

Time-integrated monitoring of polycyclic aromatic hydrocarbons (PAHs) in groundwater using the Ceramic Dosimeter passive sampling device

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Abstract

Passive sampling relies on the uptake of contaminants into appropriate sampling devices along a diffusion gradient without using pumps or bailers. Thus, for example, in groundwater sampling, changes to flow due to pumping can be avoided. If the diffusion gradient can be maintained for extended periods, contaminants can be sampled continuously over time without any action, allowing to determine time-weighted average contaminant concentrations. We here show that the Ceramic Dosimeter, a solid receiving phase passive sampler using a ceramic membrane as sorbent container and diffusion barrier, can be used without calibration for the long-term monitoring of polycyclic aromatic hydrocarbons (PAHs) in groundwater.

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1. Introduction

One of the most important steps in analyzing water samples for contaminants is the sampling of water itself [1]. Disturbances of water composition during sampling as well as alterations during transport and storage, all can irreversibly affect the outcome and subsequent interpretation of water analysis results. The conventional, and most common, sampling technique is the active removal or so-called snap-shot sampling, of a defined volume of water at a given time using bailers or pumps. The caveats of such an active sampling technique are well known. Contaminants can sorb to tubes and sampling containers. As well, they may be degraded and/or may decay during transport. For groundwater, in particular, disturbed flow regimes due to pumping may lead to the pulling in of clean or contaminated water from zones not intended for sampling. Pumping can also cause

losses of volatile compounds [2]. For these reasons, alternatives to the common way of water sampling are being sought.

One alternative to the conventional snap-shot sampling approach is the passive water sampling. In passive sampling, contaminants are being taken up into appropriate sampling devices along a diffusion gradient without the use of pumps or bailers [3]. The diffusion gradient is established and maintained by means of a receiving sorbent with a high affinity to the analytes to be explored. If the diffusion gradient can be maintained over extended periods by providing sufficient sorption capacity, contaminants can be accumulated continuously over time and time-weighted average contaminant concentrations determined. Thus, in addition to providing undisturbed water sampling, passive approaches can be used to integrate fluctuations in contaminant concentrations over time without the need for excessive snap-shot sampling.

A variety of passive sampling devices are available for water sampling [3,4]. However, only a few samplers have

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so far been applied to groundwater (e.g. [5–10]). Among them, the Ceramic Dosimeter [11] is a time-integrative passive sampling device which is based on a ceramic tube as diffusion-limiting barrier enclosing a receiving phase that consists of solid sorbent beads. Recently, the utility of the Ceramic Dosimeter as a robust groundwater sampling device was shown for benzene, toluene, ethylbenzenes, xylenes and naphthalenes, using Dowex Optipore L-493 as the receiving phase [10]. Over up to 90 days of sampling in a contaminated aquifer, the Ceramic Dosimeters showed an excellent performance, which was judged by comparing time-weighted average contaminant concentrations derived from the Dosimeters with average aqueous concentrations determined by frequent conventional snap-shot sampling. Based on the same principle, the same group postulated the use of Amberlite IRA-743 as a solid receiving phase for the sampling of polycyclic aromatic hydrocarbons (PAHs). This is an ion exchange resin on polystyrene basis which was chosen due to its capacity for binding hydrophobic contaminants and its wettability, which is of importance for use in a water-saturated sampling device [12]. Indeed, initial laboratory and field experiments focusing largely on phenanthrene showed promise for the long-term sampling of PAHs by means of Amberlite IRA-743 in the field [12–14]. Among the important features determined in these studies were the high affinity of Amberlite IRA-743 to the model PAHs and its ability to preserve the adsorption of PAHs even when the Ceramic Dosimeters were placed in PAH-free, de-ionized water for up to 100 days [12].

The aim of the current study was to explore the ability of the Ceramic Dosimeter passive sampling device, filled with Amberlite IRA-743, to perform well under field conditions with regard to the sampling of PAHs. Over the course of 1 year, a total of 51 Ceramic Dosimeters were deployed in three groundwater boreholes at a former gas works site known to be contaminated with PAHs.

2. Experimental

2.1. Passive sampler material and chemicals

The ceramic tube, caps as well as the stainless steel holder of the Ceramic Dosimeter passive sampling device were provided by IMW (Tübingen, Germany). More detailed properties of the ceramic tube can be found in Table 1. The cap material was PTFE. Caps had an inner diameter of 1 cm, thus closing the ceramic tube by a tight fit. Filled ceramic tubes were fixed in stainless steel holders of 6 cm length. Amberlite IRA-743, which was used as the receiving phase, was from Sigma–Aldrich (Steinheim, Germany). Cyclohexane (99.9%) and acetone (99.9%) for sample extraction were purchased from Roth (Karlsruhe, Germany) and Merck (Darmstadt, Germany), respectively. The internal standard for GC–MS analysis of PAHs was from Dr. Ehrenstorfer (Augsburg, Germany) and contained 200 µg/mL deuterated PAHs ($[^2\text{H}_8]$ naphthalene, $[^2\text{H}_{10}]$ acenaphthene, $[^2\text{H}_{10}]$ phenanthrene, $[^2\text{H}_{12}]$ chrysene and $[^2\text{H}_{12}]$ perylene, prepared using PAH Mix 31). Standard mixtures for determination of response factors were prepared by mixing PAH Mix 14 and PAH Mix 31 (Dr. Ehrenstorfer).

2.2. Passive sampler preparation

A total of 51 ceramic tubes were filled with the Amberlite IRA-743. Amberlite was pre-cleaned by rinsing it with water, followed by careful shaking in acetone. The acetone was decanted and replaced by new acetone until the solvent stayed clear with no signs of discoloration. The Amberlite was left to dry before about 1.5 g were filled into each ceramic tube. The tubes were then filled with distilled water, closed with the PTFE caps and clamped into stainless steel holders. Next, the devices were placed in a bottle filled with distilled water

Table 1
Parameters required for time-weighted average contaminant concentration determinations using the Ceramic Dosimeter

	Symbol according to Eqs. (1) and (2)	Value	Comment
Parameters defined by the membrane			
Thickness	Δx	0.15 cm	Flux-controlling barrier; diffusion distance
Surface area (tube length: 5 cm; tube diameter: 1 cm)	A	8.5 cm ²	Taking reduction of total surface area due to PTFE caps into account
Porosity	ε	0.305	Measured using capillary pycnometer [13]
Archie's law exponent	m	2.0	As determined and applied by Martin et al. [10,12]
Pore size	–	5 nm	Prevents entry of microorganisms and thus biodegradation of accumulated analytes
Analyte-specific parameters			
Diffusion coefficient in water	D_w	6.69×10^{-6} cm ² /s (naphthalene) to 4.44×10^{-6} cm ² /s (dibenzo[<i>a,h</i>]anthracene)	Calculated for each PAH according to Worch [25]
Accumulated mass	M	µg	Measured upon extraction of the sorbent material, Amberlite IRA-743
Parameter of sampling environment			
Temperature	–	°C	Measured during sampling; a determinant of water viscosity thus influencing diffusivity D_w

and evacuated in an exsiccator in order to remove any air within the tube and to ensure complete water saturation of the ceramic tube. Ceramic Dosimeters prepared in this way were stored in amber glass bottles filled with distilled water until deployment.

2.3. Field deployment of the Ceramic Dosimeters

Samplers were deployed in groundwater at a former gas works site in southern Germany from September 2003 until September 2004. Results from previous snap-shot sampling campaigns indicated total PAH concentrations of up to about 5000 $\mu\text{g/L}$ for the sum of 16 EPA PAHs. No unusual aquifer attributes had previously been noted. Three different groundwater boreholes (referred to as boreholes 1–3, borehole diameter = 5 or 6 in.) were chosen for sampling, with two of them being situated within 40 m of one another (boreholes 2 and 3) and the third being within a distance of 175 m (borehole 1). Groundwater flow velocity was about 2.4 m/day. Groundwater levels were 3.5 and 5.5 m below surface corresponding to 217.6–217.8 m above sea level.

Ceramic Dosimeters were transported to the field site stored in the water-filled amber glass bottles. For each sampling time and borehole, a string containing three Ceramic Dosimeters was prepared. The samplers were tied to a polyethylene string using separate nooses. The length of the string and the place where the samplers were attached was chosen such that the samplers could be positioned in the middle of the screened portion of each borehole in 6–8 m depth. Five strings were hung in each of the three boreholes so that triplicate samplers could be collected from each well for several sampling events.

Parallel to the deployment of the passive samplers, mini-pressure pumps (IMW) were installed in the three boreholes in order to allow for regular snap-shot water sampling. The mini-pressure pumps are positive displacement mini gas lift pumps for low flow sampling, which keep disturbances of the natural groundwater flow regime to a minimum.

2.4. Sampling

Snap-shot water sampling using the mini-pressure pumps was performed every second week in duplicate for the first 6 months and once in parallel to the last Ceramic Dosimeter sampling after 12 months. If Ceramic Dosimeters were removed on the same day, snap-shot samples were taken first in order to avoid erroneous PAH concentrations in the snap-shot water samples due to mixing of water during passive sampler removal. For each sample, approximately 700 mL of water was collected into 1 L amber glass bottles which already contained 10 mL of cyclohexane and 10 μL of internal deuterated standard for later extraction and chemical analysis.

The exact water sample volumes were determined gravimetrically immediately upon arrival in the laboratory. The samples were then rigorously shaken for 1 h in order to extract the aromatic hydrocarbons with the cyclohexane. A vol-

ume of 1.5 mL of the cyclohexane phase was then transferred into GC vials and directly injected into the GC–MS system within 24 h upon arrival in the laboratory (see Section 2.6).

Removal of passive samplers was done in triplicate after 1–4 months of sampling. Because the sampling behaviour remained as expected over the entire 4 months, confirming the robustness and the high capacity of the Dosimeters, it was decided to extend the exposure time to up to 1 year. Thus, after 6 months of exposure only two samplers per borehole were removed in order to leave one sampler for full 12 months of sampling. In addition to these single samplers, two new samplers were added per borehole during the 6-month sampling event. These new samplers were then removed together with the 12-month sampler so that they were exposed for 6 months in the second half of the year of this study (April–September 2004). Samplers were wrapped in tissue, soaked in distilled water, and packed in zip plastic bags. They were transported to the laboratory and processed within 24 h.

Because temperature influences diffusion coefficients of chemicals and thus the uptake of contaminants into the passive sampling devices, water temperature was determined in parallel to all sampling activities. It was found to be constant at 13.5 °C.

2.5. Processing of passive samplers after field deployment

Ceramic Dosimeters were processed as previously described by Piepenbrink [13]. In brief, Amberlite IRA-743 was transferred from the Ceramic Dosimeters to stainless steel cylinders, coupled to a vacuum manifold. The sorbent material was extracted three times with 10 mL of acetone with 10 min contact time for each extraction step and the 3 \times 10 mL combined. Ten microlitres of internal deuterated PAH standard were added to 5 mL of the combined acetone extracts for direct GC–MS analysis. Extracts contained about 5% of water. Experiments with varying water contents up to 5% did not lead to significant variations in analyses results.

2.6. Instrumental analysis

Samples were analyzed according to Griebler et al. [15] and Grathwohl et al. [16]. In brief, a HP 5890 Series II gas chromatograph with a HP 6890 autosampler was used in combination with a HP 5972 A mass spectrometer for analyses of water samples and Ceramic Dosimeter extracts. The GC column for separation of PAHs was a Zebtron ZB-5 MS (30 m \times 0.25 mm i.d., 0.25 μm film thickness; Phenomenex, Aschaffenburg, Germany). Samples were injected splitless. The MS was operated in single ion mode (SIM). Detection masses corresponded to the molecular masses of all substances. For some of them, additional qualifier ions were detected for definite identification. The internal standard with deuterated PAHs was used for quantification of the analysis results. For determination of response factors, an additional PAH mixture was utilized, containing 0.49 mg/L of the 16

EPA PAHs plus 1- and 2-methylnaphthalene (PAH Mix 14, Dr. Ehrenstorfer) and 0.2 mg/L of the deuterated PAHs from PAH Mix 31 (Dr. Ehrenstorfer). Limits of detection for the PAHs were between 0.03 and 0.08 $\mu\text{g/L}$ for the water samples and between 20 and 80 ng accumulated mass per sampler for the Ceramic Dosimeters. Dosimeter detection limits corresponded to calculated average water concentrations of 0.6–1.2 $\mu\text{g/L}$ at the first sampling time point (first month) and to 0.1–0.3 $\mu\text{g/L}$ after 12 months of sampling.

2.7. Data evaluation

Chemical analysis of the passive sampler solvent extracts yielded the mass (M) of PAHs that traversed through the available surface area (A) of the ceramic membrane over the sampling period (t) and accumulated on the sorbent material, Amberlite IRA-743. Assuming that the movement of the PAHs to the inner part of the Ceramic Dosimeter is based solely on diffusion, the accumulated mass can be described according to Fick's first law [10,12]:

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

In (1), D_e is the effective diffusion coefficient. It accounts for the altered diffusion of analytes in the porous membrane compared to water according to Archie's law:

$$D_e = D_w \varepsilon^m \quad (2)$$

where D_w is the diffusion coefficient in water, ε is the porosity of the ceramic membrane and m is Archie's law exponent, which in porous media generally ranges from 1.5 to 2.5 [17]. Further, the term Δx in (1) is the diffusion path length, i.e. the thickness of the ceramic membrane, and ΔC is the difference in aqueous analyte concentration between the sampling environment and the inner sampler part. Given the high affinity of the PAHs to bind to Amberlite IRA-743, the aqueous concentration in the inner part of the sampler can be assumed to approach zero. Thus, Eq. (1) enabled the prediction of average water concentrations from the amounts of PAHs collected in the Ceramic Dosimeter. The factors controlling the accumulation of PAHs in the Ceramic Dosimeter and Dosimeter-specific parameters required to calculate time-weighted average PAH concentrations are provided in Table 1. Dosimeter sampling rates (R) for the various PAHs, corresponding to $R = D_e A / \Delta x$, were calculated to be between 1.5 and 2.5 mL/day at 14 °C.

3. Results

3.1. Appearance of the Ceramic Dosimeters after field exposure

Sampling devices removed from boreholes 1 and 3 occasionally displayed a slight greyish discoloration whereas Ceramic Dosimeters obtained from borehole 2 showed com-

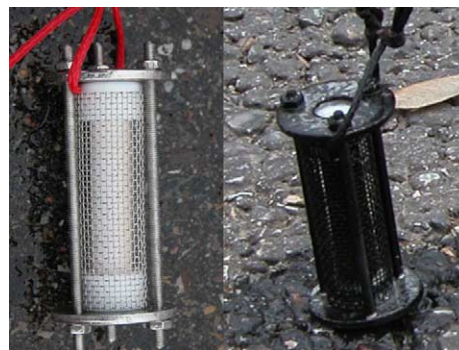


Fig. 1. Appearance of Ceramic Dosimeters before exposure (left side) and after 2 months of exposure in borehole 2 (right side). The tar oil phase led to a brownish-black discoloration of the stainless steel cage and the ceramic membrane. No such alterations to Ceramic Dosimeter appearance were observed upon exposure to borehole 1 or 3.

prising discolorations ranging from yellow-reddish to dark black (Fig. 1). These alterations in colour were visible from the first sampling point (1 month) on. They were attributable to a tar oil phase occurring unexpectedly in this borehole upon an operational change at the gas works site. The tar oil phase filled the borehole from the bottom to about half of the borehole depth and remained on the bottom due to its density, which is higher than that of water. Thus, the samplers were hanging within the oil phase. No oil phase was observed on the groundwater surface, so that no non-aqueous product was drawn down by deploying the samplers. Smearly films or biofilms were not observed on Dosimeter surfaces for any of the samplers.

3.2. Prediction of time-weighted average aqueous PAH concentrations by means of Ceramic Dosimeters

The accumulated amounts of PAHs in the Ceramic Dosimeters were applied to Eq. (1) in order to calculate the time-weighted average aqueous concentration predicted for each PAH by the passive sampling device. These values were compared to the average PAH concentrations determined by the conventional snap-shot sampling approach (Figs. 2 and 3). Dosimeter replicates showed a variation coefficient of 10% at an average. Details for three exemplary compounds can be found in Fig. 2. Snap-shot sample aqueous PAH concentrations, determined every second week for the first 6 months and then once again after 12 months, varied up to 32-, 36- and 7-fold for naphthalene (Nap, see also Fig. 2) in boreholes 1–3, respectively. For the 1- and 2-methylnaphthalene, variations were up to about 4-fold with the exception of borehole 3, where differences up to 16-fold were observed for 2-methylnaphthalene (2-MNap). Variations in concentrations generally were below 2-fold for all other PAHs (compare, for example, phenanthrene (Phe) and fluoranthene (FA) in Fig. 2). Detectable levels were observed for all sampling events and locations for PAHs ranging in molecular weight from naphthalene to fluoranthene/pyrene.

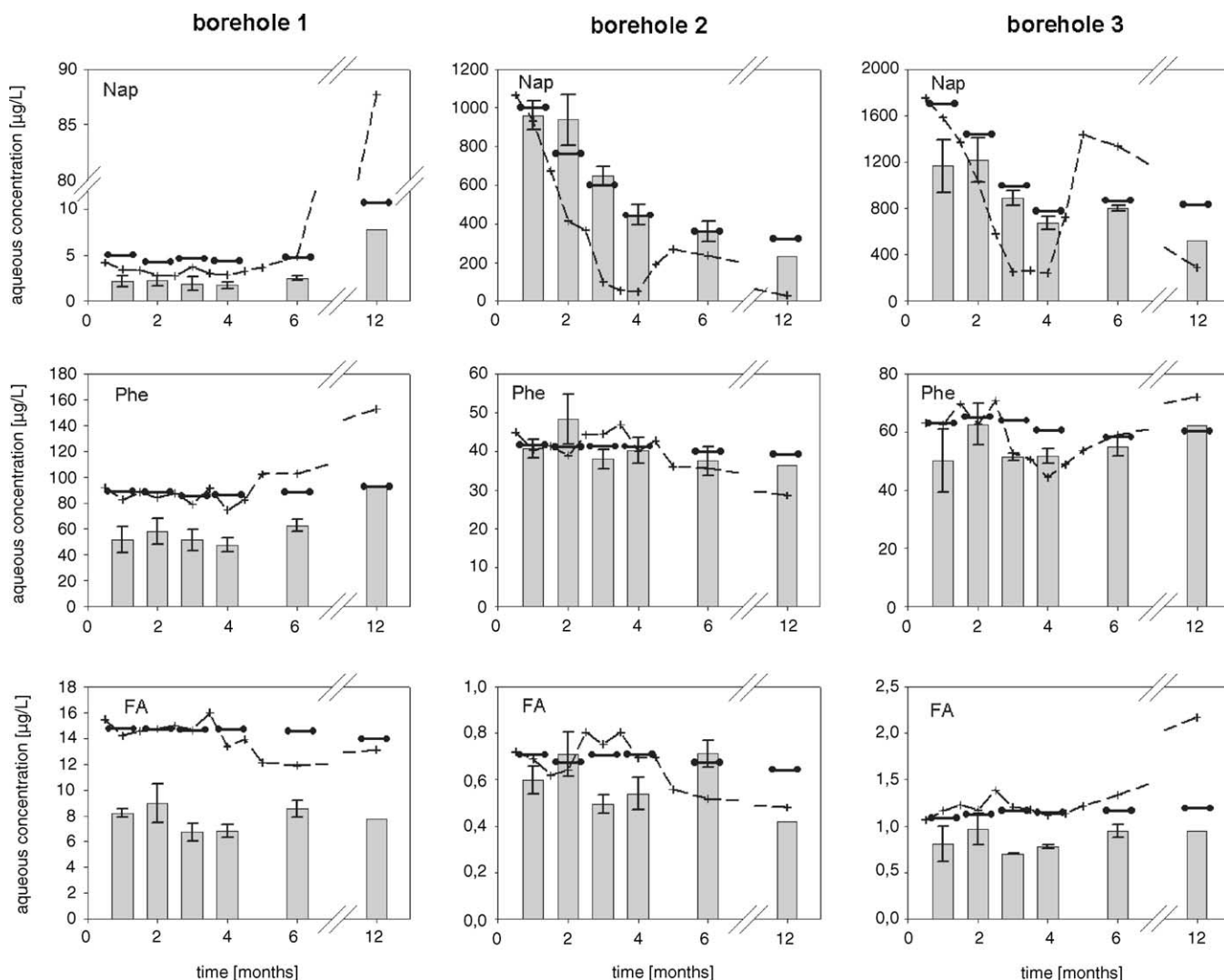


Fig. 2. Comparison of snap-shot sample determined and Ceramic Dosimeter-derived time-averaged aqueous PAH concentrations in the three boreholes. A two-ring (naphthalene, Nap), a three-ring (phenanthrene, Phe), and a four-ring (fluoranthene, FA) PAH were selected to give three examples. Grey bars represent the average of Ceramic Dosimeter samples with the vertical lines representing standard deviation of triplicate samplers for sampling point 1–4 months, and deviation from the mean for duplicate samplers after 6 months of exposure. After 12 months of exposure, only one single sampler was removed per well. The plus connected with a dashed line represent aqueous PAH concentration in the first of duplicate snap-shot samples (the deviation between the duplicate samples was negligible with a median deviation of 2%). The barbells represent the time-averaged PAH concentrations determined from the snap-shot samples over each corresponding exposure period. Thus, if the Ceramic Dosimeter yields aqueous concentrations equal to the concentrations derived by averaging repeated snap-shot sample results, the upper end of each grey bar and the corresponding barbells should exactly match.

Dosimeter-derived time-weighted average PAH concentrations very well matched those obtained by averaging results from extraction and analysis of conventional snap-shot sampling obtained over time (Fig. 3). The greatest differences ever observed were a 3.1–4-fold lower Dosimeter-derived concentration for 1-methylnaphthalene in borehole 1 after 1–4 months of sampling, and a 3.7-fold underestimation of 2-MNap in borehole 3 after 12 months of sampling. Overall, the PAH concentrations predicted by the Ceramic Dosimeter were lower than the snap-shot sample-derived PAH concentrations by a median factor of 1.2 (83% of snap-shot sample-derived concentrations). Differences were observed between the boreholes. Whereas Dosimeter-derived PAH concentra-

tions in boreholes 2 and 3 were lower than snap-shot sample-derived concentrations by a median factor of, respectively, 1.1 (91%) and 1.2 (83%), the same median factor was 1.5 (66%) for borehole 1. A greater than snap-shot sample-derived PAH concentration was predicted in 13% of all cases with the greatest level of overestimation being 2-fold for one value of anthracene in borehole 2 (Fig. 3, middle panel).

3.3. Accumulation of PAHs in the sampling device

The PAHs naphthalene (Nap), 1-methylnaphthalene (1-MNap), acenaphthene (Ace), acenaphthylene (Any), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene

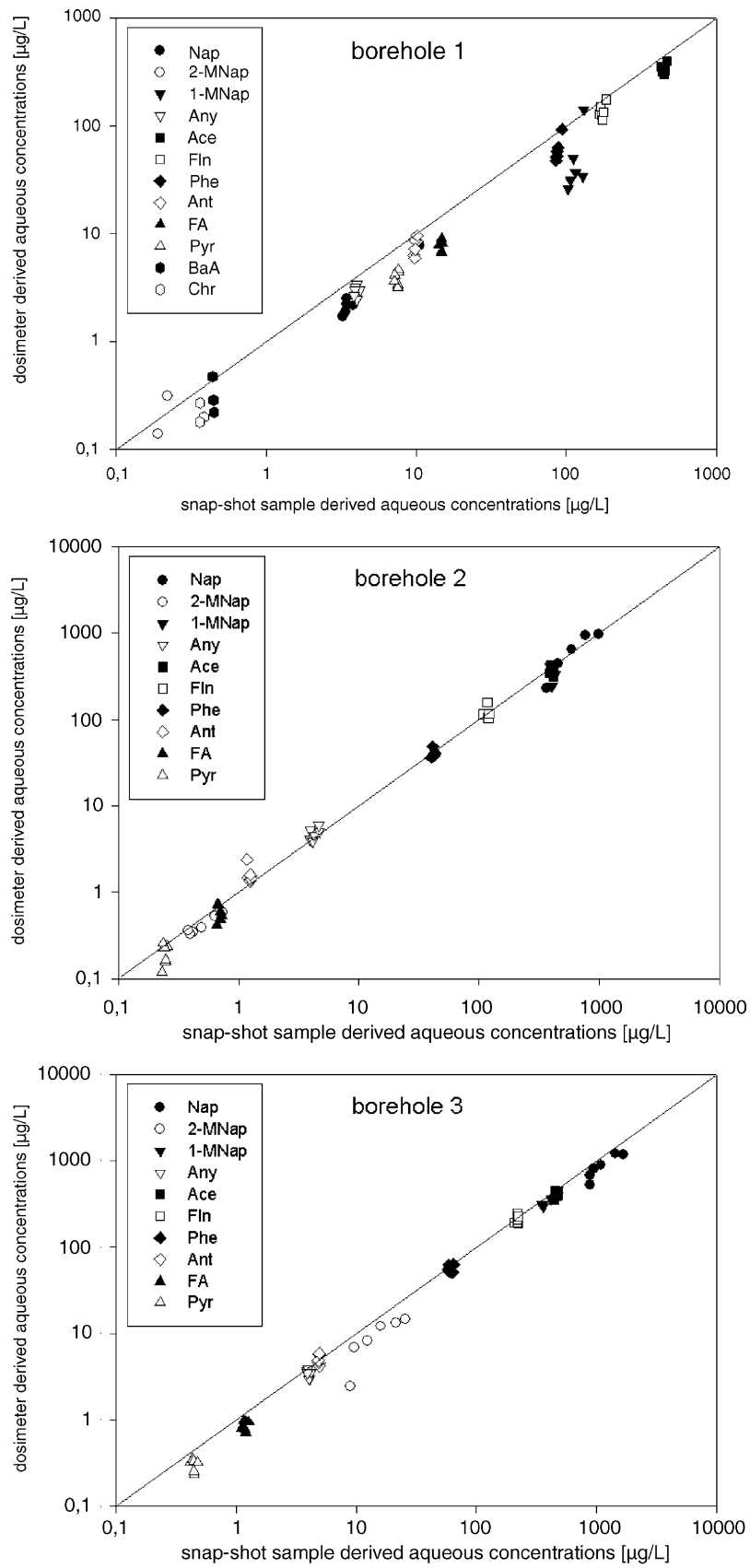


Fig. 3. Comparison of Ceramic Dosimeter-derived and time-averaged snap-shot sample determined aqueous PAH concentrations for all sampling times within the three boreholes. For absolute agreement between the two sampling methods, symbols should lie on the diagonal line.

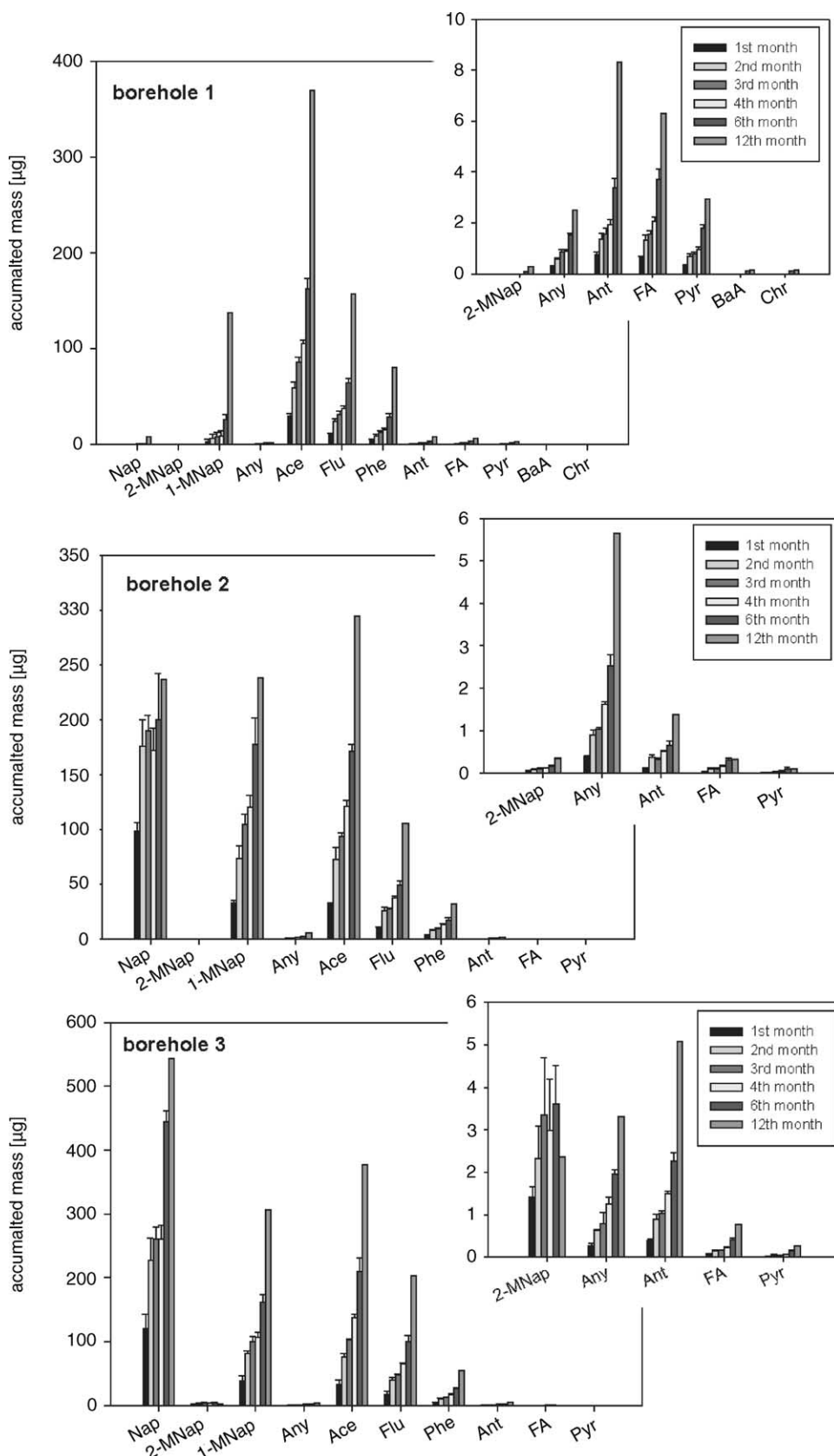


Fig. 4. Accumulated PAH masses in the Ceramic Dosimeters exposed in the three boreholes over period of 1–12 months. Insets show a magnification for the lower concentrated PAHs. Vertical lines represent standard deviation of triplicate samplers for sampling point 1–4 months, and deviation from the mean for duplicate samplers after 6 months of exposure. After 12 months of exposure, only one single sampler was removed per well.

(FA) and pyrene (Pyr) were encountered in all the Dosimeters deployed irrespective of the sampling locations. 2-Methylnaphthalene (2-MNAP) was consistently detectable in boreholes 2 and 3 but was found only after 6 and 12 months of sampling in borehole 1. As well, benzo[*a*]anthracene (BaA) and chrysene (Chr) were detectable only in borehole 1 and only after 6 and 12 months of sampling. The PAHs benzo[*k*]/[*b*]fluoranthene, benzo[*a*]pyrene, dibenzo[*a,h*]anthracene, benzo[*ghi*]perylene as well as indeno[1,2,3-*cd*]pyrene never accumulated in the sampling devices sufficiently to be reliably detectable above the detection limits of the analytical method applied. Overall, the spectrum of PAHs detected by the Ceramic Dosimeters was the same as for the snap-shot water samples.

With a few exceptions, all detectable PAHs were found to increasingly accumulate within the Ceramic Dosimeters with sampling time (Fig. 4). The exceptions were 2-MNAP in borehole 3 and Nap in boreholes 2 and 3, where uptake appeared stagnant in some time intervals, which however coincided with large drops in aqueous concentrations for these substances. In theory, if PAH concentrations in the water are constant, the Ceramic Dosimeter passive sampling device should accumulate the analytes linearly with time. This indeed was observed. When the accumulated amounts for each of the PAHs with less than 2-fold changes in aqueous concentration (acenaphthylene to pyrene) were plotted as a function of time, the uptake was found to be significantly linear with the coefficient of determination, R^2 , being generally close to 1.

To support the 12-month determinations with one sampler in each borehole, a second set of samplers (two per borehole) was deployed after the first 6 months for the second half of the year between months 7 and 12. When the sum of PAH masses accumulated in the samplers during the two half-year intervals was compared to the total mass detected after a whole year, an excellent agreement was found with one exception, the 2-MNAP in borehole 3 (Fig. 5). Thus, samplers deployed for 1 year behave no differently than samplers deployed for shorter periods. This confirms the suitability of the Ceramic Dosimeter for long-term monitoring due to the high sorption capacity of Amberlite IRA-743 as well as the robustness of the ceramic diffusion barrier.

4. Discussion

The Ceramic Dosimeter was originally developed by Grathwohl [11] for the passive, time-integrative sampling of water or air. Two key features to this simple, small device are its robust ceramic membrane and the solid receiving phase, which has to be chosen according to the analytes under investigation. Previously, Martin et al. [10] had filled the ceramic tube with Dowex Optipore L-493 as the solid receiving phase in order to derive time-weighted average concentrations of BTEX and naphthalenes in groundwater. They showed that the Ceramic Dosimeter-derived contaminant concentrations

well agreed with those obtained by repeated conventional snap-shot sampling over several months. As well, laboratory and preliminary field experiments using Amberlite IRA-743 in the Ceramic Dosimeters had illustrated the suitability of this receiving sorbent for the sampling of PAHs [13,16]. We here show that Amberlite IRA-743-filled Ceramic Dosimeters are capable of continuously accumulating PAHs over many months without exceeding the sorption capacity of the Amberlite IRA-743, thus allowing for time-weighted average concentration determinations for PAHs in a polluted aquifer.

The average aqueous PAH concentrations predicted by the Ceramic Dosimeters closely reflected those derived by averaging conventional snap-shot sampling results obtained over time. If at all perceptibly different, the Dosimeter-derived PAH concentrations tended to be lower than the snap-shot sample-derived concentrations. In the case of the snap-shot samples, whole water is extracted irrespective of particulates or colloids potentially carrying contaminants whereas in the case of the Dosimeter, only truly dissolved PAHs are being monitored. Although turbidity was not observed in the water samples and particulates were not specifically investigated, they indeed appear to be one plausible cause for the differences obtained by the two sampling approaches. This is supported by the fact that borehole 1, where the greatest differences between snap-shot sampling and Dosimeter-derived PAH concentrations were observed, was situated at only a 10 m distance to a steep slope toward a river valley, implying a higher susceptibility to particulate mobilization due to infiltrating water. On the other hand, it could be argued that in the case of sorption to particulates, higher $\log K_{ow}$ substances, such as chrysene, should be attenuated more strongly and thus be underrepresented in the Dosimeter more so than lower $\log K_{ow}$ substances, such as naphthalene. Such a difference however was not observed even in borehole 1. Taken together, while the slightly lower Dosimeter-derived PAH concentrations cannot yet fully be explained, they highlight the importance of keeping in mind the differences in whole water extraction, as in the case of snap-shot sampling, and the extraction of only truly dissolved substances, as in the case of the Ceramic Dosimeter. Overall, however, the differences were minor in this study, considering that average aqueous PAH concentrations derived with the two approaches varied by a median factor of 1.2.

A direct comparison of snap-shot sample water concentrations versus passive sampler derived water concentrations has so far only rarely been attempted. For various types of passive samplers applied for 2–4 weeks in lakes, rivers or marine environments, deviations of passively determined contaminant concentrations and directly analyzed water samples were within factors of 2–5 [18–20]. Even fewer examples exist for the use of time-integrative passive sampling devices in groundwater. Martin et al. [10] found a very good agreement for BTEX and naphthalene concentrations in groundwater determined by Dowex Optipore L-493-filled Ceramic Dosimeters and snap-shot samples. Slight deviations were explained by the fact that snap-shot samples reflect

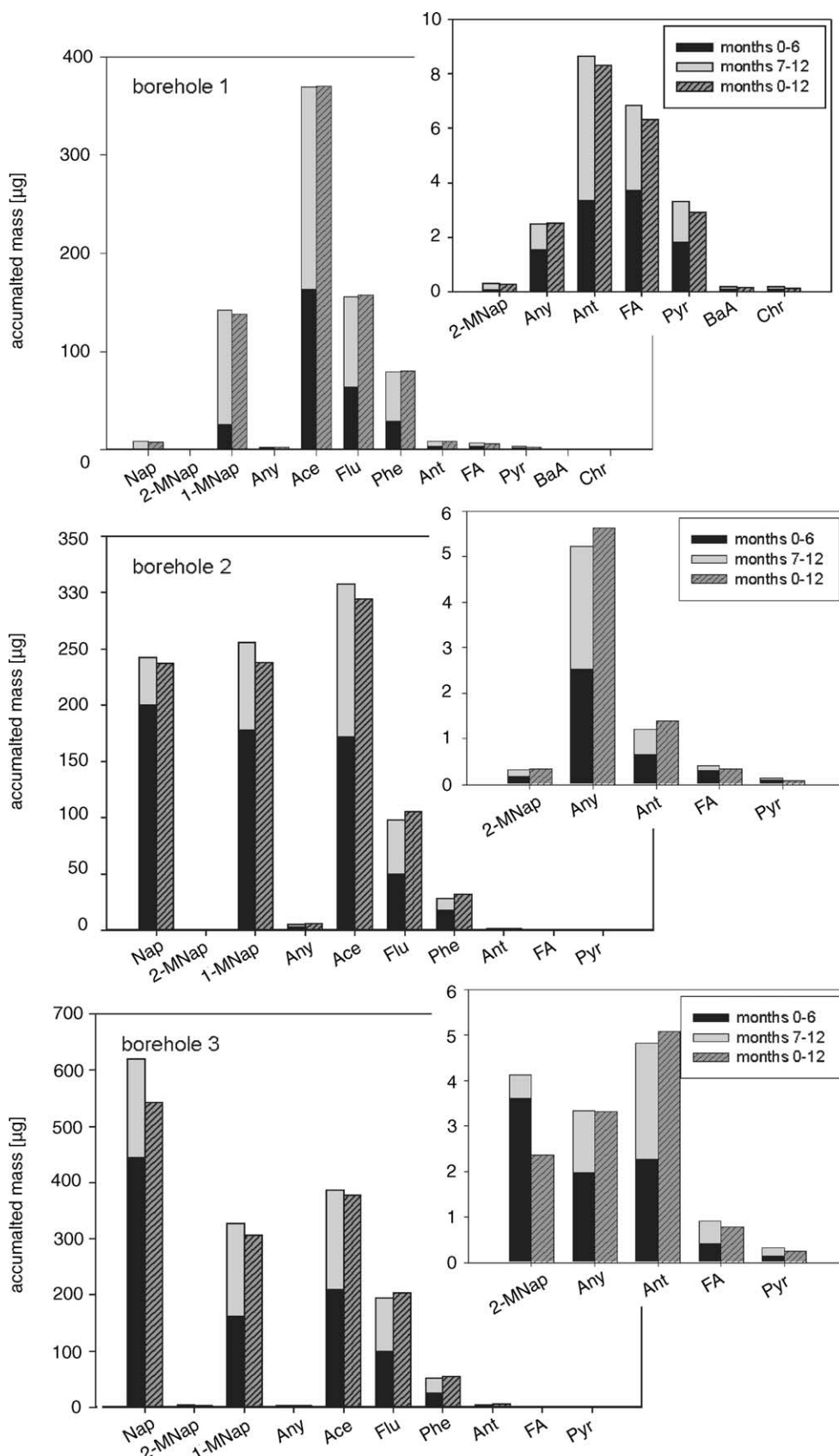


Fig. 5. Comparison of accumulated PAH masses collected over the whole exposure period in the 12 months exposed Ceramic Dosimeters and the sum of accumulated masses in the samplers exposed for the first (months 0–6) and the second 6 months (months 7–12) of the 1-year sampling campaign.

only instantaneous concentration values. Thus, their mean may differ from the average concentrations determined by the Dosimeters which collect analytes throughout the entire exposure time without interruption. Gustavson and Harkin [6] deployed semipermeable membrane devices (SPMDs) in groundwater at a PAH contaminated site. Deviations between the passive and active sampling results were between 5- and 10-fold. SPMD-derived average aqueous PAH concentrations were larger than snap-shot sample-derived concentrations in one well, which was found to contain free product. The latter, a black viscous material, had coated the SPMDs and this coating was suspected to facilitate transfer of PAHs into the devices. Such effects can be excluded for the Ceramic Dosimeter, where the presence of a tar oil phase in borehole 2 did not affect the sampling behaviour. SPMD-based average aqueous PAH concentrations were, however, lower than snap-shot sample determined concentrations in the other wells [6]. These lower concentrations were attributed to particle-bound PAHs not available for the SPMDs but included in the analysis of unfiltered water samples, which is along the lines of our arguments presented above.

The simplicity of the Ceramic Dosimeter is based, in part, on the ceramic membrane. This membrane serves to protect the solid receiving sorbent but as well as a diffusion barrier. The ceramic tube represents a relatively thick diffusion barrier. Therefore, even under low-flow conditions where a significant aqueous boundary layer may form outside of the sampling device, the sampling behaviour can be assumed to be dominated by diffusion through the ceramic alone. For example, Gale [21] reported an aqueous boundary layer thickness of 100–400 μm in quiescent aqueous systems, which is about 1/15 to 1/4 of the thickness of the ceramic tube. This is in contrast to many other sampler types which are based, e.g. on organic polymer membranes, where the aqueous boundary layer can greatly influence sampling behaviour (e.g. [18,22,23]). It is difficult to quantitatively include these effects in calculation of time-weighted average aqueous concentrations, because of difficulties in assessing flow fluctuations in field situations or calibrating for them in the laboratory. The Ceramic Dosimeter's independence of hydrodynamic parameters is of advantage because no labor-intensive calibration steps have to be performed in order to account for varying flow. Likewise, the application of performance reference compounds, which frequently are injected into sampling devices as a means to account for varying flow in the field [24], are not required. In fact, temperature remains the only parameter to be determined during sampling because of its impact on diffusivity. A temperature increase of 1 K corresponds to an increase of diffusion coefficients of about 3–4% in the range from 12 to 25 °C.

The role of the ceramic membrane as protector and robust diffusion barrier was also illustrated in this study by the unaltered performance of the Ceramic Dosimeters in the presence of an unexpectedly occurring tar oil phase in borehole 2. This represents an extreme situation which would likely have led to the disintegration of a number of other passive

sampler types. Another influence on sampling behaviour often reported especially in surface water sampling, namely the formation of biofilms, has to be considered but was not obvious in the sampling of groundwater in this and previous studies [10,16]. This might be due to lower microbial activity in groundwater compared to surface waters or a reduced ability of microbes to form biofilms on that particular ceramic membrane. Application of the ceramic membrane to a surface water rich in microorganisms, such as an effluent treatment pond, may shed light on this thus far unexplored characteristic of the ceramic membrane.

5. Conclusions

The Amberlite IRA-743-filled Ceramic Dosimeter proved to be a reliable device for long-term groundwater monitoring of PAHs at contaminated sites. It greatly reduces the sampling and analysis efforts compared to active snap-shot sampling and due to its robust design, does not require laborious calibration steps. Thus, the Ceramic Dosimeter can be recommended as a simple and straightforward alternative to conventional snap-shot sampling if contaminated groundwater needs to be monitored for extended periods of time. The only restriction that applies is that contaminant sampling rates through the ceramic membrane are relatively low so that long exposure times are required if aqueous contaminant concentrations are rather low. For example, it would take about 15 days for reaching the detection limit for accumulated masses in the Ceramic Dosimeter when exposed in water containing 1 $\mu\text{g/L}$ PAHs, as well as 150 days at water concentrations of 0.1 $\mu\text{g/L}$. Suitable areas of application therefore are, for example, sites where Monitored Natural Attenuation is accepted as a remediation strategy. Likewise, a groundwater site that underwent active remediation could be continuously monitored with little effort in order to ensure that contaminant levels stay at the envisioned levels. The application of the Ceramic Dosimeter to the monitoring of other contaminant groups as well as other sampling environments is an attractive future goal.

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