

## CERAMIC DOSIMETERS FOR TIME-INTEGRATED CONTAMINANT MONITORING

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### ABSTRACT

Sampling with ceramic dosimeters (passive samplers, patent pending) is a new method which was developed for long-term, time-integrated monitoring of organic pollutants in groundwater and surface water. This new sampling method reduces the number of necessary analyses to only a few and avoids artifacts during sampling, transportation, or storage of a water sample while monitoring the contaminant concentrations (representative mean values) over the entire sampling period. This concept of time-integrated concentration measurements can be used equally for contaminant monitoring in groundwater as well as in rivers, lakes, wastewater, etc. The dosimeter consists of a ceramic tube containing a suitable adsorbent. The porous ceramic membrane controls diffusive fluxes and therefore allows the calibration of the system. This method has been developed and tested for polycyclic aromatic hydrocarbons (PAH), volatile chlorinated hydrocarbons, and volatile aromatic compounds (BTEX), but can also be used for other organic and inorganic aqueous contaminants. During the monitoring period, the compounds accumulate in the adsorbent linearly with time and are solvent-extracted or thermo-desorbed for quantification.

### INTRODUCTION

The common sampling methods (*e.g.* pumped water samples) only detect the momentary concentration of contaminants in groundwater and surface water. In order to evaluate the contaminant concentration over a longer time period, all the variations have to be measured and their average must be found (Figure 1). When taking only a few water samples over a long time period, the values detected might only be short-term extreme values (too high or too low), which would then lead to significant interpretation errors. In addition, groundwater sampling with pumps leads to a change in the hydraulic flow field, which could cause a dilution of the contaminants. For highly volatile compounds such as BTEX, evaporation during the sampling procedure may lead to lower values in the water samples.

The main advantage of the new method presented in this paper is the time-integrated monitoring over the entire sampling period (possibly many months). This reduces the number of required analyses to only a few, avoids sources of error during sampling, transportation or storage of a water sample, and reduces costs.

The time-integrated monitoring of organic contaminant concentrations, *e.g.* in groundwater, is achieved by using dosimeters that are installed in sampling wells that continuously accumulate contaminants from the water onto a suitable adsorbent material. A ceramic membrane is used for the control of diffusive fluxes, allowing calibration of the system.

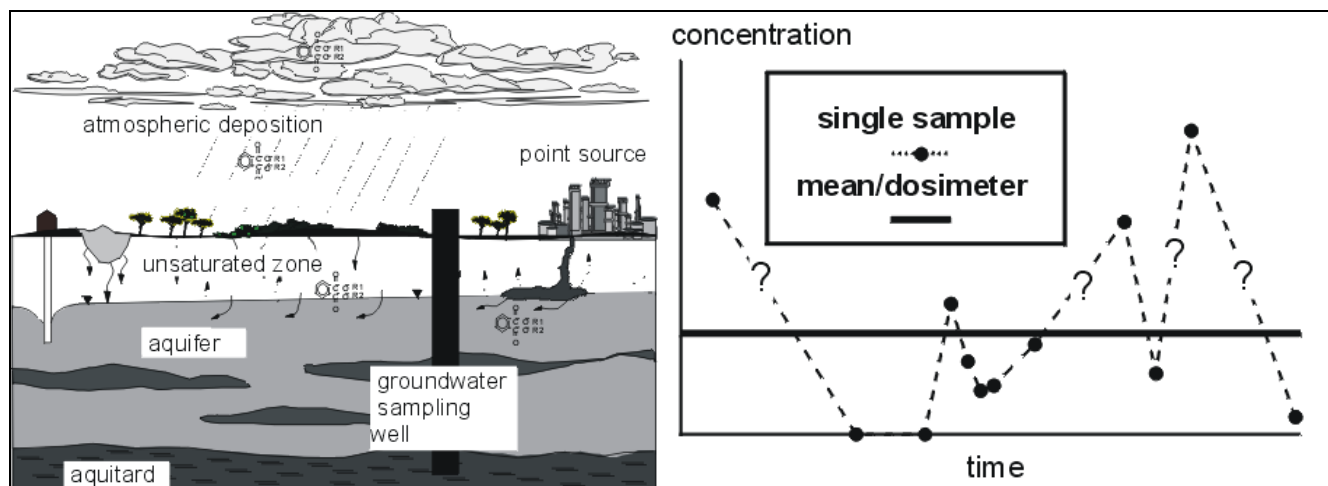


Figure 1. General scheme of the time-integrating sampling concept with a dosimeter (passive sampler) (Grathwohl and Schiedek, 1997).

Other researchers proposed passive samplers for the monitoring of surface water (DiGiano et al. 1988, Hofelt and Shea 1997). For example Lebo et al. (1995) used polyethylene membranes with triolein as adsorbent material. Gale (1998) developed a model describing the contaminant accumulation for this type of passive sampler. Mehlretter and Sorge (1995) proposed passive samplers for soil air monitoring. A system of multilevel sampling for ionic compounds in groundwater is already commercially available (Lobbe Inc.). In contrast to the ceramic dosimeter presented in this paper, all these methods rely on the equilibration of the aqueous concentration with the adsorbent material and therefore do not allow the time-integrated monitoring of contaminant concentrations over extended periods of time. They can only give information about the momentary contaminant concentration, whereas the new system determines the long-term average concentration.

#### DOSIMETER DESIGN

Dosimeters can be built according to different designs, e.g. using a water saturated or a dry adsorbent bed. In both cases, the contaminants accumulate by diffusing from the contact water through a membrane into the adsorbent bed. They accumulate with time, depending on the concentration gradient and the effective mass transfer coefficient across the membrane (diffusion coefficient/diffusion distance; see Figures 2 and 3).

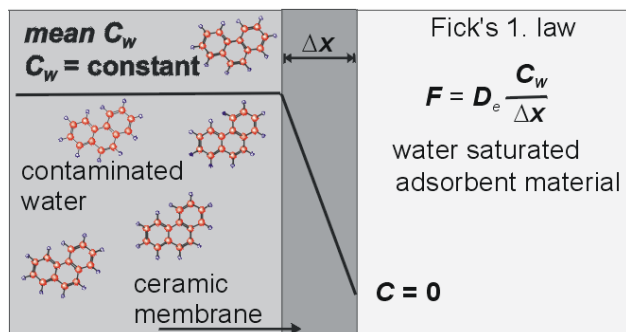


Figure 2. Concentration profile and fluxes in a dosimeter with water saturated adsorbent material.  $D_e$  denotes the effective diffusion coefficient in the porous ceramic membrane,  $t$  the contact time, and  $C_w$  the (mean) contaminant concentration in the contact water.  $F$  and  $\Delta x$  are the flux through the ceramic membrane and the diffusion distance (thickness of the membrane), respectively.

The most promising flux controlling membranes identified in this study were porous ceramic materials that are commercially available as discs or cylinders of different thicknesses, pore sizes, and porosities. These ceramic membranes allow high diffusive fluxes of the solute due to their high porosities. If necessary, they can be effectively impermeable to water due to very small pore sizes. A further advantage is that they are practically inert and do not accumulate organic solutes (which would lead to a time lag in solute uptake in the adsorbent bed).

Suitable adsorbents for organic compounds such as polycyclic aromatic hydrocarbons are ion-exchange resins (e.g. IRA-Amberlite). They are easily wetted by water and show high accumulation factors as well as recovery rates for hydrophobic organic compounds. For quantitative analysis the adsorbent is solvent-extracted after the desired sampling period. For volatile chlorinated hydrocarbons and BTEX, Tenax is a suitable adsorbent. In this case the adsorbent is thermo-desorbed and therefore should be dry. This is achieved by the use of ceramics with very small pore sizes.

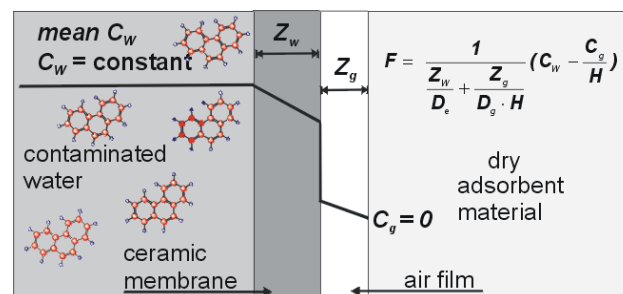


Figure 3. Double film for the flux of contaminants from water into a dosimeter with dry adsorbent material.  $C_w$  denotes the concentration in water.  $C_g$ , the concentration in air next to the adsorbent material, is kept close to zero.  $Z_w$  is the thickness of the water film (= the thickness of the ceramic membrane), and  $Z_g$  is the thickness of the air film. The organic compound shown here is phenanthrene.

The average contaminant concentration of the water which has been in contact with the dosimeter can be calculated from the accumulated mass of contaminants during the sampling period according to the following models.

During the monitoring period the contaminant diffusion through the membrane occurs at steady state and therefore is solely controlled by a water saturated membrane of thickness  $\Delta x$  (Fick's first law). The cumulative mass ( $M$ ) which has diffused through the membrane into the adsorbent bed can be calculated by equation 1:

$$M = F \cdot A \cdot t = D_e \cdot \frac{\Delta C}{\Delta x} \cdot A \cdot t \quad (1)$$

where  $F$ ,  $A$ ,  $t$ ,  $D_e$  denote the mass flux through the ceramic membrane [ $M \text{ t}^{-1} \text{ L}^{-2}$ ], the membrane surface area [ $\text{L}^2$ ], the sampling time [ $t$ ], and the effective diffusion coefficient, which is given by:  $D_e = D_w \cdot \varepsilon^m$ , where  $D_w$ ,  $\varepsilon$  and  $m$  denote the diffusion coefficient in water [ $\text{L}^2 \text{ t}^{-1}$ ], the porosity of the ceramic material and Archie's law exponent (approximately 2, obtained by the calibration), respectively.  $\Delta C/\Delta x$  is the concentration gradient.

If a dosimeter with dry adsorbent material is used, the contaminants (e.g. phenanthrene, BTEX, or volatile chlorinated hydrocarbons) first have to diffuse through the water saturated ceramic membrane and then through an air film into the adsorbent bed (Figure 3).

The steady state flux into the dosimeter is given by the double film diffusion model which leads to equation 2:

$$F = \frac{1}{\frac{Z_w}{D_e} + \frac{Z_g}{D_g}} \left( C_w - \frac{C_g}{H} \right) \quad (2)$$

where  $D_g$ ,  $C_w$ ,  $C_g$ ,  $H$  denote the diffusion coefficient in air [ $L^2 t^{-1}$ ], the concentration in water, the concentration in air next to the adsorbent material [ $M L^{-3}$ ], and Henry's law constant ( $H = C_g/C_w$ ), respectively.  $Z_w$  and  $Z_g$  are the thicknesses of the water saturated ceramic membrane [L] and the air film [L] (*i.e.* the effective distance between the adsorbent material and the ceramic membrane).

For the proper operation of either the dry or water saturated dosimeter, it is important to use an adsorbent material with a high sorption capacity in order to keep the concentration gradient at a maximum during the entire sampling period (thus guaranteeing linear uptake). In the ideal case, the accumulation of contaminants on the adsorbent material can be described with a partition coefficient ( $K_p$ ) independent of the concentration:

$$K_p = C_s/C_w \quad (3)$$

where  $C_s$  and  $C_w$  denote the adsorbed and aqueous concentrations. Usually  $K_p$  increases with decreasing water solubility of the compound.

For field applications in the subsurface environment, the dosimeters can be placed in a cage (Figure 4), which allows the groundwater to flow easily to the ceramic dosimeter even if they are placed in multilevel groundwater wells containing packer systems.

## EXPERIMENTAL RESULTS

### Calibration

In order to check the performance of the dosimeter in laboratory experiments, dosimeters were exposed to a saturated solution of phenanthrene in water for 13 different lengths of time; these time periods varied from two to more than 70 days. To prevent water flowing into the ceramic tubes of the dosimeters during immersion, the tubes were closed with a silicone plug at each end after being filled with adsorbent material. To ensure that the concentration of phenanthrene remained constant (solubility concentration) throughout the experimental period, excess phenanthrene was added to the solution, thereby providing an *in situ* reservoir of organic contaminant. After the dosimeters were removed from the "contaminated" water, phenanthrene was extracted with suitable solvents, such as acetone. The concentrations in the extracts were quantified based on internal standards and GC-MS analysis. The solute masses recovered from the water saturated adsorbent material of the dosimeters are presented in Figure 5 as a function of time of exposure of the dosimeter to the contaminated water. Samples were taken in triplicate to check reproducibility.

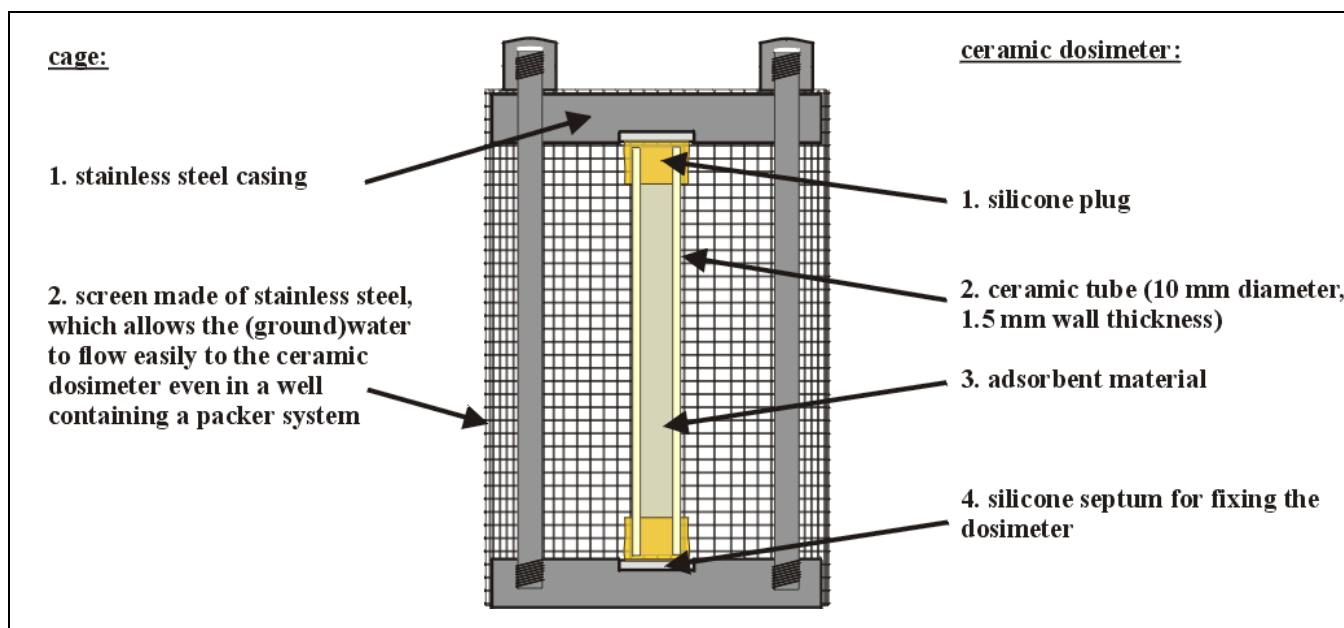


Figure 4. Cross-section of a ceramic dosimeter for groundwater monitoring.

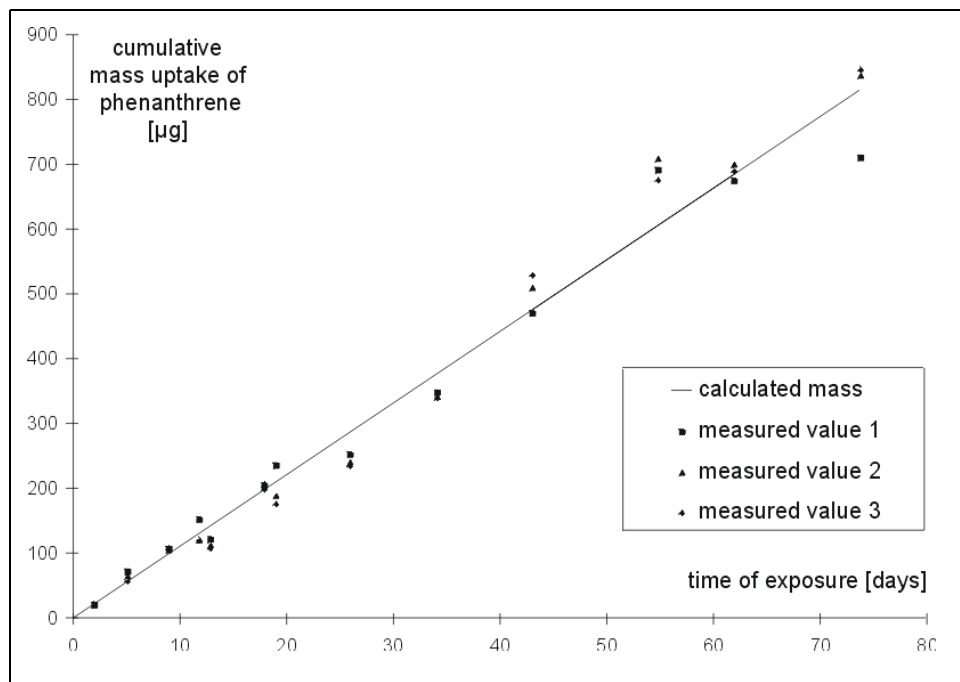


Figure 5. Linear uptake of phenanthrene in a porous ceramic tube with water saturated adsorbent material (10 cm length, 100 nm pore size) measured over more than 70 days. The solid line represents the calculated cumulative uptake following equation 1 ( $\epsilon = 31.9\%$ ;  $m = 1.56$ ;  $D_e = 1.12 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ;  $\Delta C = 1 \mu\text{g cm}^{-3}$ ;  $\Delta x = 0.15 \text{ cm}$ ;  $A = 17 \text{ cm}^2$ ) (Martin et al. 1999).

### Memory and Long-Term Stability

A further advantage of the ceramic dosimeters is that once collected, contaminants do not significantly desorb and diffuse out of the adsorbent bed back into the water when the concentration in the water declines. In order to investigate this possibility, loaded dosimeters (*i.e.*, containing a specified contaminant concentration) were immersed in clean water for different periods of time, up to almost 100 days. The concentration of the contaminant found within the dosimeters after this period was compared with the initial concentration.

In detail, twelve dosimeters were exposed for about two weeks to a saturated solution of phenanthrene in water, after which the contaminant concentration of three of them was measured using the procedure described above and the remaining nine dosimeters were immersed for the different length of time in flowing clean water. The recovered masses from this experiment (Figure 6) showed almost no decline with time. Thus, no desorption occurs if contaminated dosimeters are exposed to water of low or no contaminant concentration. This shows that the partition coefficient (equation 3) is sufficiently high to keep the contaminants (as shown for phenanthrene) sorbed in the dosimeter and enables the ceramic dosimeters to detect short term high concentrations even in a long term monitoring period. The results also prove that no losses, *e.g.* due to degradation of phenanthrene, occur even over extended periods of time.

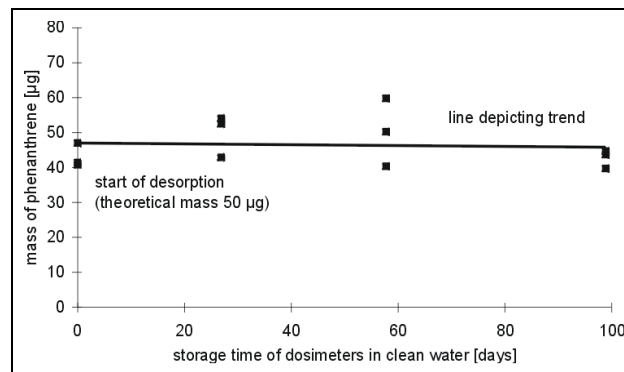


Figure 6. Tests for the long-term stability of phenanthrene in ceramic dosimeters (5 cm length, 5 nm pore size) over extended periods of time (two weeks of uptake of phenanthrene from saturated water followed by up to 100 days in clean water).

### FIELD TESTS IN GROUNDWATER

In field tests, five ceramic dosimeters (three with water saturated and two with dry absorbent material) were placed in a multilevel groundwater well (Figure 7) at a former manufactured gas worksite in Stuttgart (southern Germany) for about one month.

In Figures 8 and 9 the average concentrations calculated from the masses extracted from the ceramic dosimeter are plotted against the concentrations actually measured in multilevel groundwater samples. The plots are linear over a wide range of concentrations.

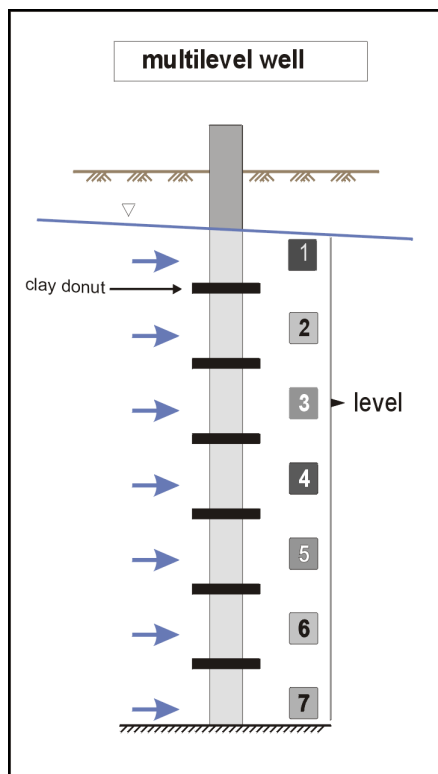


Figure 7. Schematic drawing of a multi-level groundwater well.

### CONCLUSIONS

Ceramic membrane dosimeters are suitable devices for monitoring contaminant concentrations over long time periods (many months) in surface water and groundwater.

The dosimeters show very good reproducibility and a linear solute uptake over an extended period of time (two months in laboratory tests) for the compounds investigated in this study. The dosimeters also exhibited the ability to retain a once sorbed contaminant (see Figure 6) and therefore to detect even short term events in long term monitoring periods. These promising laboratory results were confirmed by several field tests at a former manufactured gas work site.

Further research focuses on the calibration of the dosimeter for various other compounds (single ones or mixtures), mainly volatile contaminants such as volatile chlorinated solvents and BTEX. Another aim is to prove the applicability in field sites over extended long term periods.

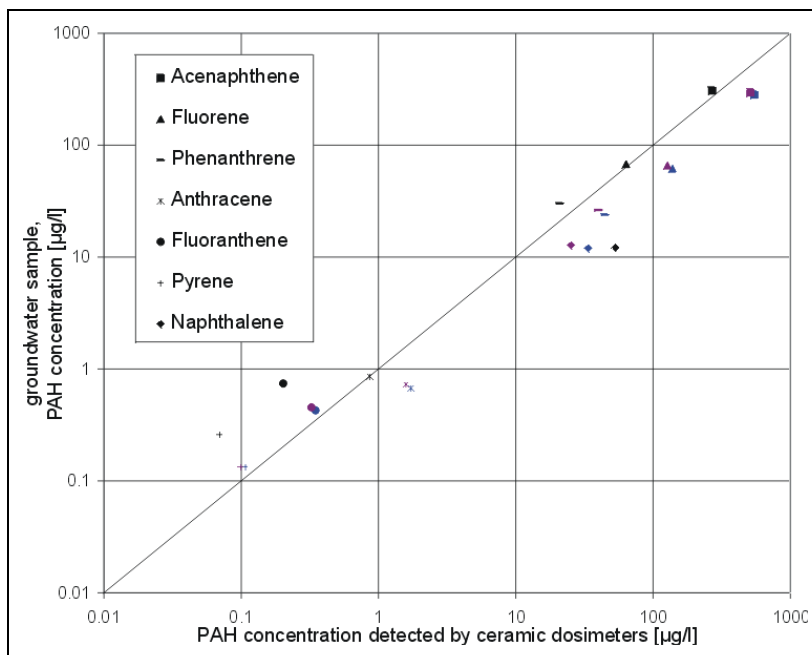


Figure 8. Field tests with three ceramic dosimeters with water saturated absorbent material in a multilevel groundwater well at a former manufactured gas work site.

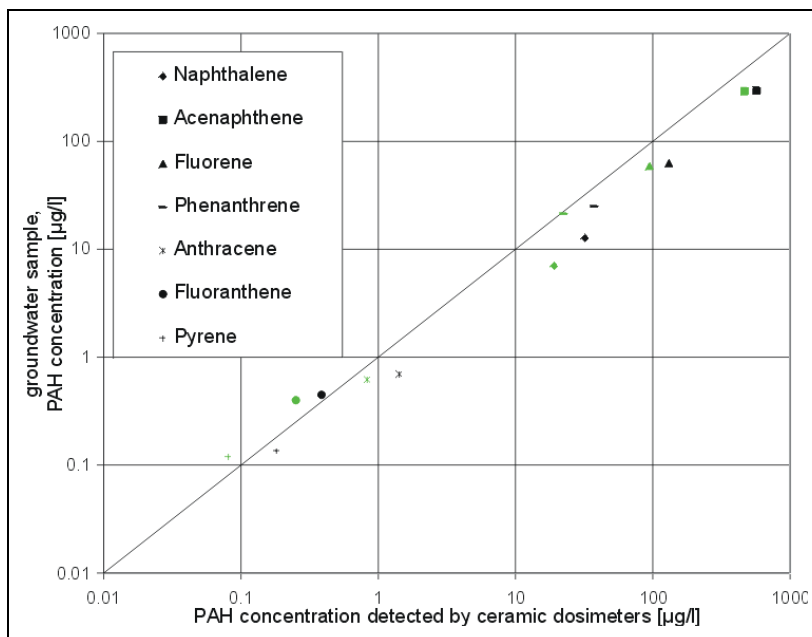


Figure 9. Field tests with two ceramic dosimeters with dry absorbent material in a multilevel groundwater well at a former manufactured gas work site.

### ACKNOWLEDGMENTS

This work has been supported by the state of Baden-Württemberg through the research programs PWAB (PW 97 195) and BWPLUS (BWSW 99001).

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