the glass core is an absorptive material effective for passive sampling.

Possibility to deploy device directly in the environment make it results very accurate due to minimized contamination. Equally important is the exclusion of power requirements and need for only one device at sampling location, which altogether lead to substantial reduction of analytical costs. Moreover, equipment applied at

sampling stage is relatively convenient, even for an untrained person, does not cause oversaturation of the site and due to the size can be easily mailed to and from remote locations. Another apparent advantage is possibility to be deployed in the working process for several days or even longer providing thus a time-average concentration at the sampling stations. Named vantages should allow significantly more extensive spatial and temporal monitoring of metals in the aquatic and gaseous environments than has previously been possible.

#### 2.3 Sampler design

Design of specific sampling device mostly depends on the field, which is being studied and can vary greatly from liquid to gaseous environment. In this work all known media will be discussed.

#### 2.3.1. Gaseous medium

For gaseous environment equally applicable both diffusive or permeative devices which in principle formed as tubes or boxes (badges) and characterized by a long, axial diffusion path and a low cross-sectional area resulting in relatively low sampling rates. Badge-type samplers that have a shorter diffusion path and a greater cross-sectional area typically exhibit higher uptake rates. These two structures act as a basis for further modifications added to improve efficiency or reduce sensitivity to weather fluctuations. Among the other passive samplers used for this compartment, permeative devices are less subjected to the weather fluctuations due to several-times-lower permeability constants of analytes then their diffusion coefficients in air. Nonetheless they required to be calibrated for each target analytes. See most common passive samplers design for air monitoring in the figure 2.

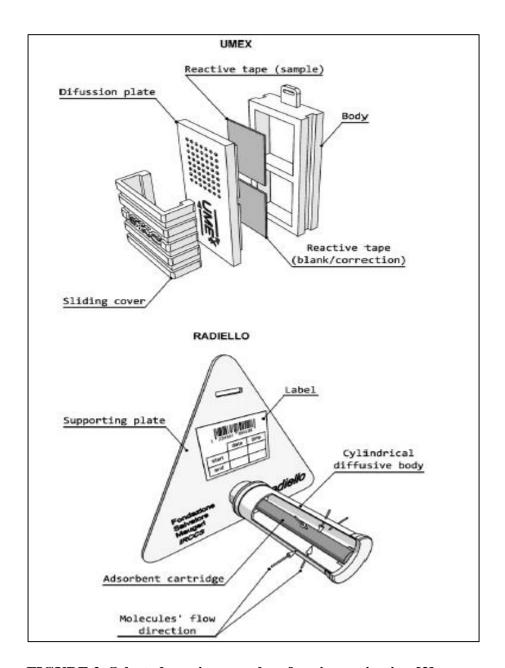


FIGURE 2. Selected passive samplers for air monitoring [3]

Second device, Radiello, was designed in the mid 1990's and is noticeable for its revolutionary radial symmetry design.

#### 2.3.2. Liquid medium

In passive sampling, the reference (or receiving) phase is exposed to the water phase, without aiming to quantitatively extract the dissolved contaminants and the exchange kinetics between the sampler and water can be described by the first-order one-compartment model. [3] Chosen for evaluation devices shown in the figure 3.

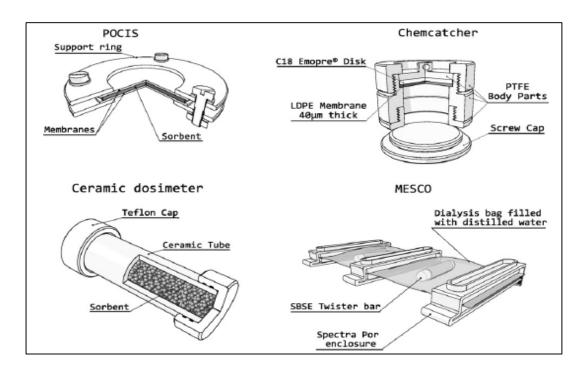


FIGURE 3. Selected passive samplers for water environment analysis [3]

These devices are suitable for monitoring a range of non-polar and polar organic chemicals, including pesticides, pharmaceutical/veterinary drugs and other emerging pollutants of concern have recently been developed. Among them are illustrated ceramic dosimeter, MESCO, SPATT, Chemcatcher, and POCIS [4].

Devices for this compartment can range from each other based on the time needed for the equilibrium between the contaminants concentration in the water and in the receiving phase to be achieved and can be divided into equilibrium and non-equilibrium. In the first case, deployment time is sufficiently long and stable concentrations are reached after a known response time. Whereas non-equilibrium samplers characterized by a high capacity for collecting the contaminants and enable to collect time weighted concentrations (TWC) over the sampling period. Whether a passive sampler behaves as an equilibrium or non-equilibrium sampler is also dependent on the partitioning properties of the chemicals. Samplers may be in equilibrium for some environmental pollutants during field sampling, while still being in the non-equilibrium phase for other compounds [16].

#### 2.3.3. Sediments and soil

Development of samplers for this compartment are the most recent compared to others. Typically, this type of sampling involves the collection of vapours, which is a combination of air, water vapour, naturally occurring organic compounds and other constituents capable of partitioning from liquid and soil materials. [7] Despite of slow development of these devices they have one significant advantage over others as they enable to detect volatile and semivolatile compounds under a wider range of site conditions. The design of sampling devices (PETREX and GORE SORBER) is schematically presented in the figure 4.

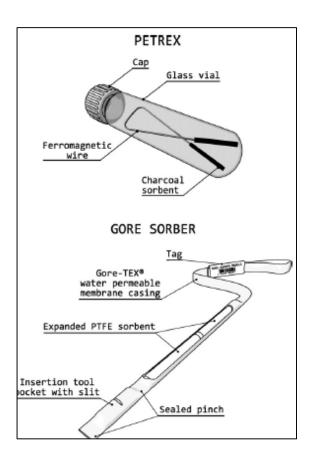


FIGURE 4. Selected passive samplers for sediment and soil analysis [3]

The GORE SORBER module is beneficial device as prevent soil particles and liquid water from affecting integrity, suitable for duplicate and back up analysis. PETREX sampler is mostly suitable for detection of volatile organic compounds (VOCs) and

semivolatile organic compounds (SVOCs), petroleum hydrocarbons, polynuclear aromatic hydrocarbons, and other compounds present at different depths [7].

#### 3 METHODOLOGY

Methodology of this thesis is dealt by reviewing existing sampling devices for monitoring of contaminated environmental divisions.

Firstly, information from different sources are gathered with advantages and limitations, state of the art, technological structure, total costs and challenges for the future applications as the main elements for comparison. All collected data is then summarized and synthesized so to make the pivot table containing relevant information on each sampling device.

Several questions are answered by dint of this thesis: what has already known in the area of passive sampling, what existing theories are, are there any inconsistencies and shortcomings presented, how current situation has changed over the last few years and what effects existing development may have of future elaboration.

Main source which i am referring to in this report is a "Passive sampling technologies in environmental monitoring: 48 (Comprehensive Analytical Chemistry)", edited by Greenwood R., Mills, G. and Vrana, G. Book has a comprehensive review of passive sampling - covering air, water and majority of available technologies in addition to the theory and applications, providing background information and guidelines for use in the field.

Another frequently used article is belongs to Washington's Interstate Technology & Regulatory Council (ITRC) Diffusion Sampler team implemented as a preparation for ITRC Technical and Regulatory Guidance for Using Polyethylene Diffusion Bag Samplers to Monitor VOCs in Groundwater. Source contain technical overviews of 12 sampling devises and summary table highlighting the important attributes of each technology.

#### 4 EXPLOITATION OF PASSIVE DEVICES

This part describes stages that are always included when taking measurements with passive samplers. They are preparation, deployment, recovering and storing.

#### 4.1 Selection of sampling material

When selecting particular sampler for application, relevant characteristics should be thoroughly considered to ensure validation of the results. See Figure 5 for various consideration when selecting passive sampler, which are not restricted though.

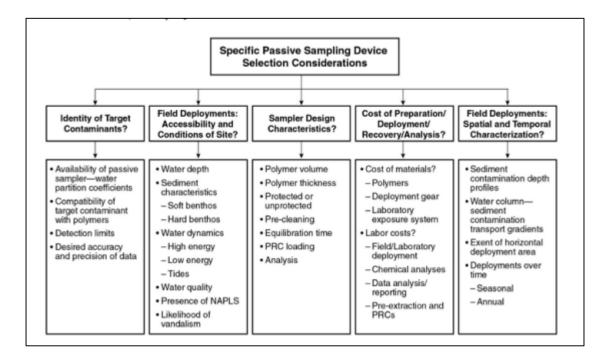


FIGURE 5. Selected passive samplers for sediment and soil analysis [3]

These steps typically include:

- Required detection limits. For example, PO and POM sheets have lower detection limits than PDMS-coated SPME fibers due to their larger sorptive capacities. Thus, a relatively large polymer absorptive mass is generally preferable when low detection limits are desired.
- Equilibrium kinetics. Thinner and less sorbing polymers have faster kinetics thus more preferable for static in-situ measurements [3].

• Sampler fouling. However, there is a lack of clear understanding on polymer susceptibility to fouling and additional studies are needed to address this issue.

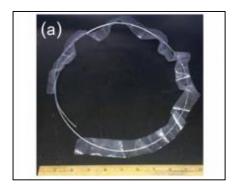
The use of commercially available polymers is advantageous because they are expected to be more uniform and homogeneous and are also available to the general public, which increases the possibilities for standardization [5]. For example, SPME fibers with various thicknesses of PDMS (e.g., 7, 30, and 100  $\mu$ m) are commercially available, can be cut to desired lengths, and have been calibrated and utilized in both laboratory and field exposures for several classes of HOCs [13].

#### 4.2 Preparation

Before the deployment, every passive device should be purified from any possible contaminates. Typically, this involves soaking them in organic solvent for several hours to days before deployment, followed by soaking or rinsing with clean water [13]. It is also a critical part to eliminate risk for potential recontamination from the surrounding conditions as laboratory, air, vehicles and water. Sometimes for greater reliability the samplers are often wrapped in aluminum foil, placed inside a plastic bag, and frozen (-4°C) until they are ready for deployment [5].

#### 4.2 Deployment

Different samplers required different deployment mechanism. PE and POM samplers can be deployed in the liquid environment on stainless steel wire loops thus maximizing the number of dissolved contaminates (see picture 2).



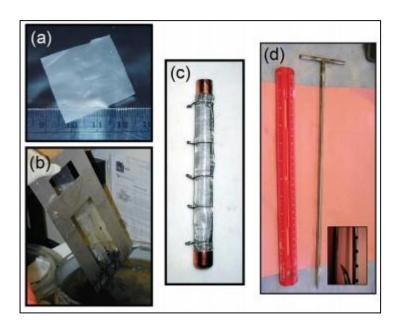
## PICTURE 2. Passive samplers designed for water column deployments: long strip of polyethylene on a stainless steel wire loop [12]

They can also be deployed in enclosures to avoid harmful environmental conditions and prevent subsequent sampler loss (see picture 3).



PICTURE 3. Passive samplers designed for water column deployments: polyethylene and polyoxymethylene strips fastened to the interior of a fish trap [8]

SPME can be rather fragile and should be actuate in a protective container which can be paneled with stainless steel or copper mesh envelopes or tubing (see picture 4).



PICTURE 4. Passive samplers designed for whole sediment deployments: (a) small piece of polyethylene, (b) polyethylene arrayed in a metal frame, (c) copper tubing holding SPME fibers, and (d) stainless steel tubing containing SPME fibers [2]

This option can enhance overall sensitivity of the analysis and interstitial water and surface water concentrations can be measured simultaneously to assess the gradient of contaminants between the sediment bed and the water column.

Passive samplers can with equal success be applied in both freshwater and saltwater systems, as uptake of sediment is the same regardless of the salinity except for once difference: the presence of the salt dissolved in seawater will make the colloidal organic carbon (COC) accumulate into the organic polymer more readily than in freshwater.

Samplers can also be used in *ex-situ* conditions where sediments collected in the field and delivered to the laboratory and samplers than added to the bioaccumulation and partitioning studies [13]. This type is often less expensive however it departs greatly from the natural conditions that reflect reality at contaminated sites [6]. Table 2 below lists factors to consider when choosing between *ex-situ* and *in-situ* approaches.

TABLE 2. Factors to consider when selecting between *ex-situ* and *in-situ* application [8]

Factor	Approach			
	Ex-situ	in-situ		
Ability to estimate equilibrium C <sub>6+4</sub>	Laboratory conditions can be controlled to better attain equilibrium.	Uncertainty can occur; need to use performance reference compounds (PRCs), multiple polymer thicknesses, or time series sampling to confirm equilibrium. Time series interpretation can be impacted by temporal changes in the field.		
	Comparison to independent confirmatory methods (e.g., air bridge) can be applied.			
Spatial scale (e.g., to differentiate between biologically active zones and underlying sediments or contaminant migration through a cap)	Sediments are frequently composited and/or homogenized to avoid concentration variability caused by vertical and horizontal spatial heterogeneity.	Fine-scale spatial (vertical and horizontal) patchiness in concentrations can be measured (e.g., identify gradients).		
	Coring followed by passive sampling in intact cores can maintain spatial characteristics if not influenced dramatically by site dynamics.	Best approach to capture field conditions.		
Contaminant depletion	Mixing (e.g., tumbling of sample) during equilibration period is used to limit localized depletion.	Confaminant depletion may occur in the zone around samplers; use of multiple polymer thicknesses or time series analysis may be used to evaluate depletion.		
Statistical design	Multiple treatments and replication are possible; hypothesis testing can be performed.	Multiple treatments, replication, and hypothesis testing are possible, but logistically challenging and expensive.		
Ease of experimentation	Experiments are simpler to perform under laboratory conditions.	Expense, achieving experimental and statistical design goals, safety concerns, weather, adverse site conditions, and vandalism.		
Ability to capture field conditions (e.g., currents, tidal cycles, groundwater intrusion, sediment-water column fluxes, bioturbation, temperature and salinity change)	Laboratory conditions are frequently standardized, but can be altered to attempt to replicate some field conditions.	Best approach for capturing field conditions.		

#### 4.3 Recovering and storing

After the deployment step which usually lasts for 28 days, the sampler are recovered typically with laboratory tissues to ensure removal of site water, sediments and any biological growth. If the samplers retain a film of residual sediment or biological growth, they should be rinsed with clean water for about a minute or wiped with a damp laboratory tissue to remove as much remaining material as possible without damaging the samplers [14]. And final step here as in the first stage is wrapping in aluminum foil and storing in an ice-filled cooler for a short period of time before delivering back to the laboratory the next analysis.

#### 5. APPLICATION OF PASSIVE SAMPLERS

Even though passive sampling is relatively young approach for organic and inorganic pollutants evaluation, it has already been used in gaseous, aqueous and soil environments. See Figure 5 for summarized milestones in passive techniques development.

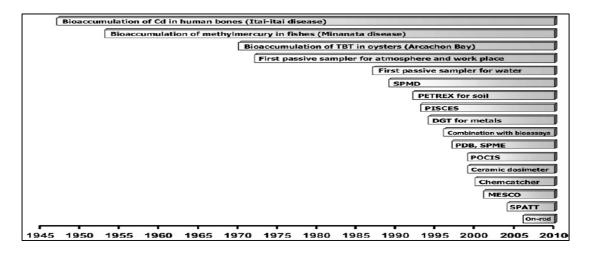


FIGURE 5. Milestones in the passive techniques development from different compartments [3, p.143]

As may be concluded first recognition passive devices had received in the early 1950s and already in that time they receive public recognition as an effective tool in

environmental research. Nowadays passive samplers utilized in a versatile fields of study included at least the following:

- a) monitoring of pollutants;
- b) determination of tendencies in levels of waterborne, airborne and soil-borne pollutants [2];
- monitoring spatial contaminant distribution and tracing point and diffusive pollution sources;
- d) assessing distribution of pollutants between environmental compartments;
- e) evaluation TWA concentrations of waterborne, airborne and soil-borne pollutants;
- f) comparing contaminant patterns in biota and passive samplers biomimetic sampling to estimate organism exposure [5].

#### 5.1 In gaseous medium

Until this moment, wide acceptance of passive technologies was mostly recognized for gaseous medium as indoor air, air at the workplaces and in the atmosphere air quality monitoring. Particularly this type has called *passive dosimetry*. This term somewhat highlights distinctions between this passive approach and dynamic one. Though both techniques are based on absorption or adsorption of analytes in/on the trap, and passive sampling is on the *free* flow (according to Fick's first law of diffusion) of analyte molecules from the sampler to a collecting medium. Driving force for diffusion here is difference of chemical potential of analytes of sampled and collected medium. [3]

In this compartment, passive devices are mostly used for persistent organic pollutants (POPs) measuring, which are organic compounds resistant to environmental degradation. Potential uses include also monitoring of regulatory compliance and identification of potential pollution sources; cheap and efficient reconnaissance surveys of the spatial distribution of gases, VOCs and POPs; investigation of the environmental processes affecting VOCs and POPs cycling [3]. In recent years, measurement are recommended to be produce in the form of maps generated based on the point measurements at large scales. This option not only allows prediction of the values and application in further mathematical analysis but

also more importantly contributes to the cost reduction of environmental quality investigations. The applicability of known passive samplers for air monitoring assembled in the summery table in attachment 1.

#### 5.2 In liquid medium

Comparing development of passive devices for air and water monitoring, last type has significantly fell down substantially due to research limitations as well as a lack of information in the scientific and commercial communities. Howether for known advantages these devices have a lot of potential to become robust, reliable and cost-effective tool around the world and already now being considered as a part of an emerging strategy for monitoring a range of priority pollutants and assessing of time-weighted average (TWA) concentrations. Moreover, passive devices has recently been widely used for groundwater sampling especially in point of long term monitoring (LTM). In this case groundwater being sampled within a screened interval of a permanent monitoring well without pumping or purging. Passive samplers devices that have been utilized in this field can be distinguish into following groups:

1) **Equilibrium samplers** - devices that establish an equilibrium with the groundwater.

Most common here are PDB sampler and Regenerated Cellulose Dialysis Membrane (RCDM) samplers (see picture 5). However they can identify relatively limited number of pollutants such as VOCs, polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs).



## PICTURE 5. Regenerated Cellulose Dialysis Membrane Equilibrium Sampler [29]

2) **Sorptive samplers** - devices that accumulate analytes from groundwater over time.

Samplers in this group rely on sorption of organic compounds to a matrix during the exposure period to accumulate a measurable mass [25]. Widely used sampler is GORE Module now referred to as AGI Universal Sampler (see picture 6).



PICTURE 6. AGI Universal Sampler – A Sorptive Sampler [25]

3) **Grab samplers** - devices that collect water samples at a specific depth and time

Passive grab samplers are pre-deployed devices that are activated in place to directly obtain depth and time-specific samples from monitoring wells [15]. Devices here are HydraSleeve and SNAP sampler (see picture 7).



PICTURE 7. Deployment of the Snap Sampler [15]

Passive devices in liquid medium operate in kinetic and equilibrium regimes follow first one-compartment model shown in the figure below.

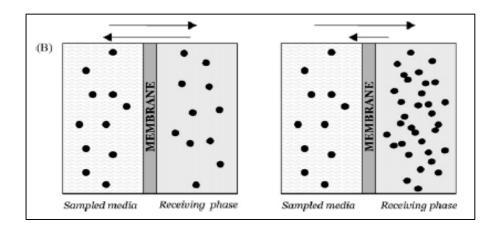


FIGURE 6. Graphical presentation of equilibrium and non-equilibrium passive sampler [2]

These regimes, being the most common among the operation of passive devices, describe how kinetics exchange between the samplers and the receiving phase. See attachment 2 for the matrix summery table of passive samplers applicable for water monitoring.

#### 5.3 In sediments and soil

Terrestrial investigations by passive samplers also recognized as relatively new. Typically, it involves the assemblage of vaporous recreating in soil. The vapours are composed of air, water vapour, naturally occurring organic compounds, human-inducted organic compounds, organic compounds migrating from deep fossil fuel reserves, and other constituents capable of partitioning from liquid and soil materials into the vapour phase under ambient conditions. In effect, reliability of the obtained results is ensured. See Table 3 below for applications of selected types of passive samplers for sampling of different types of contaminants present in soils.

TABLE 3. General information on the use of passive samplers in studies of soil and sediments pollutants [8]

Type of passive unit	Element of soil	Type of analytes	
		Chlorinated and aromatic	
PETREX® sampling	Sandy bottom	hydrocarbons vapours, Volatile	
tubes	sediments Bottom	chlorooganics vapour	
	sediments	(trichloroethene, tetrachloroethene,	
		dichloroethene)	
GORE SORBER®	Soil vapours	BTEX, PAH's, TPH	
DGT device (diffusive	Pore water, soils	Cd, Zn, Ni, Fe, Sn, Pb, Al, Cr, Mn,	
gradients in Thin films)	Tore water, sons	Co, Cu, As; P (availability)	
Adsorbent tubes	Soils air	Chloroform, tetrachloro-methane,	
Ausorbent tubes	Sons an	1,1,1-trichloroethane	
Passive sampling			
devices according to Soil		Bioavailability of explosive	
Awata. C18 placed into	3011	metabolites (MNX and TNX)	
PE bag			
SPME	Sediment	Hydrophobic organic contaminants	
SI IVIL	porewater	Trydrophobic organic containmants	
SPMD	Sediment	PAH's, PCB	

Compared to the conventional methods passive technologies with regard to the soil investigation are less sensitive to changes in ambient conditions, capable of detecting volatile and semi volatile compounds and do not disturb the natural equilibrium of the vaporous in the subsurface. Named advantages can provide profound and rigorous research. However, the interpretation of results obtained with the use of passive dosimetry at the analyte collection stage from soil and sediment

samples requires conducting further studies in strictly defined (modeled) conditions [5].

#### 6. ACCURACY OF THE RESULTS

There are great number of factors that could cast doubt on the exactitude of the sample and in many ways alter performance of passive sampling. This may include changing weather conditions, presence of water, time events, and so forth.

There are two precautionary measures possible to apply during the sampling campaign to avoid false interpretation:

- 1) Ensure sample state is met objective requirements. This could be due to the unexpected presence of free phase when the intention is to analyze dissolved phases, the significant presence of suspended matter, etc. Turbid samples must always be considered as dubious. [9]
- 2) Respect all factors affecting sampling process. Since decision whether to apply sample or reject it may be very fragile, documentation of all deviations occurred is required. This may include equipment decontamination, accession of additional agents and reagents, period, and so on.

Apart from such factors as simplicity, safety, device composition and convenience to users, through-out design of the sampler can noticeably increase accuracy of the results. For instance, if sampler filled with organics, biofouling can be reduced by slower seeping out of organic liquid through the membrane. Diffusion process simply described as trapping of chemicals in the devices and partitioning of them between the receiving and external environment phases can also be modified due to design characteristics. For example, in order to increase sensitivity, a sampler design should hive higher A/L ratio, where A is the area and L is the length of the sampler. At that point, tube type samplers are less sensitive compared to badge type samplers therefore most devices are configured in latter type. [14] Regardless to the design, almost any sampler has a barrier between phases, which helps to identify the sampling rate. Some barriers have defined openings resulting into diffusion-based samplers. Others have the

barrier in the form of a non porous membrane, referred to as permeation-based samplers [1].

#### 6.1 Calibration of the passive samplers

It is a known fact that the major purpose of every research is to give precise and true picture of the investigate object. In case of passive sampling, it is an actual conditions and composition of studied environmental area. In this regard, good precision (<5%) can be obtain if samplers are calibrated in the laboratory rather than in the field. For example, in the review of the passive sampling devices made by L. Chimuka et al. 2005, was noted that the average percentage relative standard deviations for aquatic passive samplers ranged from 10%-32%. However, calibration process itself may take a lot of time even though it is not so complicated. In order to calibrate the passive sampler, user just have to build an appropriate exposure system with constant temperature conditions and water flow in the calibration system.

#### 6.2 Environmental factors affecting sampling

Even though, as mentioned previously, calibration and bioassays conducted together with passive sampling can bring a lot of benefit in determination of maximally precise results, there is still a room for optimization. Environment factors may bring beneficial effects for the passive sampling procedure as well as cause difficulties for result interpretation. For example, if face velocities less than 25 ft/min and air is stagnant, it can significantly reduce the sampling rate and conversely high air velocity may result in poor diffusion in samplers. Uptake of chemicals also depends on temperature and flow conditions. In this case, compared diffusion of lower temperatures indicated lower sampling rates and higher temperature contrariwise higher rate. To avoid such deviation, laboratory optimization has to be done to bring temperature closer to real environmental conditions. Moreover, humidity rate and excessive concentration of the compounds may result in lower capability of the sampler to adsorb or retain contaminant for further analysis. [13] Even hydrophobicity can alter the results significantly.

#### 6.3 Other factors affecting sampling

Apart from environmental issues, timing can also adversely influence the results. For instance, for one substances less time is required than for another to accumulate. In contrast with slowly accumulating substances, those that amass relatively faster the overall toxicity will tend to be underestimated in passive sampling extract, even if both mixtures would be equally toxic to aquatic organisms. [12] In this respect, user should follow all the instructions for application issued by the supplier whereby sampler devices would not be overload and accuracy of laboratory analysis will be more accurate.

In some cases, environmental factor as turbulence can be mixed together with such characteristic as sampler material. For example, it was studied that for membrane based passive samplers, permeation of compounds through the membrane is seen as the rate-limiting step and is more pronounced for polar compounds (logKow < 2, where logKow is the log of the octanol-water partition coefficient) (membrane/permeation controlled samplers). At high turbulence, the uptake rates for such compounds are reduced. On the other hand, for non-polar compounds (log-Kow >3), diffusion through the unstirred layer and sampler controls the mass transfer (donor/diffusional controlled). [14] To avoid such discrepancy, sampler could be enclosed in a container, which act as shelter and reduce the effects of turbulence.

#### 7. QUALITY CONTROL AND ASSURANCE

To ensure accuracy of the results and meet of sampling research objectives, quality control program (QC) have to be conducted. Typically, it consists of several steps adjusted to particular project and analytic procedures involved to identify whether the results are consistent with the purpose and. This quality program also complement by quality assurance procedure (QA) to guarantee representative and precise data, which has to be obtained in accordance with application instructions.

#### 7.1 Quality control

Application of proper QC measures is a compulsory step in both sampler deployment and subsequent laboratory analysis.

In the field, technical steps to ensure control of qualitative sampling materials are being implemented. Commonly these steps include blank preparation (fabrication, process, reagent, field and sampler spikes), cleaning procedure of the devices, proper transportation, consideration of possible risks, retrieval of documents and storage. In some campaigns, field duplicates may be an essential step as well. However, since only few methods, other than passive samplers, can truly measure dissolved contaminant fractions, accuracy and comparison of the results may be difficult. [1] At least 10-15% of duplicates samples can increase the precision of the results especially if analyze the same data in different laboratories. In this case, comparable and meaningful methods in all laboratories are required. In many situations, additional elements can be added for control. Quality control may be visualize in the program with several steps (figure 7).

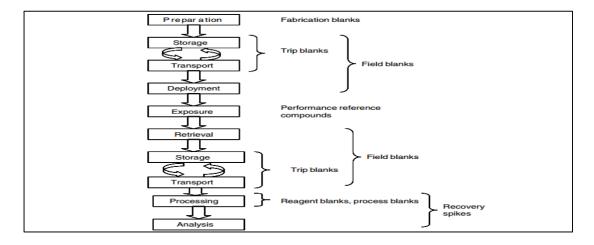


FIGURE 7. QC samples involved in passive sampling [9]

Quality program in the laboratory analysis includes use and analysis itself of those procedure blanks, field blanks and others prepared the stage before. When all received data collected, it compiled and interpret for presentation.

#### 7.2 Quality assurance

Quality assurance is a set of operating principles that, if properly applied, will obtain data of known and justifiable quality. [9] It has to be conducted both in the field and laboratory stages as well.

In the first stage, the principle of quality assurance should govern the following elements in particular:

- -planning the campaign;
- -following recommendations and procedures for the choice of sampling methods and the equipment needed to collect, conserve and transport samples;
- -following recommendations and procedures when collecting samples and performing field measurements;
- -documenting the work in sufficient detail to verify whether the points cited above were carried out according to the procedures in application. [5]

Primary requirement in the laboratory analysis is to perform analysis in accredited and qualified laboratory in accordance with quality assurance program. This can be done either by international standardization such as ISO/IEC 17025 or by regional accreditation body. More reliability can be added if accredited body certified by independent organization.

#### 8. LIMITATIONS FOR WIDE ACCEPTANCE

Despite its relatively long history, passive sampling is still developing and so far gain a great number of advantages as applicability for spatially resolved data collection and identification of the sources of contamination. Moreover, these technologies conduct more meaningful and accurate results than any other technologies. Nevertheless, they have a number of limitations to fully penetrate into the market of sampling devices and broader regulatory acceptance would be required.

#### 8.1 Standardization and legislation

Steps have been taken to assess and ensure the applicability and quality of data produced by passive samplers, including the publication of the British Standards Institute's (BSI) standard method Determination of priority pollutants in surface water using passive sampling (BSI PAS 61:2006) and Water quality - Sampling - Part 23: Guidance on passive sampling in surface waters (ISO 5667-23 : 2011) [8]. Further efforts are have to be done, however, if passive samplers are to become a standard inventory in the toolbox for regulatory monitoring.

Some problems may also occur when incorporating passive sampling methods into the legislation framework and establishing guidelines values.

#### 8.2 Scientific problems

Fist problem is to identify correctly, when equilibrium between the dissolved phase and the sampler is archived by the contaminants. This issue may seems minor and one may think that current technologies are already available to do that with great success. Unfortunately, this is only half the truth as the need to understand better how and when equilibrium occurs still remains vital. In addition, alternative options is required also for evaluating concentration data when equilibrium does not occur.

A second scientific challenge deals with interpreting the meaning of resulting contaminants. In this respect additional laboratory, research has to be provided. In some way it can be resulted in a statistically robust but simple linear model that predicts organism bioaccumulation based on knowing how much e.g. COC contaminants accumulated in a passive sampler [8]. And, finally, there is a clear need for standard set development of passive sampler-dissolved phase partition coefficients (Kps-d) for a range of passive samplers. However last one is not so much a problem but a complementary task to compile a scientifically sound values that can be used universally and consistently by the entire passive sampling community.

#### 9 FUTURE TENDENCIES

Based on latest development in sampling and monitoring technologies, several trends can be applied to existing passive sampling methods to increase overall efficiency.

It was already noted that mapping seems very promising tool, especially in air monitoring, both indoor and outdoor. Space visualization of analyte concentration distribution in the form of maps of pollution levels presents a valuable source of information nowadays. See Attachment 3 for samplers applicable for pollutants mapping.

Another promising option is to combine several samplers together to cover broader spectrum of analytes. For example the use of SPMD and POCIS as combined samplers allows for the concentration of waterborne hydrophobic and hydrophilic organic contaminants a somewhat provide a base for holistic approach for the assessment of anthropogenic stressors in aquatic systems. [20] Different suites of integrative samplers e.g. the stabilized liquid membrane device (SLMD) and the polar organic chemical integrative sampler (POCIS), provide a means to sequester and concentrate a broad spectrum of waterborne contaminants present as complex mixtures in aquatic ecosystems and enable assessment of an organism's exposure and the potential consequences. [22]

Other powerful option is to conjoin traditional chemical analysis with bioassays. It is not only deliver accurate and reproducible data but provide users with information concerning the relative toxicological significance of contaminants. Assays that have been used to assess SPMD extracts or diluents include the following: Microtox®, Mutatox®, mixed-function oxygenase induction-ethoxyresorufin-o-deethylase (EROD) activity, sister chromatid exchange, vitellogenin induction via interperitoneal injection of test species, enzyme-linked immunosorbent assay, and Ames mutagenicity test. [22] Moreover, the integration of passive air sampling with genotoxicological analysis may provide an effective tool for air monitoring on various scales, and for the screening of the genotoxic potential of ambient air samples, which can be further applied for exposure assessment as part of a human health risk assessment. [15]

Finally, latest trend in passive sampling technologies is directed towards miniaturization of the devices, which therefore decreases transportation costs to and from the sampling site, and lowers consumption of solvents during sampling treatment. What is more, standard passive samplers like SPMD devices can be combined together with modern

sample preparation techniques, such as microwave assisted extraction (MAE) or accelerated solvent extraction (ASE) which altogether lead towards "green" chemistry.

#### 10 CONCLUSION

After five months working on this thesis, it is a great satisfaction to deepen my knowledge in such promising up-and coming passive sampling technologies. As far as my research is concerned, several unexpectedly advantageous features of those technologies have been found. They are relative simple and convenient for users, do not require a lot of laboratory costs as well as complicated and inconvenient equipment, could enable frequent screening and time-weighted average concentrations, do not required electricity and provide more accurate and reliable information than any other technologies available. All these characteristics make them very attractive for researchers as an alternative for traditional more established technologies. However, much development of efficient Quality Assurance, Quality Control and method-validation schemes is necessary to obtain broader acceptance for deployment. Several limitations inherent to this technologies should be controlled and reduced where possible likewise. Especially environmental conditions such as water turbulence, air humidity, wind velocity and temperature as they are too difficult to overcome.

The long-term aim of using these technologies for in situ monitoring in the marine environment is even further away. Even though many devices have been developed to proof concept of prototype stage, the development work to convert these into robust and validate instrument that can be deployed for prolonged periods has not been undertaken. As for air and soil monitoring, due to its comparatively long usage period they has already gained a general recognition among users.

Overall, it is clear that the full potential of passive sampling techniques is not yet fully realised. Hopefully, this will change in the not-too distant future.

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# ATTACHMENT 1: Passive sampling devices applicable for air monitoring

Passive sampler		Type of monitored air	Type of analytes	Deployment remarks	Sample Volume	Limitations	Approxi mate commerci al costs	Link to user guide
		Indoor air	Benzene, 1,3-butadiene, Aldehydes	From 1 to 7 days exposure time,				
			Benzene, Volatile organic compounds, toluene, etylobenzene, xylene	2 and 6 days exposure time			commerci	
Radiello diffusive sampler	liffusive	Ambient air	1,3-Butadiene, 2-Butanone, tetrachloroethylene, xylene dimethyldisulfide, benzoic acid b-pinene, limonene, phenol, benzene, toluene	From 1day to 1 week exposure time, From 2 to 8h exposure time	packed with a desorbent with a time, T,	effect of time, T, RH on uptake rate		http://www.sig maaldrich.com/ analytical- chromatograph y/air- monitoring/radi ello/learning- center/applicati
			Ozone	8h exposure time; the distribution represented using the SURFER program (Kriging method–Linera Variogram Model)				ons.html
		Indoor air	VOC, Benzene, toluene, xylene	4 weeks to 2 days exposure time				http://www.skc
Group of SKC samplers	Ambient Air Volatile compoundioxide  Personal Personal etyloben		Volatile organic compounds, nitrogen	3 days weekend to 1 month exposure time	>300 mg of sorbent	low 2 ppb limit of detection for	Uncertain price	inc.com/catalo g/index.php?cP ath=200000000 _203000000_2
		Benzene, toluene, etylobenzene, xylene, VOC, Ethylene oxide	Around 30 min exposure time to 18 days exposure time		sampling pri formaldehyde	price	03000150_203 000151	

	Workplace exposure	2-Methoxyethanol, 1,3-Butadien, 1,3-Butadien, styrene, N,N-Dimethylformamide, methyl ethyl ketone, toluene	The work-shift exposure time, 8h exposure time, 1 day exposure time				
Perkin-	Ambient air	1,3-Butadiene, benzene, toluene, etylobenzene, xylene, VOC	From 1 to 14 days exposure time	packed with	preferred for low concentration		http://www.per
Elmer tubes	Personal Exposure	Benzene	2 days exposure time	approximately 200 mg of Tenax TA with surface area of 35 m2 g-1	levels because of its very high analytical sensitivity	20 \$ each, reusable	kinelmer.com/p roducts/default. xhtml
Gabie sampler (badge type)	Worplace exposure	n-Butanol, isobutanol, toluene, m-xylene, etylobenzene, methylisobutyloketonr, methylethylketone, ethyl acetate, butyl acetate	7h exposure time	Badge has a geometric diffusion surface of 7 cm2 and contains 550 mg ofcoconut charcoal sorbent		576.00 EUR	
XAD-2 filled	Ambient air	Persistent organic pollutants	From 1 to 12 months exposure time	resin-filled container (long thin of stainless steel mesh)		\$185-285 each including analysis	
	Ambient air	Carbon dioxide	From 1 to 6 weeks exposure time	consist of glass vials filled with a	Polymer coating is		
Solid Phase Microext ractio Sampler (SPME)	Personal exposure	Ethylene oxide	30 min for three successive days	hydroalcoholic solution. A plastic screw-cap, perforated in the centre, retains a vertically inserted, glass tube, which passes through the cap and provides a suitable diffusive path length and surface.	fragile, easily broken, and have limited lifetime, reduced concentration capability due to the small volume of polymer coating	35.10 EUR, 126 EUR, 235 EUR	http://www.sig maaldrich.com/ analytical- chromatograph y/analytical- products.html? TablePage=964 4862

	Indoor air	Polychlorinated biphenyls	0, 4, 24, 48, 72, 120, 168, 336 and 504h exposure time	consist of a thin film	Detection		
Polymer- coated glass (POG) sampler	Ambient air	Polychlorinated biphenyls, polycyclic aromatic hydrocarbons, polychlorinated napthalenes, polybrominated diphenyl ethers, polycyclic aromatic hydrocarbons	7 days exposure times; mapping pollutants	of ethylene vinyl acetate coated onto the inside and outside surfaces of a hollow glass cylinder	Detection limits, sensitivity to nature conditions		
Personal air allergen sampler (PAAS)	Personal exposure	Airbone coarse particle - aeroallergens	From 6h to 6 days exposure time	consists of two planetary rings in which a substrate holder can rotate in all directions; $5 \times 4 \times 4$ cm; $\sim 50$ g		\$49 to \$69 per sample	

### **Explanation of Table Categories:**

Passive Sampler: Abbreviated identifier of the technology

Type of air: Lists all gaseous medium that can be sampled by the technology

Common Analytes: Generalized list of common analytes for which the technology is appropriate

Deployment remarks: Identifies major deployment issues, if any and structure of the device

**Sample Volume:** Range of sample volumes a typical sampler would collect.

Limitations: Primary limitations of the technology, specifics listed in document section

**Cost:** Range of approximate price scale

Link: To primary contact or vendor of the technology if known

**ATTACHMENT 2: Passive sampling devices applicable for water monitoring** 

Passive sampler	Type of sampling environ ment	Type of analytes	Deployment remarks	Sample Volume	Limitations	Approximat e commercial costs	Link to user 49 guide
Semiper meable membra ne devices (SPMD)	Air, water, sediment , wastewa ter	PAHs, PCBs, organotin compounds	Up to several months exposure time; Accumulate mass by diffusion and sorption; Exposure to sunlight should be minimized to prevent photolysis of certain analytes	A typical 1-mL triolein SPMD (5-mL volume) will extract from as much as 5 to 160 liters (water) or cubic meters (air) after a 30-day Exposure, Weight of standard SPMD: 4.4–4.6 g; Triolein: 99% purity (1.0mL used for standard 91.4cm length)	Exposed SPMDs require processing and cleanup prior to analysis. Biofouling (water) may occur with extended exposures, but corrections for reduction in sampling rates can be made	~\$100, includes analyte recovery from the device	http://www.ce rc.usgs.gov/
Ceramic dosimete r	Ground waterriv ers, lakes, wastewa ter sewers	Polycyclic aromatic hydrocarbons (PAHs) volatile aromatic compounds, volatile chlorinated hydrocarbons	The contaminants accumulate by diffusing from the contact water through the membrane into the adsorbent bed. They accumulate with time, depending on the concentration gradient and the effective coefficient of mass transfer across the membrane	Made of a ceramic membrane (outer layer) and adsorbent material; filled ceramic tubes are fixed in stainless steel holders of 6 cm length; the receiving phase: Amberlite IRA-743; membrane thickness 0.15 cm; surface area (tube length: 5 cm; tube diameter: 1 cm) is 8.5cm2	Low sensitivity	~ 340.00\$	http://www.a mazon.com/re f=nav logo
Chemcat cher (passive sampler using Empore disk)		Polar or nonpolar organics, some persistent organic pollutants (POPs): organochlorine pesticides, PCBs, PAHs	Accumulation rates and selectivity are regulated by the choice of both the diffusion-limiting membrane and the solid-phase receiving material; 14 days to 1 month exposure time	Uses a diffusion-limiting membrane and a bound, solid-phase receiving phase; A diffusion-limiting membrane and the solid-phase receiving material are supported and sealed in place by inert plastic housing	Calibration is the must		http://www.pe rkinelmer.co m/products/de fault.xhtml
Diffusive gradients in thin film sampler (DGT)	Natural waters (fresh water, deep sea water,	The content of trace metals (Cd, Ca, Mg, Zn, Mn)	Is the establishment of a constant concentration gradient in the diffusive layer that forms the basis for quantitively measuring metal concentration in a	The whole sampler is made from plastic and consists of three layers. The first one (a filter membrane) consist of a resin-impregnated gel layer (metal-binding	Problems with measurements when the sample is very diluted (an ionic strength less than 0,2mmoll-1)	£12.50 each- £68.00 each	http://www.dg tresearch.com /WebProducts .aspx?CATID =HOM

			14:	1 A -1		
	rivers,		solution without the need for	layer). A plastic outer-sleeve		
	lakes,		separate calibration	is placed over the base in		
	estuaries			order to secure the layers, to		
	)			maintain an even surface, and		
				to inhibit water ingress into		
				the resin-gel; The content of		
				trace metals (Cd, Ca, Mg, Zn,		
				Mn); Natural waters (fresh		
				water, deep sea water, rivers,		
				lakes, estuaries) The resin-		
				layer is overlain by a		
				diffusive layer of hydrogen		
				and a filter. Ions have to		
				diffuse through the filter and		
				the diffusive layer to reach		
				the resin layer		
				The selectivity of the		
				MESCO extraction		
				technique is enhanced in two		
Manulan			The complete of the	ways		
Membra			The sampler consists of a	(1) The dissolved molecules		
ne-		Pesticides,	hydrophobic solid receiving	become separated from	Degradation of the	
enclosed		PCBs, PAHs,	phase enclosed in a water	colloids during their	membrane,	
sorptive		selected	filled hydrophilic	diffusion across the	Biofouling, Sampler	
coating		POPs	semipermeable membrane; 1	dialysis membrane	must be kept wet	
(MESCO			day to several weeks	(2) Hydrophobic target	•	
) sampler			exposure time	analytes are selectively		
				extracted from the inner		
				aqueous solution by the		
				PDMS sorbent coating		

Polar Organic Chemical Integrati ve Sampler (POCIS)	Wasterw ater effluents , fresh and salt water	Pesticides, phenoxyacids, pharmaceuticals , sulfa drugs antibiotics, tetracycline—antibiotics, methamphetami ne, MDMA (Ecstasy) estradiols and estrone, estriol, alkylphenols benzophenone, caffeine, actibacterial and actifungal agents, organic waster water originated contaminants	Diffusion of the substances through a membrane. Contaminated water penetrates the membrane and infiltrates the sequestration polymers which sorb and immobilize water-soluble compounds. Chemicals are thereby cumulatively collected in the sorption medium and the method is less sensitive to variations in the water since sampling continues over a long period of time	Constructed of two 130  m thick by 47mm diameter hydrophilic polyethersulfone membranes (0.1  mpore size). The membranes enclose resin/adsorbent admix which serves as sequestering medium and consisting of 80mg of solute ENV+ and 20mg of Biobeads S-X3 with surface dispersed powdered Ambersorb 1500 carbon or 100mg of Oasis HLB resin alone. The total surface area corresponding to the 47mm interior diameter (i.d.) is 18cm2	For accurate concentrations to be calculated, calibration studies need to be conducted on the analytes of interest; Field samples require special processing prior to laboratory analysis	Reusable disk is holder is about \$60. Membranes orbentm disk for chemical sequestratio n is disposable	http://www.es t-lab.com/
Peeper Sampler	Personal exposure	Pure water concentration	Equilibrium concentration by diffusion	Typically 1-20 mL	Small sample volume; Analytes are specific to the Membrane material	Peeper Plate consisting of membrane and skeleton is approx. \$312 pre sampler Cost Uncertain for PsMS	http://www.ri ckly.com/

## ATTACHMENT 3: Passive sampling devices applicable for pollutants mapping

Type of passive	Type of	Type on analytes	Remarks
sampler	monitored air	Type on analytes	Kemarks
Radiello diffusive sampler	Ambient air	Benzene	1 day exposure time, mapping pollutants with geostatic computer program ISATIS
ORSA-type sampler	Ambient air	Benzene, toluene, xylene	15 day exposure time, mapping pollutants
Perkin-Elmer tubes	Ambient air	VOC	2 weeks exposure time; contour maps were developed to illustrate the spatial distribution of the different variables, using the kriging method
Shibata glass-tube sampler	Ambient air	VOC	1 day exposure time; mapping pollutants
Palmes diffusion tube	Indoor air	NO2	7 days exposure time; the locations of all the sites were plotted on a TNRIS base map of El Paso using ArcView 8.1 GIS software (ESRI)
The PAS*	Ambient air	Polychlorinated biphenyls ethers, polybrominated biphenyl ethers	1 year exposure time; mapping pollutants
Puf sampler	Ambient air	Polychlorinated biphenyls, organochlorine pesticides, polycyclic aromatic hydrocarbons	Selected data was processed using the geographic information system (ArcView 3.2, ESERI); the geostatistical gridding kriging method was used to produce maps;
Polymer-coated glass (POG) sampler	Indoor air	Polychlorinated biphenyls, polycyclic aromatic hydrocarbons, polychlorinated napthalenes, polybrominated diphenyl ethers, polycyclic aromatic hydrocarbons	7 days exposure times; mapping pollutants
Badge type passive sampler developed by IVL (Institute f or Vatten-och Luftv ° adsforskining	Ambient air	Sulfur trioxide, ozone, ammonia	1 month exposure time; mapping pollutants

<sup>\*</sup> The PAS consists of a resin-filled container placed in a protective sampling shelter with an opening at the bottom. The sampling container is a long thin cylinder made of a fine stainless steel mesh held in shape by two end caps The entire cylinder is filled with XAD-2 resin as the sampling medium.