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Sampling Trace-Level Organics with Polymeric Tubings
Dynamic Studies

Louise V. Parker and Thomas A. Ranney

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Abstract: This study is the second phase of a two-year effort to determine the effects that sampling tubings have on organic analyte concentrations. In the first year, 20 different tubings were compared, under static conditions, with respect to sorption of organic contaminants and leaching of organic constituents. In this study, we examined what occurs under dynamic conditions when TCE-contaminated water is pumped through several different types of polymeric tubings. Sorption of organic solutes, leaching of organic constituents, and desorption of sorbed organic contaminants were all examined.

Five tubings were selected for this study: a rigid fluoropolymer, a flexible fluoropolymer, low-density polyethylene (LDPE), and two plasticized polypropylene tubings. These materials were selected because our static studies had shown that these tubings leached little or no organic constituents (as determined by HPLC analyses with an ultraviolet [UV] detector) and ranged from being the least sorptive tubings tested to among the most highly sorptive. The effects of tubing length and flow rate were examined.

Results from these studies indicate that if water is pumped through tubing at a slow flow rate (100 mL/min), fluoropolymers should be used to prevent extensive losses of TCE and more sorptive analytes, especially if the tubing is 50 ft or longer. If a faster flow rate (1 L/min) is used, it appears that LDPE tubing can be used to sample TCE and other less sorptive analytes, although time for equilibration (2–4 hr) should be allowed to reduce losses in the deepest wells.

We were unable to detect (using HPLC analyses and a UV detector) any constituents leaching from any of the tubings used in these studies, even when a slow flow rate was used. However, desorption of sorbed analytes is a concern for all the tubings tested, including the rigid fluoropolymer.

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PREFACE

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INTRODUCTION

It is important that the reported concentrations of contaminants in samples taken from groundwater monitoring wells accurately reflect in-situ values, or else decisions on whether remedial actions are necessary can be erroneous. Recent studies suggest that among the currently used sampling methods, low-flow-rate (~100 mL/min) purging and sampling may cause the least disturbance to the well during the sampling process. Samples taken using this method have lower turbidity (Kearl et al. 1992, Puls and Powell 1992, Puls et al. 1992, Backhus et al. 1993) and yield perhaps the most accurate values for inorganic contaminants among the currently used sampling methods (Puls and Powell 1992, Puls et al. 1992). Furthermore, there is evidence indicating that low-flow-rate purging and sampling may also produce samples that reflect the in-situ values of at least some organic contaminants, such as polycyclic aromatic hydrocarbons (Backhus et al. 1993).

One concern with the slow-rate pumping methods for sampling groundwater is that the longer residence time in the tubing may allow possible interactions that could affect analyte concentrations. The tubing could either leach inorganic or organic constituents, which may be analytes of concern, or interfere with the methods of analysis and thereby give inaccurate values. The tubing may also sorb contaminants present in the sample, thereby leading to inaccurate low values. In addition, if the tubing is not dedicated to a particular well, it is possible that tubing used previously to sample a well with high contaminant concentrations could release sorbed contaminants into the next sample, leading to inaccurate high values. Also, gases such as oxygen can dif-fuse through certain types of tubing, thereby possibly affecting the solution chemistry of the sample as it is pumped to the surface (Holm et al. 1988, Kjeldsen 1993). In this paper, we will focus on the effects tubing materials can have on groundwater samples with respect to sorption of organic contaminants, leaching of organic constituents, and desorption of sorbed organic contaminants.

Sorption of organic contaminants

Several studies (Ho 1983, Barcelona et al. 1985, Reynolds and Gillham 1985, Devlin 1987, Pearsall and Eckhardt 1987, Gillham and O'Hannesin 1990, Reynolds et al. 1990) have shown that polymeric tubing materials can lower analyte concentrations. In most cases, losses of organic solutes to polymers were attributed to absorption within the polymer matrix (Barcelona et al. 1985, Reynolds and Gillham 1985, Gillham and O'Hannesin 1990, Parker et al. 1990, Reynolds et al. 1990). Uptake of organic compounds by polymers is considered to proceed first by sorption by the polymer surface, followed by diffusion into the polymer matrix (Serota et al. 1972, Yasuda and Stannett 1975, Reynolds and Gillham 1985, Gillham and O'Hannesin 1990). Flexible tubing materials (e.g., silicone rubber, latex rubber, flexible PVC) have been shown to be highly sorptive of organic solutes (Ho 1983, Barcelona et al. 1985, Devlin 1987, Pearsall and Eckhardt 1987). In contrast, the more rigid polymers appear to be much less sorptive of organic solutes (Barcelona et al. 1985, Reynolds and Gillham 1985, Gillham and O'Hannesin 1990). As an example, Figure 1 shows sorption of ppm levels of benzene by rigid and flexible PVC in a static study conducted by Gillham and O'Hannesin (1990). Barcelona et al. (1985) attributed the reduced sorption by the more rigid poly-
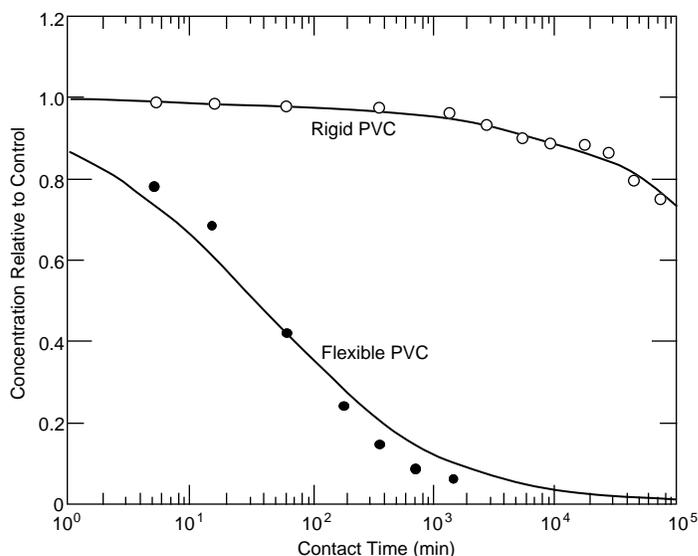
Figure 1. Sorption of benzene by rigid and flexible PVC (Gillham and O'Hannesin 1990).

mers to the greater density and crystallinity of those polymers. Of all the types of polymeric tubings that have been tested, PTFE (Teflon) was among the least sorptive (Ho 1983, Barcelona et al. 1985, Reynolds and Gillham 1985, Devlin 1987, Pearsall and Eckhardt 1987, Gillham and O'Hannesin 1990).

Recently, we (Parker and Ranney 1996) con-ducted a study that compared sorption of organ-ic solutes by twenty sampling tubings, including thirteen rigid tubings and seven flexible tubings, of which eight were fluoropolymers (Table 1). The tubings were filled with a test solution that contained low mg/L concentrations of eight or-ganic analytes (two nitroaromatic compounds and six volatile organic compounds). We found

Table 1. Materials used in Parker and Ranney (1996) study.

	Cost per ft.[a] ($)
Flexible polymers [b]	
polypropylene-based material with plasticizer, formulation 1 (PP1)	0.58
polypropylene-based material with plasticizer, formulation 2 (PP2)	2.48
polyvinyl chloride (PVC)	0.89
thermoplastic elastomer[c] (TPE)	0.96
linear copolymer of vinylidene fluoride and hexafluoropropylene [P(VDF-HFP)]	1.99
polyurethane	0.64
fluoroelastomer	8.70
Rigid polymers [d]	
polyethylene, low density (LDPE)	0.19
polyethylene, cross-linked high density (XLPE)	0.43
polyethylene liner in ethyl vinyl acetate (EVA) shell	0.57
polyethylene liner cross-linked to EVA shell	1.08
co-extruded polyester lining in PVC shell	0.77
polypropylene (PP)	0.27
polyamide (nylon)	0.71
polytetrafluoroethylene (PTFE)	4.27
perfluoroalkoxy (PFA)	5.58
ethylene tetrafluoroethylene (ETFE)	5.50
polyvinylidene fluoride (PVDF)	1.80
fluorinated ethylene polypropylene (FEP)	3.90
FEP-lined polyethylene	3.00

a 1994 prices; cost varies with quantity, dimensions, and supplier.
b Finger pressure can collapse tubing.
c Styrene-ethylene-butylene block copolymer modified with silicon oil.
d Can be stepped on without collapsing the tubing.

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Figure 2. Sorption of tetrachloroethylene by the 10 least sorptive tubings studied (Parker and Ranney 1996). (Values for PTFE, ETFE, and polyamide were adjusted to comparable surface-area-to-solution-volume ratios.)
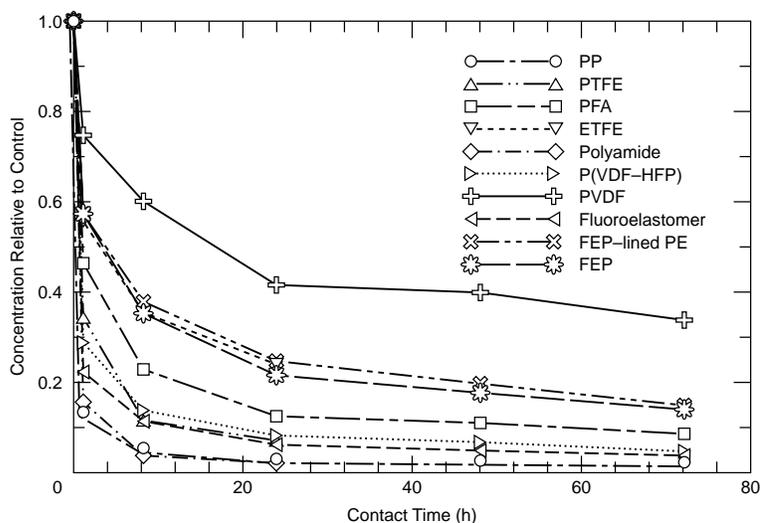
Figure 3. Sorption of p-*dichlorobenzene by the 10 least sorptive tubings studied (Parker and Ranney 1996). (Values for PTFE, ETFE, and polyamide were adjusted to comparable surface-area-to-solution-volume ratios.)*
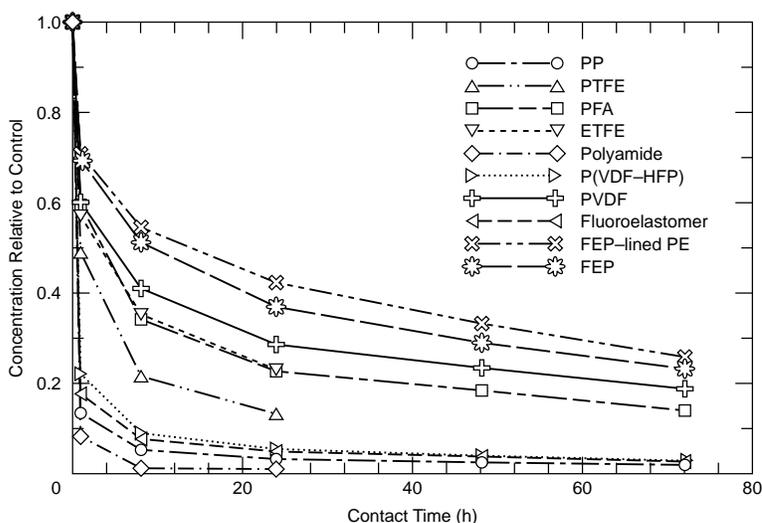
that the rigid fluoropolymers (Table 1) were the least sorptive. As an example, Figure 2 shows sorption of tetrachloroethylene (PCE) and Figure 3 shows sorption of *p*-dichlorobenzene (PDCB) by the ten least sorptive materials tested. Among the rigid fluoropolymers, the fluorinated ethylene (FEP), FEP-lined polyethylene (PE), and polyvinylidene fluoride (PVDF) tubings were the three least sorptive materials. However, even though these three tubings were the least sorptive, it should be noted that they were still highly sorptive of the more hydrophobic analytes tested. For example, FEP-lined PE sorbed the least amount of PDCB, and yet loss of this analyte was nearly 30% after only 1 hr!

In some instances a more flexible tubing may be required, such as in the head of a peristaltic pump. Among the flexible tubings tested, the two fluorinated tubings, a fluoroelastomer and a copolymer of PVDF and hexafluoropropylene [P(VDF-HFP)], were much less sorptive of organic solutes than the other flexible tubings (Parker and Ranney 1996).

Only a few studies have examined losses of organic solutes from solutions that were pumped through various types of tubings, i.e., under dynamic conditions. Pearsall and Eckhardt (1987) found that concentrations of two VOCs tested were 8–15% lower in samples pumped through silicone rubber tubing than in samples pumped through Teflon tubing (at flow rates of 0.7–1.0 L/min). Ho (1983) reported that concentrations of organics were up to 15% lower in samples pumped through silicone rubber tubing than in the initial test solution (flow rates were 2.6–4.0 L/min). Ho also reported that there were signifi-

cant losses of two VOCs from a test solution that was pumped through PTFE tubing but did not quantify what those losses were. Only one study (Devlin 1987) has addressed what happens to analyte concentrations when the test solution is pumped through tubing for an extended period of time, i.e., whether equilibration occurs. Devlin (1987) reported that representative samples could be obtained through 100-ft sections of PE tubing after first flushing the tubing for 5–10 min, and that the equilibration time depended upon the length of the tubing and the pumping rate. However, Devlin did not provide any data that showed this.

Therefore, while we know that concentrations of some organic analytes can be affected when contaminated water is pumped through some tubings, we do not know the full extent of this effect. Other unanswered questions include 1) Do losses decrease with time? 2) Is equilibrium achieved? 3) How long does it take to reach equilibrium? 4) What is the extent of loss at equilibrium? and 5) Does flow rate affect the amount of loss or when equilibrium is achieved?

Leaching of organic constituents

Several studies (Junk et al. 1974, Curran and Tomson 1983, Barcelona et al. 1985, Parker and Ranney 1996) have shown that some polymeric tubings leach organic constituents under either static or dynamic conditions. This is especially true for flexible tubings such as PVC and various types of rubber (e.g., black latex, silicone) (Curran and Tomson 1983, Barcelona et al. 1985). One reason some flexible products tend to leach organic constituents is that they contain large percentages of plasticizers. For example, flexible PVC contains 30–50% plasticizers (by weight) (Junk et al. 1974, Aller et al. 1989), while rigid PVC contains less than 0.01% (Barcelona et al. 1984). In contrast, PTFE and other fluoropolymers have been shown not to leach any organic constituents (Junk et al. 1974, Curran and Tomson 1983, Barcelona et al. 1985). These materials do not contain plasticizers and generally do not contain many additives.

We (Parker and Ranney 1996) evaluated twenty tubings for evidence of leaching after 24 and 72 hr, using reversed-phase high performance liquid chromatography (RP-HPLC) analysis and an ultraviolet (UV) detector. Some of the organic compounds were later identified by gas chromatography–mass spectrometry (GC–MS). Among the rigid tubings, we found that after 72 hours' contact, several constituents had leached from the polyester-lined PVC and polyamide tubings (Table 2). In contrast, we were unable to detect that any constituents had leached from the six

Table 2. Number of spurious peaks and possible identity (from Parker and Ranney 1996).

| Material | Contact time | | Possible identity |
	1 hr	72 hr	
Flexible tubings			
plasticized PP1	1	1	not identified
plasticized PP2	0	0	
PVC	3	8	hexacosane
TPE	1	4	hexanedioic acid, dioctyl ester
P(VDF-HFP)	1	1	not identified
polyurethane	5	12	hexanoic acid, 2-ethyl
fluoroelastomer	1	1	not identified
Rigid tubings			
LDPE	0	0	
XLPE	0	0	
PE in EVA shell	0	0	
PE x-linked EVA shell	0	0	
Polyester-lined PVC	1	4	not identified
PP	1	1	hexanedioic acid, dioctyl ester
polyamide	2	9	benzene sulfonamide, N-butyl
PTFE	0	0	
PFA	0	0	
ETFE	0	0	
PVDF	0	0	
FEP	0	0	
FEP-lined PE	0	0	

rigid fluoropolymers and four polyethylene tubings, and detected only one constituent that had leached from the polypropylene tubing. Among the flexible tubings, we found several constituents leached from the PVC, thermoplastic elastomer, and polyurethane tubings (Table 2). The two fluoropolymer tubings and one of the plasticized polypropylene tubings (PP1) each leached one constituent; we were unable to detect that any constituents leached from the other plasticized polypropylene tubing (PP2). Our findings for the polypropylene (PP) and PE tubings are in general agreement with those of Junk et al. (1974) and Curran and Tomson (1983).

Two of the previous studies (Junk et al. 1974, Curran and Tomson 1983) were conducted under dynamic conditions (with flow rates of 60 and 30 mL/min, respectively). However, only one study has examined the effect flow rate (or linear velocity) has on leaching. Junk et al. (1974) observed that increasing the linear flow rate of water through flexible PVC tubing increased leaching. They attributed this to erosion of the polymer matrix. Curran and Tomson (1983) noted that the total amount of contaminants they observed leaching from the PE and PP tubings was less than what Junk et al. (1974) had observed. They attributed this to differences in flow rate, tubing conditioning, or manufacturing. However, there can also be several different formulations of the same polymer, and some constituents (additives) are more readily leached than others.

It is not clear what effect continued pumping has on leaching. Several leaching studies (Packham 1971a and 1971b, Gross et al. 1974, Boettner et al. 1981) have shown that leaching of organic constituents from PVC pipe decreases with time. This may also be true for some polymeric tubings. On the other hand, leaching may remain the same or increase with time, as Junk et al. (1974) observed with flexible PVC tubing. They reported that extensive rinsing of flexible PVC served no useful purpose and attributed this to the fact that flexible PVC tubing contained "an almost inexhaustible source of plasticizers." Thus, relatively little is known about the effect of flow rate and continued pumping on leaching of organic constituents.

Desorption of sorbed organic contaminants

Desorption of sorbed organic compounds by polymers proceeds in the opposite order of sorption, i.e., diffusion through the polymer matrix to the surface followed by partitioning/dissolution back into the aqueous solution. Because it has been shown that sorption of organic solutes by tubings can be substantial, desorption of sorbed organic contaminants has the potential to bias samples if tubing is used for more than one sampling event, especially if it is moved from a well containing high analyte concentrations to one with low analyte concentrations. Only a few studies have addressed this issue.

Barcelona et al. (1985) studied the release of organics from five flexible tubings: PP, PE, PTFE, flexible PVC, and silicone rubber. These tubings had been previously exposed to two test solutions, one containing ppb levels of chloroform and one containing ppb levels of four chlorinated organic solvents. Conditions for these tests were static, and desorption was followed for only 1 hr. They reported that most (80–90%) of the desorption occurred during the first 5 min, but by the end of the hour, most (> 50%) of the sorbed organic solutes had not been recovered. They also found that while the rate and extent of sorption was greatest for the PVC and silicone rubber tubings, the percent desorbed relative to the amount sorbed was greatest for PP and PE tubings, intermediate for PTFE, and lowest for the PVC and silicone rubber tubings.

Devlin (1987) also found that the PE tubing released contaminants over a longer period than Teflon tubing. A test solution containing fifteen VOCs (ppb levels) was pumped through both tubings, and PE was the more sorptive. Devlin found that pumping 5 L of deionized (DI) water through the fluoropolymer tubing reduced concentrations of the analytes in the rinse water to less than 1 ppb, but did not do so for the PE tubing. No information was provided relative to which tubing desorbed the analytes most relative to the amount sorbed, or what flow rate was used in the study. Devlin concluded that carryover of organic contaminants may be a problem unless a fluoropolymer tubing is used.

Thus, very little is known about the kinetics of desorption, especially when water is pumped through the tubings. Furthermore, the effect that flow rate has on this process is unclear.

OBJECTIVE

The purpose of these studies was to determine whether, under dynamic conditions, polymeric tubings sorbed TCE from contaminated well water, leached organic constituents, or desorbed sorbed TCE. In our sorption/leaching studies,

we quantified losses when the flow rates were moderately fast (1 L/min) and slow (100 mL/min), determined if equilibration occurs and when, and investigated whether organic constituents or constituents that interfered with organic analyses were leached. In our desorption study, we determined whether TCE was released from contaminated sampling tubings when organic-free water was pumped through them at a slow flow rate, and again looked for leaching of organic constituents or compounds that interfered with organic analyses.

MATERIALS AND METHODS

Materials

The five tubing materials used in this study were LDPE, one rigid fluoropolymer (PVDF), one flexible fluoropolymer [P(VDF-HFP)], and two formulations of plasticized polypropylene (PP1, PP2). We selected these tubings because, in our previous study (Parker and Ranney 1996), we found that these tubings ranged from relatively highly sorptive (PP1 and PP2) to least sorptive (PVDF) and that they leached little or no organic constituents under long-term static storage (as determined by HPLC analyses with a UV detector). All the tubings had an inside diameter of 0.25 in. and were not pre-cleaned prior to the study.

Water contaminated with trichloroethylene (TCE) was obtained from an artesian well that can supply up to 380 gal/min, located at our facility. The water from this well is used by our facility for cooling after it is treated to remove the TCE.

Experimental design for the sorption studies

For these studies, we tapped the outflow pipe from the TCE-contaminated well and drew water off at flow rates that varied from 100 mL/min to 3 L/min. The well water was diverted from the outflow pipe to a water distribution system consisting of a master flow valve; an electronic flow meter connected to a Linear 555 chart recorder; a three-port valve, which allowed samples to be siphoned off but still allowed flow to continue through the tubings; and a bank of five multi-turn needle valves, where up to five tubings could be connected (Fig. 4). The materials used in the distribution system consisted primarily of copper, brass, and glass. There was a small amount of Teflon, perfluoroalkoxy, and Kel-F that were used in the O-rings, three-port valve, and needle valve body. To flush the system, the well water was pumped through the system for several hours prior to connecting the tubings. Strip chart recordings showed that the flow rate into the distribution system varied by approximately 10%. The rate of flow through each tubing was routinely monitored by collecting a volume of water from the outflow of the tubing in a graduated cylinder and measuring the time with a stopwatch. Flow through each tubing was regulated by turning the appropriate multi-turn needle valve at the end of the distribution system. To expel air from the tubings as they filled with water, the tubings were wound around a 55-gallon metal drum in an upward spiral fashion.

In our first study, all five tubings [PVDF, P(VDF-HFP), LDPE, PP1, and PP2] were tested. TCE-contaminated well water was pumped through three different lengths (10 ft, 50 ft, 100 ft) of tubing at a slow flow rate (100 mL/min). In our second study, the TCE-contaminated well water was pumped through 500 ft of LDPE at the same flow rate (100 mL/min). In our third study, the contaminated well water was pumped through 100-ft sections of three tubings (PP1, LDPE, and PVDF) at a much faster flow rate, 1 L/min.
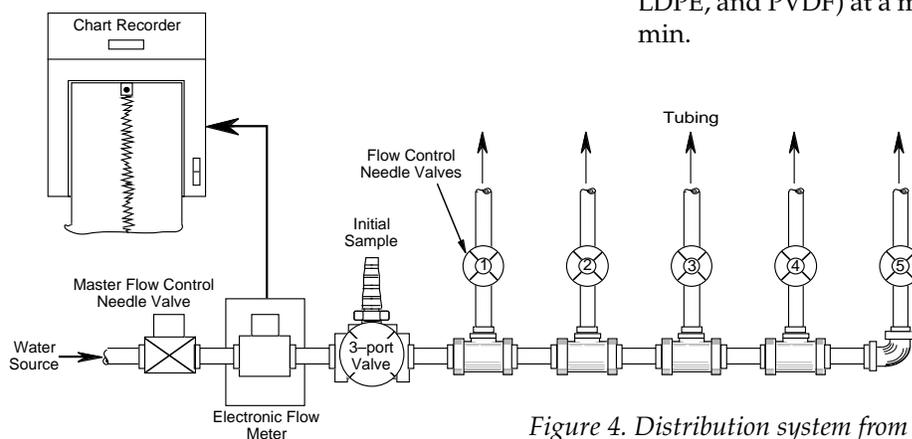
Figure 4. Distribution system from water source to tubings.

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Table 3. Sampling times during sorption studies.

	First study			Second study	Third study
	10-ft tubing	*50-ft tubing*	*100-ft tubing*		
10 min	X	X	X	X	X
30 min	X	X	X	X	X
1 hr	X	X	X	X	X
4 hr	X	X	X	X	X
8 hr	X	X	X	X	X
13 hr	X				
1 day (24 hr)	X	X	X	X	X
2 days (48 hr)	X	X	X	X	X
3 days (72 hr)	X	X	X	X	X
4 days (96 hr)		X	X		X
6 days (144 hr)				X	
7 days (168 hr)		X	X		X
8 days (192 hr)		X		X	
9 days (216 hr)		X			
10 days (240 hr)		X			
11 days (264 hr)			X		
16 days (384 hr)			X		

The times that the samples were collected in these three studies are given in Table 3. For each tubing material and sampling time, three samples were collected by filling 1.8-mL HPLC autosampler vials directly from the tubing outflow. To determine the initial concentration of TCE in the well water for a given time, three control samples were obtained by collecting water from the three-port valve (Fig. 3). The samples were analyzed immediately after collection.

Experimental design for the desorption/leaching study

Three of the tubing materials from the sorption/leaching study were selected for this study (PVDF, LDPE, and PP1). Of the polymeric tubings tested previously (Parker and Ranney 1996), these materials ranged from the least sorptive to highly sorptive. These tubings were contaminated by pumping contaminated well water through them at a flow rate of 1 L/min for seven days (168 hr). The needle valves in the distribution system were closed to stop flow into the tubings. The distribution system (Fig. 4) was then disconnected from the well's pump and the complete system was moved from the well house to the laboratory. The distribution system was then connected to the laboratory's DI water source, and DI water was pumped through each tubing at a flow rate of 100 mL/min. Samples were collected after 10 min, 30 min, 1 hr, 4 hr, 8 hr, 24 hr, 48 hr, 72 hr (three days), and 96 hr (four days).

Analyses

Analytical determinations were performed using RP-HPLC. A modular system was employed consisting of a Dynatech LC–241 autosampler with a 100-μL injection loop, a Spectra Physics SP8810 isocratic pump, a Spectra Physics SP100 variable-wavelength UV detector set at 215 nm, and a Hewlett Packard 3396 series II digital integrator. Separations were obtained on a 25- × 0.46-cm (5 μm) LC–18 column (Supelco) and eluted with 1.5 mL/min of 65/35 (V/V) methanol/water. The detector response was obtained from the digital integrator operating in the peak height mode. A primary TCE standard was made by weighing neat TCE into methanol in a 100-mL volumetric flask, giving a final concentration of 3,000 mg/L. This standard was kept in the freezer. Each day a series of water standards was made from the primary standard by serial dilution using pipets and volumetric flasks. These standards ranged in concentration from 3.0–0.006 mg/L.

The Method Detection Limit (MDL) for TCE (0.0026 mg/L) was determined by using the protocol described in the Federal Register (1984).

Data analysis

For each time, analysis of variance (ANOVA) tests were conducted to determine whether the tubing had any significant effect (at the 95% confidence level) on the TCE concentrations when compared with control values. When significant differences were found, Fisher's Protected Least Significant Difference Test was performed to determine which tubing materials were significantly different from the controls and each other.

The mean normalized concentrations of TCE were obtained by taking the mean concentration

of a sample exposed to a tubing for a given sampling time and dividing it by the mean concentration for the control samples for the same time. Thus a mean normalized value of 1.00 represents no loss of TCE for a given tubing and time.

The total amount desorbed (mg) from each tubing was determined by 1) plotting the concentration desorbed vs. time, 2) taking the sum of the areas under lines drawn from time 1 to time 2, time 2 to time 3, etc., and 3) multiplying the total area by the flow rate.

The total amount sorbed (mg) by the PP1 tubing was determined by 1) subtracting the concen-

tration (mg/L) after passing through the tubing from the control concentration (mg/L), 2) plotting the difference (mg/L) vs. time, 3) taking the sum of the areas under the lines drawn from time 1 to time 2, time 2 to time 3, etc., and then 4) multiplying the total area by the flow rate.

RESULTS AND DISCUSSION

Sorption/leaching studies

Sorption findings for the first study
    Figures 5, 6, and 7 show the normalized con-
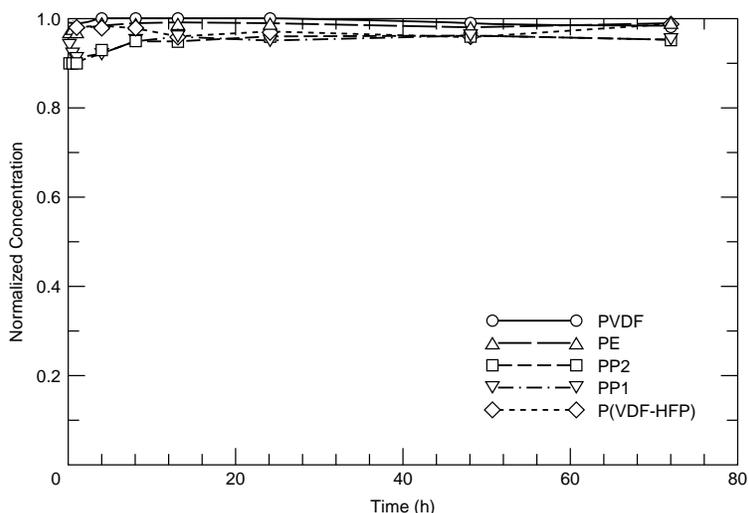
Figure 5. Normalized concentration of TCE in water pumped through 10 ft of tubing at 100 mL/min.
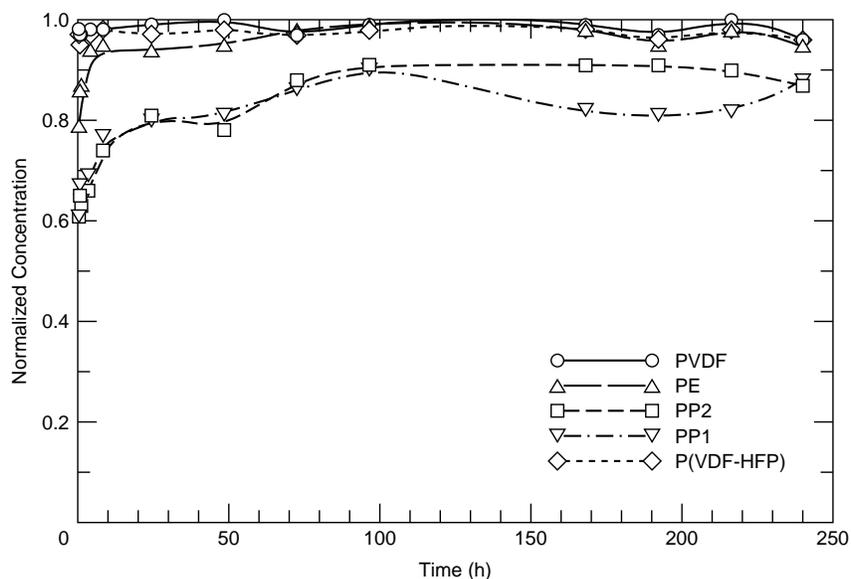
Figure 6. Normalized concentration of TCE in water pumped through 50 ft of tubing at 100 mL/min.

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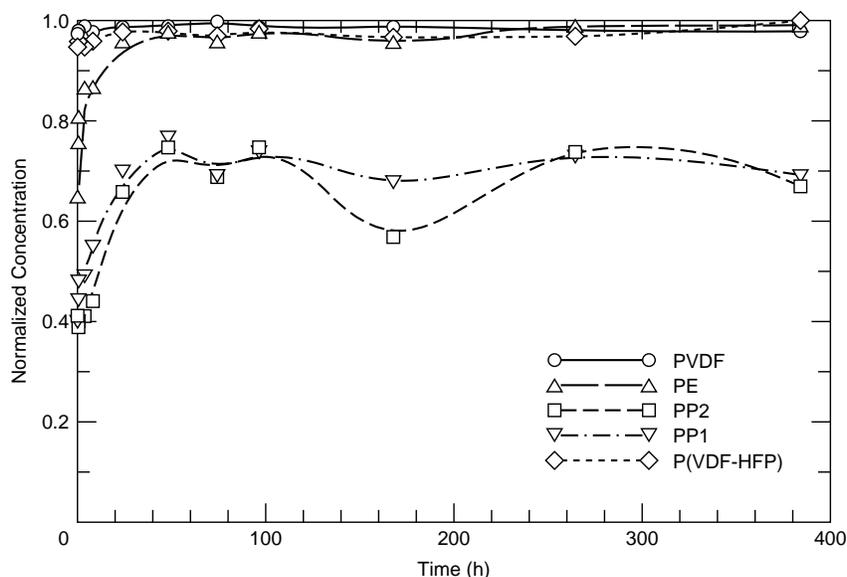
Figure 7. Normalized concentration of TCE in water pumped through 100 ft of tubing at 100 mL/min.

centration of TCE in well water that was pumped through 10-ft, 50-ft, and 100-ft lengths of PVDF, P(VDF-HFP), PP1, PP2, and LDPE tubings at a flow rate of 100 mL/min. (Appendix Table A1 gives the mean normalized concentrations, and Appendix Table B1 gives the actual concentrations of TCE [in mg/L] in the well water before and after pumping it through the various tubings. Appendix Table B1 also shows the results of the statistical analyses.) The two fluoropolymers, PVDF and P(VDF-HFP), were clearly the least sorptive tubings tested. Sorption of TCE by these two fluoropolymers was always 5% or less, even for the 100-ft sections. For the other polymers, sorption was minimal (<10%) for the 10-ft sections of tubing but became substantial when longer tubings (50 ft and 100 ft) were used. Losses were greatest initially but then approached some type of equilibrium value.

For LDPE, initial losses of TCE were 20% for the 50-ft and 35% for the 100-ft lengths. However, these losses were reduced to ~5% after 4 hr of pumping for the 50-ft lengths and after 24 hr for the 100-ft lengths. It appears that the tubing and TCE-contaminated water reached equilibrium at these times. The large losses observed initially were most likely due to adsorption on the polymer surface. The residual losses that were found at equilibrium most likely resulted from diffusion through the polymer matrix.

The pattern of losses was similar for the two plasticized polypropylene tubings (PP1, PP2). However, losses were much greater for these materials, both initially and at equilibrium. For example, after ten minutes' contact, ~60% of the TCE was sorbed by the 100-ft sections of these tubings. However, losses were still substantial at equilibrium with losses of 10–20% for the 50-ft sections and 30% for the 100-ft sections. We are not certain what accounts for the pronounced dip in the curves around 150–200 hr for the 50-ft length of PP1 or 100-ft length of PP2. It may be due to breakthrough of the TCE through the tubing walls to the atmosphere.

These results agree well with the results from our static study (Parker and Ranney 1996). That is, among the tubings tested in this study, the plasticized PP tubings sorbed the most TCE and the fluoropolymers were the least sorptive.

Based on these findings, it appears that LDPE could be used to sample TCE if there is an adequate equilibration period. This does not appear to be true for the plasticized polypropylene tubings. Because there would be a substantial cost savings if LDPE tubing could be used, the next experiment was designed to see how much TCE would be lost with a much longer length of LDPE tubing (500 ft) and when equilibration might be expected. A five-hundred-foot well would be one of the deeper wells one might sample, but certainly not the deepest.

Sorption findings for the second study

Figure 8 shows the mean relative concentration of TCE in water that was pumped through 500 ft of LDPE tubing at a flow rate of 100 mL/

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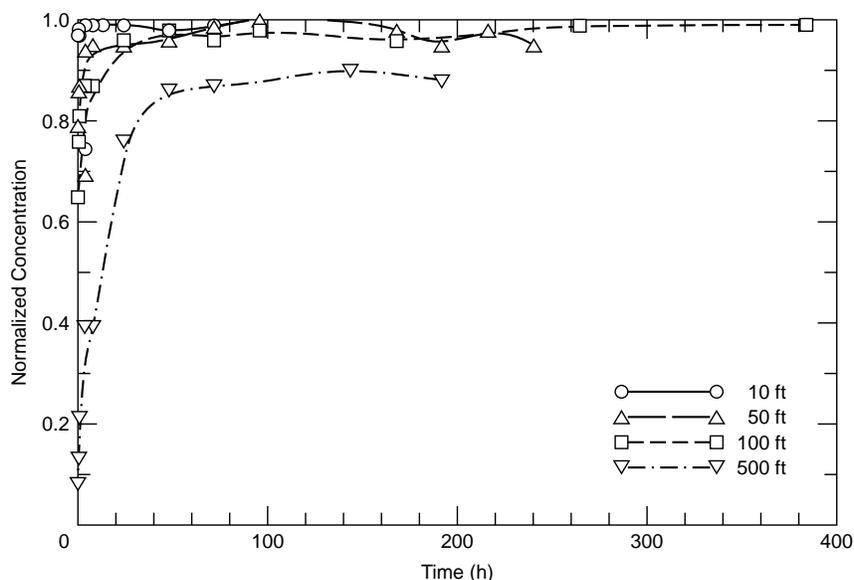
Figure 8. Comparison of losses of TCE by different lengths of LDPE tubing.

min. (Appendix Table A2 gives the mean normalized concentrations of TCE, and Appendix Table B2 gives the concentrations of TCE [in mg/L] in the water before and after pumping it through the tubing.) For this length of tubing, sorption was much more pronounced initially, with 92% loss after 10 min. Equilibration appears to occur after 48 hr of pumping, with residual losses of 10–15%. For comparison, Figure 8 also shows losses of TCE from water pumped through the 100-ft, 50-ft, and 10-ft lengths. The relationship

Table 4. Relationship between the pumping time (t) and the relative concentration (C_t) of TCE in water pumped through various lengths of LDPE tubing at 100 mL/min.

Length (ft)	Contact time (min)*	Relationship	r†
10	1	$C_t = 0.978 + 0.0067 \log(t)$	0.709
50	5	$C_t = 0.873 + 0.0495 \log(t)$	0.890
100	10	$C_t = 0.785 + 0.0932 \log(t)$	0.954
500	50	$C_t = 0.244 + 0.309 \log(t)$	0.975

* Time for water to pass through tubing.
† Correlation coefficient.

between the pumping time (t) and the relative concentration (C_t) for the various lengths of tubings is given in Table 4. It is clear that for the longer tubings or contact times, sorptive losses can be adequately described by a log function.

Sorption findings for the third study

In this study, we wanted to determine what

effect a faster flow rate had on sorption. Because of physical limitations we had with the delivery system, only three tubings could be used in this study. We selected PP1, LDPE, and PVDF. We eliminated PP2 because its performance was very similar to PP1 and P(VDF-HFP) because its performance was very similar to PVDF.

Figure 9 shows the relative concentrations of TCE in water that was pumped through 100-ft sections of these tubings at a flow rate of 1 L/min. (Appendix Table A3 gives the mean normalized concentrations and Appendix Table B3 gives the initial and final concentrations [in mg/L] and the results of the statistical analyses.) Statistical analyses indicated that the concentrations of TCE in samples pumped through the PP1 tubing were significantly lower than the controls. However, these losses were always less than 10%. In general, concentrations of TCE in water pumped through the PVDF and LDPE tubings did not differ significantly from the controls.

Figures 10a and 10b compare sorption of TCE in water pumped through 100 ft of LDPE and PP1 tubing, respectively, at the two flow rates (1 L/min and 100 mL/min). The relationship between the pumping time and the relative concentration of TCE for each of the two tubings and flow rates is given in Table 5. We see a similar trend to the one we observed with the longer lengths of tubing, namely that at the slower flow rate (or longer contact time) sorption can be adequately described by a log function. There is good agreement between the expression for the relative concentration of TCE in water pumped through 100

10
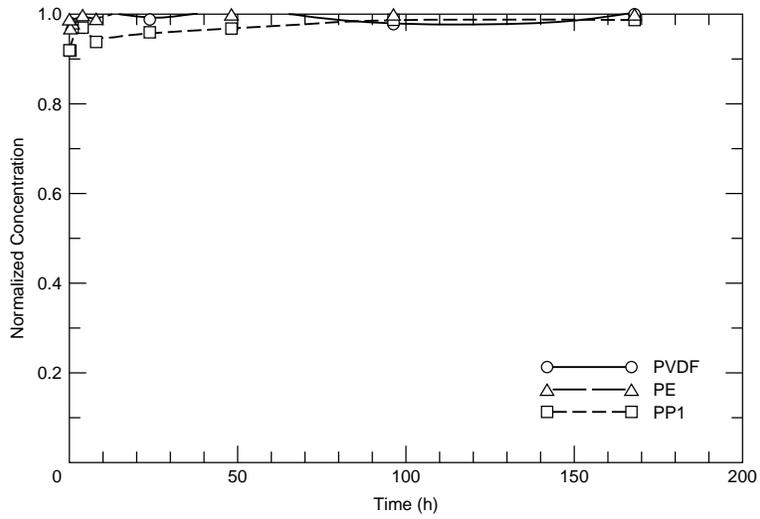
Figure 9. Normalized concentration of TCE in water pumped through 100 ft of tubing at 1 L/min.
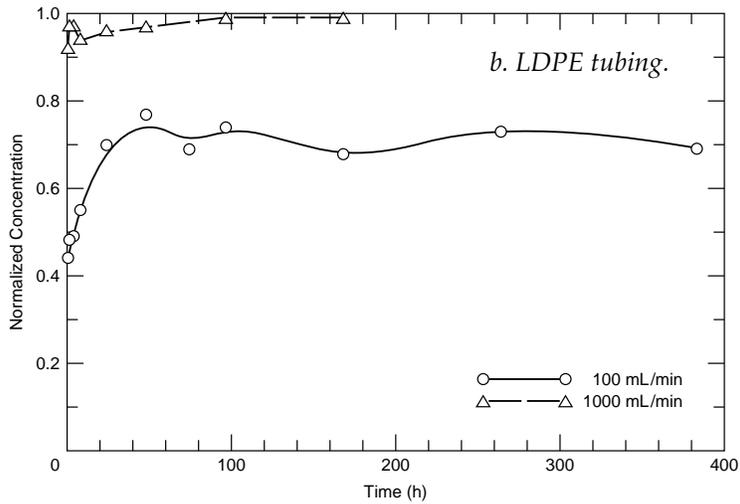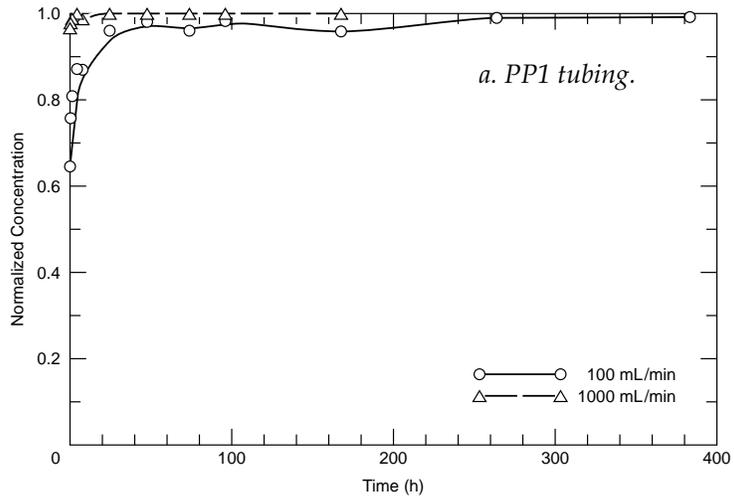
*Figure 10. Comparison of losses of TCE in water pumped through 100 ft of tubing at different flow rates.*

Table 5. Relationship between the pumping time (*t*) and the relative concentration (C_t) of TCE in water pumped through 100 ft of tubing at different flow rates.

Flow (mL/min)	Contact time (min)*	Relationship	r†
LDPE			
100	10	$C_t = 0.785 + 0.0932 \log(t)$	0.954
1,000	1	$C_t = 0.986 + 0.0082 \log(t)$	0.706
PP1			
100	10	$C_t = 0.492 + 0.102 \log(t)$	0.909
1,000	1	$C_t = 0.941 + 0.0205 \log(t)$	0.811

* Time for water to pass through tubing.
† Correlation coefficient.

Table 6. Predicted normalized concentrations of TCE following pumping at 1 L/min for various pumping times.

Tubing length (ft)	Sample contact time (min)*	Pumping time (hr)	Predicted normal conc. TCE
100	1	4	0.98
500	5	4	0.90
1,000	10	4	0.84
100	1	2	0.98
500	5	2	0.88
1,000	10	2	0.81

* Time for water to pass through tubing.

ft of LDPE at 1 L/min (Table 5) and water pumped through 10 ft of LDPE tubing at 100 mL/min (Table 4). In both cases, the contact time was 1 min. Thus, it appears that contact time can be used to predict losses.

We used the relationships derived in Table 4 for 5- and 10-min contact times to predict what the losses might be for TCE-contaminated water pumped through 500 ft and 1,000 ft of LDPE at 1 L/min, after allowing the tubing to equilibrate for either 2 or 4 hr. We see that if only 2 hr were allowed for equilibration, the estimated losses would be only slightly greater than 10% for 500 ft (Table 6). Only for the 1000-ft lengths would a longer equilibration time (4 hr) be required if the flow rate was 1 L/min. Thus, we would predict that longer lengths (500 ft and greater) of LDPE could be used to sample TCE at a flow rate of 1 L/min if 2–4 hr is given for equilibration. However, these predictions need to be verified by additional testing, and other analytes need to be considered.

General discussion on sorption

Our low-flow-rate studies indicate that although the more sorptive plasticized polypropylene tubings do reach equilibrium with the contaminated well water, the change in the normalized concentration of TCE at equilibrium is large enough to bias results. It appears that the less sorptive LDPE could be used to sample TCE in all but the deepest wells (> 100 ft) if the tubing were equilibrated (pumped) for 2–4 hr. The question that then remains is what would happen with the other analytes that are more readily sorbed by this tubing, such as PCE and PDCB (Parker and Ranney 1996). Based upon our previous findings (Parker and Ranney 1996), we expect that losses of PDCB and PCE would be substantially greater at equilibrium than what we observed with TCE. However, currently this is unproven.

Clearly, the fluoropolymers tested in this study [PVDF, P(VDF-HFP)] did not sorb much TCE. We were surprised to find there was no significant difference between the concentrations of TCE in samples exposed to the PVDF and P(VDF-HFP) tubings. In our previous study (Parker and Ranney 1996), losses were always much greater for test solutions exposed to the flexible fluoropolymers than those exposed to the rigid fluoropolymers. We suspect that we would have detected some differences between these two materials if a longer length of tubing or a more sorptive analyte had been tested. However, this also remains unproven.

If the samples are to be pumped at a rapid rate (1 L/min), it appears that LDPE tubing can be used to sample most wells for TCE, although 2–4 hr should be allowed for equilibration in wells 500 ft and greater. However, additional tests should be conducted with longer lengths of tubing and more sorptive analytes to prove this.

Leaching findings

We did not detect any spurious peaks, using RP-HPLC analysis and a UV detector, in any of the samples that had been pumped through any of the tubings used in these experiments, even the longest lengths. However, we should mention that because the concentration of our analyte of interest, TCE, was in the low mg/L range, these analyses were not highly sensitive. Also, UV detectors are not universal detectors and many organic constituents that might be leached would not be found using this type of detector. UV detectors are most sensitive for conjugated bonds and sulfur-, nitrogen-, bromine-, and iodine-

containing compounds (Johnson and Stevenson 1978). These results agree reasonably well with the findings from our static study (Parker and Ranney 1996) where we did not find any spurious peaks in any of the test solutions exposed to the PVDF, LDPE, and PP2 tubings, and found only one spurious peak in the test solutions exposed to the PP1 and P(VDF-HFP) tubings.

Desorption/leaching study

Desorption findings

Another concern in the monitoring industry is whether there is carryover when a tubing is used to sample more than one well. It is not known how long a tubing would continue to desorb sorbed contaminants. This study looked at the dynamics of this process for three tubings that ranged from relatively nonsorptive to highly sorptive (PVDF, PP1, and LDPE). These tubings were contaminated by pumping TCE-contaminated well water through them at a flow rate of 1 L/min for seven days. Figure 11 shows the mean concentration (mg/L) of TCE that was released into the DI water pumped through these three tubings at a flow rate of 100 mL/min. (Appendix Table B4 gives all the data.) After 30 min, which corresponds to rinsing the tubing with three tubing volumes of water, DI water pumped through the PP1 and LDPE tubings contained high µg/L concentrations of TCE (776 and 396 µg/L, respectively), while water that was pumped through the PVDF tubing contained only low µg/L concentra-

tions (14 µg/L) (Appendix Table B4). After 8 hr, the TCE concentration in water that was pumped through the PVDF tubing was below the detection level (< 2.6 µg/L). In contrast, both the LDPE and PP1 tubings continued to release high µg/L concentrations of TCE into the DI water for 8–24 hr and low µg/L concentrations for the remainder of the experiment (four days or 96 hr).

These results and those of Devlin (1987) show that while contaminants are removed from fluoropolymer tubing much more readily than from other types of tubing, simply rinsing fluoropolymer tubing with organic-free water is not adequate for removing sorbed organic contaminants.

The relationship between the pumping time and the concentration desorbed for each of the three tubings is given in Table 7. In this instance, a negative log function adequately describes desorption from the more sorptive polymers (LDPE, PP1).

Table 7. Relationship between the pumping time (t) and the concentration, mg/L (C_d), of TCE desorbed into water pumped through 100 ft of contaminated tubing at 100 mL/min.

Material	Contact time (min.)*	Relationship	r[†]
PVDF	10	$C_d = 0.971 - 0.0696 \log(t)$	0.625
LDPE	10	$C_d = 0.419 - 0.248 \log(t)$	0.925
PP1	10	$C_d = 0.647 - 0.343 \log(t)$	0.992

*Time for water to pass through tubing.
† Correlation coefficient.
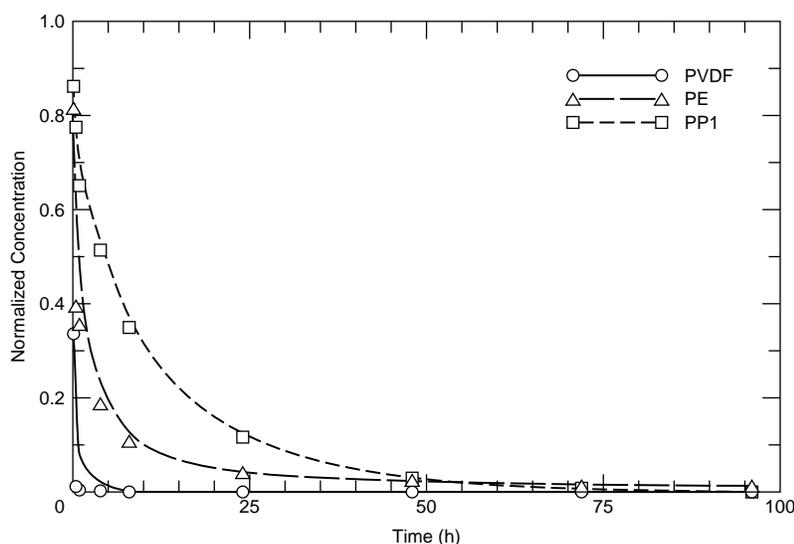
Figure 11. Desorbed concentration of TCE in organic-free water pumped through 100 ft of contaminated tubing.

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Table 8. Total amount of TCE sorbed and desorbed by tubing.

Tubing	Sorbed[1] (mg)	Desorbed[2] (mg)
PVDF	—	0.91
LDPE	—	28.7
PP1	273	62.6

[1] After pumping contaminated water through 100 ft of tubing at 1 L/min for seven days.
[2] After pumping DI water through tubing at 100 mL/min for four days.

Table 8 gives the amount desorbed by these three tubings and also shows the amount sorbed by the PP1 tubing. No estimate was made for sorption by the other two tubings because losses of TCE were not significant for them. After four days, it appears that only 23% of the TCE was recovered from the PP1 tubing.

Leaching findings

We did not observe any spurious peaks, using RP-HPLC analyses with a UV detector, in the water samples that were pumped through the PVDF, LDPE, or PP1 tubings at 100 mL/min. In this case, the sensitivity of the analyses was much greater because we were looking for low μg/L concentrations. However, our analysis time was not as long in this experiment as in our previous study (Parker and Ranney 1996) where leaching was observed. The results from this study are consistent with the results from our static study (Parker and Ranney 1996), where only one constituent was detected leaching from any of the tubings, PP1.

CONCLUSIONS

The results from this study along with those from our previous study (Parker and Ranney 1996) show that, with respect to sorption, 1) generally rigid fluoropolymers should be used when sampling for organic contaminants using slow-rate pumping (100 mL/min), especially if the contaminants are unknown, and 2) if a flexible tubing is required, then P(VDF-HFP) or a fluoroelastomer are the least likely to bias test results. It appears that there are instances when a less expensive tubing such as LDPE can be used to sample less sorptive (more hydrophilic) analytes such as TCE. These conditions are when 1) a slow

pumping rate (100 mL/min) is used to sample a shallow well (<50 ft), and 2) a faster flow rate is used (1 L/min) in deeper wells, although 2–4 hr should be allowed for equilibration in the deepest wells (500 ft and greater). However, we realize that equilibration for 2–4 hr may not be practical in all instances. We also recommend that there be additional testing with other analytes.

In this study, we were unable to detect (using an HPLC with a UV detector) that any organic constituents leached from any of the five tubings tested when either a slow rate (100 mL/min) or a moderately fast rate (1 L/min) was used to pump water through the tubings. These results agree reasonably well with our previous static study (Parker and Ranney 1996), where, using similar methods of analysis, we detected only one constituent that leached from two of these tubings [PP1, P(VDF-HFP)].

This study also shows that desorption of sorbed organic solutes, such as TCE, can be a problem if slow-flow pumping is used. This is true whether the tubing is relatively nonsorptive (e.g., PVDF) or highly sorptive (e.g., PP1). Furthermore, pumping organic-free water through these tubings at this flow rate is not an effective way to remove TCE.

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APPENDIX A: MEAN NORMALIZED CONCENTRATIONS OF TCE

Table A1. Mean normalized concentrations of TCE sorbed by various lengths of tubing at a flow rate of 100 mL/min.

Time (hr)	PVDF	LDPE	PP2	PP1	P(VDF-HFP)
10 ft					
0.17	1.02	0.97	0.90	0.94	1.01
0.5	1.01	0.98	0.90	0.92	0.98
1	0.98	0.97	0.90	0.91	0.98
4	1.00	0.99	0.93	0.92	0.98
8	1.00	0.99	0.95	0.95	0.98
13	1.00	0.99	0.95	0.96	0.96
24	1.00	0.99	0.96	0.95	0.97
48	0.99	0.98	0.96	0.96	0.96
72	0.98	0.99	0.95	0.95	0.99
50 ft					
0.17	0.98	0.79	0.61	0.63	0.96
0.5	0.97	0.86	0.65	0.67	0.95
1	0.97	0.87	0.63	0.64	0.97
4	0.98	0.94	0.66	0.69	0.97
8	0.98	0.95	0.74	0.77	0.98
24	0.99	0.95	0.83	0.82	0.97
48	1.00	0.96	0.80	0.83	0.99
72	0.97	0.99	0.90	0.87	0.97
96	0.99	1.00	0.91	0.90	0.98
168	0.99	0.98	0.91	0.82	0.98
192	0.97	0.95	0.91	0.81	0.96
216	1.00	0.98	0.90	0.82	0.98
240	0.96	0.95	0.87	0.88	0.96
100 ft					
0.17	0.97	0.65	0.41	0.44	0.96
0.5	0.98	0.76	0.39	0.44	0.95
1	0.98	0.81	0.40	0.48	0.96
4	0.99	0.87	0.41	0.49	0.95
8	0.98	0.87	0.44	0.55	0.96
24	0.99	0.96	0.66	0.70	0.98
48	0.99	0.98	0.75	0.77	0.98
74	1.00	0.96	0.69	0.69	0.97
96	0.99	0.98	0.75	0.74	0.98
168	0.99	0.96	0.57	0.68	0.97
264	0.98	0.99	0.74	0.73	0.97
384	0.98	0.99	0.67	0.69	1.00

Table A2. Mean normalized concentrations of TCE sorbed by 500 ft of LDPE tubing at a flow rate of 100 mL/min.

Time (hr)	Concentration
0.17	0.08
0.5	0.13
1	0.21
4	0.39
8	0.39
24	0.76
48	0.86
72	0.87
144	0.90
192	0.88

Table A3. Mean normalized concentrations of TCE sorbed by 100 ft of tubing material at a flow rate of 1,000 mL/min.

Time (hr)	Treatment		
	PVDF	LDPE	PP1
0.17	1.06	0.99	0.92
0.5	0.98	0.97	0.92
1	1.03	0.98	0.97
4	1.02	1.00	0.97
8	1.00	0.99	0.94
24	0.99	1.01	0.96
48	1.00	1.00	0.97
96	1.00	1.00	0.99
168	1.00	1.00	0.99

APPENDIX B: CONCENTRATION OF TCE

Table B1. Concentration of TCE (mg/L) in well water before and after flowing through various lengths of tubing at a rate of 100 mL/min.

					Time (hr)				
Treatment	0.17	0.5	1	4	8	13	24	48	72
10 ft of tubing									
initial	0.086	0.099	0.109	0.208	0.293	0.441	0.884	1.207	1.846
initial	0.088	0.095	0.110	0.212	0.297	0.443	0.907	1.269	1.912
initial	0.090	0.099	0.108	0.206	0.290	0.440	0.896	1.239	1.762
$\overline{X}$	0.088[a,b]	0.098[a,b]	0.109[a]	0.209[a]	0.293[a,b]	0.441[a]	0.896[a]	1.238[a]	1.840[a]
PVDF	0.091	0.098	0.107	0.211	0.291	0.439	0.893	1.227	1.801
PVDF	0.089	0.099	0.105	0.210	0.294	0.441	0.897	1.221	1.858
PVDF	0.089	0.100	0.109	0.206	0.298	0.441	0.891	1.218	1.777
$\overline{X}$	0.090[a]	0.099[a]	0.107[a,b]	0.209[a]	0.294[a]	0.440[a]	0.894[a]	1.222[a]	1.812[a]
LDPE	0.086	0.095	0.105	0.201	0.288	0.437	0.884	1.195	1.896
LDPE	0.085	0.095	0.107	0.210	0.296	0.439	0.889	1.223	1.695
LDPE	0.086	0.098	0.105	0.211	0.288	0.438	0.885	1.214	1.877
$\overline{X}$	0.086[b]	0.096[b]	0.106[b]	0.207[a]	0.291[a,b]	0.438[a]	0.886[a]	1.211[a,b]	1.823[a]
PP2	0.077	0.087	0.097	0.196	0.278	0.416	0.863	1.183	1.681
PP2	0.081	0.089	0.097	0.194	0.273	0.418	0.856	1.181	1.709
PP2	0.081	0.088	0.099	0.195	0.281	0.419	0.852	1.188	1.860
$\overline{X}$	0.080[c]	0.088[c]	0.098[c]	0.195[b]	0.277[c]	0.418[b]	0.857[c]	1.184[b]	1.750[a]
PP1	0.079	0.090	0.097	0.196	0.274	0.422	0.852	1.174	1.672
PP1	0.084	0.090	0.100	0.179	0.281	0.423	0.855	1.211	1.807
PP1	0.084	0.091	0.100	0.200	0.279	0.424	0.858	1.171	1.767
$\overline{X}$	0.082[c]	0.090[c]	0.099[c]	0.192[b]	0.278[c]	0.423[b]	0.855[c]	1.185[b]	1.749[a]
P(VDF-HFP)	0.088	0.096	0.106	0.204	0.289	0.432	0.871	1.184	1.839
P(VDF-HFP)	0.088	0.094	0.107	0.210	0.290	0.432	0.861	1.188	1.865
P(VDF-HFP)	0.090	0.098	0.108	0.202	0.282	0.412	0.873	1.199	1.752
$\overline{X}$	0.089[a,b]	0.096[b]	0.107[a,b]	0.205[a]	0.287[b]	0.425[b]	0.868[b]	1.190[b]	1.819[a]

For a given time, values with the same letter are not significantly different from each other.

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Table B1 (cont'd). Concentration of TCE (mg/L) in well water before and after flowing through various lengths of tubing at a rate of 100 mL/min.

	Time (hr)												
Treatment	0.17	0.5	1	4	8	24	48	72	96	168	192	216	240
50 ft of tubing													
initial	2.34	2.42	2.51	2.53	2.59	2.50	2.46	2.36	2.30	2.51	2.53	2.33	2.29
initial	2.38	2.39	2.47	2.58	2.66	2.51	2.42	2.36	2.33	2.55	2.52	2.38	2.27
initial	2.38	2.42	2.53	2.58	2.61	2.53	2.47	2.37	2.44	2.55	2.60	2.33	2.27
$\overline{X}$	2.37[a]	2.41[a]	2.50[a]	2.56[a]	2.62[a]	2.51[a]	2.45[a]	2.36[a]	2.36[a]	2.54[a]	2.55[a]	2.35[a]	2.28[a]
PVDF	2.33	2.32	2.40	2.52	2.57	2.51	2.41	2.33	2.34	2.51	2.37	2.31	2.15
PVDF	2.32	2.32	2.43	2.51	2.56	2.53	2.45	2.29	2.38	2.53	2.53	2.35	2.16
PVDF	2.32	2.34	2.44	2.52	2.58	2.45	2.50	2.29	2.29	2.50	2.52	2.35	2.23
$\overline{X}$	2.32[b]	2.33[b]	2.42[b]	2.52[b]	2.57[b]	2.50[a]	2.45[a]	2.30[c]	2.34[a]	2.51[a,b]	2.47[a,b]	2.34[a,b]	2.18[b]
LDPE	1.86	2.06	2.20	2.42	2.50	2.37	2.36	2.33	2.35	2.51	2.47	2.31	2.18
LDPE	1.89	2.04	2.15	2.41	2.48	2.37	2.30	2.33	2.35	2.48	2.42	2.27	2.12
LDPE	1.87	2.09	2.16	2.42	2.50	2.42	2.36	2.33	2.36	2.48	2.42	2.31	2.16
$\overline{X}$	1.87[d]	2.06[d]	2.17[c]	2.42[d]	2.49[c]	2.39[b]	2.34[b]	2.33[b]	2.35[a]	2.49[b,c]	2.44[b]	2.30[b]	2.15[b]
PP2	1.46	1.55	1.57	1.70	1.94	2.10	1.90	2.11	2.15	2.32	2.34	2.11	1.95
PP2	1.45	1.58	1.54	1.70	1.92	2.10	2.03	2.13	2.15	2.31	2.28	2.12	2.02
PP2	1.45	1.57	1.59	1.69	1.92	2.04	1.96	2.11	2.16	2.32	2.34	2.09	1.97
$\overline{X}$	1.45[f]	1.57[f]	1.57[d]	1.70[f]	1.93[e]	2.08[c]	1.96[c]	2.12[d]	2.15[b]	2.32[d]	2.32[c]	2.11[c]	1.98[c]
PP1	1.51	1.65	1.62	1.74	2.01	2.12	2.02	2.06	2.13	2.08	2.06	1.96	1.98
PP1	1.49	1.59	1.62	1.75	2.00	2.06	2.05	2.07	2.14	2.07	2.07	1.89	2.00
PP1	1.51	1.62	1.58	1.78	2.01	1.98	1.99	2.08	2.11	2.07	2.06	1.94	2.00
$\overline{X}$	1.50[e]	1.62[e]	1.61[d]	1.76[e]	2.01[d]	2.05[c]	2.02[c]	2.07[e]	2.13[b]	2.07[e]	2.06[d]	1.93[d]	1.99[c]
P(VDF-HFP)	2.28	2.30	2.42	2.49	2.56	2.46	2.42	2.30	2.31	2.47	2.43	2.31	2.18
P(VDF-HFP)	2.27	2.26	2.40	2.48	2.57	2.42	2.42	2.30	2.31	2.47	2.47	2.28	2.19
P(VDF-HFP)	2.26	2.29	2.43	2.46	2.56	2.46	2.38	2.29	2.31	2.49	2.45	2.33	2.17
$\overline{X}$	2.27[c]	2.28[c]	2.42[b]	2.48[c]	2.56[b]	2.45[a,b]	2.41[a,b]	2.30[c]	2.31[a]	2.48[c]	2.45[b]	2.31[a,b]	2.18[b]

	Time (hr)											
Treatment	0.17	0.5	1	4	8	24	48	72	96	168	264	384
100 ft of tubing												
initial	2.15	2.12	2.13	2.07	2.14	2.09	1.94	2.21	1.97	1.97	2.06	2.19
initial	2.16	2.07	2.19	2.11	2.12	2.16	1.92	2.21	2.06	1.94	2.30	2.17
initial	2.25	2.12	2.20	2.04	2.14	2.12	1.97	2.04	2.02	2.05	1.94	2.12
$\overline{X}$	2.19[a]	2.10[a]	2.17[a]	2.07[a]	2.13[a]	2.12[a]	1.94[a]	2.15[a]	2.02[a]	1.99[a]	2.10[a]	2.16[a]
PVDF	2.08	2.06	2.17	2.07	2.10	2.14	1.98	2.10	1.98	2.01	1.95	2.07
PVDF	2.20	2.03	2.09	2.05	2.07	2.08	1.91	2.13	1.98	1.97	1.99	2.15
PVDF	2.11	2.08	2.14	2.06	2.09	2.08	1.89	2.23	2.03	1.95	2.25	2.13
$\overline{X}$	2.13[a,b]	2.06[b]	2.13[a,b]	2.06[a]	2.09[b]	2.10[a]	1.93[a]	2.15[a]	2.00[a]	1.98[a]	2.06[a]	2.12[a]
LDPE	1.43	1.62	1.78	1.78	1.90	2.04	1.91	2.02	1.95	1.98	2.09	2.15
LDPE	1.48	1.59	1.76	1.80	1.81	2.06	1.94	2.09	1.98	1.87	1.85	2.09
LDPE	1.37	1.56	1.74	1.81	1.85	2.00	1.87	2.12	2.02	1.90	2.01	2.15
$\overline{X}$	1.43[c]	1.59[d]	1.76[c]	1.80[c]	1.85[d]	2.03[b]	1.91[a]	2.08[a]	1.98[a]	1.92[a]	1.98[a]	2.13[a]
PP2	0.93	0.84	0.87	0.83	0.96	1.39	1.43	1.47	1.55	1.09	1.69	1.43
PP2	0.86	0.84	0.85	0.84	0.95	1.43	1.49	1.50	1.53	1.07	1.45	1.45
PP2	0.91	0.79	0.86	0.86	0.94	1.40	1.46	1.52	1.49	1.22	1.52	1.46
$\overline{X}$	0.90[d]	0.82[f]	0.86[e]	0.84[e]	0.95[f]	1.41[d]	1.46[b]	1.50[b]	1.52[b]	1.13[c]	1.55[b]	1.45[b]
PP1	0.97	0.93	1.05	0.99	1.18	1.47	1.47	1.44	1.45	1.40	1.66	1.49
PP1	0.93	0.92	1.01	1.01	1.16	1.49	1.52	1.49	1.52	1.32	1.52	1.47
PP1	0.98	0.95	1.06	1.02	1.16	1.50	1.52	1.52	1.54	1.33	1.45	1.49
$\overline{X}$	0.96[d]	0.93[e]	1.04[d]	1.01[d]	1.17[e]	1.49[c]	1.50[b]	1.48[b]	1.50[b]	1.35[b]	1.54[b]	1.48[b]
P(VDF-HFP)	2.14	1.97	2.12	1.97	2.05	2.10	1.90	2.21	1.99	1.99	1.85	2.14
P(VDF-HFP)	2.10	2.00	2.04	1.96	2.04	2.06	1.87	1.95	1.99	1.91	1.81	2.17
P(VDF-HFP)	2.03	2.01	2.08	1.97	2.03	2.10	1.92	2.13	1.94	1.90	2.12	2.14
$\overline{X}$	2.09[b]	1.99[c]	2.08[b]	1.97[b]	2.04[c]	2.09[a]	1.90[a]	2.10[a]	1.97[a]	1.93[a]	1.93[a]	2.15[a]

For a given time, values with the same letter are not significantly different from each other.

Table B2. Concentration of TCE (mg/L) in well water before and after flowing through 500 ft of LDPE tubing at a rate of 100 mL/min.

					Time (hr)					
Treatment	0.17	0.5	1	4	8	24	48	72	144	192
initial	2.11	2.22	2.23	2.25	2.28	2.29	2.23	2.31	2.22	2.33
initial	2.11	2.23	2.16	2.25	2.27	2.31	2.24	2.21	2.21	2.32
initial	2.23	2.23	2.21	2.21	2.28	2.26	2.24	2.27	2.27	2.35
$\overline{X}$	2.15[a]	2.23[a]	2.20[a]	2.24[a]	2.28[a]	2.29[a]	2.24[a]	2.26[a]	2.23[a]	2.33[a]
LDPE	0.177	0.305	0.457	0.864	0.894	1.77	1.91	1.96	2.02	2.06
LDPE	0.177	0.298	0.460	0.860	0.899	1.72	1.91	1.97	2.01	2.03
LDPE	0.172	0.290	0.457	0.860	0.902	1.74	1.92	1.96	2.01	2.04
$\overline{X}$	0.175[b]	0.298[b]	0.458[b]	0.861[b]	0.898[b]	1.74[b]	1.91[b]	1.96[b]	2.01[b]	2.04[b]

For a given time, values with the same letter are not significantly different from each other.

Table B3. Concentration of TCE (mg/L) in well water before and after flowing through 100 ft of tubing at a rate of 1 L/min.

					Time (hr)				
Treatment	0.17	0.5	1	4	8	24	48	96	168
initial	1.21	1.20	1.17	1.16	1.16	1.14	1.08	1.14	1.10
initial	1.15	1.22	1.16	1.16	1.16	1.15	1.11	1.12	1.10
initial	1.20	1.21	1.18	1.19	1.19	1.18	1.10	1.14	1.11
$\overline{X}$	1.19[b]	1.21[a]	1.17[b]	1.17[a]	1.17[a]	1.16[a]	1.10[a]	1.13[a]	1.10[a]
PVDF	1.22	1.19	1.19	1.19	1.18	1.14	1.11	1.12	1.10
PVDF	1.27	1.15	1.22	1.21	1.15	1.15	1.09	1.15	1.10
PVDF	1.27	1.22	1.21	1.20	1.17	1.14	1.10	1.15	1.11
$\overline{X}$	1.25[a]	1.19[a]	1.21[a]	1.20[a]	1.17[a]	1.14[a]	1.10[a]	1.14[a]	1.10[a]
LDPE	1.19	1.17	1.14	1.17	1.17	1.13	1.10	1.14	1.10
LDPE	1.11	1.20	1.16	1.20	1.15	1.14	1.10	1.13	1.11
LDPE	1.21	1.18	1.14	1.16	1.13	1.23	1.08	1.15	1.09
$\overline{X}$	1.17[b]	1.18[a]	1.15[c]	1.18[a]	1.15[a]	1.17[a]	1.09[a]	1.14[a]	1.10[a]
PP1	1.10	1.11	1.12	1.12	1.10	1.12	1.07	1.12	1.11
PP1	1.10	1.12	1.14	1.12	1.09	1.11	1.06	1.11	1.09
PP1	1.08	1.09	1.14	1.16	1.10	1.11	1.07	1.12	1.08
$\overline{X}$	1.09[c]	1.11[b]	1.13[c]	1.13[b]	1.10[b]	1.11[a]	1.07[b]	1.12[b]	1.09[a]

For a given time, values with the same letter are not significantly different from each other.

Table B4. Concentration of TCE (mg/L) in deionized water flowing through contaminated tubing at 100 mL/min.

Treatment	Time (hr)								
	0.17	0.5	1	4	8	24	48	72	96
initial	LD	LD	LD	LD	LD	LD	LD	LD	LD
initial	LD	LD	LD	LD	LD	LD	LD	LD	LD
initial	LD	LD	LD	LD	LD	LD	LD	LD	LD
$\overline{X}$	LD	LD	LD	LD	LD	LD	LD	LD	LD
PVDF	0.377	0.014	0.008	0.005	LD	LD	LD	LD	LD
PVDF	0.329	0.013	0.007	0.004	LD	LD	LD	LD	LD
PVDF	0.306	0.014	0.007	0.006	LD	LD	LD	LD	LD
$\overline{X}$	0.337	0.014	0.007	0.005	LD	LD	LD	LD	LD
LDPE	0.818	0.397	0.351	0.188	0.108	0.043	0.030	0.016	0.012
LDPE	0.809	0.387	0.370	0.187	0.105	0.040	0.025	0.015	0.011
LDPE	0.820	0.403	0.343	0.185	0.108	0.043	0.024	0.016	0.011
$\overline{X}$	0.816	0.396	0.355	0.187	0.107	0.042	0.026	0.016	0.011
PP1	0.859	0.767	0.673	0.479	0.367	0.113	0.035	0.008	LD
PP1	0.861	0.779	0.628	0.515	0.347	0.117	0.034	0.009	0.004
PP1	0.863	0.782	0.660	0.547	0.344	0.120	0.031	0.006	0.003
$\overline{X}$	0.861	0.776	0.654	0.514	0.353	0.117	0.033	0.008	<0.003

LD = Values less than MDL (0.0026 mg/L).

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13. ABSTRACT (*Maximum 200 words*)

This study is the second phase of a two-year effort to determine the effects that sampling tubings have on organic analyte concentrations. In the first year, 20 different tubings were compared, under static conditions, with respect to sorption of organic contaminants and leaching of organic constituents. In this study, we examined what occurs under dynamic conditions when TCE-contaminated water is pumped through several different types of polymeric tubings. Sorption of organic solutes, leaching of organic constituents, and desorption of sorbed organic contaminants were all examined.

Five tubings were selected for this study: a rigid fluoropolymer, a flexible fluoropolymer, low-density polyethylene (LDPE), and two plasticized polypropylene tubings. These materials were selected because our static studies had shown that these tubings leached little or no organic constituents (as determined by HPLC analyses with an ultraviolet [UV] detector) and ranged from being the least sorptive tubings tested to among the most highly sorptive. The effects of tubing length and flow rate were examined.

Results from these studies indicate that if water is pumped through tubing at a slow flow rate (100 mL/min), fluoropolymers should be used to prevent extensive losses of TCE and more sorptive analytes, especially if the tubing is 50 ft or longer. If a faster flow rate (1 L/min) is used, it appears that LDPE tubing can be used to sample TCE and other less sorptive analytes, although time for equilibration (2–4 hr) should be allowed to reduce losses in the deepest wells.

14. SUBJECT TERMS

See reverse

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13. ABSTRACT (cont'd)

We were unable to detect (using HPLC analyses and a UV detector) any constituents leaching from any of the tubings used in these studies, even when a slow flow rate was used. However, desorption of sorbed analytes is a concern for all the tubings tested, including the rigid fluoropolymer.

14. SUBJECT TERMS

Desorption	Polypropylene	Trichloroethylene
Hexafluoropropylene	Polyvinylidene fluoride	Tubing
Leaching	Sorption	Vinylidene fluoride
P(VDF-HFP)	TCE	Volatile organics
Polyethylene	Teflon	