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EFFECTS OF POLYVINYL CHLORIDE (PVC) PIPE ON THE SAMPLING OF ORGANIC CONTAMINANTS IN GROUNDWATER

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Introduction

Use of Polyvinyl Chloride (PVC) rigid pipe as a well casing material in groundwater monitoring networks has been extensive due to its low cost, low corrosion potential, light weight, and high strength properties (Parker et al., 1988). In recent years, however, regulators and owner/operators of groundwater monitoring systems have been questioning the suitability of PVC for certain groundwater monitoring applications, in particular sampling for organic compounds. Specifically, it has been implied that PVC desorbs organics (vinyl chloride, plastisizers, or solvents) into solution or adsorbs organic contaminants from solution. This paper addresses the desorption and adsorption of organic compounds to PVC rigid pipe under appropriate groundwater monitoring conditions.

Background

In 1985, the Environmental Protection Agency (EPA) issued a draft RCRA guidance document titled "RCRA Groundwater Monitoring Technical Enforcement Guidance Document" which was intended to clarify to EPA/state enforcement agencies and owners/operators of groundwater monitoring systems if their monitoring systems met RCRA requirements. This guidance document recommended Teflon or stainless steel over PVC when installing new wells to monitor for volatile organics (EPA, 1986).

EPA cited three main reasons (Skyes et al., 1986; Sara et al., 1987):

1) PVC casing was susceptible to deterioration when exposed to high concentrations of some organic compounds.

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2) Plastisizers and monomers in the PVC casing could desorb into the surrounding aqueous compounds, thereby creating a false positive reading or masking the presence of other pollutants.

3) Organic compounds present in the groundwater could adsorb to the well casing. EPA considered this critical since removal of contaminants from solution could result in a false negative reading.

Teflon and stainless steel were not considered to present the deterioration, desorption, or adsorption problems associated with PVC exposed to organic compounds (Sara et al., 1987).

Desorption from PVC Casing

The belief that rigid PVC casing desorbs constituents into the groundwater may stem from misinterpretation of earlier research (Dressman et al., 1978) conducted with PVC formulations containing high concentrations of leachable residual vinyl chloride monometer or on flexible PVC tubing containing high amounts of leachable plasticizers (Sara et al., 1987; Nielsen, 1988). In addition, desorption of solvents such as tetrahydrofuran, methylethyleketone, and cyclohexanone from the solvent-cemented PVC joints into the surrounding groundwater also implicated PVC (Sosebee et al., 1982; Barcelona et al., 1983; Gibb et al., 1984; Sara et al., 1987).

The PVC material typically used in monitoring well casing is tested and approved by the National Sanitation Foundation (NSF) and is expected to be essentially clear of monomers and plastisizers which could leach out and bias sample results (Barcelona et al., 1983; Parker et al. 1986; Nielsen, 1988).

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Research was conducted to compare the desorption effects of rigid PVC as compared to Teflon. In the results, PVC was found to be a less active desorber than Teflon (Curran et al., 1983 quoted in Sara et al., 1987).

Adsorption of Organic Compounds to PVC Well Casing

The adsorption issue may stem from the EPA's misinterpretation of Barcelona's (1983) work (Sara et al., 1987). Based on the material's compatibility with typical ground water contaminants, Barcelona concluded the Teflon and stainless steel were the materials of choice, since PVC had the potential to deteriorate in a highly contaminated groundwater environment (Barcelona et al., 1983). Sorption effects were not considered. The EPA extended this conclusion to prefer use of Teflon or stainless steel, regardless of the water quality being monitored (Sara et al., 1987).

Adsorption Research

The research does not support the conclusion that PVC is an unacceptable groundwater monitoring well casing material where appropriate sampling protocols are adhered to.

Sykes conducted a study to determine differences in the effect of PVC, Teflon, and stainless steel on the adsorption of six organic compounds. The experiment was designed to simulate typical groundwater monitoring protocols in which the well casing is exposed to contaminants for an indefinite length of time, purged of stagnant water, then sampled within 2 to 24 hours of purging. Results indicated that no statistical difference exists between adsorption of the organic compounds tested to PVC,

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Teflon, or stainless steel when exposed to concentrations approximating 100 ppb (Sykes et al., 1986).

Sara et al. conducted a similar experiment. PVC was exposed to organic-contaminated groundwater allowing a sufficient period of time for any adsorption equilibrium to occur. The stagnant solution was then removed and replaced with a fresh organic-contaminated solution. Results indicated a net sorption rate of zero.

Research was conducted to compare the effect of casing materials (PVC, Teflon tubing, and stainless steel) to the adsorption of five organic compounds. Results are shown in Table 1 (Reynolds et al., 1985 quoted in Sara et al., 1987). Note that Teflon tubing and rigid PVC have, in general, comparable adsorption affinities.

Table 1. Comparison of Well Material Adsorption

	Adsorption (ug/L)	
Chemical	Teflon	PVC (rigid)
Chloroform	10	16
Tetrachloroethylene	41	0
1,1,2,2-Tetrachloroethane	0	8
Hexachloroethane	4	4
Bromoform	0	5
Average	**11**	**6**

Barcelona conducted research into the effect of well casing materials (Teflon, stainless steel, and PVC) on the variability of results obtained from groundwater sampling for organic compounds. Although results indicated some variations in analytical results as a function of well casing material, these

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variations were not consistently higher or lower for any one material tested. Well purging techniques proved the most sensitive process affecting variability of analysis results (Barcelona et al., 1986).

Another study was conducted to determine the adsorption rate of solvents to finely ground PVC particles. Grinding the PVC increases the adsorption contact area was from what would be expected in the surface area of an actual monitoring well. Results showed that when the contact period was minimized, accurate reading of solvents could be attained (Kresse, 1985 quoted in Sara et al., 1983).

Conclusion

Desorption of organic compounds from PVC rigid is not known to occur with the use of NSF tested and approved rigid PVC pipe joined by threaded flush joints versus solvent-cemented joints (Sosebee et al., 1982; Gibb et al., 1984; Barcelona et al., 1986; Nielson, 1988).

Adsorption of organic compounds to PVC well casing has not been substantiated by the research data (Sara et al., 1987). Studies, particularly Sykes et al., 1986 and Sara et al., 1987, designed to simulate actual groundwater sampling protocol both indicate that adsorption of organic compounds to PVC does not interfere with obtaining representative groundwater samples when proper well purging procedures are used.

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Much Ado About Nothing: The Monitoring Well Construction Materials Controversy

by David M. Nielsen

It's about time we ended all of the senseless arguments over which casing material is "the best" for ground water monitoring wells and focused our attention on some of the more important issues confronting ground water professionals involved in conducting monitoring programs. Much has been said over the past few years, and much effort and money has been spent in attempts to substantiate one position or another regarding the use of the various types of casing and screen materials in monitoring wells. Virtually all of the arguments relate to monitoring wells installed for the purpose of complying with RCRA ground water monitoring requirements. The catalyst for most of the heated discussions was the initial draft (August 1985) of the U.S. EPA's RCRA Ground Water Monitoring Technical Enforcement Guidance Document (TEGD), which made the absurd statement that "in constructing wells, the owner/operator should use Teflon, stainless steel 316, or other proven chemically and physically stable materials." The subsequent furor resulted in a slight softening of the language in the final (September 1986) version of the TEGD, but by then the damage had been done.

Both versions of the TEGD, as many people predicted, were grossly misapplied by inexperienced federal and state regulatory agency personnel grasping desperately for guidance that would provide answers to questions that were never posed to them in college. Some less-than-learned regulatory personnel were, in fact, attempting to use the guidance offered by the TEGD in lieu of informed professional judgment, and were attempting to apply the TEGD guidance, much of which is unsubstantiated, as a regulation of regulatory requirement. The TEGD itself states, "it is not a regulation and should not be used as such," but a much stronger, more prominent statement relating to the use of the document was needed. A similarly strong statement relating to the need for the use of informed professional judgment applied by trained and experienced agency personnel may have helped us to avoid the current situation.

Fortunately, in a recent decision (NSWMA v. U.S. EPA), the U.S. Court of Appeals for the District of Columbia Circuit made a stronger statement in ruling that "the TEGD is not a regulation or requirement, the TEGD has no binding legal force on (owner/operators) and, in any future enforcement proceeding regarding a ground water monitoring system, the methods set forth in the TEGD are subject to challenge." This may be the first step in correcting a situation that should have been anticipated and headed off by the EPA long ago.

Perhaps the most notorious misapplication of the TEGD to date has been the blind insistence of many federal and state regulatory agency personnel that every well installed for the purpose of monitoring ground water, whether for RCRA compliance or not, be installed using fluoropolymer or 316 stainless steel casing and screen. When asked for the basis of their decision, these folks answer, "because the blue book (the TEGD) says so." Some states have already adopted or are considering adopting this stance as regulation, even though the available scientific evidence suggests that this is not a defensible position. And, if you consider the practicability of requiring the use, for example, of fluoropolymer well casing and screen (to say nothing of the cost), it simply doesn't make good sense. Fluoropolymers are by no means the panacea many people would like to believe.

The plain fact is, fluoropolymers aren't well suited for use as well casing materials; their physical properties simply do not lend themselves well to applications in vertical boreholes completed as wells. Why not? Consider the following: (1) the very low tensile strength and high weight per unit length of fluoropolymer materials (especially compared to other plastics) results in a significant limitation on installation depth and a high potential for failure at casing joints; (2) the materials's low compressive strength, high weight per unit length and ductile behavior results in the partial closing of fluoropolymer well screen openings and a consequent reduction of well efficiency; (3) the extreme flexibility and lack of rigidity of fluoropolymer well casing causes casing strings to become bowed and non-plumb in the borehole during installation; (4) because of the lack of compressive strength and the cold-flowable nature of fluoropolymers, screens are only available in slotted casing, which can clog easily and make well development difficult; (5) the non-stick nature of fluoropolymers that makes them so desirable in other applications results in the lack of formation of a competent annular seal with neat cement grout; and (6) recent research at the University of Waterloo suggests that even

materials is suspect — they m ndeed sorb certain organic chemicals at rates and amounts faster and higher than other plastics.

On the other hand, the research that is commonly cited as condemning PVC has its roots in work conducted some years ago on PVC tubing, which has high levels of plasticizers added to it to enhance flexibility, or on rigid PVC that contained high levels of residual vinyl chloride monometer (RVCM). In the first place, PVC casing is a hardened, rigid material whose formulation does not include plasticizers that could potentially leach out, and in the second place, today's formulations of PVC used in rigid pipe are controlled by NSF Standard 14, and do not leach RVCM or vinyl chloride. More recent research suggests that rigid, hardened Type 1 PVC performs better in laboratory sorption/leaching studies than fluoropolymer materials.

Those who have followed the casing materials issue know that the great bulk of research done to date has been conducted under laboratory conditions, where casing materials were usually exposed to a solution over prolonged periods of time (several days to several months), allowing an extended period of time over which the materials could exhibit sorption or leaching effects. While this may be comparable to a field situation in which ground water is exposed to well casing as it may be between sampling rounds, few studies have considered the fact that prior to sampling, the well is usually evacuated of stagnant water that would have been in contact with the casing between sampling rounds. Thus, the water that would have been affected by sorption or leaching effects (if they were present at all), will ideally have been removed and replaced with aquifer-quality water. Because the sample is generally taken immediately after the casing has been purged of stagnant water and, further, because the pump intake or bailer is usually placed within or just above the screen to take a sample, the water that is taken as a sample will have had a minimum of time (seconds or fractions of a second) with which to come in contact with casing materials. Is this long enough to produce the oft-mentioned sorption or leaching effects? Not very likely. Several researchers have pointed out that potential sample bias effects due to sorptive interactions with well casing materials may be discounted or eliminated for this reason. They further suggest that these effects are far more critical in sample transfer and storage procedures employed prior to sample analysis.

Assuming that you accept this argument, isn't it apparent that the focus of much of the effort in solving problems related to ground water monitoring has been on the wrong issue? Is casing materials even an issue? I would argue that it is close to last on the list of issues that should be dealt with in the establishment of monitoring programs. Preceding it should be such important issues as proper location of wells, establishment of site-specific well design criteria (other than casing) that will ensure acquisition of representative samples (avoiding such ubiquitous problems as siltation and grout contamination), development of a thorough understanding of site pling protocol, selection of a laboratory that can provide analytical results in which one can have confidence. We must place the casing materials issue in its proper perspective. Doc No: CLEJ-00596-12.05-11/11/90

Unfortunately, a great deal more effort and money will probably be expended by the U.S. EPA and others in an attempt to resolve the casing materials issue, but Uninformed, experienced ground water professionals already know the answers. As in all other situations in which decisions hinging on definition of the hydrogeologic system must be made, "it depends." It depends on a unique set of site-specific and logistical factors, including geologic environment, natural geochemical environment, anticipated well depths, types and concentrations of known or expected contaminants, well drilling method and type of well completion, among other factors. This is a fact that is well-recognized by experienced practitioners of hydrogeology. Despite what some would have us believe, there is no "best" well casing material applicable over the wide range and variety of natural and man-induced site-specific conditions. Rather, it is important that the site-specific conditions be properly characterized and evaluated so that casing material can be tailored to meet the unique set of conditions that exists at each site. Thus, where natural geochemical conditions indicate a high corrosion potential and where synthetic organic contamination of water is present at levels high enough to chemically degrade other plastic casing materials (measured in percent), fluoropolymer casing/screen materials may, in fact, be the best choice. Where corrosion potential is low and synthetic organic contamination of water is at high levels, stainless steel may be the best choice. Fiberglass casing materials may have applications. But in the vast majority of cases, where corrosion potential is low and where synthetic organic chemical contamination may be encountered at levels that are not high enough to produce chemical degradation effects, PVC casing will probably suffice, as it has in tens of thousands of wells already in use around the country. What it takes to make these determinations, however, is a properly trained, well-informed professional who can make sound professional judgments based on scientific evidence.

In my view, the effort and money that will be spent on the casing materials issue could be better spent in properly developing more critically needed guidance, in educating those people who are new to the profession, and in hiring more qualified, experienced, well-informed professionals to staff regulatory agencies. I'm either optimistic or naive enough to believe that we can purge the system of the people who cannot exercise professional judgment and who must therefore rely on ill-conceived guidance written by bureaucrats and idealists rather than practitioners and realists. The time will come when people who understand the technical issues and who can gather the scientific evidence required to support professional judgment will sit on both sides of the table, but it will be a frustrating experience waiting for that time to arrive. Until then, I suggest we focus our attention on more serious issues than debating which casing material is best.

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Do Casing Materials Affect the Integrity of Ground Water Samples Obtained After the Well Is Purged?

This is the last of four "Point-Counterpoint" articles planned to appear in this column. These articles are based on discussion sessions held at the Sixth National Aquifer Restoration and Ground Water Monitoring Conference. A brief article outlining each speaker's opinion is offered first, followed by the transcript of the discussion session during which attendees have a chance to ask the speakers questions on the subject.

Opinion 1.

by Martin N. Sara

I'm going to talk today first about the regulations, then about the literature of casing materials — instant surface chemistry and recent tests performed to simulate ground water sampling and finally, I'll discuss problems with Teflon®.

Introduction

In my opinion, ground water monitoring has become the single most important regulatory issue concerning waste storage, treatment and disposal facilities. The federal government has enacted specific codes within the Resource Conservation and Recovery Act (RCRA) to address ground water monitoring at regulated facilities.

The purpose and goal of the ground water monitoring program is to "determine a facility's impact on the quality of ground water in the uppermost aquifer underlying the facility." To accomplish this goal, each facility must "install a ground water monitoring system that is capable of yielding ground water samples for analysis and must consist of: (1) monitoring wells (at least one) installed hydraulically upgradient . . . ," "(2) monitoring wells (at least three) installed hydraulically downgradient. Their number, locations, and depths must ensure that they immediately detect any statistically significant amounts of hazardous waste . . . " (40 CFR Part 265). RCRA further states, "All monitoring wells must be cased in a manner that maintains the integrity of the monitoring well borehole. This casing must be screened or perforated and packed with gravel or sand, where necessary, to enable sample collection at depths where appropriate aquifer flow zones exist."

Since little or no guidance was provided on appropriate use of casing material at the time of the RCRA regulations were promulgated, most operators installed polyvinyl chloride (PVC) casing in both the original and subsequent monitoring systems. This material was readily available, fairly inexpensive, and had a long history of use in water supply. In the intervening years, a number of questions were raised concerning exactly which casing material is appropriate for use in a monitoring well, and some research was initiated to provide guidance in this area.

Initially, many wells were installed using glued joints. Not until the EPA started requiring extensive organic analyses was it discovered that glued joints contaminate a monitoring well with such chemicals as tetrahydrofuran, methylethylketone, and cyclohexanone. Such chemicals would normally be washed out of a traditional water well used for domestic purposes, but for monitoring wells used only once per quarter, the organics would not likely be totally washed out for years. The reputation of PVC was thus tainted as some people, unaware of the actual cause, believed the organics were desorbing from the PVC.

The second factor that raised some questions was the availability of alternate casing materials. Materials such as Teflon and 316 stainless steel were suggested because of their apparent "inertness" primarily with respect to organics. Teflon has long been thought to be a stable, unreactive, inert material. This led to the suggestion that Teflon or 316 stainless steel would be preferable to PVC. Barcelona et al. (1983) stated, "A preliminary ranking of commonly used materials (for well construction) was performed on the basis of chemical compatibility and manufacturer's recommendations. Compatibility was judged from the point of view of potential deterioration of each material. No second order effects such as adsorption, absorption or leaching were considered."

The preliminary ranking presented was: Teflon, Stainless Steel 316, Stainless Steel 306, PVC I, Lo-Carbon Steel, Galvanized Steel and Carbon Steel.

The intent of Barcelona's paper was, presumably, to show that under certain circumstances, such as highly contaminated ground water, PVC might not stand up and that it would be prudent to consider Teflon or stainless steel. However, his conclusion has been extended by the U.S. EPA to include all monitoring wells without consideration of water quality. This misinterpretation of the facts forms the background for the current controversy.

The Controversy

The controversy surrounds the August 1985 draft guidance document titled *RCRA Groundwater Moni-*

toring Technical Enforcemen Guidance Document (TEGD), which was intended to help EPA and state enforcement officials decide whether specific elements of an owner/operator's ground water monitoring system satisfy the RCRA requirements. The guidance document states that only Teflon or stainless steel are acceptable for use as screen or casing in new well installations. While the agency has backed off on requiring the use of these materials for the fully cased well to only that portion located within the saturated zone, the guidance requirement raises serious questions as to its technical validity.

There are three primary reasons why the U.S. EPA has decided that PVC is unacceptable as casing material in the saturated zone.

1. The U.S. EPA believes that PVC will not be sufficiently resistant to attack by concentrated organics. This belief stems from reports of PVC casing installed at CERCLA sites collapsing after being softened by high concentrations of organics.
2. The U.S. EPA believes that PVC desorbs or emits contaminants to otherwise uncontaminated ground water. This misconception originates from confusion regarding the previously described problem with glued joints and also from published work that describes the release by PVC of some compounds that are used as plasticizers.

   The U.S. EPA believes that PVC adsorbs chemicals from the water, thus delaying the detection of contamination. This belief is based on the misinterpretation of the work of Barcelona.

The U.S. EPA believes that Teflon and stainless steel do not exhibit any of the preceding problems.

Discussion

The first issue regarding PVC raised by the guidelines is related to its ability to stand up to high concentrations of chemical solvents. This, we believe, is a moot point in this discussion. The issue is whether PVC is adequate for use in detection monitoring wells at RCRA facilities. Our experience with almost 3000 monitoring wells suggests that interim status facilities designed to RCRA specifications, i.e., double liners, leachate collection systems, etc., have yet to detect migration of organic constituents in high concentrations that would threaten the integrity of PVC casing. Even in cases where contaminants have reached the parts per million level, no instance of PVC casing failure has occurred to the best of our knowledge. Finally, if levels of organics from a product spill, there are alternate materials.

The second issue involves the reported desorption of contaminants to otherwise clean ground water. The use of only National Sanitation Foundation (NSF) tested and approved PVC formulations can be expected to reduce the possibility of desorption of either residual monomer, fillers, stabilizers or plasticizers. Proper cleaning of the well casing material and well installation equipment will further reduce the possibility of later desorption of contaminants.

The exclusive use of threaded flush joints prevents any residual chemicals from solvent-cemented joints from contaminating the ground water sample. Curran and Thomas (1983) investigated the leaching characteristics of rigid PVC and various other plastics used in well construction and sampling. Looking at their data, it is clear that desorption from rigid PVC is at least as low as from Teflon and may be slightly lower. They concluded, "... that rigid PVC is an acceptable alternative to Teflon for monitoring wells ..."

The final issue, that of adsorption or absorption (collectively referred to as sorption) of ground water constituents on PVC casing, is cited as the major problem in the guidance documents. The guideline suggests that sorption would tend to lower the amount of contaminant in a monitoring well sample to the point where it might go undetected (false negative). The possibility of a false negative is of prime concern to the U.S. EPA and other regulatory agencies.

Absorption is the process in which molecules enter the spaces between other molecules, much like water absorbed as a sponge. The process is not an equilibrium process, but will continue as long as there is a driving force pushing the molecules into the matrix and capacity exists in the substrate to absorb additional molecules.

In the case of organic molecules in aqueous solution in a monitoring well casing, the rate of adsorption is proportional to the concentration and one can calculate this rate. For concentrations of organics up to 25 percent the steady-state rate of permeation even after 6000 years would be only 20 micrograms per square meter of surface area. Clearly, this rate of permeation is negligible.

Adsorption is an equilibrium process in which molecules that contact a surface adhere to it for some period of time.

All surfaces adsorb. The forces that hold a molecule to a surface are electric in nature (Van der Waal's forces) and are dependent on the structure of the molecule and the temperature and nature of the adsorbing medium. The rate of adsorption is controlled by two factors, the length of time each molecule adheres to the surface and the rate of diffusion of the molecule to the surface.

Only one layer of molecules can be adsorbed on a surface at one time, which is commonly referred to as a monolayer. Thus, for any given surface area, only a many molecules can be adsorbed at equilibrium.

At least three notable experimental efforts to determine the magnitude of adsorption of organics on PVC, Teflon, and other materials have appeared in the literature.

The first is a paper by Barcelona (1983), which deals exclusively with sorption of organics on various polymeric tubing materials associated with sampling equipment.

Barcelona's experiments involved only fresh ¼-in. I.D. tubing of various polymeric types. The experiments show that 10 to 20 minutes are required to reach equilibrium, i.e., for the rate of sorption to drop to zero. While his experiments are valid for sample tubing materials, he concedes that these materials (except Teflon) contain up to 50 percent foreign ingredients (plasticizers) included in the formulation to produce the necessary flexibility.

The second experimental work performed by

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olds dealt with rigid PVC, but unfortunately included a comparison with only Teflon tubi

Reynolds concludes, "Of particular interest in this study were the results with PVC and Teflon. PVC only adsorbed four of the five compounds, and the rate of absorption was sufficiently slow that absorption bias would likely not be significant for these compounds should well development and sampling take place in the same day. Teflon showed similar results."

The preceding two studies were performed for different test periods. The Barcelona experiment was conducted over 10 minutes to 60 minutes, and the Reynolds experiments over 10 minutes to 50,000 minutes. Both tests determined the sorption of each compound for the different well materials.

The results of the two studies are presented in Table 1. The results clearly show a significant difference between rigid PVC and flexible PVC. Although two of the chemicals tested by Barcelona and three of the chemicals tested by Reynolds are not the same, chemicals used by Barcelona show an average sorption rate for flexible PVC of 25 times more than the sorption rate of chemicals used by Reynolds for rigid PVC. The Barcelona study further shows that flexible PVC sorbs roughly three times as much as the Teflon tubing, while the Reynolds study shows that, on the average, the rigid PVC sorbs slightly less than the Teflon tubing.

TABLE 1
Comparison of Well Material Sorption
(in μg/mL)

	Test Time			
	Barcelona et al. 60 min.		Reynolds et al. 200 min.	
Chemical	TFE	PVC (flexible)	TFE	PVC (rigid)
Chloroform	40	150	10	16
Trichloroethane	10	145		
Trichloroethylene	70	160		
Tetrachloroethylene	105	160	41	0
1122-Tetrachloroethane			0	8
Hexachloroethane			4	4
Bromoform			0	5
Average	56	154	11	6

You can calculate sorption for a hypothetical case using a well casing 4 inches in diameter, 10 feet long, filled with water contaminated with one of the chemicals used in the preceding tests at the 10 parts per billion (PPB) level. If the well casing were Teflon and the chemical were tetrachloroethylene, the maximum that would be sorbed would be 16 percent. None would be sorbed by the rigid PVC. If the chemical were trichloroethane, the maximum sorbed by the rigid PVC would be 6 percent. In neither case would the analytical uncertainty levels be exceeded.

More recently, a paper by Kresse (1985) describes a test performed on ". . . finely ground PVC to increase the surface contact area between the sample containing the solvent and the °C, so the test shows a much higher potential for adsorption than would be expected to occur in a well. The test shows that if the contact time between PVC casing and the ground water is minimized, representative samples to test for the solvents can be obtained. Therefore, the use of more expensive materials for well construction is wasteful."

Since none of the experiments reported to date addressed what I feel is a key issue with regard to the use of these materials in well construction, a series of experiments were conducted to address the absorption issue. (The experimental protocol may be obtained by request.) This series of experiments address the absorption of organics on previously exposed casing surfaces. The idea, then, is the exposure of monitoring well casing material to contaminated formation water for a sufficient length of time to allow dynamic equilibrium to be established between the material surface and various organic molecules. We observed some adsorption (up to 20 percent) when the material is fresh.

However, proper sampling techniques require that the stagnant water be removed (purged) from a well prior to sampling. This has the effect of removing water from the well that may have lost up to 20 percent of the organics through sorption and replacing it with formation water representative of the ambient organic conc tion. Because this new water is in contact with the already saturated surface of the well casing for as short a time one hour, and probably no longer than 24 hours. issue is how much sorption takes place under these tions. In both cases, and for all materials exposed net sorption is nominally zero. While admittedly there will be some experimental error associated with these the result still is obvious — rigid PVC well casing performs as well as, if not better than, Teflon or stainless steel. In general, there is little, if any, real justification for the substitution of Teflon or stainless steel for PVC as the material of choice for construction of monitoring wells for RCRA facilities.

Let's look at a more likely reason for contamination of ground water samples.

I've defended PVC for long enough; let's take a look at problems with Teflon.

What's so good about Teflon?

Problems with Teflon casing:

- Strength of materials
  - High (medium-density) — low strength
  - 300 pounds hanging weight allowable
  - Safety problems with more than 80 feet of Schedule 80 casing hanging
- Threads too flexible and slick
  - Caused leakage at joints with one psi pressure
- Cold creep
  - Affects slot size required
  - Makes design of slots difficult
  - Closing of slots with time?
- Difficult to set and install
- Extremely porous material
- Grout will not stick to Teflon.

To sum up, Teflon is not a very good casing material

and we, as scientists and engin s, should not end up like Louis Agazise, the 19th centu Swiss geologist after the 1906 San Francisco earthquake — with our head in the pavement.

In closing, let's put Teflon and stainless steel back where they belong — in our frying pans.

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Opinion II

by Don Shosky

The question posed to the speakers this evening is "do casing materials really affect the integrity of ground water samples obtained after the well has been purged?"

There is a little bit of controversy on this subject; a lot of people feel strongly about casing materials. There are many types of casing available on the market today. To name a few, we've got stainless steel, carbon resins, PVC and fiberglass.

A few of those compounds have never been used very much in monitoring wells until recently.

I'd like to discuss my opinions concerning the factors that influence the leaching or absorbing of contaminants on these different casing materials. Then I'll ease my way into the purging issues because they're separate, yet they're the same.

It's known that there are certain factors that influence the leaching and/or absorbing of contaminants on well casing.

Sometimes those things can be a basic chemical affinity to a particular contaminant. For example, perhaps certain chemical classes such as hydrocarbons, through hydrogen bonding, could absorb into PVC. The reverse is also true since after saturation occurs we can have release of those same contaminants back into the environment.

We also know that under certain conditions waste leaching can be a problem with some casing material. You certainly can't purge three casing volumes out of your well if your well doesn't exist. We've run into this problem at a lot of facilities that treat wood products, use a lot of creosote, PCP, things of that nature. One day the 2-inch piece of pipe is sticking out of the ground, the next day it's gone.

We also know that geologic conditions affect the integrity of a particular well casing material. We know that high and low pH environments sometimes raise havoc with casing materials such as stainless steel, but then so does the chemistry in certain ground waters. With high TDs, say 150,000 parts per million, we've had a real issue of what types of wells to install.

The point I'm trying to get at here is that we should be looking at selecting casing material for particular si tions. What are the waste materials that we're dea with? What is the ability of that particular casing mat to work well in the environment that it's going to exposed to? If it doesn't have long life for its inten purpose, why put it in? Why go out and put in ano well in five or six years, because the one you have rotted away? Which gets us into the question of how adequate purging of the well make a difference in sample that's obtained.

My experience in taking ground water samples comparing our data with that that's being selecte facilities is more often than not we don't have an adeq well purge.

Right now I have several applications where a fa using PVC is starting to see some contaminant phthalates. It so happens that the same facility has streams that contain phthalates and we're seeing 10 parts per billion in these wells. The company claim PVC casing leaching this material out.

These are questions that are posed to me, regulator.

The point that I'm making here is that in this situ the phthalates may be or may not be coming fro PVC casing. I also know a little bit of history about particular sites and I know that the purging that's done at those sites have been highly variable over

Sometimes as much as seven casing volumes been pumped out of a particular well, other time casing volume. Phthalates show up at different co trations, at different times. Is it a plume, or is it the material that's leaching?

I'm not trying to put one type of casing materia the other, but I do have a strong opinion that we s always be looking at the most compatible casing m for a particular situation.

There's another thing that causes some intere confusion at these particular locations. We're only p ing out these wells once every three months, on a q sampling basis.

Is the well purge adequate with that kind of res time? With higher yield wells, the residence time pr isn't going to be that long, even when we don't go o

purge the well except at three- and four-month intervals.

In lower yield situations, the [illegible] the residence time could be a lot longer. What we're seeing there is longer exposure of the water to the casing material, so there is a greater opportunity for whatever is in the casing material to come out.

Now the real question becomes, can I go out and take out my one casing volume before the well dries up and is that going to be adequate to totally flush the well of contaminants that could be in there due to the casing material, regardless of what kind it is?

Quite frankly, the answer in my mind at this point is I don't know. Data seems to suggest that there is a chance that a lot of that material will still be in the well.

Another interesting point that I'd like to make is to take a look at the wells that are out at your site. Do they look dirty?

I look at a variety of different wells and how they're constructed. A lot of times well casing appears dirty from leached material that's been slopped on the sides or maybe absorbed into the casing material.

How is that casing material going to react? Over time, is it going to start releasing those contaminants? You could have cleaned up the aquifer and you're monitoring what your casing is releasing over time, or you've instigated a correcti[illegible]tion program for 20 years longer than you need because you are monitoring those same contaminants over time.

The last thing I'll discuss is structural integrity. What I'm trying to push here is finding appropriate casing material for the conditions. What is the waste material that we're dealing with? What are the constituents? What are the constituents and life expectancy of the casing material?

Nothing is more frustrating than to go out and take a water level measurement and have the well fall over because everything has rotted underneath it. Nobody believes me, but it happens.

Based on the data that's come across my desk from a variety of different types of facilities, these facilities believe that part of their contamination problems are from the casing material that they use.

My advice is, let's use some type of inert material and let's go for the highest quality ground water sample that we can get, so that we don't have to argue about whether or not the contaminant is coming from the casing material or the site.

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Discussion

From the Floor: I've got a question for both parties. I've been hearing a lot lately about the magic of fiberglass and epoxies. Have you run across anything, either for or against them?

Sara: When the systems are so sensitive, I would hesitate to use anything that doesn't have a long history of use.

Shosky: I would say that any new type of casing material or any casing material that hasn't gone through both field testing and real lab evaluation should be looked at with speculation until adequate testing is provided. This does not reflect the opinion of the agency, but is a personal opinion.

From the Floor: I have a question for both. The reason for purging a well is to get fresh formation water in, therefore taking a molecule some distance from the casing and bringing it up to the surface. We're assuming that we're not getting any contact. How do you address the issue?

Shosky: Well, the real issue is what's an adequate purge? One of the best documents that I've found on this subject is one produced by the American Petroleum Institute, which discusses theories about well purging and recommends that under certain conditions, if the well is designed properly, purging should be kept to a minimum. They're considering the well as a dynamic system where there is flow continually through the well.

If you operate under the assumption that certain casing materials will absorb or adsorb contaminants then release them over time, my concern would be that the purging was done adequately.

How much purging is enough if there is contaminant that's being released in the well, and does that fit in with the rest of the sampling scheme that you have for a particular facility?

I'm not in the habit of OK'ing excessive purge volumes out of a well, like 70, 80 casing volumes.

If anything is being released into the well, it's my feeling that probably within two to three casing volumes, you'd be removing most but possibly not all of the contaminants from the well.

Sara: Well, I'm probably not going to be able to add much to that other than I personally believe that all monitoring wells or piezometers should be tested for the ability to yield water. I think that's very important. It's one that people miss a lot. It doesn't do much good to say that you have to pull three casing volumes of water out of a hole that has an overall transmissivity of .1 meter monitoring point in a situation where you are going to get at least enough yield to be able to get an adequate sample. That means more than one casing volume.

From the Floor: I'd like to ask if in spite of all the evidence and the fact that there are few people who are credible scientists who side strongly for the use of Teflon 100 percent of the time, what flexibility exists on the part of EPA?

Shosky: There's a couple options we have as regulators. One, throw the book on the table and say you'll follow this or you'll be in trouble. Normally what we do is sit down and we look at the site conditions and the type of casing material that best fits those conditions.

Now this is my personal style, but if somebody comes in to me with an argument on cost only, I don't listen to it. I'm being honest with you, I don't. The thing that matters to me the most is that the best casing material is installed that will yield the best

quality sample given a particular situation.

If it happens to be Teflon then that's what I ask to be installed. If it happens to be stainless steel, then that's what I ask to be installed. On a few of the sites that I've looked at, because of certain conditions that exist at that particular facility, we've allowed PVC. Educated regulator and educated facility person or consultant should come in and negotiate which casing material can be used based on site-specific data.

From the Floor: What kind of cost differential are we talking? I imagine there is significant cost in the beginning, but over the entire course of a 30-year monitoring program, is that significant?

Shosky: The cost differentials for the casing material alone aren't that much when compared with the entire cost of installing a well.

Most of us know that the real cost in installing a well is the time that the guy spends out there putting the well in. The cost of the casing is insignificant when you're talking about paying somebody 50 or 70 bucks an hour plus driller's time.

Sara: The whole context of my talk was not that PVC is less expensive, which it might happen to be. The most important thing is that experience with PVC proves it is generally acceptable for RCRA. No matter what the cost, I happen to think PVC is OK, but this issue isn't just EPA.

From the Floor: Martin, in your presentation you showed data relating to up to 200 minutes, then later you talked about you should only put monitoring wells where wells will yield water. What if there's not a place on the site where the well will yield water at 80 feet? This is continuous, very thin sand lenses over a thin shale. Is there such a thing as an exemption from ground water monitoring?

Sara: That's never really ever accepted but, you know, at least you make the offers, just to be a nice guy.

Moderator Graves: What material do you recommend for use for dedicated bailers that you're going to reuse in sampling wells that have extensive volatile organics in their concentrations, let's say between 50 and 5000?

Sara: What I would normally probably do is not use bailers but use dedicated bladder pumps. With a bailer of any material, you still end up with a situation where you are dealing with material properties, and material properties are based on adsorption, desorption properties.

If you have stagnant water well that is going to be difficult to sample, no matter what kind of bailer you use.

Shosky: I like to use those clear Teflon bailers over the stainless steel because I still like to look at and smell the water when it comes out of the well.

Sara: Looking for TCE you might not want to use Teflon. You might want to use PVC.

From the Floor: I have a question for Martin. On what do you base your statement that Teflon will deteriorate with time?

Sara: Just open up the Merck Manual and turn to the page where it talks about Teflon, and read it for yourself.

alluded to where Teflon would be better than [illegible] especially i[illegible] have product spill.

Shosky: It is one thing to deal with the problems [illegible] extremely contaminated sites when you're talkin[illegible] about the lower levels and the company is telling yo[illegible] that it's coming from their PVC well casing, but the[illegible] is a real good possibility that could be coming fro[illegible] their site. Those are the kind of decisions that we fa[illegible] as regulators every day.

Sara: Actually I agree with Don. If you have to take t[illegible] approach that in order to defend your site that you[illegible] got to blame your wells for organics results, I thi[illegible] you deserve to put in Teflon wells.

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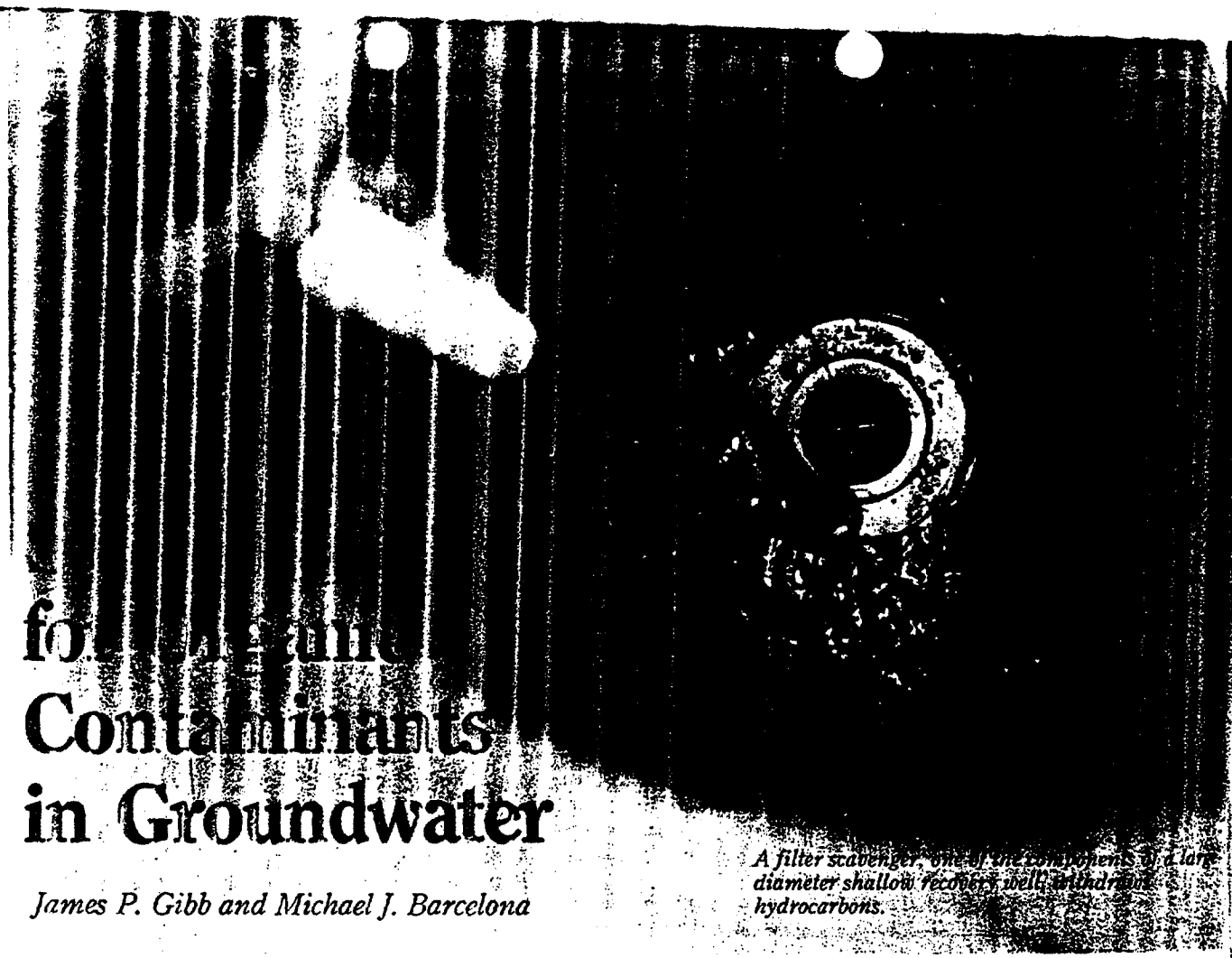

fo[illegible] Contaminants in Groundwater

A filter scavenger, one of the components of a large-diameter shallow recovery well, withdrawing hydrocarbons.

James P. Gibb and Michael J. Barcelona

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Samples taken for analyzing the quality of groundwater can be altered by certain materials used in the construction of monitoring wells and even by the containers used to collect samples. Similar problems can occur with samples taken from a distribution system. Further research is needed to refine analytical procedures so that actual in situ data pertaining to organic compounds in groundwater can be obtained.

The base flow of perennial streams can be attributed to groundwater. Groundwater is also the source of half of US drinking water supplies.[1] Yet groundwater has received only token scientific attention in terms of its quality and protection. Almost no attention has been given to proper sampling procedures to determine accurately the quality of groundwater.

The passage of the Safe Drinking Water Act (PL 93-523) in 1974 finally recognized groundwater as a major source of drinking water and established standards of groundwater quality protection. Later, the Toxic Substances Control Act (PL 94-469) and the Resource Conservation and Recovery Act (PL 94-480) further recognized the significance of groundwater resources and the importance of their protection against the increasing threats posed by human activities.

Since the beginning of the industrial age, a variety of new chemicals have been introduced into the environment by man's indiscriminate use and waste disposal practices. Since World War II, the explosive development of the synthetic chemical industry has added thousands of chemicals to the environment. *Chemical Abstracts* announced in March 1972 that it had registered two million unique chemicals since January 1965.[2] These chemicals enter both surface water and groundwater—not only through waste disposal but also as a result of normal use.

The presence of many trace organics in groundwater, even at very low concentrations, may create short-term or long-term health hazards.[3] The inclusion of approximately 113 organic compounds on the US Environmental Protection Agency (USEPA) priority pollutant list indicates the significance accorded these chemicals by US health officials.

The identification of organics, particularly in drinking water supplies, has always been a difficult problem, although in recent years significant progress has been made in the development of analytical separation and identification techniques. Considerable attention has also been given to proper procedures for preserving samples to ensure that collected samples undergo minimal chemical change between collection and analysis. However, almost no effort has been made to determine what procedures could ensure collection of groundwater samples that are representative of the quality of the resource in its natural environment. This article addresses some of the problems associated with sampling public water supply wells and constructing groundwater monitoring wells.

Principles affecting organic compounds

Scalf et al[1] correctly noted that a positive sample from a monitoring well may prove the presence of a contaminant in groundwater, provided the integrity of the well and the sampling procedure are intact. However, a negative sample does not necessarily prove the absence of contamination in the aquifer. This dicussion points out some factors that tend to bias analytical results and may compromise the credibility of both positive and negative sample results.

The relatively unstable nature of many chemical, physical, and microbial constituents in groundwater contributes to the complexity of securing representative groundwater samples. Because th

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physical, chemical, and biological aspects of the subsurface environment are so closely interrelated, it is difficult to deal with one without the others being affected. In devising groundwater sampling protocols, the effects of collection, preservation, and handling procedures on each of these aspects must be considered to ensure sample integrity. (See Westrick, page 52.)

The act of sampling may cause changes in water temperature and pressure that may, in turn, affect the water quality. Groundwater is usually well insulated and, therefore, normally experiences a narrow range of temperatures. When withdrawn from the subsurface, it may undergo temperature changes of 15–25°C and rapid changes in pressure. Degassing, aeration, and temperature variations can cause significant changes in the solubility of volatile compounds and alter the chemical speciation of many dissolved chemical constituents. Pressure and temperature effects on the carbonate system may shift the pH or redox potentials and affect the chemistry of iron, manganese, sulfur, oxygen, and other mineral equilibria. Gibb et al[4-6] indicated how the selection of sampling apparatus alone may drastically affect the pH and chemical speciation of the pH- and redox-sensitive elements.

Temperature and pressure also affect microbial growth. In order to assess the in situ activity of subsurface microorganisms, sampling methods must be selected that will not disturb the groundwater or contaminate it with foreign organisms.[7]

In addition to altering water chemistry and subsurface microbiology, sampling can influence the integrity of groundwater samples by contamination or loss by means of contact with materials in the sample delivery system. Certain materials in contact with the sample can cause organic chemicals to be sorbed from the water samples or leached from the materials into the samples. For example, Miller[8] studied three types of well casing exposed under static conditions to two metal pollutants and six volatile organic pollutants. He reported that polyvinylchloride (PVC) pipe caused less monitoring interference with volatile organics than polyethylene or polypropylene under the conditions of the experiment. Junk et al[9] determined that organic contaminations ranging from 1 to 5000 μg/L by weight were observed in organic-free water that had flowed through tubes of polyethylene, polypropylene, black latex, six different formulations of PVC, and a plastic garden hose. Among the contaminants leached from PVC were *o*-cresol, naphthalene, butyloctylfumarate, and butylchloroacetate. Curran and Tomson[10] measured the leachate concentrations found in organic-free water that had been circulated through five different types of plastic tubing (polypropylene, polyethylene, PTFE, vinyl chloride and vinyl acetate copolymer, and PVC, with and without solvent-cemented joints). Their results indicated low levels of leaching from all of the tubing tested except PTFE. Numerous contaminants were leached from solvent-cemented PVC and vinyl chloride and vinyl acetate copolymer.

Pettyjohn et al[11] and Barcelona et al[12] compared the merits of preferred well construction materials in relation to the cost of construction and the quality of resulting data. The materials in order of preference are: glass, PTFE, stainless steel, polypropylene, other plastics and metal, and rubber. Each monitoring situation must be assessed to determine appropriate materials for well construction in order to reduce bias in analytical results. This consideration is particularly significant for hydrologists and consultants who must justify additional costs involved in using more expensive, inert materials.

The materials used in wells and pumps can also affect water quality from public water supply wells. Well casing and pump materials are normally chosen on the basis of strength and durability, whereas little or no attention is given to the possible impact the materials may have on the quality of water delivered to the surface. Similar problems exist with regard to distribution systems for public water supplies. Studies by Schreiber[13] showed that contrary to the expected results of increasing trihalomethane (THM) concentrations throughout distribution systems, the highest concentrations of THMs often were found at the treatment plants. Studies conducted by the PVC pipe industry and the USEPA[14] for five public water supply systems using PVC pipe detected no vinyl chloride in water conveyed through the pipe. Dressman and McFarren[15] found vinyl chloride monomer in concentrations of 0.03–1.4 μg/L in distribution systems ranging in age from new to nine years old.

Studies conducted by Boettner et al[16] demonstrated that low levels of akyl tin species may be leached from both PVC and chlorinated PVC (CPVC) pipes by water. Volatile organic solvents (e.g., methyl isobutyl ketone, tetrahydrofuran, and cyclohexanone) used in sealing cements continued to leach into water from PVC and CPVC pipe joints for more than 14 days. The quantities leached ranged from 10 μg/L to 10 mg/L during the 15 days of sampling. Factors influencing the leaching process included pH, temperature, ionic composition of the water, exposed surface area, and surface porosity of the pipe material. Water-soluble polymer additives or reaction products may migrate to the pipe's surface, and many factors can affect the degree and type of leaching from the pipes.

Sampling public water supplies for organic contamination

Public water supply wells (raw water) and finished drinking water are routinely sampled in response to regulatory requirements. Sampling taps are located at the well heads and at various points throughout distribution systems for obtaining samples from which to analyze the inorganic and bacterial constituents of the water. Water is allowed to flow through the taps into prepared sample containers, which encourages aeration, degassing, and loss of volatile organic compounds.

The raw water samples collected at the well head are not representative of the finished water delivered to the consumer through the distribution system. Water delivered to the distribution system is often maintained under positive pressure throughout the treatment procedure and in the distribution mains. Not only are volatile organics retained in the water delivered to the consumer, but they also may be transformed through reaction with oxidants or disinfectants such as ozone, chloride, and chlorine dioxide.

Because of possible chemical transformation within the distribution system, there is no substitute for a carefully conceived and comprehensive program for sampling raw water at the well head and finished water at various points throughout the distribution system. An attempt to develop a mass balance of organic compounds delivered to and obtained from the distribution system would be desirable; however, the frequently used indicator of organic content, dissolved organic carbon (DOC), is not recommended. Most methodologies for determining DOC do not include volatile constituents and rarely indicate more than 10 percent of the DOC actually identified. Such inadequate sampling of distribution systems may give a false sense of security. A carefully planned sampling program to test all portions of the distribution system should be undertaken if any contaminants are suspected in the raw or finished water within the system. To ensure that the expense of conducting such a program is warranted, special care must be taken to collect samples that will not bias analytical results through the loss of volatile organics.

Water samples collected from public water supply wells represent the integrated or average quality of water contained within the aquifer. Radial flow of water toward the well integrates water from different sources along the horizontal plane. Similarly, water from the entire saturated thickness of the aquifer

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being pumped is drawn into the well. Therefore, the effect of a comparatively small plume of contaminated water captured by the pumping well may go undetected in the sampling of relatively large water supply wells.

To provide more detailed water quality information, monitoring wells, designed to determine "point water quality data" horizontally and vertically, are desirable. Data obtained from properly located, constructed, and sampled monitoring wells are essential to a realistic picture of water quality within the aquifer.

The construction of groundwater quality monitoring wells

Scalf et al said:[1] "The success of a groundwater quality monitoring program depends on numerous factors; however, the location, design, and construction of the monitoring wells is usually the most costly and nonrepeatable factor." It is extremely important that the siting and construction of monitoring wells be properly done.

The number and locations of monitoring wells depend on the geologic and hydrologic conditions at each site. The horizontal location of monitoring wells in relation to a pollutant source determines whether contaminated water can be intercepted. Further, the vertical location of the well screen also affects the quality of water collected from the well. The development of a successful monitoring well program depends on the skills of the hydrogeologist and the driller who design and install the wells. Flexibility must be maintained to change well locations and depths as new information is obtained during program development and well drilling. Under no circumstances should the entire drilling budget be spent on a series of monitoring wells based only on initial predictions of the direction of movement of pollutants.

The diameter of monitoring wells should be no larger than necessary to accommodate the sampling apparatus. The diameter of the bore hole into which the casing is placed must accommodate the casing and be at least 5 cm (2 in.) larger to permit placement of a grout seal around the outside of the casing. Casings and bore holes that are larger than necessary can have undesirable effects on the data obtained from the well. For example, in formations with very low permeability, excessive storage in an unnecessarily large boring or well casing can result in erroneously low water levels for days or even months. Also, because it is necessary to remove the water standing within the well casing before collecting a sample, unnecessary pumping of water from within the well casing can prolong the sampling procedure.

The materials normally used for the construction of monitoring wells are either metal or plastic. Alteration of groundwater samples may occur because of chemical reactions with casing materials, pipe-cutting oils, threading compounds, cleaning solvents, or cement. Choosing casing material is more complex than simply using metal casing if organic constituents are to be determined and plastic casing if metals are to be determined. Iron oxides from aged steel casing may be a source of adsorption losses of trace metals or organic compounds. Adsorption on PVC is presumed to be limited; however, absorption into this material can contribute to the loss of organic compounds. As a well is purged, casing material in equilibrium with stored water may exert other effects on newly entered water from a geologic formation with a different water quality. Barcelona et al[12] recommended using PTFE, stainless steel, or rigid threaded PVC pipe for well casing materials. A nearly ideal construction material for wells is PTFE. Inertness to attack, poor sorptive properties, and low leaching potential are clear advantages of rigid PTFE.

Alteration of groundwater samples may occur because of chemical reactions with casing materials.

Solvent cement should be avoided to prevent the diffusion of organic solvents into samples. Threaded couplings should be used for joining segments of the casing and screens. Monitoring wells in unconsolidated geologic formations should have openings that permit free entry of groundwater into the well without the intrusion of earth materials. The use of commercially manufactured well screens is recommended, since hand-sawed or torched slots may enhance the diffusion of organic compounds from some types of pipe and cause clogging or other difficulties in developing the well. The length of the screen or slotted section of the casing is important. The use of long screens can result in dilution of (and possible failure to detect) thin lenses of contamination in groundwater. Screens that are too short and do not have an adequate open area restrict the entrance of groundwater, resulting in slow recovery rates of the water level after the casing is evacuated. In most cases, a 0.6-3-m (2-10-ft) length of screen is adequate. An artificial gravel pack is normally placed around the screen or slotted section of a monitoring well to allow water to move freely to the well and to retain aquifer materials.

The annular space between the casing and the bore hole above the gravel pack should be backfilled with a sealant to the ground surface. Proper backfilling prohibits migration of water from the surface or from other geologic formations and provides support for the casing. Care in selecting the grouting materials is also important to ensure that the grouting does not interfere with the chemicals of interest in the monitoring program. Claylike bore-hole cuttings, bentonite, and cement grout are commonly used sealants. Each of these has limitations. Bore-hole cuttings are the least satisfactory because they are difficult to compact during placement. The swelling properties of bentonite are reduced when it is mixed or in contact with highly mineralized waters. Additives are available that can be combined with the bentonite to offset this reduction, but their effectiveness is not documented. Biodegradable additives may encourage microbial growth. Subsequent breakdown may cause seals to fail as a result of gas formation or the generation of mobile microbial metabolites. Cement grout has a tendency to shrink and crack during in-place curing. Cements or cement-bentonite mixtures that expand are preferred by most researchers.

After a well is installed, it must be developed by pumping or surging or both until sediment-free water is produced. One technique of surging involves the use of a surge block or plunger to create a vacuum on the upstroke and a positive pressure on the downstroke. During the positive pressure stroke, fine-grained materials in the immediate area of the well screen are loosened, and on the upstroke they are pulled into the well. Similar actions may be accomplished by alternately turning a pump on and off or alternately increasing and decreasing the rate of discharge. All fine-grained materials brought into the well during development should be removed. Airlift mechanisms have proved successful in developing monitoring wells in highly permeable formations. In geologic materials of limited permeability, circulation of clean water down through the well casing and screen, through the gravel pack, and up the bore hole prior to placement of the bore hole sealant often removes the mud cake on the bore hole and renders the well usable for sampling with minimal turbidity. Until adequate time has elapsed, newly constructed and developed wells may not yield representative water samples because of the effects of drilling.

Types of sampling devices

There are five basic types of sampling devices for collecting samples from groundwater monitoring wells. They include grab samplers (e.g., bailers and syringes), gas-driven devices, positive-

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displacement submersible pumps, suction pumps, and airlift devices. Studies by Gibb et al[4-6] indicated that bailers and positive-displacement bladder pumps yield samples for inorganic analysis that are most representative of the water contained in an aquifer. The airlift devices tested by Gibb stripped dissolved carbon dioxide from the water, thereby increasing the pH and altering the chemical composition before the water reached the surface. Barcelona et al[17] showed that bladder (no-gas contact) pumps are superior for most organic sampling applications. Significant bias and poor precision may be expected in sampling for organics with gas-driven mechanical-displacement systems and suction mechanisms. Ho[18] recently reported on the loss of volatile compounds as a result of suction sampling mechanisms.

Recommendations for organic sampling of groundwater

Prior to the initiation of a sampling program for organic compounds, the goals of the sampling or monitoring project must be clearly understood. The materials used for well construction, the pumps, and the sampling devices should be compatible with the goals of the sampling program and consistent with the desired limits of accuracy and precision for detecting the chemical constituents of interest. In many cases, the level of detail demanded by scientific or research studies is greater than that required for routine monitoring purposes. A clear understanding of the hydrogeology and suspected chemical contaminants is also essential to a successful sampling program. The possible alteration of the chemistry of water samples caused by an inappropriate sampling mechanism or by contact with the well casing or sample delivery tubing should be considered. Pumping rates and times must be sufficient to purge the well of stagnant water without inducing excessive migration of water toward the well. For the sampling of public water supply distribution systems, it is essential to know which materials are used in the system.

The success of a sampling or monitoring program depends on careful planning prior to the initiation of actual sampling. In many instances, the cost of analysis incurred over a monitoring period of 5-10 years is large compared with the costs of construction of monitoring wells. Analysis of the costs involved in properly constructing and developing monitoring wells and purchasing pumps should be undertaken to ensure that costs are not increased unnecessarily by adherence to false economies in the initial phases of the project.

Careful consideration must be given to the pumping mechanisms in the well, the type of treatment that the water undergoes before it enters the distribution system, and the kinds of piping contained in the distribution system. All of these factors may alter the chemical quality of the water prior to use by the consumer. The selection of the points within the distribution system where samples are to be taken should be made by a hydraulic engineer who is familiar with the flow paths and by a chemist who is familiar with the types of chemical reactions that may be expected to occur. Proper planning and judicious selection of sampling points throughout the system can result in considerable cost savings in terms of eliminating unneeded samples. An understanding of the chemistry within the system will also ensure that the monitoring program adequately protects the health of the consumers.

Summary

Too little is known about the chemical changes that occur in groundwater samples during the collection process. Because of the potentially dangerous or toxic nature of many organic compounds found in groundwater throughout the United States and in Europe, this type of research can no longer be avoided. The analytical data collected to date on organic compounds in groundwater are not actually representative of in situ conditions. Only in cases of gross contamination, where the concentrations of organic compounds are so large that bias from the sampling procedure is unnoticed, can it be determined with certainty that contamination has occurred. When organic compounds occur only at trace levels, inappropriate sampling procedures or mechanisms may prevent their detection by subsequent chemical analysis. The crucial task of groundwater protection can be accomplished only by recognizing the importance of proper sampling and by accelerating research to address these critical problems.

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FIELD REPORT

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(5)

Sorption of Organics by Monitoring Well Construction Materials

by A.L. Sykes, R.A. McAllister and J.B. Homolya

Introduction

In August of 1985, the Environmental Protection Agency released a draft guidance document titled "RCRA Groundwater Monitoring Technical Enforcement Guidance Manual," which was intended to help EPA and state enforcement officials decide whether specific elements of an owner/operator's ground water monitoring system satisfy the RCRA requirements. The guidance document states that polytetrafluoroethylene or Type 316 stainless steel are the materials of choice as screen or casing in new well installations where volatile organics are the parameters of interest. Since no guidance was provided on appropriate use of casing material at the time the RCRA regulations were promulgated, most operators installed PVC casing in both the original and subsequent monitoring systems because this material had been used for years in the water well industry, is readily available, and is fairly inexpensive.

The EPA has cited a number of reasons why PVC is not an acceptable material for well construction. These include:

- Potential for casing attack and fatigue by exposure to high concentrations of certain organic compounds
- Desorption of plasticizers and additives from the well casing to otherwise uncontaminated ground water (false positive)
- Sorption of organic compounds into the well casing exposed to contaminated ground water (false negative).

Sorption was cited as the major problem in the guidance document, since the possibility of a false negative is of prime concern to the EPA and other regulatory agencies.

In August of 1985, Waste Management Inc. (Jarke 1986) conducted a preliminary research program designed as a practical and realistic evaluation of the potential for sorption to occur for PVC and other materials of construction expected in monitoring wells. This study was designed to address the potential for sorption of previously exposed casing surfaces. Proper monitoring well sampling protocols require that the stagnant water (in equilibrium with the casing) be pumped from a well prior to sampling. The recharge of formation water would then be representative of the ambient organic concentration and would be in contact with the saturated surface of the well casing for a period of between one and 24 hours before sampling. Therefore, a series of experiments were conducted to investigate the potential of exposed casing materials to further sorption by recharge of the well. Results of those experiments demonstrated that for all materials exposed for both the one and 24 hour cases, the net sorption was nominally zero. These results, however, were only preliminary because the study was limited to a small number of exposure samples, making a statistical interpretation of the data impossible.

The major technical question resulting from WMI's preliminary research program was the use of methanol as a means of dissolving sorbates of interest into water for material exposure studies. Since the final level of methanol in water was significantly greater than the sorbates, it is possible that the exposed material surfaces became saturated with a mono-layer of methanol, preventing any sorption of other organics. Radian's studies were designed to address the criticisms of the WMI work. Consequently, methanol was not used as a vehicle for introducing sorbates to the water matrix. Each component was spiked directly into pure water. Also, each experiment was done in triplicate with full quality assurance and control procedures followed throughout.

Technical Approach

Well Material Coupons: All materials were obtained from Brainard-Kilman Drill Co. (Stone Mountain, Georgia). The PVC was "TriLoc Monitor Pipe," 2-inch (51mm) I.D. by 2⅜-inch (60mm) O.D. The stainless steel was "Armco Welded 2-inch Type 316," 2½-inch (56mm) I.D. by 2⅜-inch (60mm) O.D. The polytetrafluoroethylene (virgin PTFE) was 2⅛-inch (52mm) I.D. by 2⅜-inch (60mm) O.D. All coupons were cut to a length of 53mm, which produced a surface area of 100cm² per coupon. Each coupon was then cut once lengthwise to allow placement into a 237 mL jar. The tube edges were not considered to be a factor in this study.

Exposure Jars: The exposure jars were "Qorpak Clear with TFE-Lined" screw caps 237 mL capacity (actual 260 mL with no head space). These jars were

obtained from Fisher Scientific, catalog #03-230-7D. All jar cap liners were covered with foil to minimize possible jar liner effects.

Solvents: All solvents were purchased as chromatography grade and were used without further purification. A stock spiking solution containing methylene chloride (MeCl2), 1,2-dichloroethane (1,2-DCE), trans-1,2-dichloroethylene (DCEE), toluene and chlorobenzene at a concentration of 10 ppm each was prepared in distilled/deionized water. A second spiking solution was prepared containing 0.5 ppm trichloroethylene (TCEE) in distilled/deionized water. This separate spike was prepared because of TCEE's much lower solubility in water (1.1 ppm) than the other compounds.

Water: Distilled/deionized carbon filtered water was used.

Procedure

Preparation of Glass Jars: The glass jars and lids were each cleaned with soap and water followed by distilled/deionized water rinse. Each jar and lid was then dried at 100 C.

Solution Stability Studies: Prior to the material exposure studies, the 10 ppm and 0.5 ppm spiking solutions were evaluated for stability and the suitability of the test protocol design. Six 260 mL jars with foil-lined caps were filled (without head space) with aliquots of the spiking solutions and pure water to yield approximately 100 ppb of each component. An additional six jars were filled with pure water and represented water blanks for the study. After a one-hour period, an aliquot from each jar was transferred to a Volatile Organic Analysis (VOA) vial (polytetrafluoroethylene-lined cap) and stored in a refrigerator at 5 C for a seven-day period. At the end of the seven days, the original stock-spiking solution was used to prepare a 100 ppb component solution mixture which was then aliquoted to 2 VOA vials for analysis. Additional VOA aliquots were taken from the original 260 mL jars and used for analysis. On day nine, all VOA vial samples were again analyzed and compared to freshly prepared spiked water. Originally, these exposures were to be at two levels, 10 ppb and 100 ppb, but due to the unacceptable variance of compound recoveries from the spiked water at 10 ppb, only the 100 ppb level was used for the exposures.

Well Material Coupon Exposure Studies: Well material coupons were placed in foil-covered glass jars and filled with spiked water solution so that no head space remained. The water solutions were spiked at levels to yield component concentrations between 90 and 150 ppb. The jars were stored at 5 C in a refrigerator for seven days and agitated daily. After the seven-day conditioning period, an aliquot was pipetted into a 40 mL VOA vial with zero head space for analysis. A second aliquot was also pipetted into a 40 mL vial and stored at 5 C as a preserved sample. The remaining solution in the jar was discarded. The jars, with the original coupons, were then refilled with organic-spiked water of the same concentration as in the seven-day conditioning period. After a contact time of one hour, aliquots were again taken for analysis and preservation. The jars were refilled with organic-spiked water again for a contact time of 24 hours, after which a third aliquot was taken for analysis. Control samples, consisting of spiked water with no well material coupons were carried through the entire procedure. Blank samples, consisting of pure, unspiked water and no coupons were carried through as well.

Sample Analysis

The analytical procedure followed was EPA Method 602 (EPA 1984), which uses gas chromatography with flame ionization detection. The procedure incorporates a purge and trap technique to concentrate the volatile organics from water samples. The instrument used was a Varian 3700, and the data system was a Varian Vista 402. The column was 1.3m x 2mm, stainless steel, packed with 1 percent SP-1000 on Carbopack B 60/80 mesh. The temperature of the oven was initially at 45 C for three minutes, then programmed to 200 C at 15 C per minute. The nitrogen carrier gas was set at 30 mL per minute through the column and 40 mL per minute through the Tekmar LCS-1 Purge and Trap. Each sample analyzed was transferred to a 5 mL gas tight syringe equipped with a sample valve. Ten microliters of a three-component internal standard mix (15 ng/μL) was added to each sample through the syringe to produce a concentration of 30 ppb. The three internal standards were bromochloromethane, 1-chloro-2-bromopropane and 1,4-dichlorobutane.

One exposure level for each compound was studied. These ranged between 87 and 150 ppb. The concentrations varied because the same mass of each compound was used to prepare the stock-spiking solution of each compound. The density was then used to calculate exact concentrations.

The following is a list of each compound studied and the concentration level prepared in the exposure medium:

methylene chloride	133 ppb
1,2-dichloroethane	126
trans-1,2-dichloroethylene	128
trichloroethylene	147
toluene	87
chlorobenze	110

Calibration and Quality Control

The calibration procedure used for the volatile organic analysis was the external standard technique, with internal standards added to each standard and sample for quality control of the analysis. A calibration curve was constructed by preparing three concentration levels of each compound at approximately 10 ppb, 50 ppb and 100 ppb levels. A system blank of pure water was used as a zero point on the curve. A stock solution was prepared from the pure materials in chromatography grade methanol by accurately measuring microliter portions into a known volume. The concentration of each component was then calculated based on its density (mg/μL). The

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working standards were prepared fresh each day by dilution of the stock into pure water. The three-point curve was prepared initially at the beg ng of the stability study and again at the beginning of the exposure study. Linear regression equations were calculated for each curve, then plotted for visual agreement with linearity. Subsequently, only the 100 ppb standard was used to ensure that the calibration curve was within the EPA protocol of <10 percent CV (percent coefficient of variation). The linear regression plots are shown in Figure 1. In addition, three internal standards were used to verify system control. Each 5 mL sample and standard received 10 μL of the three-component mix (15 μg/mL), which was equivalent to 30 μg/L (ppb), immediately before analysis. Figure 2 is a plot of the internal standards with the calculated percent CVs. This data shows that throughout the study the percent CVs were 5 percent, which, according to EPA Method 602 <10 percent is acceptable. The mean concentration of all the blanks analyzed during the exposure study shows that methylene chloride was 13 ppb; 1,2-DCE was 3 ppb; DCEE and TCEE were 2 ppb; and toluene and chlorobenzene were 1 ppb.

Results and Discussion

Results of Stability Study

The objective of the stability study was to evaluate each compound for recovery variability excluding well-casing material sorption effects. Analyses of duplicate samples determined precision; and analyses at day one, day seven and day nine determined the potential storage effects. Analysis of water blanks also determined background contamination due to the glass jars, liners and storage. The stability study also established a reference for evaluating analytical precision and quality control of

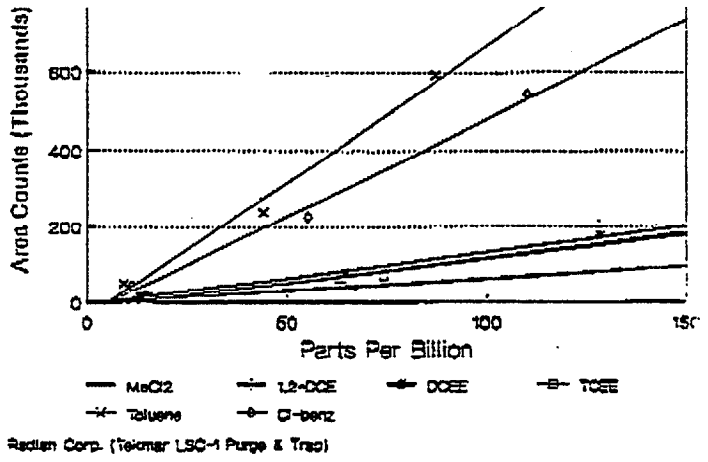

Figure 1. Volatile organic analysis calibration curves of coupon exposures

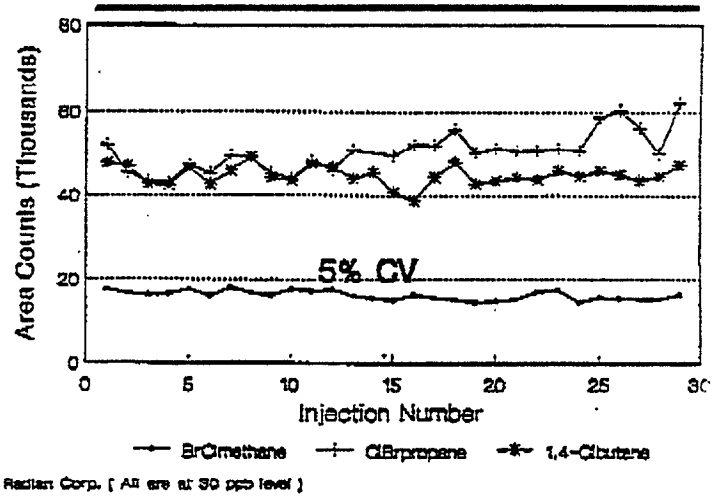

Figure 2. Percent coefficients of variation of three internal standards for coupon exposures

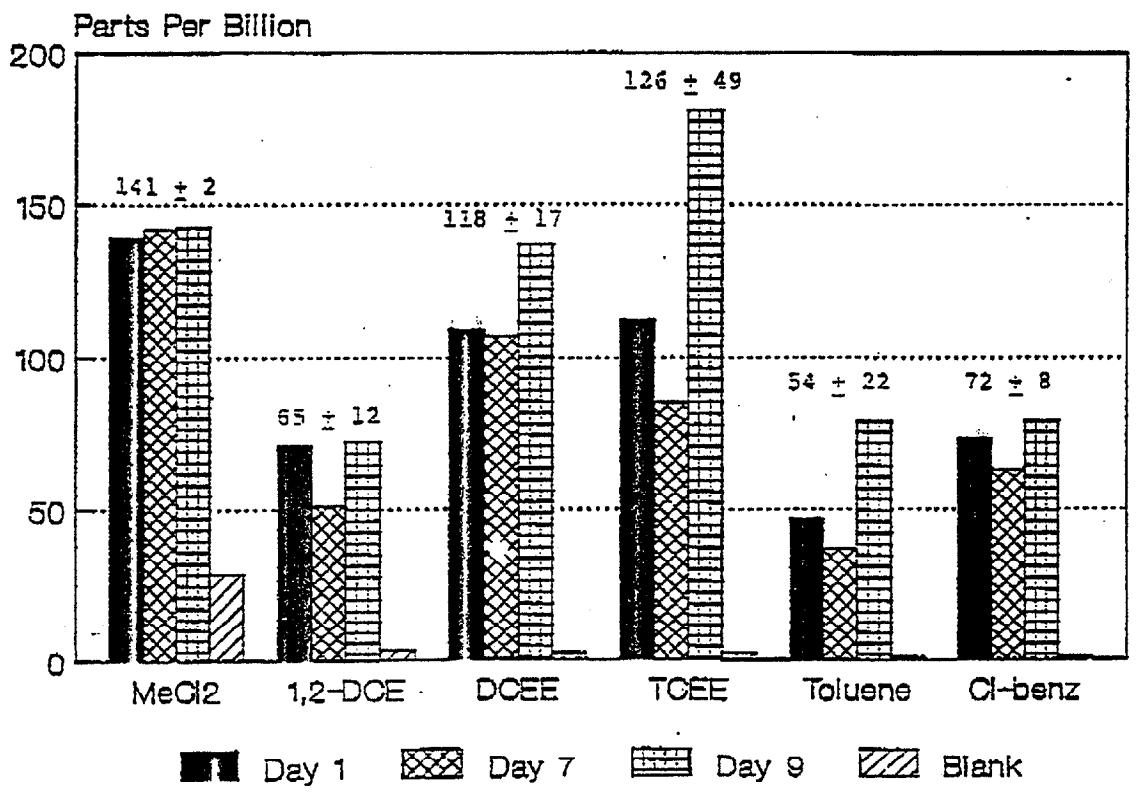

Figure 3. Stability of volatile organics in 5 degree C. water for nine days

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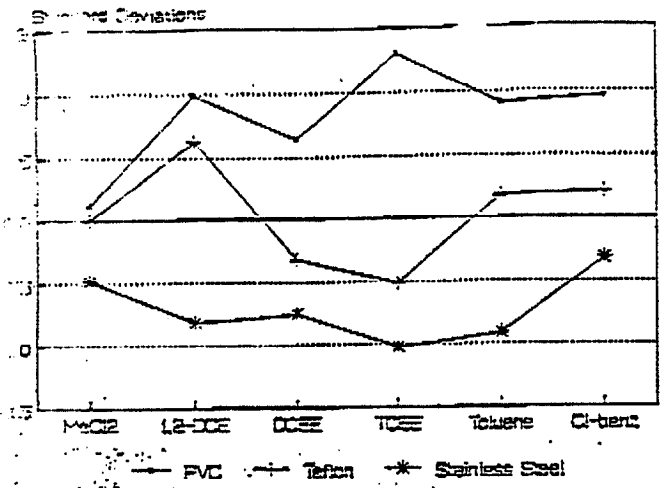

Figure 4. Standard deviation of one hour coupon exposures vs. controls

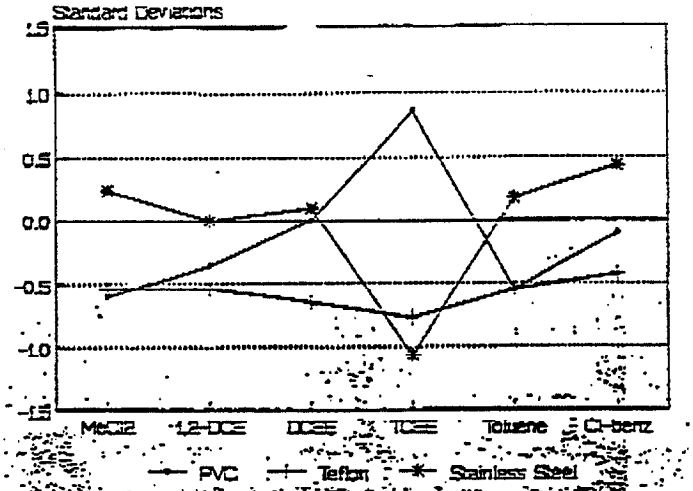

Figure 5. Standard deviation of 24-hour coupon exposures vs. controls

the method.

The results of the stability study show that for the compounds studied, there is some variability. This variability seems to be associated with the solubility of each compound in water. Figure 3 graphically displays the results for each compound at day one, day seven, and day nine, and a blank water sample.

Results of Material Exposure Study

The objectives of the material exposure study were to determine if there were significant differences in compound sorption between PVC, polytetrafluoroethylene, and stainless steel well-casing materials when exposed to volatile organic hydrocarbons in a simulated "well" environment. The laboratory experiments were designed to simulate actual conditions of sampling ground water containing approximately 100 ppb of hydrocarbons normally found in contaminated waters. In addition, the experiments were designed to determine adsorption or desorption effects of these materials when exposed to these compounds over time. It is necessary to determine if false positive or false negative results bias the actual concentrations of the samples. The study did not, however, determine if the materials released compounds into non-contaminated water.

The results of the material exposure study are shown in Figures 4 and 5. Nine control samples were analyzed for each compound studied. These nine controls were averaged and a standard deviation obtained. The three replicate values for each compound for each type of material studied were also averaged. Figures 4 and 5 represent the effect of sorption at one hour and 24 hours, respectively, for the six compounds on the three casing materials. All results are approximately one standard deviation of the mean for all compounds and all casing materials. A more rigorous analysis of these data will be performed at a later date.

The results of these experiments show that statistically, there is no significant difference between PVC, polytetrafluoroethylene, and 316 stainless steel well casing materials when exposed to approximately 100 ppb contaminated water for seven days and 5 C, then exposed for one hour, and then for 24 hours.

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adsorption studies

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DISCUSSION

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The Use of PVC Casing and Screen in the Presence of Gasolines on the Ground Water Table

by G.W. Schmidt

The purpose of this discussion is to extend the conclusions of the Field Report by A.L. Sykes, R.A. McAllister and J.B. Homolya titled "Sorption of Organics by Monitoring Well Construction Materials," published in *Ground Water Monitoring Review*, v. 6, no. 4, 1986.

The authors should be commended for statistically demonstrating that there are no significant differences in organic compound sorption between polyvinyl chloride (PVC), polytetrafluoroethylene and stainless steel well casing when exposed to dissolved volatile organic hydrocarbons of approximately [illegible]0 ppb concentrations (Sykes [illegible] 1986). The U.S. Environmental Protection Agency (EPA) [illegible] incorrectly concluded that PVC is not an acceptable material for monitoring well construction because it "deteriorates when in contact with . . . aromatic hydrocarbons" (EPA 1986). It has also been implied over the past several years by both federal and state regulatory agencies that PVC casing will swell and deteriorate in the presence of the aromatic fraction of liquid gasoline. Therefore, many regulators do not allow the use of PVC casing, and especially PVC screen, in monitoring wells because they erroneously believe that the swelling of PVC in the presence of gasolines will cause the screen slots to close and the casing to deteriorate.

It has been my observation in using PVC screen and casing in monitoring liquid gasoline on the ground water table in many thousands of wells, over 13 years, that there is neither swelling nor deterioration of PVC casing or screen. To demonstrate these field observations, small sections of rigid 2-inch diameter, Type I PVC screen (0.006 slot size) were placed in different gasolines to record any changes in slot opening sizes or any other alterations. Each PVC screen was cut to [illegible] two slots, as well as being cut at right angles to the [illegible] The [illegible]ions were completely submerged in premium [illegible]n-[illegible]ed regular, and leaded regular grades of [illegible] gasolines. A control sample was retained that was not placed in contact with any gasoline. After the sections of PVC screen were in the gasolines for 6.5 months, they were removed and, along with the control sample, were photographed under a scanning electron microscope (Amray Model 1000B) to observe any swelling or alteration. The results are shown in Figure 1. [illegible]otograph 1 (premium gasoline), photograph 2 (unleaded [illegible]gular), photograph 3 (leaded regular), and photo[illegible] control sample not in any gasoline).

The photographs (samples 1, 2 and 3) clearly show no changes in slot size of any of the PVC screens in contact with gasolines compared to the control (sample 4 [illegible] the fragments on the "cut face" of each of the [illegible] show no alteration from long-term exposure to [illegible] gasolines. From this study, the conclusion is clear that Schedule 40, rigid, Type I PVC casing and screen can be used with confidence when monitoring for the occurrence of gasolines on the ground water table [illegible] Thoreau said, "The question is not what you [illegible] what you see." The EPA and state regulatory [illegible] should recognize such confirmation d[illegible] unsubstantiated conclusions such as [illegible] the use of PVC casing and screen in the [illegible] gaso[illegible]

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lowest rankings are for some benzoic acid, aniline, and phenol derivatives; of course, if some other criteria were used, the ranking might have been somehow different, but probably not too much. For example, the ranking obtained by using Freitag and co-worker's chlorobenzene data and the ranking using Ribo and Kaiser's data are very similar. When a new chemical is developed and its properties are known, it can be easily ranked and compared with other known chemicals or any arbitrary standards. The availability of the program in microcomputer form make the routine applicability easy.

A final comment: the development of a suitable index for environmental risk has been widely discussed in the literature (*3, 4, 12*). An index is a suitable scalar function of the vector distance components with the best chemicals having the lowest index. Since an index is a scalar quantity, problems concerned with the noncomparability of chemicals cannot arise since the chemicals can always be ranked and represented as a chain in a Hasse diagram. Unfortunately, the choice of a particular index affects the results (*7*).

A simple example can clarify the previous arguments: Let C' and C'' be the vector distance components of a chemical C and let $F = C' + 2C''$ be the chosen index. The chemical C2 previously considered has the components $C'_2 = 2$ and $C''_2 = 3$; thus, $F_2 = 2 + 2 \times 3 = 8$. Analogously, for the chemical C3, $C'_3 = 3$, $C''_3 = 2$, and $F_3 = 3 + 2 \times 2 = 7$. As $F_3 < F_2$, the chemical C3 would be considered safer than C2. Conversely, if the index were $G = 2C' + C''$, then $G_2 < G_3$ and C2 would have to be considered safer than C_3. The conclusions are opposite to each other. They depend only on the index chosen. As a consequence, every time the definition of an index cannot be firmly grounded on a theoretical basis, the results can be completely biased, and the index becomes biased toward a subjective meaning.

Registry No. 1, 108-88-3; 2, 108-86-1; 3, 1817-47-6; 4, 611-06-3; 5, 82-68-8; 6, 65-85-0; 7, 586-76-5; 8, 50-30-6; 9, 62-53-3; 10, 106-47-8; 11, 25265-76-3; 12, 92-87-5; 13, 634-93-5; 14, 91-94-1; 15, 108-95-2; 16, 108-39-4; 17, 123-31-9; 18, 100-02-7; 19, 87-86-5; 20, 128-39-2; 21, 120-83-2; 22, 88-06-2; 23, 92-52-4; 24, 13029-08-8; 25, 34883-43-7; 26, 16606-02-3; 27, 62796-65-0; 28, 39485-83-1; 29, 71-43-2; 30, 108-90-7; 31, 106-46-7; 32, 120-82-1; 33, 608-93-5; 34, 118-74-1; 1,2-dichlorobenzene, 95-50-1; 1,3-dichlorobenzene, 541-73-1; 1,2,3-trichlorobenzene, 87-61-6; 1,3,5-trichlorobenzene, 108-70-3; 1,2,3,4-tetrachlorobenzene, 634-66-2; 1,2,3,5-tetrachlorobenzene, 634-90-2; 1,2,4,5-tetrachlorobenzene, 95-94-3.

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Well Construction and Purging Effects on Ground-Water Samples

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■ Multiple well installations of selected casing materials [i.e., poly(tetrafluoroethylene) (PTFE), 304 stainless steel (SS), and poly(vinyl chloride) (PVC)] were constructed and sampled to determine if well purging and construction procedures would significantly bias chemical constituent determinations in ground water. Water quality results from six monthly sampling dates indicate that proper purging of stagnant water from monitoring wells and isolation of cement seals are essential for the collection of representative chemical data. Significant differences in purged samples taken from PTFE, SS, or PVC wells were observed for total organic carbon and volatile halocarbons, which may be linked to the materials' interaction with ground water. The well casing interferences were not predictably high or low for any of the materials.

Introduction

The effects of well construction procedures and sampling protocols on the reliability of ground-water chemistry investigations have been the subject of a number of research efforts in the past 10 years. The published literature has dealt mainly with the potential error introduced by water sampling or analysis (*1–3*) and by the selection of materials that are appropriate for specific monitoring applications (*4, 5*). A recent publication details procedures by which ground-water sampling protocols may be developed to control systematic sources of sample collection (*6*). These errors include artifacts of well siting or construction, well purging, and sample retrieval from the well. In general, sample collection errors cannot be accounted for by traditional laboratory quality control measures. Also, large sampling errors coupled with analytical errors of similar severity can result in the collection of grossly biased data.

Recent work has shown that potential sampling bias due to both sampling mechanisms and flexible tubing materials is of the same order of magnitude (i.e., ±5–20%) as analytical errors for volatile organic compounds (*7, 8*). These results support the need for very careful consideration of volatilization, sorption, and desorption effects in the selection of sampling pumps or tubing for ground-water investigations.

The effects of drilling fluids, grouts, or well casing interactions with the geologic formation or ground water are

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more difficult to evaluate for a number of reasons. Foremost among these reasons is that natural variability in ground-water quality has not been studied in detail. Also, there have been no systematic field studies reported on the effects of well purging or casing materials on organic compound levels in ground water where inert materials have been used as controls. Houghton and Berger (*9*) have reported significant differences in ground-water dissolved organic carbon and trace metal levels in samples from stainless steel and thermoplastic well casing materials. The observed differences were of the order of analytical bias (i.e., ±10–50%). Laboratory investigations may help in evaluating sources of sampling imprecision or bias; however, systematic field studies are needed to evaluate the actual severity of such errors. The unique details of well construction, completion, development, and the in situ geochemical conditions for an actual ground-water monitoring installation may enhance or limit the potential effects of materials or mechanisms that have been observed in controlled laboratory testing (*10*).

This study was undertaken to compare the effects of well purging and well construction materials on the reliability of determinations of inorganic and organic chemical constituents in ground water at two sanitary landfill sites in east-central Illinois. Due to the fact that the materials' related errors have been documented for ferrous metal well casing materials other than stainless steel, these materials were not considered in the study (*5*). Similarly, no solvent cements, nonthreaded joints, or uncommon materials were employed in well construction.

Procedures

Site Descriptions and Well Construction. The two 85–100-acre sites had been operated as municipal landfills/dumps for at least 15 years. Household trash, some light industrial wastes, and other refuse made up the 5–10 million tons of waste emplaced at each site prior to closure. Sampling installations were constructed in May 1983 with hollow-stem auger (10-in o.d., 6-in. i.d.) drilling techniques. All drilling equipment, well casings or screens, split-spoon samplers and steel tapes, etc. were steam-cleaned before they were used to minimize the introduction of foreign materials into the subsurface. Geologic conditions at both sites were characterized as till deposits (i.e., clayey silt with traces of fine to coarse sand) from below the surface topsoil to depths of 6–8 m (20–25 ft). Sand or sand and gravel lenses were observed in split-spoon samples of the till deposits at depths between 8 and 14 m (25–45 ft). All wells were 2 in. in o.d. and were completed at the depth where substantial (>0.5 ft) sand or sand/gravel lenses were observed (see Table I). Wells were placed within 2 m of each other at each location to minimize the potential effects of horizontal inhomogeneities in the formations at the completion depths. At site 1, upgradient and downgradient wells of poly(tetrafluoroethylene) (PTFE, Teflon), stainless steel (SS), and poly(vinyl chloride) (PVC) were constructed. At site 2, stainless steel and PVC wells were completed at upgradient and downgradient locations, and a Teflon/Al oxide, gas-drive dedicated sampler (Barcad) was installed in place of a PTFE (Teflon) well. All wells were completed with 2-ft screens and packed with Ottawa silica sand from the bottom of the screened interval to at least 1 ft above the top of the screen at site 1. Mortar slurry seals of 2–5 ft were placed in the bore holes above the sand pack of the site 1 wells. The slurry mix consisted of 1.5:1.0 mixtures by weight of the silica sand with Chem-Comp II shrinkage-compensating cement. The wells were finished by backfilling the bore holes to 4–6 ft from the surface with silica sand, and a cement surface seal was then placed to seal the bore hole from surface water influx. At site 2, the native sand or sand/gravel heaved up above the screened interval from 6 to 15 ft. These installations were completed by placing a cement seal from the top of the heaving material to the land surface.

Table I. Field Installations Data

location	material[a]	depth of screened interval (below land surface), ft
site 1 (upgradient)	PVC	36.5–38.5
	stainless steel (304)	34.5–36.5
	PTFE	35.5–37.5
site 1 (downgradient)	PVC	25.5–27.5
	stainless steel (304)	26.0–28.0
	PTFE	26.0–28.0
site 2 (upgradient)	PVC	32.5–34.5
	stainless steel (304)	32.0–34.0
	gas-drive sampler (Teflon/Al oxide)	30.75–32
site 2 (downgradient)	PVC	40.5–42.5
	stainless steel (304)	40.5–42.5
	gas-drive sample (Teflon/Al oxide)	41.25–42.5

[a] Materials used in the study were as follows: PVC, rigid poly(vinyl chloride) schedule 40 NSF approved for potable water uses; SS, 304 stainless steel; PTFE, poly(tetrafluoroethylene) (PTFE) (Teflon, Du Pont).

The wells at both locations were developed within a week of the construction date by use of filtered, compressed air (170 cfm) and procedures described previously (*3*). The wells at site 2 did not require further development work. Although the wells at site 1 were redeveloped at intervals for a period of 12–15 months, turbid water samples were encountered on all sampling dates due to the presence of cement fines.

Well Purging and Sampling. Hydraulic conductivity testing was done on all of the wells at each location to establish their hydraulic performance. The well purging requirements necessary to isolate stagnant water in the well bore were determined by a previously published method (*6*). Positive-displacement bladder pumps constructed of stainless steel and PTFE with PTFE delivery tubing were utilized for well purging and sampling operations (QED Well Wizard). The pumps were driven by a single controller through a gas manifold, which permitted a simultaneous supply of drive gas (air or N_2) to each pump. Pump intakes were set at the top of the screened interval for both purging and sampling operations.

The experimental design included the measurement of the well purging parameters [pH, Eh, temperature, and conductivity (Ω^{-1})] by use of an in-line flow-through electrode cell prior to well purging. Stagnant water was then collected for NO_2^-, S^{2-}, Fe^{2+}, total organic carbon (TOC), alkalinity, and selected volatile organic compounds. After collection of these samples, the outputs of the pumps were reconnected to the manifold of a flow-through electrode cell to monitor the progress of purging the wells simultaneously. Pumping rates during well purging were controlled between 500 and 1000 mL·min^{-1}, and the purging was continued until the levels of the well purging parameter stabilized to within approximately ±10% over a minimum of 4–5 L pumped (~25% of 1 well volume). All adjacent wells were purged of an equal volume of stagnant water before sampling. The volume depended on site hydrologic conditions and measured hydraulic conductivities. Once well purging was completed, pumping rates were reduced to 100–500 mL·min^{-1}, and samples were taken for the following parameters in order: alkalinity,

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Table II. Well-Purging Effects on Ground-Water Quality

	stagnant	purged	difference (+, −)	change (factor of)
Dissolved Ferrous Iron, mg·L⁻¹, Site 2 (8/6/85)				
upgradient				
PVC	0.03	0.18	0.15	+5
SS	0.02[a]	0.25	0.23	+12
downgradient				
PVC	0.04	4.57	4.53	+113
SS	1.23	4.37	3.14	+2.6
Dissolved Sulfide, mg·L⁻¹, Site 1 (7/9/85)				
upgradient				
PVC	0.048	0.242	0.194	+4
SS	0.010[b]	0.012	0.002	+1.2
PTFE	0.031	0.172	0.141	+4.5
downgradient				
PVC	0.308	0.047	0.261	−0.85
SS	0.024	0.384	0.360	+15
PTFE	0.166	0.230	0.064	+0.39

[a] Method detection limit = 0.02 mg·L⁻¹ [accuracy 90% (−10% bias), precision ±15% rsd]. [b] Method detection limit = 0.010 mg·L⁻¹ [accuracy 80% (−20% bias), precision ±20% rsd].

TOC, volatile organic compounds, dissolved inorganic constituents, and acid and base/neutral organic compounds. Pressure filtration of samples for dissolved constituent determinations was performed in the field. TOC and volatile organic compound samples were collected in 40-mL glass vials, sealed without head space by PTFE-lined septum caps.

Analytical Methodologies and Quality Control. Organic and inorganic chemical constituents were determined by USEPA-recommended methods (*11, 12*). Total organic carbon (TOC) determinations were performed by a methodology described previously (*13*). Field determinations of alkalinity were performed by potentiometric titration, and the results were analyzed by Gran end-point analysis procedures. On each sampling date, a series of field standards and blanks were used to account for transport and storage errors, which supplemented the daily analytical procedure control standards for both laboratory and field methods. Replicate samples were analyzed at intervals during analytical sessions to establish the precision and accuracy of the water chemistry data.

Results and Discussion

Well Purging. Stagnant water samples analyzed for pH, alkalinity, reduced inorganic constituents [S^{2-}, Fe(II)], and organic constituents showed higher temporal (i.e., month to month) variability than did the samples obtained after proper well purging. In most cases, well purging resulted in the stabilization of the gross solution chemistry parameters (i.e., pH, E_h, Ω^{-1}, alkalinity) although the concentrations shifted in varying degrees. For example, at site 2, alkalinity levels in stagnant water samples were generally ~25% lower than those measured in water samples after purging. The average magnitude of the alkalinity differences between samples from SS or PVC wells was not significantly different over the course of the study.

In general, the levels of reduced chemical constituents [i.e., Fe(II), S^{2-}] shown in Table II would be expected to be lower in the stagnant water in monitoring wells than in ground water obtained from the formation after purging. The actual concentration differences observed between stagnant and purged samples reflected this trend. However, the magnitude of the differences was quite variable and may have been influenced by well casing materials and small-scale heterogeneities in water quality, even in wells that were finished in the same formation less than 5-ft apart. In downgradient wells at both sites, the *stagnant water* from the SS well frequently (i.e., four of six sampling dates) showed higher levels of ferrous iron and lower levels of dissolved sulfide than those from the adjacent PVC or PTFE wells. This would be consistent with leaching of iron from the stainless steel and precipitation of sulfide by the excess iron during stagnant periods. Obviously, PVC and PTFE would not be expected to leach iron in this fashion. Example results for ferrous iron given in Table II show stagnant water values from PVC and SS wells that were significantly different at least at the reducing downgradient location. Upon purging, however, ferrous iron values in samples from both upgradient and downgradient locations increased substantially, and the formation water values from both sets of PVC and SS wells were equal within experimental error. It would seem from these observations that either PVC or SS well casing would be appropriate for ferrous iron determinations if purging is complete. Typical results for dissolved sulfide, an example of which is shown in the lower portion of Table II, reflect somewhat random changes on purging. These changes do not consistently correspond to potential well casing effects or the introduction of more reducing formation water. Rather, it seems that variability well above the detection limit and analytical precision can result from natural heterogeneities in water chemistry for some chemical constituents. These average chemical differences in reduced species between stagnant water samples and those obtained after purging were frequently a factor of 5 greater than the errors involved in either the sampling or analytical procedures. Also, purging-related variations in TOC were observed to increase or decrease by ±50% in all wells over the range of 1.20–30.0 mg of C·L⁻¹. No consistent trends in TOC as a function of purging could be associated with the different casing materials. Purging a particular well at either site frequently resulted in greater differences in water quality than was observed between upgradient and downgradient ground locations. Improper well purging can obviously cause gross bias in ground-water monitoring results that far exceeds that due to materials's effects or sampling mechanisms.

Cement Grout Contamination. Despite the fact that all the drilling and well completion operations were held constant, the wells at site 1 exhibited significant water quality differences in both stagnant and formation water samples that could not be attributed to well purging or casing materials. For example, upgradient and downgradient wells at site 1, with the exception of the downgradient PVC well, exhibited pH values in excess of 12 pH units, and the alkalinity was primarily associated with hydroxyl ion. The downgradient PVC well yielded formation samples with pH values between 7 and 8 pH units (mostly bicarbonate alkalinity), and the stagnant water values ranged from 8 to 12 pH units.

Anecdotal references to monitoring well contamination by cement grouts have been reported (*14*). The usual symptom that has been observed is very high solution pH (i.e., 10–12 pH units), even after exhaustive well development. In this study a total of 12 sampling installations was constructed, and the bore holes were sealed above the screen and gravel pack, as well as at the surface with a sand/shrinkage-compensating cement mixture. The grout seals were introduced as thick slurries into standing water in the bore hole after the well had been constructed.

At site 1, either native geochemical conditions or differential settling of the cement mixture prevented the grout seals from setting up properly. The wells at this site

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Table III. Comparison of Ground-Wa... Quality and Grout/Water Mixture Analytical Results

	contaminated ground water (field site 1, upgradient)[a]	grout-contaminated water (laboratory)[a]
major species		
pH, pH units	12.7	>13
alkalinity (OH^-), milliequiv·L^{-1}	31.6	167
sulfate	35.9	1076
calcium	190	1069
potassium	8.21	578
sodium	26.6	62
silicate	5.84	0.7
conductivity, μS	1975	11 500
other species		
magnesium	0.05	0.02
aluminum	<0.10	0.17
chloride	11.0	1.04
iron (total)	0.09	0.10
manganese (total)	0.02	<0.02

[a] Unless otherwise specified, units are mg·L^{-1}.

consistently showed high pH, alkalinity (>90% hydroxyl or caustic), Ω^{-1}, and Ca^{2+} with the exception of the downgradient PVC well, which showed only slightly elevated levels of caustic alkalinity. The apparent cement contamination problem persisted more than 18 months after construction, despite at least 10 redevelopment attempts. The installations at site 2 did not show any evidence of cement contamination, although several early pH measurements of formation water exceeded the long-term mean of ~7.4 pH units.

The cause of this persistent contamination was investigated by careful analysis of a number of cement/sand/water mixtures prepared in the laboratory from the same materials used in well construction. The data in Table III show the comparison of average solution chemistry results from an upgradient well and the aqueous phase of grout/water mixtures prepared in the laboratory. Clearly, the major ionic species identified in the grout-contaminated ground water are represented in the laboratory grout/water mixture aqueous phase. The alkalinity, conductance, and the calcium values in the ground-water samples were all approximately one-fifth their respective levels in the laboratory sample. Attempts to calculate an ion balance on the basis of OH^- as the major anion resulted in ion balances that seldom agreed to better than 40%. There was always an apparent excess negative charge in solution. The possibility of a polymeric or gel phase (e.g., polysilicates) that might interfere with the analytical data or confute the dissolved ion charge balance was examined by $NaHCO_3$ digestion of the aqueous samples prior to analysis (*15*). It was verified that no unusual forms of silica or common alkali or alkaline earth cations were present that might cause gross errors in the alkalinity titrations or wet-chemical analytical methods. Therefore, the grout-contamination problem remains an enigma, although it should be obvious that grouting materials can drastically effect the reliability of ground-water chemistry data for long periods after well construction.

The cement grouts should have been placed either after water had been removed from the well bore or by tremie pipe. Also, the sand pack could have been isolated from the cement grout by a bentonite seal.

Well Casing Material Effects. Apart from the differences noted above (Tables II and III) in the stagnant water samples, no consistent effects on the inorganic chemical constituent data from the two sites were observed

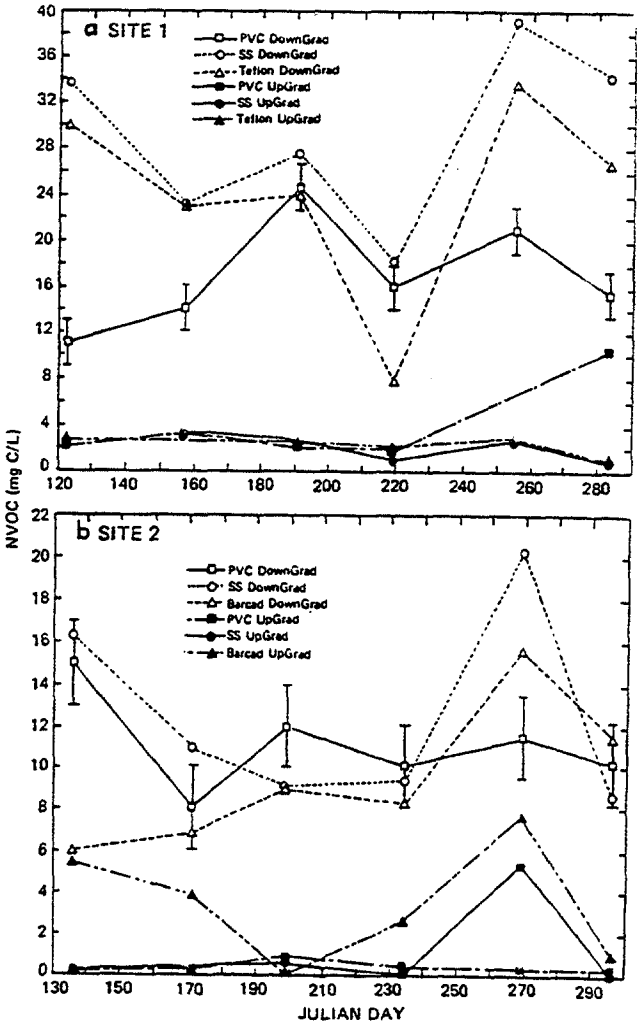

Figure 1. Total organic carbon (mg of C·L^{-1}) in ground water at site 1 and 2. The error bars indicate two standard deviations from the mean of triplicate determinations.

that might be attributed to well casing material exposure alone. Total Fe and Mn concentrations were not significantly different in samples from the SS wells as compared to those from the PVC or PTFE wells. These observations contrast with the elevated metal levels reported by Houghton and Berger on results from a single sampling event (*9*). The divergent results from this study reflect the influence of actual site conditions, temporal variability, and well purging practices on the type and relative severity of sampling and well construction related errors.

At the downgradient locations, all of the installations showed the effects of apparent landfill leachate contamination (i.e., elevated Cl^-, Na^+, K^+, specific conductance, and TOC). The observed levels of TOC or specific organic compounds, however, did not provide evidence of major organic (i.e., volatiles, base–neutrals, and phenols) contamination of these locations.

The observed levels of the nonvolatile fraction of TOC (i.e., NVOC) in ground water from the upgradient and downgradient wells at site 1 after purging are plotted in Figure 1a as a function of time during the summer and fall of 1984. The upgradient samples from each type of well showed negligible differences from the mean TOC of ~3 mg of C·L^{-1}. The downgradient location, however, generally showed higher levels of TOC in samples from the stainless steel and Teflon wells than did samples from the PVC well. On four of the six sampling dates, the positive differences were significant at the 0.05 confidence level.

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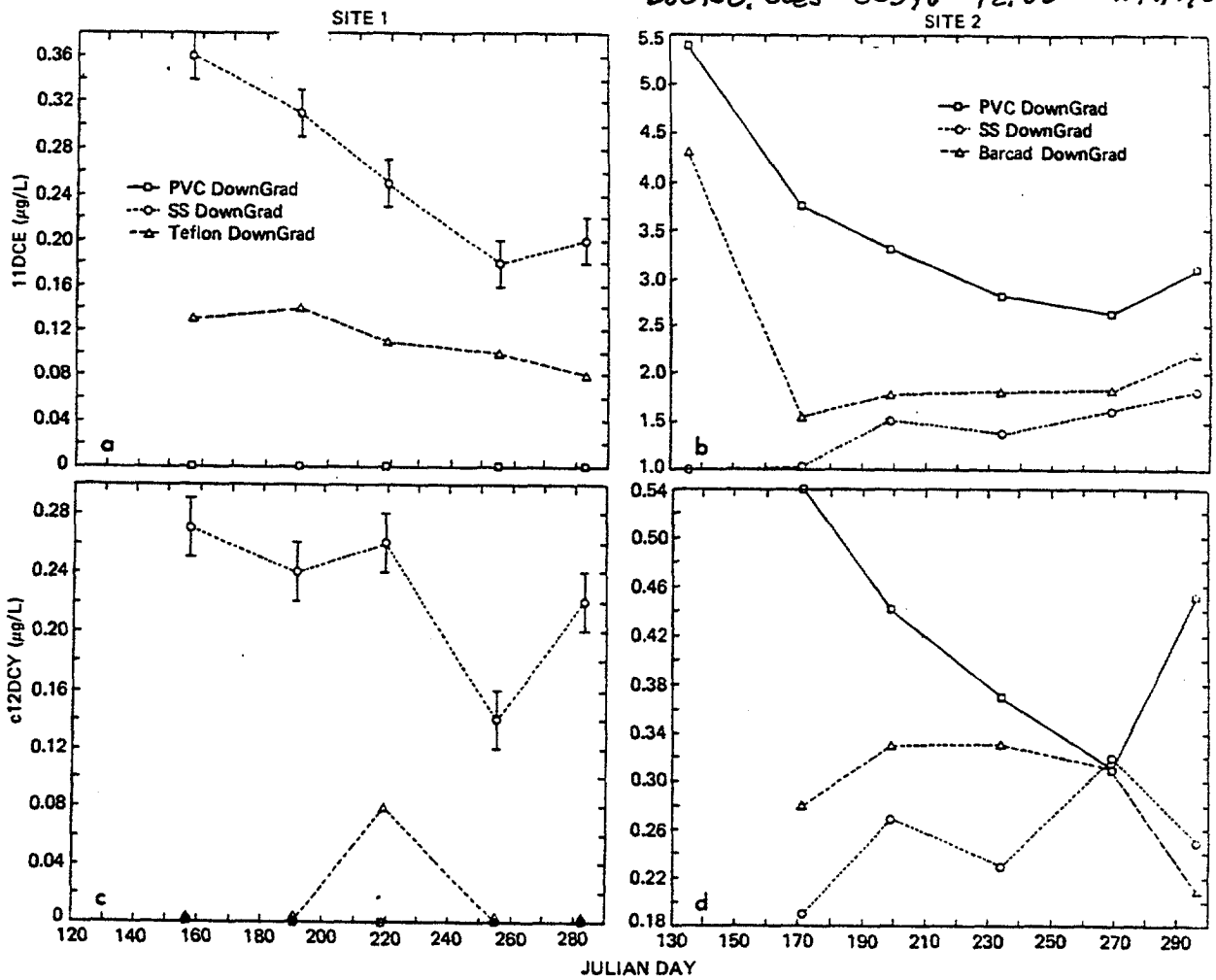

Figure 2. Levels of 1,1-dichloroethane (11DCE) and *cis*-1,2-dichloroethylene (C12DCY) ($\mu g \cdot L^{-1}$) in ground water at sites 1 and 2. The error bars indicate two standard deviations from the mean of triplicate determinations. Detection limit = 0.08 and 0.10 $\mu g \cdot L^{-1}$, respectively.

The TOC results at site 2 showed a similar pattern; however, the differences in samples from the individual well casing materials were not statistically significant when compared to the analytical and sampling errors.

At site 1, levels of 1,1-dichloroethane (11DCE) and *cis*-1,2-dichloroethylene (c12DCY) after purging also were higher generally in the samples from the downgradient Teflon and stainless steel wells than in those from the PVC well (Figure 2a,c). The error bars on the figure represent two standard deviations from the mean determined by analysis of replicate samples and standards. In these cases, the "stainless steel" results were significantly higher (at the 0.05 level) than either the Teflon or the PVC data. These concentration levels are all quite low but in the range of quantitation of the purge and trap analytical methodology. Therefore, systematic differences in observed trace organic compound distributions may arise from the sorptive effects of polymeric well casings as compared to stainless steel. The samples from the differently cased wells at site 1 showed more net difference in purgeable organic compounds than any single well showed over the study period.

Overall, the levels of 1,1-dichloroethane at site 2 (Figure 2b,d) were 10 times above the levels measured at site 1. In contrast with the other results, levels of purgeable organics in samples from the PVC well were consistently higher than those in samples from either the stainless steel well or the gas-drive sampler. It is unlikely that the paired wells actually intercepted ground water of different microconstituent quality, as they were finished only ~1 m (4 ft) apart. Yet, the PVC and stainless steel results for 11DCE differ by a factor of 2. This is more than 10 times greater than the precision established for analytical determinations of these compounds. This order of materials-related effect could result in systematic under- or overestimates of the extent of ground-water contamination, under some conditions. This type of error cannot be accounted for in statistical comparisons of data from upgradient and downgradient locations unless an "inert" artifact-free well casing material can be identified.

The observations noted for site 2 above are also supported by the levels of total volatile halocarbons in the PVC and stainless steel wells before and after purging. With the exception of the September 25 sampling date, the stagnant levels of volatile halocarbons from the PVC well are nearly a factor of 2 or more greater than those from the stainless steel installation (see Table IV). On the average, the PVC well yielded samples with higher total levels of volatile halocarbons than did the stainless steel well. It may be that under these conditions the sorptive and leaching properties of PVC tend to maintain a higher background level of organic compounds in ground water exposed to this material relative to stainless steel.

Conclusions

The purging of stagnant water from monitoring wells is essential to the collection of reliable ground-water quality data. In this study, the variations in water chemistry on

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Table IV. Total Volatile Halocarbon[a] Levels in Site 2 Wells, $\mu g \cdot L^{-1}$

	PVC		SS	
date	stagnant	purged	stagnant	purged
5/15	7.4	6.2	3.7	1.1
6/19	8.7	7.8	1.4	7.5
7/17	8.8	8.3	3.0	4.8
8/21	7.0	6.8	1.9	4.2
9/25	12.9	6.1	12.2	4.6
10/23	11.2	6.5	6.2	3.9
average	9.3	7.0	4.7	4.4

[a] Included total methylene chloride, dichloroethylene, dichloroethane, trichloroethane, trichloroethylene, tetrachloroethane, and tetrachloroethylene after individual separation and quantitation by gas chromatography with HECD detection.

well purging were generally greater than errors associated with either sampling mechanism, tubing, or apparent well casing material effects.

Cement grout seals, which for one reason or another do not properly set up in the bore hole, can cause severe, persistent contamination of both stagnant and formation water from monitoring wells. Determinations of dissolved inorganic chemical constituents are affected by cement contamination, which significantly changes the background solution composition.

Well casing materials exerted significant, though unpredictable, effects on the results of total organic carbon and specific volatile organic compound determinations. Systematic differences ranging from a factor of 2 to 5 in concentration were observed between samples taken after purging from wells cased with different materials. Though the differences were not consistently higher or lower from site to site, materials' performance may limit the conclusions that may be drawn from ground-water quality results in the low ppb ($\mu g \cdot L^{-1}$) range.

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(7)

Sampling Tubing Effects on Groundwater Samples

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Volatile organic compounds pose a challenge to groundwater sampling protocols, since they can be lost as a water sample degasses or lost due to sorption on tubing or pump materials. Laboratory sorption experiments have been conducted with five common flexible tubing materials to determine the impact of sorptive bias for chloroform, trichloroethylene, trichloroethane, and tetrachloroethylene. Tubes made of Teflon, polyethylene, polypropylene, poly(vinyl chloride), and silicone rubber were all found to sorb the test compounds in short exposure periods. Virgin tubing materials introduce substantial amounts of leachable organic matter in similar exposures. Tubing made of Teflon showed the least absorption and leaching problems and should be the tubing material of choice for detailed organic sampling purposes. Absorption into the polymer matrix is the likely mechanism for the errors.

The results of analysis of environmental water samples have seen far more attention in the literature than sampling protocol considerations. For many types of samples, e.g., atmospheric precipitation, effluents, and groundwater, the sampling steps which precede separation and analytical procedures are critical to the overall determination of the analytes of interest. Field standards and blanks can account for storage and analytical errors in the determination of organic compounds in groundwater. However, the effects of sampling mechanisms (*1*), well casing, and sampling materials (*2, 3*) on the integrity of the samples must be evaluated independently.

Evaluations of sampling materials' related sources of bias and imprecision are complicated by the wide range of hydrogeologic conditions encountered in groundwater monitoring situations. The chemistry of the subsurface environment may be dominated by considerable overpressures of CO_2 or N_2 due to microbial or geochemical processes. Investigations at waste disposal sites frequently require the collection of aqueous solutions of organic solvents or highly mineralized acidic solutions which may vary considerably in time or between sampling locations. It is difficult to adequately assess the magnitude and impact of aggressive groundwater/waste admixtures on the integrity of well casing, sampling pumps, or transfer tubing. In cases where severe deterioration may be expected, the use of appropriate materials is required.

The secondary effects of sample handling and material exposures are more difficult to evaluate. Matrix interferences (*4*), volatilization losses (*5, 6*), leaching (*7–9*), and sorptive (*5, 10*) sources or error have been addressed by a number of research groups concerned with effective water sampling for organic compound determinations. Sampling methods which do not involve exposure to flexible materials have a clear advantage in this regard (*6*). Interpretation of the results from these studies have been hampered by the diversity of experimental procedures utilized and the lack of data available under controlled conditions of material exposure which approximate actual sampling conditions. It is clear from previous results that sampling operations can bias subsequent analytical determinations of organic compounds at trace (ppb) levels. Many plastic materials in wide use in well casing and sample transfer tubing have considerable affinity for low molecular weight organic contaminants of interest in groundwater monitoring applications. Flexible, polymeric materials, in particular, have been shown to sorb or leach a number of priority pollutant organic compounds. Indeed, several of these materials have been evaluated as prospective "adsorbents" for the preconcentration and separation of organic compounds from aqueous solution (*10, 11*).

Groundwater sampling for volatile organic compounds, on a routine basis, generally requires that the choice of an unbiased sampling mechanism (e.g., positive displacement bladder pump) and optimum tubing material selection should be made part of the sampling protocol. The tubing material is more critical than that used for well casing under most conditions. Well purging and normal sample flow rates (~100 $mL \cdot min^{-1}$) entail approximately ten times the nominal surface area contact per unit time for sampling tubing as compared to the well casing material. The present study was initiated to investigate five common flexible tubing materials under simulated sampling conditions for the recovery of volatile halocarbons (chloroform, trichloroethylene, trichloroethane, and tetrachloroethylene) frequently identified in contaminated groundwater samples (*12*). The analytical procedures for these compounds are very well documented and are in routine use. In this way, analytical errors were kept under control while the effect of sampling tubing could be identified.

EXPERIMENTAL SECTION

Apparatus. Sorption studies were performed in 75–100 cm lengths of the tubing materials ($^1/_4$ in. i.d.). Tubing loops were joined by 4 mm i.d. glass T's, which had been modified to accept the tubing diameter at each end. The third opening of each T was closed by a screw cap which served to hold a silicone rubber septum with a face made of Teflon for subsampling at specified intervals of exposures. This arrangement allowed for the handling of samples and replicates without exposure to the atmosphere and volume to nominal surface area ratios of approximately 1.7 $L \cdot m^{-2}$.

The analytical method used for specific compound determinations was conventional purge and trap concentration (*13*) followed by gas chromatographic separation using a fused silica capillary column and a Hall electrolytic conductivity detector. The analytical work was done on a Varian 3740 GC, equipped with a Vista 402 data system. Dissolved organic carbon determinations for the poly(ethylene glycol) PEG studies were performed by the method described previously (*14*).

Materials and Reagents. Laboratory grade Silicone rubber, linear polyethylene, polypropylene, and poly(vinyl chloride)–Tygon tubing lengths were purchased from a local supplier. Tubing made of Teflon (TFE) was obtained directly from the manufacturer. The tubing segments were cut and rinsed with hot, soapy water, followed by exhaustive rinsing with double distilled water. The tubing was allowed to air-dry prior to construction of the loops.

The organic solvents used were ACS reagent grade or Distilled in Glass (Burdick and Jackson) and were used without further purification. Standards were made up in doubly distilled water or in 10^{-3} M $NaHCO_3$ solution, depending on the needs of the experiment. Dichlorobutane internal standards were spiked into the samples prior to analysis and all samples, standards, and blanks were analyzed in triplicate.

Poly(ethylene glycol) (400 MW, Aldrich, Milwaukee, WI) was used to provide an organic background in two series of experiments to evaluate the effects of extraneous organic matter. PEG was chosen because it is water soluble and its use does not interfere

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with the purge and trap analysis procedure (*15*).

Procedures. Three series of experiments were run in the course of the study. Initial screening runs were made with chloroform as the test compound at 100 ppb ($\mu g \cdot L^{-1}$) in both distilled water and bicarbonate solutions of ionic strength varying from 0.001 M to 0.1 M. Fresh tubing loops were constructed of each material, cleaned, and rinsed with the appropriate test solution. The loops were then filled to exclude any headspace, closed with the septum cap, and placed on a holding rack. At each exposure interval (5, 10, 20, 40, and 60 min), a single tubing loop was emptied into a 15 mL glass vial with a Teflon-lined septum. Replicate samples were then taken by syringe for analysis. The sampled loops were rinsed and refilled with distilled water and then replaced on the holding rack for the same time interval to observe desorption effects. The temperature of the experiments was that maintained in the laboratory, 25 ± 1 °C. Due to the short experimental exposure periods and the use of closed systems, the potential effects of other loss mechanisms (e.g., volatilization, reaction, etc.) were minimized. A mass balance was not attempted, since handling blanks amounted to less than a 1% loss of sorbate in transfers and desorption was found to be incomplete for all the test compounds.

The second set of volatile halocarbon experiments was performed by using the four test compounds, each at 100 ppb in a mixture in both distilled water and distilled water spiked with PEG to provide a 5 ppm-C background. PEG sorption and desorption were evaluated in separate experiments under the same conditions as the work described above. Freshly cleaned tubing loops were used for all experimental runs.

RESULTS AND DISCUSSION

Chloroform Sorption Studies. The five tubing materials were screened, employing timed sorption runs with ~100 ppb $CHCl_3$ distilled water solutions followed by desorption against distilled water alone. Average results of three sorption runs are shown in Figure 1. Initial solution concentrations were established for each of the exposure replicates at zero time. They have been blank corrected and initial concentrations were normalized to 100 ppb for purposes of comparison. Error bars have been included for the TFE data, which were typical of the ±9% relative standard deviation at ±5% accuracy achieved in the course of all of these experiments. The results demonstrate the rapid sorptive removal of $CHCl_3$ by both PVC and silicone tubing to the extent that 80% depletion of the dissolved concentration occurred within 1 h. PE, PP, and TFE showed somewhat lower initial rates of sorption and the net amount removed from solution was less than half that of PVC or silicone rubber. Thus, the sorptive affinity of the materials for $CHCl_3$ followed the order TFE < PP < PE < PVC < SIL.

Just as the bulk of the net sorptive removal occurred in the initial period (20 min) of exposure, 80–90% of the desorption of $CHCl_3$ into distilled water took place almost immediately. The amount desorbed constituted less than 10% of the total $CHCl_3$ sorbed. PVC and silicone tubing desorbed no more than 3% and 15% of the maximum amount sorbed (60 min), respectively. With these materials the bulk of the desorption (80–90% of maximum) occurred during the first 5 min of exposure to distilled water. PP and PE tubing desorbed somewhat more of the total $CHCl_3$ sorbed (20–48% of maximum) in 5 min than did PVC and silicone. TFE, which sorbed the least amount of $CHCl_3$ of all the materials, desorbed 9–12% of the total within 10 min. It seems very likely that sorption of chloroform takes place by absorption into the polymer matrix, rather than by a specific adsorptive surface mechanism. This hypothesis is supported by the results of previous $CHCl_3$ sorption experiments reported by Cook and Hartz (*10*), which were conducted in batch exposures over much longer time periods. They observed apparent "adsorption" of chloroform on PE and PVC tubing at surface coverages which far exceeded monolayer coverage. Indeed, the sorptive capacity of these tubing materials approached that of granular activated carbon, which had a nominal exposed surface area exceeding that of the polymeric materials by at least a factor of 1000.

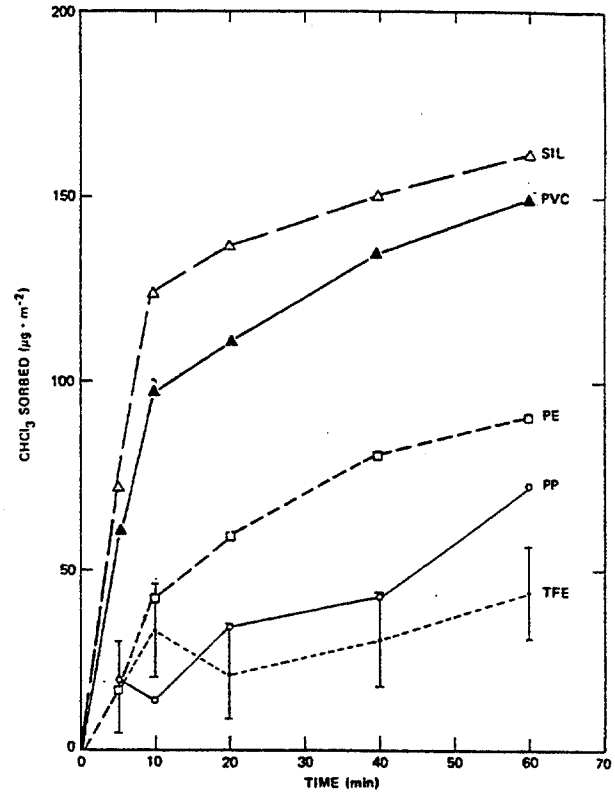

Figure 1. Concentration of chloroform sorbed. The sorbed concentration ($\mu g \cdot m^{-2}$) of chloroform from distilled water solutions is shown as a function of time in exposure to the tubing materials: Teflon, TFE (●); polypropylene, PP (○); polyethylene, PE (□); poly(vinyl chloride), PVC (▲), and silicone rubber, SIL (△).

Background Solution Composition. The $CHCl_3$ sorption experiments in this study were repeated over a range of ionic strengths (10^{-3} to 10^{-1} M $NaHCO_3$) and no significant differences from the previous absorption or desorption results were observed. Dissolved organic matter in natural waters has a marked effect on the sorptive behavior of trace organic compounds on metal oxides and sediments (*16*, *17*). The direction and magnitude of the effects of background organic matter are difficult to predict. Since the preceding sorption runs were performed under "clean" laboratory conditions, an attempt was made to investigate the effect of sorbing organic matter on the net absorptive and desorptive properties of the tubing materials. This portion of the work included the study of the effect of adding PEG to the background solution, as well as the effect of the levels of organic carbon contributed to the solution by the leaching of the tubing materials.

Substantial amounts of organic matter leached from the cleaned virgin tubing materials and contributed to the background organic concentrations. The data in Table I show that, with the exception of TFE, all the tubing materials leached more organic carbon into the background solution within 30 min than was present as PEG. It was, therefore, not possible to determine the extent to which PEG was sorbed by PVC, silicone, polyethylene, and polypropylene in these experiments. Although the conditions of leaching were not identical with those of Junk et al., 1974 (*2*), PVC tubing was found to leach the most organic matter as it had in their work. Assuming that Teflon sorbed the least amount of PEG (~400 $\mu g \cdot m^{-2}$), it is reasonable to infer that at least 2 to 3 times the nominal surface coverage of the tubing available for $CHCl_3$ sorption (~150 $\mu g \cdot m^2$) could be affected by background organic matter.

The leaching of organic matter from the tubing materials

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Table I. Leachable Organic Matter and PEG Sorption[a]

material	leached organic carbon: total carbon, mg-C·m^{-2}	leached organic carbon: volatile carbon (% of total)	% PEG sorbed of 10 ppm-C spike
SIL	30.6	7.2	N.D.[b]
PVC	33.2	20.0	N.D.
PE	20.6	5.7	N.D.
PP	23.5	8.6	N.D.
TFE	0.66	<25	20

[a] Data presented for 30-min exposure period. [b] N.D. denotes that organic carbon leached far exceeded the PEG added and net sorption could not be calculated.

Table II. Sorption[a] of $CHCl_3$ with Increased Organic Background

sorbent	$CHCl_3$ sorption, no PEG, $\mu g \cdot m^{-2}$	$CHCl_3$ sorption with PEG (5 ppm-C) ($\mu g \cdot m^{-2}$)	% of max sorption[b]	% diff
Teflon	40	42	26	+5
polypropylene	61	52	44	−15
polyethylene	71	52	50	−27
PVC	126	183	86	+45
SIL	139	163	97	+17

[a] 60-min exposure runs. [b] Calculated on the basis of complete sorption of $CHCl_3$ from the solution.

may account for the mixed effect of the PEG addition on $CHCl_3$ sorption. Table II contains a summary of $CHCl_3$ sorption data in the presence of 5 ppm-C as PEG. The addition of PEG had a negligible effect on the sorptive properties of TFE, while significant decreases were observed for PP and PE. Increased sorption of $CHCl_3$ was measured for PVC and Sil under the same conditions. The experiments did not result in the total depletion of $CHCl_3$ from the background solution. Tubing made of Teflon showed consistently the least amount of leaching or sorption of organic matter (including $CHCl_3$) as compared to the other tubing materials.

Chlorinated Hydrocarbon Sorption. The sorptive properties of the five tubing materials for the four chlorinated hydrocarbons in equal concentration mixtures were very similar to those noted for chloroform. The results of this series of experiments are shown in Figure 2. With the exception of the tetrachloroethylene, each compound showed the same relative order of sorption on the five tubing materials: TFE < PP < PE < PVC ~ SIL. The least sorptive tubing materials (i.e., TFE, PP, and PE), as a group, sorbed significantly less than PVC and SIL, probably as a result of their higher density and greater crystallinity. The more flexible PVC and SIL likely present more active surfaces for sorption. Tetrachloroethylene did show enhanced sorption on polyethylene which may be related to the similarity of the molecule to the ethylene monomer unit of polyethylene. Otherwise, the saturated halocarbons (i.e., chloroform and tetrachloroethane) were less actively sorbed than the unsaturated compounds. The total amount of the halogenated mixture sorbed by the other materials was substantially greater than that observed for Teflon. Polypropylene and polyethylene showed about twice the amount sorbed and PVC and silicone sorbed nearly three times that sorbed by Teflon.

Table III contains the maximum sorption values and percent desorbed within an hour for the five tubing materials. The values for chloroform in the halocarbon mixture were not statistically different (*t* test) from those when it was the sole sorbate. As one can see from these data, the presence of leachable and sorbing background organic matter had mixed effects on the sorption/desorption of the halocarbons. A

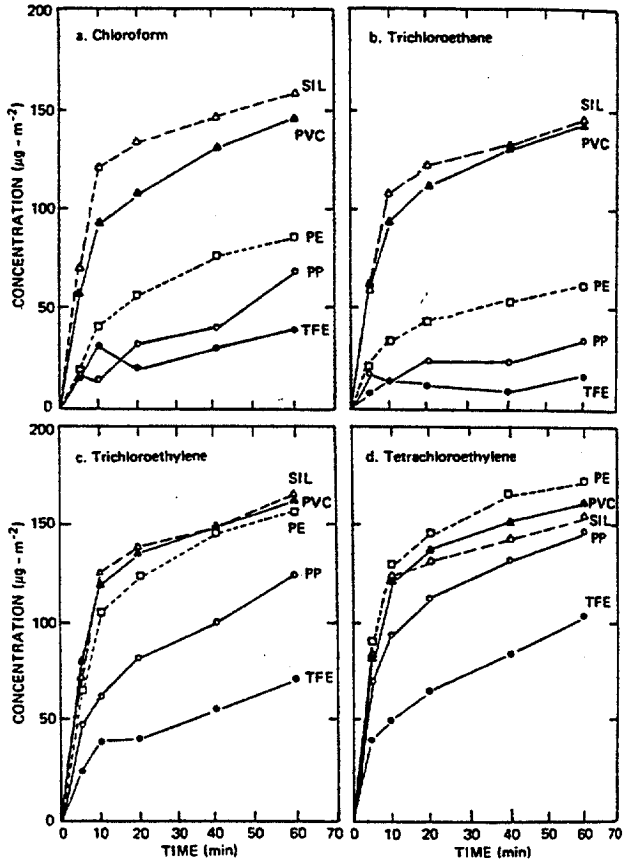

Figure 2. Concentration of sorbed chlorinated organics. The sorbed concentration ($\mu g \cdot m^{-2}$) of the four test compounds from distilled water solutions is shown as a function of time in exposure to tubing materials: (a) chloroform, (b) trichloroethane, (c) trichloroethylene, (d) tetrachloroethylene. Dissolved concentrations were initially between 90 and 120 ppb of each compound.

Table III. Comparison of Maximum Sorption and Desorption of Halocarbon Mixtures

material	low carbon background[a]: max sorption, $\mu g \cdot m^{-2}$	low carbon background[a]: max % desorbed	high carbon background[b]: max sorption, $\mu g \cdot m^{-2}$	high carbon background[b]: max % desorbed
TFE	237	13	170	28
PP	384	17	330	16
PE	483	18	372	13
PVC	622	8	700	6
SIL	624	2	624	<1

[a] Sorption of 400 ppb halocarbon mixtures from bicarbonate buffered distilled water background. [b] Sorption of 400 ppb halocarbon mixtures with 5 ppm organic-C background added to buffered distilled water.

20–25% reduction in the maximum sorption was observed for Teflon, PP, and PE. PVC increased by 12%, while silicone's desorptive behavior was barely affected by the PEG. Tubing made of Teflon sorbed significantly less and desorbed somewhat more of the halocarbon mixture in the presence of PEG. The amounts of sorbed materials expressed on a mass per nominal tubing surface area basis are very similar to those reported by Cook and Hartz (*10*) for chloroform and other halomethanes in much longer exposures. In both tubing studies, sorption was at least 2 orders of magnitude greater than that observed by Miller, 1982 (*18*), for rigid PVC, PE, and PP well casing materials.

The rates of the sorption/desorption processes were not significantly affected by the presence of the PEG. The curves of sorption vs. time for the halocarbon mixtures are shown

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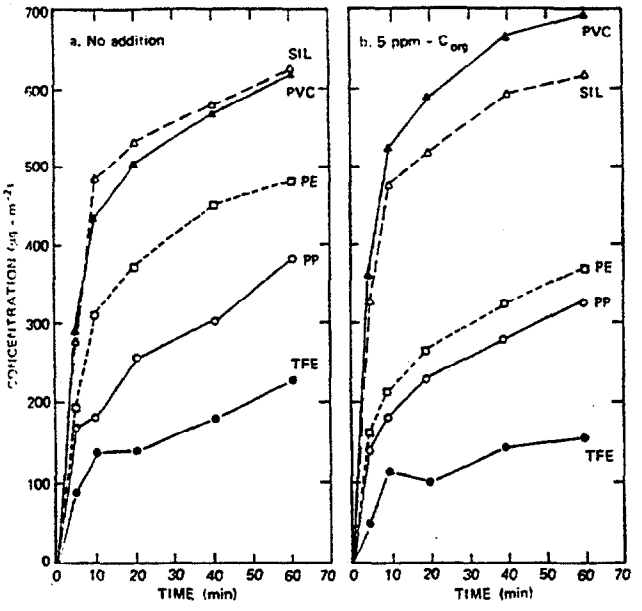

Figure 3. Concentrations of total sorbed chlorinated organics. The sorbed concentration ($\mu g \cdot m^{-2}$) of total chlorinated organics from 400 ppb mixed solutions on each of the five tubing materials: (a) no addition of organic matter; (b) with 5 ppm-C_{org} as poly(ethylene glycol).

in Figure 3. The presence of background organic matter seemed to accentuate the differences between the low sorption affinity materials (TFE, PP, and PE) relative to the more sorbent materials (PVC and SIL).

As noted for chloroform, the initial rate of sorption was 2–5 times more rapid in the first 5–10 min of exposure than that observed from 15 to 60 min. In the desorption runs, the bulk of the previously sorbed material remained in the tubing material over comparable time periods (Table III). About 5–15% of the sorbed material could be leached with either distilled water or bicarbonate solution. Desorption was observed only in the initial 5–10 min of repeat exposures.

These data support the hypothesis that the sorption of chlorinated solvents by flexible tubing materials occurs by absorption into the polymer matrix. The flexible materials therefore represent a virtual sink for the chlorinated solvent sorbates which should be very carefully considered in planning groundwater sampling protocols. Under equivalent conditions, the sorptive capacities of the corresponding rigid well casing materials are much below those of the tubing materials. The flexible tubing materials more rapidly sorb greater amounts of the halogenated hydrocarbons. Desorption data for the rigid materials are not available to complete the comparison.

The recent work of Rice and Gold (1984) with polypropylene supports the general conclusions of this study. They observed impressive recoveries of polynuclear aromatic hydrocarbons, aryl phthalate esters, and dodecanol from 1 to 400 ppb solutions on packed beds of polypropylene sorbent. It is not obvious whether these functional classes of compounds would be either adsorbed or absorbed by the flexible tubing materials. However, in at least one case (pyrene) lower recoveries may be attributed to diffusion into the polymer. Sorption behavior is controlled by both the chemical properties of the sorbate and the polymer matrix of the sorbent. The compounds used as sorbates in the present study are persistent, mobile, and only moderately hydrophobic. They are similar to many dissolved organic contaminants in groundwater. Thus, the results strongly suggest that flexible tubing choices must be very carefully made to ensure good sampling recovery and precision.

The magnitude of the impact of sorptive processes on groundwater sampling results is difficult to predict a priori.

Table IV. Predicted Percent Sorptive Loss of Chlorinated Hydrocarbons due to Tubing Exposures[a]

tubing diameter, in.	% loss				
	TFE	PP	PE	PVC	SIL
1/4	4	6	10	14	15
	(4)	(6)	(7)	(17)	(15)
3/8	1	2	3	4	4
	(1)	(2)	(2)	(5)	(5)
1/2	1	1	1	2	2
	(0.5)	(0.7)	(1)	(2)	(2)

[a] 40 ppb mixture of chloroform, trichloromethylene, tetrachloroethane, and tetrachloroethylene calculated on the basis of initial sorption rates on passage through 15 m of tubing at 100 $mL \cdot min^{-1}$. Percent loss values are tabulated for the original solution (with) and without organic carbon background.

From the static, short exposure laboratory results of this study, we have made some preliminary estimates. Take, for example, a monitoring situation in which a ~15 m length of flexible tubing is used to transport samples at ~100 $mL \cdot min^{-1}$ from a well bore to the land surface. Using conservative initial sorption rates from this study, of approximately 10 $\mu g \cdot m^{-2} \cdot min^{-1}$, the percent sorptive loss of halocarbon mixtures in transport may be calculated. The calculated initial sorption rates ranged from 3 to 50 $\mu g \cdot m^{-2} \cdot min^{-1}$. Table IV contains the results of such a calculation for a 40 ppb solution of the compounds for three commonly used tubing diameters. The calculated sorptive losses for $^1/_4$ in. i.d. tubing are in the range of controlled analytical bias for trace organic analysis methodologies. The effective losses are clearly more dependent on the materials than on the tubing diameter. Larger internal diameters minimize the effect of sorptive bias. The impact of sorptive losses is concentration dependent. At the 4 ppb trace organic range, the percent losses range from 6 to 150% for $^1/_4$ in. i.d. tubing. Therefore, it appears that gross errors in trace organic determinations can occur in the parts-per-billion concentration range due to tubing effects alone. The rates and extent of sorptive removal of the volatile halocarbon suggest that well purging and preexposure of the tubing material may not alleviate the overall impact of sorptive bias. Although the conditions used in this study are not directly comparable to those which may be encountered in field sampling, the potential for such problems clearly exists. A comprehensive evaluation of sampling mechanisms, sample transport tubing, and storage precautions should be made a part of the planning of all groundwater sampling protocols. Sampling performance may well exert control over the levels of various contaminants which may be regulated practically in these systems.

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"Phase Distortions" in Absorption-Mode Fourier Transform Ion Cyclotron Resonance Spectra

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Fourier transform ion cyclotron resonance (FT-ICR) mass spectra are almost always presented in the magnitude mode, although it has long been known that absorption-mode FT-ICR spectra would give superior resolution. It is shown in this work that typical, perfectly phased, discrete absorption-mode FT-ICR spectra will show a distortion, similar to the distortion seen in absorption spectra contaminated by some dispersion component. The importance of this distortion in discrete absorption-mode spectra can be predicted from a knowledge of T/τ, the ratio of the acquisition time to the relaxation time of the FT-ICR signal. This distortion in absorption-mode FT-ICR spectra can be obviated by extended zero-filling, exponential apodization, or apodization with resolution-enhancement window functions. For the situation where the maximum possible resolution is desired, apodization with a resolution-enhancement function and extended zero-filling will obviate the distortion and is the data treatment method of choice.

Fourier transform ion cyclotron resonance mass spectroscopy (FT-ICR or FTMS) (*1–9*) is a type of mass spectroscopy in which the cyclotron motion of an ensemble of gaseous ions is excited in a short period of time. The excited cyclotron motion at each cyclotron frequency, ω_0,

$$\omega_0 = qB/m \tag{1}$$

for each ion mass, m, in the ensemble induces a signal (*10*) in the detection circuitry of the spectrometer. This signal is sampled and stored in the memory of a computer. Equation 2 is the continuous form of the signal for a particular frequency, ω_0 (*11*).

$$F(t) = 2\pi K \exp(-t/\tau) \cos(\omega_0 t),\ 0 < t < T \tag{2}$$

In eq 2, K is called (*12*) the scaling factor and is proportional to the number of ions, ω_0 is the cyclotron frequency, τ is the relaxation time, and T is the acquisition time of the signal. Since frequency measurement is tantamount to mass measurement via eq 1, numerical Fourier transformation of the sampled time domain signal gives the ion cyclotron resonance (ICR) mass spectrum. Depending upon how the numerical frequency data is handled, the spectra can be presented in the magnitude mode or in the absorption mode (*3, 13–16*). Although the absorption mode has higher resolution (*11*) and is therefore preferred, it is almost never used in FT-ICR. This is unfortunate as the higher resolution of the absorption mode does not require the sacrifice of any other desirable instrumental feature, such as sensitivity. Absorption spectra do require more data processing but procedures are known (*3, 13, 14*) which should give pure absorption spectra. In this work we show that procedures which should give pure absorption spectra free of any dispersion component typically give spectra appearing to contain a dispersion component. Moreover, as described below, the distortion is more pronounced in exactly those cases where the higher resolution of the absorption mode is most needed. The origin of the distortion is discussed, and several methods of obviating the distortion are described. It is concluded that for the typical case of broad-band FT-ICR spectra where the acquisition time of the signal is limited by the available computer memory, apodization of the time domain signal (eq 1) with a "resolution-enhancement" window function combined with extended zero-filling (*17*) is the data treatment method of choice.

THEORY

Continuous FT-ICR Spectra. Consider a truncated, continuous time domain function of the form in eq 2. The analytical Fourier cosine transform of eq 2 is given by eq 3 (*11, 12*).

$$A(\omega) = \frac{K\tau}{1 + (\omega - \omega_0)^2\tau^2}\left[1 + \exp\left(\frac{-T}{\tau}\right) \times ((\omega - \omega_0)\,\tau \sin[(\omega - \omega_0)T] - \cos[(\omega - \omega_0)T])\right] \tag{3}$$

Equation 3 is called the continuous absorption spectrum of eq 2. The width at half height of the absorption line shape ranges from $3.791/T$ (when $T/\tau = 0$) to $2/\tau$ (when $T/\tau = \infty$) (*11*).

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Contamination of Water by Synthetic Polymer Tubes

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■ Organic contamination ranging from 1-5000 parts per billion (ppb) by weight was detected in the water which had flowed through tubes of polyethylene, polypropylene, black latex, six different formulations of polyvinylchloride, and a plastic garden hose. The contaminants in the effluent water were isolated by sorption on macroreticular resin beads contained in a small glass column. The sorbed organic compounds were then eluted with diethylether, the eluate was concentrated by evaporation, and the organic contaminants were separated and measured quantitatively by gas chromatography. Identifications of plasticizers and other polymer additives were made by combination gas chromatography–mass spectrometry. The described method is accurate and convenient for testing polymer tubes intended for use in situations which require flowing water or water solutions.

Data have recently appeared concerning the production (*1, 2*) and use (*2*) of certain plasticizers and other additives used to formulate polymers with properties desirable for their use in medicine, transportation, home furnishings, construction, apparel manufacture, food packaging, beverage production, and milk processing. The total production of phthalic acid esters, which represent only one of several classes of additives, has been over 1 billion lb per year during the period 1967 to 1973 (*1, 2*). This amount of synthetic material repetitively distributed throughout the environment naturally causes some concern, especially in view of the many recent toxicity studies of additives (*3–16*).

Phthalates have been found in plants (*17*), fungus (*18*), air (*1, 19*), food (*20, 21*), milk (*22, 23*), soil (*24–27*), blood (*3, 5, 28–32*), lipoid solutions (*3, 5, 29*), oil (*33*), body tissue (*34*), and water (*5, 9, 35–40*). Thus, the ubiquity of phthalates as well as other additives is clearly established. Although some of these may be present in the environment because of natural processes, there is little doubt that the major share of the current distribution is due to contamination from various polymers.

This report describes an accurate method for the determination of the organic contamination of water by various polymer tubes. The method accommodates test conditions similar to those encountered in the eventual use of the polymer tubes to transport water or aqueous solutions.

Experimental

XAD-2 Resin. This macroreticular resin was obtained as 20–60 mesh beads from Rohm and Haas, 5000 Richmond St., Philadelphia, Pa. 19137. The resin was purified by sequential Soxhlet extractions with methanol, acetonitrile and diethyl ether (*41*) prior to its use in the extraction columns described later.

Solvents. All solvents were either spectrograde or analytical grade. Whenever blank determinations suggested impurities detectable by flame ionization gas chromatography, these solvents were further purified by fractional distillation.

Test Water. The distilled water used in the contamination tests was purified by passage through a column filter containing 20 grams each of XAD-2 resin and activated charcoal. Water treated in this manner contained less than one part per billion (ppb) by weight of detectable organic material. This purified test water is referred to as "pure" water in this report.

Synthetic Polymer Tubes. All polymer tubes used in this study were purchased from commercial suppliers in 1973. These suppliers are not identified because polymer formulations are frequently changed and the results of our tests suggest that all commercial polymer tubes contaminate the water passed through them. The tubes were either $^1/_2$ in. or $^3/_8$ in. i.d. and cut to 25-ft lengths for test purposes. Pretreatment consisted of flushing ~25 liters of "pure" water through each tube immediately before each contamination test.

Instrumental. A single column, Varian 1200 gas chromatograph equipped with a linear temperature programmer and a flame ionization detector (FID) was used to separate, detect, and quantify the contaminants isolated from the water samples. All extracts of the contaminants were chromatographed using 6 ft × $^1/_8$ in. o.d. stainless steel columns packed with 80–100 mesh AW-DMCS treated chromosorb W coated with 5% w/w OV-1 liquid phase. Carrier gas flow was 20 ml/min for all separations and each chromatogram was obtained by injecting 3.0 μl of the ether concentrate into an off-column injector at 250°C. After an initial hold at 50°C for 1 min, the column was programmed to 250°C at 15°C/min. The detector temperature was 250°C. The detector response was calibrated for quantification using an aliquot of a standard solution of indan, naphthalene, and acenaphthylene in ethyl ether.

A Du Pont model 21-490-1 combination gas chromatograph–mass spectrometer (gc–ms) was used to obtain mass spectral data from which many of the chromatographically separated components were identified. The same chromatographic conditions used with the Varian 1200 gas chromatograph were employed with the Varian 1400 gas chromatograph interfaced to the Du Pont 21-490 mass spectrometer via an all-metal jet separator. The separator and connecting lines were held at 225°C and the ion source at 275°C.

A Digital Equipment Corp. (DEC) PDP-12/40 minicomputer was interfaced to the gc–ms to assist in data logging, reduction, and manipulations for interpretation purposes. Updated MASH (mass spectrometer data handling) software as supplied by DEC was employed. This software allowed for calibration of the computer for mass marking and acquisition of approximately 250 mass spectra acquired at six second intervals for each gc–ms run. The mass range covered was from 26–600. Data manipulations, such as generation of total ion mass chromatograms, selected ion mass chromatograms, background subtraction, spectra averaging, and ion series tables were used at the discretion of the operator on an interactive basis after data accumulation and transfer onto magnetic tape by the minicomputer. These programs were used to aid in the interpretation of each mass spectrum. A visual display on a cathode ray tube was used for inspecting line diagrams of each mass spectrum to determine if a tabulation of the displayed spectrum via a Model 33 Teletypewriter was desired. In most cases, component identifications were suggested by a manual search of the Eight

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Peak Index of Mass Spectra obt d from the British Information Sources, 845 Third Ave., New York, N.Y. 10022. When necessary, the DCRT/CIS Mass Spectral Search System, developed at the National Institutes of Health (*42*) and now available through the General Electric Mark III computer services (write to G.E. Information Services, 777 14th St., N.W., Washington, D.C., 20005), was also employed for identification purposes.

Tube Contamination Test Procedure

Apparatus and Quantification. A schematic diagram of the sampling apparatus is shown in Figure 1. All connections, adaptors, and valves are standard fittings except the upstream connection of the polymer tube to the valved intake manifold and the downstream connection to the glass extraction column which are both friction fit connections.

The extraction columns are easily prepared by inserting a small silanized glass wool plug near the stopcock and pouring a methanol slurry of clean XAD-2 resin into the glass column. Then a second glass wool plug is inserted above the resin bed, and the column is capped to maintain the resin in a methanol-wetted condition.

To test a polymer tube for contamination, the cap is removed from the column and the methanol is displaced with five 20-ml portions of "pure" water. The stopcock is closed when the last water wash level reaches the top of the upper glass wool plug. This procedure ensures complete displacement of the methanol and adequate water wetting of the resin. A 25-ft length of the polymer tube to be tested is then attached to one of the intake valves. The valve is opened and ~25 liters of "pure" water are allowed to flow freely through the tube. This action flushes the tube prior to test and removes air bubbles which can cause undesirable turbulence during the test run. When the tube is free of air bubbles, the water flow is decreased and the downstream end of the tube is attached to the extraction column and the stopcock is opened immediately. The intake valve is adjusted to achieve a flow of 60 ml/min through the tube and extraction column. The simple expediency of checking the effluent water flow periodically with a graduated cylinder and a stopwatch is sufficiently accurate for calculating the total volume flow during a given test period. When the desired amount of water has passed through the tube, the intake valve and effluent stopcock are closed, and the extraction column is removed from the polymer tube.

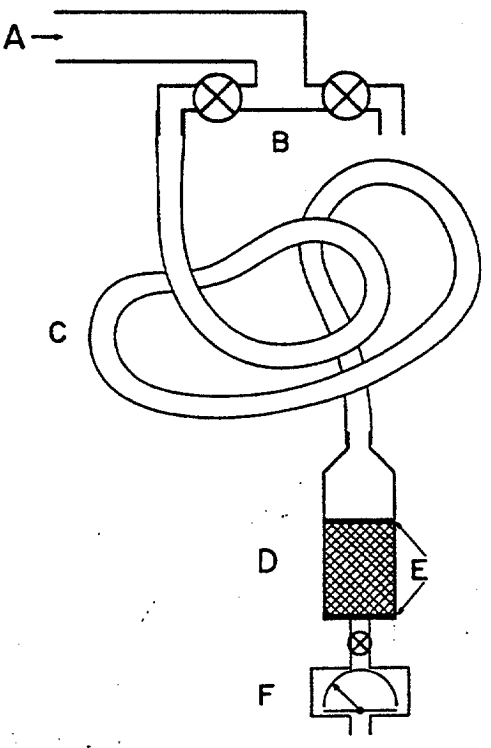

Figure 1. Sampling apparatus for contamination tests: (A) point of attachment of the combination XAD-2 and charcoal filter for purifying the distilled water. The arrow indicates the direction of water flow; (B) valved inlet manifold for simultaneous testing of several polymer tubes; (C) polymer under test; (D) glass extraction column containing 2 grams of clean 40–60 mesh XAD-2 resin; (E) glass wool plugs; (F) effluent stopcock and metering device for measuring total water flow through the polymer tube

The procedure for eluting and quantifying the organic compounds sorbed on the resin has been described in detail by Junk et al. (*41*). Briefly this procedure is as follows: open the stopcock to drain most of the remaining water from the extraction column; add 25 ml of ethyl ether and allow 5–10 min for equilibration; open the stopcock and collect the ether eluate in a 20 × 150-mm test tube; plunge the test tube into liquid N_2 for ~20 sec to freeze out the 0.5–1.0 ml of residual water; decant the cold ether eluate into a modified Kuderna-Danish evaporator vessel; concentrate the ether solution to 0.5 ml; and use a 3.0-μl aliquot of this concentrate for gas chromatographic analysis employing the conditions described in the instrumental section of this report.

The chromatogram peak areas are then measured and the amount of contamination due to each separated component is calculated using the equation,

$$\frac{(P_i) \times (S) \times (V_1)}{(V_i) \times (V_w)} = \frac{\mu g}{\text{liter}} = \text{ppb}_i$$

where

P_i = peak area of the ith chromatographic peak in cm^2, S = detector response factor in $\mu g/cm^2$, V_1 = volume of ether concentrate in μl, V_i = injected aliquot of ether concentrate in μl, V_w = volume of water passed through the polymer tube in liters, and ppb_i = parts per billion by weight of the ith component in the water.

The total contamination equals $\sum_{i=1}^{n} \text{ppb}_i$ where n equals the number of components detected. The reproducibility is generally ±10%. Blank determinations are made using the same volume of water and procedure, but deleting the polymer tube and connecting the extraction column directly to the intake valve.

Identifications. Since the gc–ms results are used solely for identification purposes, the normal procedure is to concentrate the ether eluate further from 0.5 ml to ~0.05 ml using a stream of N_2 gas or free evaporation. This additional concentration facilitates the gc–ms operation and although some losses of the more volatile components occur, no difficulty is encountered in relating the peaks observed on the conventional FID chromatogram to those observed on the gc–ms total ion monitor (TIM) chromatogram. Aliquots of 1.5 μl are injected for the gc–ms identification experiments using the chromatographic-mass spectrometric conditions described in the instrumental section.

Preliminary identifications were made from the computer manipulated mass spectral data. These were usually confirmed by matching both the gas chromatographic retention times and the mass spectral fragmentation patterns of the unknowns with those obtained for authentic samples. When necessary, additional confirmatory evidence for the identifications was obtained using other instrumental analyses of fraction-collected components.

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Results and Discussion

Separation and Quantification. Tracings of the FID chromatograms, accumulated on the Varian 1200 gc (see Instruments section) for the various polymer tubes tested, are shown in Figures 2–4. The response is scaled for each chromatogram to make possible a rapid visual comparison of the number and the intensity distribution of contaminants. The total contamination, listed in the figure legends, varies from a l[illegible] of 1 ppb for polyethylene tubes to a high of 5000 ppb for Food-Beverage Grade PVC tubes.

To aid in the comparison of chromatograms, the chromatographic conditions and the time scales are identical in each figure. These comparisons reveal that a number of the contaminants have similar gc retention volumes. Also, from 50–90% of the total contamination normally involves four to six contaminants.

The complexity of the chromatograms and the relatively

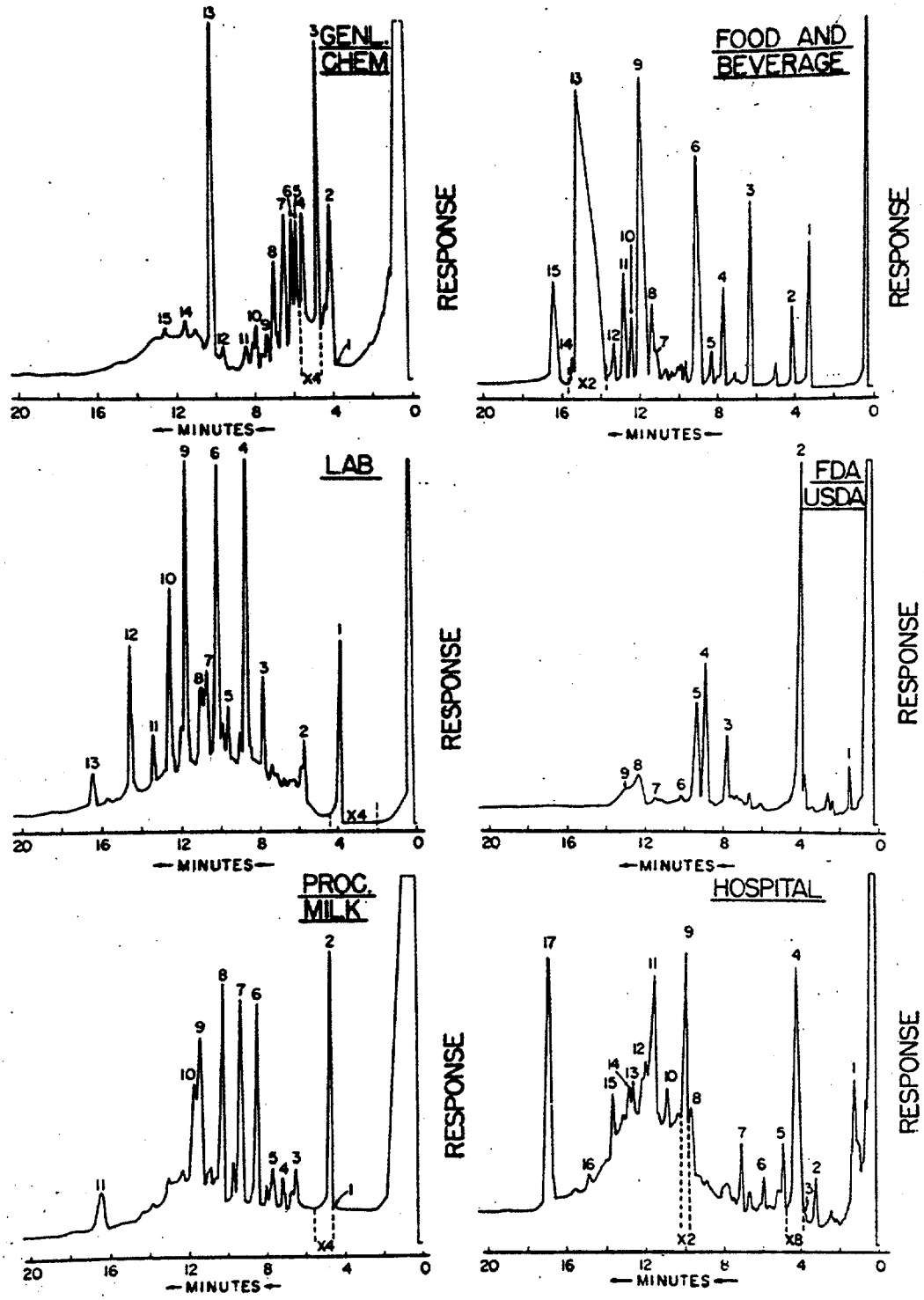

Figure 2. Chromatograms from tests of polyvinyl chloride (PVC) tubes—25 ft × ½ in. i.d.: general chemical grade (11 ppb); laboratory grade (4 ppb); processed milk grade (6 ppb); food-beverage grade (5000 ppb); FDA–USDA approved grade (9 ppb); hospital–surgical grade (6 ppb). Vinyl chloride monomer, if present, is not detected because it is masked by the large solvent peak

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high level of contamination from al ymers except polypropylene and polyethylene are due primarily to the use of large amounts of plasticizers and other additives in these polymers. Also, impurities in the starting materials which become trapped in the polymerization process contribute to the observed contamination. For polyethylene and polypropylene, the contaminants present in the water are probably due solely to impurities in the starting materials and nonplasticizer additives such as stabilizers.

The changing mass spectral fragmentation patterns observed across many of the apparent monocomponent gc peaks in Figures 2–4 suggested that the contamination mixtures were much more complex than indicated by the packed column chromatography employed for these separations. Preliminary work using support-coated open tubular (SCOT) columns reveals that as many as 100 components may be present in the water passed through some of the tubes.

Identifications. Although identifications of several contaminants present in minor amounts have been made, the primary purpose of this report is to focus on the major contaminants. To this end, detailed identification and quantification data compilations as illustrated by Table I for General Chemical Grade PVC were used to prepare a summary of the five st intense gc peaks observed for each polymer tube. This summary is given in Table II where the gc peak numbers refer to those given in Figures 2–4.

From Table II, the phthalate esters appear most frequently among the five most dominant contaminants. Relatively large amounts of 2-ethylhexanol are present in the water from several of the polymer tubes and this may be due to hydrolysis of the phthalate ester and/or impurities present in the DEHP plasticizer employed in the production of the tubes. This observation, along with that of contaminants such as phthalic anhydride, lauric acid, and stearic acid used as additives only in the chemically combined state, indicates that the identification of contaminants from plastics is complicated by chemical transformation in addition to those problems associated with the use of proprietary additives.

The total contamination profile for the various polymer tubes is summarized in Table III where both the major and minor contaminants in the water passed through the tubes are listed. An X designates that positive evidence for the contaminant exists. The absence of an X should not be construed as conclusive negative evidence. For example, the level may be below our detection limit, or a

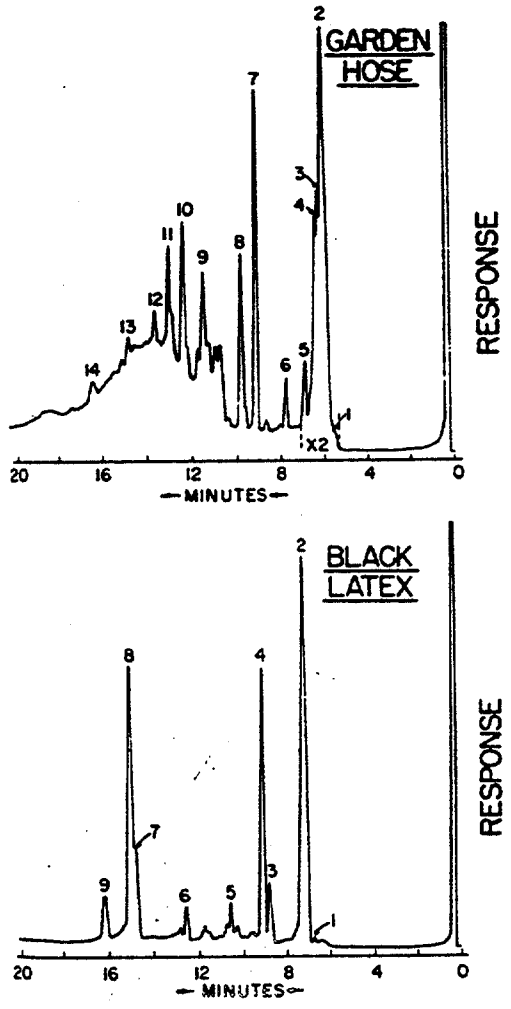

Figure 3. Chromatograms from tests of plastic garden hose and black latex tubes—25 ft × ½ in. i.d.: garden hose (170 ppb), black latex (26 ppb)

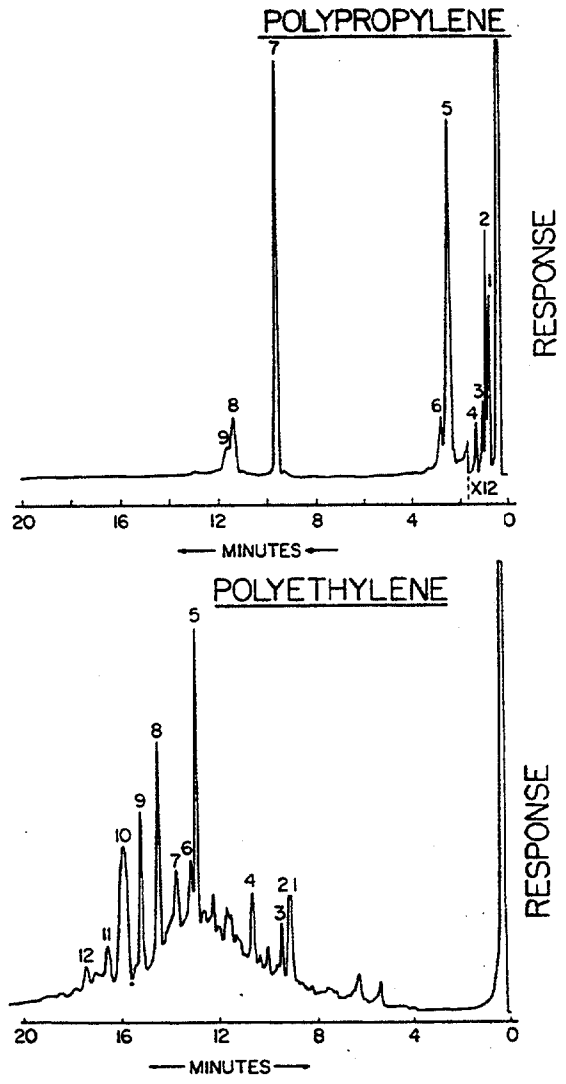

Figure 4. Chromatograms from tests of polyethylene and polypropylene tubes—25 ft × ⅜ in. i.d.: polyethylene (1 ppb), polypropylene (4 ppb)

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particular component cannot be identified positively because of unresolved gc peaks, or a major contaminant masks a minor component.

The identification results for the polyethylene and polypropylene tubes are not included here since these results are not yet definitive enough to be discussed.

Static vs. Flowing Water. Interpretation of several experimental observations suggested that the amount of contamination from various polymer tubes may be related to the linear velocity of the water flow through the tube. An increase in the amount of contamination occurred when: the water flow rate was increased from 20 to 60 ml/min to reduce the sampling time, sharp bends existed in the polymer tube, and air bubbles were present in the tube during part or all of the sampling time. These observations, coupled with the implication that agitation of aqueous solutions may increase the contamination from PVC containers (*22, 29, 34*), suggested that linear velocity and contamination were indeed related. To test the validity of this proposal, "pure" water was passed through a 6-ft length of $^1/_2$-in. i.d. Food-Beverage Grade PVC for 48 hr at 60 ml/min. The total measured contamination of the effluent water, at a calculated linear velocity of 46 cm/min, was 0.6 ppm. Then a 3-ft length of $^3/_8$-in. glass rod was inserted into the center of the 6-ft PVC tube. The head pressure was increased to achieve the same flow of 60 ml/min and this flow was continued for 48 hr. Under these conditions, the linear velocity across the restricted 3-ft section was 105 cm/min, and the contamination in the effluent water increased to 1.6 ppm. This represents a dramatic enhancement of the contamination and suggests that it is directly related to linear velocity when the amount of water sampled, the sampling time, and the exposed polymer surface area are held constant.

Previous investigations by others (*22, 43, 44*) have related the contamination mechanism to the migration of water into the polymer, to the diffusion of plasticizers and other additives through the polymer network, and to the dissolution rate of the additives. Our results suggest that an erosion mechanism occurring at the polymer–water in-

Table I. Identification and Quantification Data for Contaminants in Water Passed Through a $^1/_2$-In. I.D. Tube of General Chemical Grade PVC

Peak i[a]	Mass spectral data[b]	Gc data: R_t (unkn)[c]	Gc data: $R_t(k)$[d]	Concentration, ppb[e]	% of total concn	Identification
1	I	3.80	3.60	0.66	6.14	Butylchloroacetate
2	CL	4.00	3.95			2-Ethylhexanol
3	CL	4.50	4.25	4.62	43.01	*o*-Cresol
4	CL	5.45	5.40	1.72	16.02	Naphthalene
5	CL	5.75	N	0.24	2.23	*p*-Ethylphenol
6	HM	6.00	N	0.30	2.79	Isopropyl subs. phenol
7	HM	6.40	N	0.54	5.02	Methyl–ethyl subs. phenol
8	HM	6.90	N	0.35	3.25	Methyl-ethyl subs. phenol
9		7.30		0.16	1.48	Unidentified
10		7.80		0.18	1.67	Unidentified
11		8.40		0.11	1.02	Unidentified
12	CM	9.70	9.60	0.08	0.74	Diethylphthalate
13	I	10.00	N	1.45	13.49	Butyloctylfumarate
14	CL	11.50	11.80	0.08	0.74	Diisobutylphthalate
15	CL	12.50	12.40	0.05	0.46	Dibutylphthalate

[a] See Figure 2. [b] CM = a complete match of ms data with an authentic sample of the ICI–Aldermaston index; CL = close match; HM = match of four largest peaks; I = no match and fragmentation pattern interpretation required. [c] Retention time of unknown gc peak. [d] Retention time of authentic sample. N indicates that an authentic sample check was not made. [e] Concentration of the contaminant in the water in parts per billion by weight.

Table II. Total Contamination and Identifications of Major Contaminants in Water Passed Through Various 25-Ft Lengths of $^3/_8$–$^1/_2$ In. I.D. Polymer Tubes at 60 Ml/Min

Polymeric tube	Total contamination, ppb	Identifications[a] Major contaminants/gc peak no.[b]				
General chemical PVC	11	*o*-Cresol/3	Naphthalene/4	BOF/13	2-Ethyl hexanol/2	2-Ethyl-1-methylphenol/8
Laboratory grade PVC	4	2-Ethyl hexanol/1	Stearic acid/12	DIBP/9	BOF/6	3,4-Dimethoxy acetophenone/4
Processed milk PVC	6	2-Ethyl hexanol/2	DIBP/9	*p*-Nonyl phenol/10	DEHP/11	DEP/8
Food–beverage PVC	5000	BGBP/13	DIBP/9	DEP/6	DEHP/15	EGEP/11
FDA–USDA PVC	9	2-Ethyl hexanol/2	3,4-Dimethoxy acetophenone/5	Unkn./4	DIBP/8	DBP/9
Hospital–surgical PVC	6	2-Ethyl hexanol/4	Lauric acid/9	DEHP/17	DIBP/11	Phthalic anhydride 7
Garden hose	170	Alcohol[c]/2	Alcohol[c]/3	Alcohol[c]/4	DBM/7	DIBP/10
Black latex	26	Decyl amine/2	Unkn./8	Ionol/4	DAP/9	Diisopropyl *p*-xylene/3
Polyethylene[d]	1	Unkn./1	Unkn./2	Unkn./7	Unkn./5	Unkn./8
Polypropylene[d]	2	Unkn./2	Unkn./4	Unkn./6	Unkn./10	Unkn./14

[a] Abbreviations used for common contaminants: BOF = butyloctylfumarate; DIBP = diisobutylphthalate; DEHP = di-2-ethylhexylphthalate; DE[illegible] = diethylphthalate; BGBP = butylglycolylbutylphthalate; EGEP = ethylglycolylethylphthalate; DBP = dibutylphthalate; DBM = dibutylmaleate; DAP = diamylphthalate. [b] Refer to appropriate chromatograms in Figures 2–11. [c] Mass spectra and retention times used to tentatively identify the unresolved gc peak as a mixture of alcohols. [d] Insufficient water sampled to make any positive identifications.

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terface should be included as a p ble significant factor in the contamination mechanism.

This relationship between contamination and the linear velocity of the water flowing through the polymer tube is currently being more fully investigated. Preliminary results show that the contamination of the water will increase as the flow rate is increased for a given diameter tube. Other factors being constant, larger diameter tubes and lower head pressures are recommended to minimize the contamination. An additional conclusion is that contamination levels, based on static water tests, cannot be extrapolated to flowing water conditions.

Contamination vs. Usage. The possible decrease in the level of contamination after a polymer tube has been used for transporting large quantities of water was investigated. When 1000-liter volumes of "pure" water were used to flush Laboratory and Hospital-Surgical Grade PVC tubes, the amount of contamination measured immediately after the flushing action was reduced by a significant factor of ~3 over that measured when only 25-liter volumes of "pure" water were employed for flushing. Subsequent flushings of the same tubes with as high as 3000 liters of water failed to decrease significantly the contamination.

These results show that although initial flushing of PVC tubes with a large quantity of water has a salutary effect in lowering contamination, extensive washing serves no useful purpose. The amount of plasticizers in the highly flexible PVC tubes is approximately 40% by weight and this represents an almost inexhaustible supply of contamination. Should th ipply eventually become appreciably depleted, the contamination will decrease, but the tubing will also have lost its flexibility and strength and will undoubtedly need to be replaced, thus causing a return to the original high level of contamination.

For the relatively rigid polyethylene and polypropylene tubes the source of the contamination may not be inexhaustible, and these tubes may eventually become noncontaminating. Long-range tests of these tubes and various cleaning procedures are currently in progress.

Conclusions

The method described here for testing the contamination of water by various polymer tubes is sensitive to amounts corresponding to < 1 ppb for most organic materials. Contamination tests are made, conveniently using flow conditions which duplicate or closely approximate the use of the polymer tube to transport water or other aqueous solutions. These tests can be made in most analytical laboratories and the results used to aid in the selection of polymer tubes. Since the critical apparatus in the method is a very simple and portable extraction column, accurate on-site sampling of a production solution is possible by connecting an extraction column parallel to a production stream until the desired volume is sampled. The extraction column may then be transported readily to the laboratory where the remainder of the scheme is completed at the convenience of the analyst.

The contamination tests reported here were made using

Table III. List of Contaminants in Water and Polymer Tubes Which Caused This Contamination

Contaminant	Tube abbreviations[a]								Comment
	GC	LB	PM	FB	FU	HS	GH	BL	
2-Ethylhexanol	X	X	X	X	X	X	X		Impurity or transformation[b]
C_8 satd. alcohol				X					Probably octanol
Unkn. alcohols							X		Not present in PVC
o-Cresol	X								Suspected stabilizer
o-Ethylphenol	X								Same
p-Ethylphenol	X								Same
2-Ethyl-4-methylphenol	X								Same
2,4-Di-*t*-butyl-6-methylphenol				X					Same
2,6-Di-*t*-butyl-4-methylphenol			X		X				Same
p-Nonylphenol			X		X				Same
p-Dodecylphenol					X				Same
p-*t*-Butylphenol								X	Same
Ethyl acetate						X			—
Butylchloroacetate	X		X	X		X			Highly toxic
Naphthalene		X			X				Common impurity
2-Ethylhexanal						X			—
3,4-Dimethoxyacetophenone		X			X				Suspected stabilizer
Decylamine								X	—
Stearic acid		X							Transformation of Zn salt
Lauric acid						X			Same
Myristic acid						X			Same
Phthalic anhydride		X				X			Impurity or transformation
Butylbenzoate							X		Known plasticizer
Butyloctylfumarate	X	X							Suspected plasticizer
Dibutylmaleate							X		Same
Ethylglycolylethylphthalate				X					Same
Butylglycolylbutylphthalate				X		X			Known plasticizer
Dimethylphthalate				X					Same
Diethylphthalate	X	X	X	X	X	X	X		Same
Dibutylphthalate	X			X	X	X		X	Same
Diisobutylphthalate	X	X	X	X	X	X			Same
Diamylphthalate						X		X	Same
Di-2-ethylhexylphthalate		X	X	X	X	X			Same

[a] Abbreviations are: GC = general chemical PVC; LB = laboratory PVC; PM = processed milk PVC; FB = food–beverage PVC; FU = FDA–USDA PVC; HS = hospital–surgical PVC; GH = garden hose plastic; BL = black latex tube. X indicates that the contaminant was found in the designated tube. [b] Here impurity refers to materials found in solvents, starting chemicals, and additives used in the polymerization process.

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distilled water because these contamination results are considered to represent minimum values. The presence of minerals, inorganic acids or bases, and lipoid materials in the water would all result in either the same or an increased level of contamination. In the presence of large amounts of minerals and inorganic acids and bases, the method has been shown (*41*) to be accurate for all neutral organics and therefore is not limited to distilled water tests. Whether the procedure is useful for beverage testing where lipoid materials are present has not yet been ascertained.

The complexity of the chromatograms for all the tests of polymer tubes reported here suggests that conclusions concerning toxicity based on the tests of single pure components must be tempered with the knowledge that plasticizers and other additives almost always occur as a complex mixture.

Several conclusions, based on the results reported here, suggest that risk/benefit ratios associated with the widespread use of many polymers may not be nearly so favorable as suggested by sole consideration of the reported low level of contamination. First, the contamination profiles represent a very complex mixture of components, many of which are not identified and may be toxic. Second, some of the identified components are obviously toxic, for example butylchloroacetate. Third, the presence of myristic, stearic, and palmitic acids in some polymer tests suggests that some toxic metals may also be present. Fourth, contamination level predictions based on static water tests of polymers are usually not valid.

When these conclusions are coupled with the observations of other investigators, the case for reassessment of the risk/benefit ratio becomes even more convincing. Autian (*3*) discusses the documented increase in contamination of PVC containers when the contacting solution becomes more lipid; several investigators have established the rapid biomagnification of many plasticizers and other additives (*9, 15, 37, 39*); while little is known about cumulative toxicity and the synergistic effect of mixtures (*3*), some investigators (*3, 12, 35*) have shown these to be appreciable; and finally, recent studies (*26, 27*) suggest that plasticizers may be readily transported as water-soluble complexes with natural humic materials.

Our results and the summary outlined above suggest that the expressed concern of some scientists (*3, 8, 32, 37, 39*) is certainly valid. Unfortunately, definition of the true problem and the development of an adequate solution are severely complicated by the continuously changing and expanding list of allowable additives in the manufacture of polymer tubes and containers.

Acknowledgment

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Suitability of Polyvinyl Chloride Well Casings for Monitoring Munitions in Ground Water

by Louise V. Parker and Thomas F. Jenkins

Abstract

A number of samples of polyvinyl chloride (PVC) well casings used for ground water monitoring that varied in schedule, diameter or manufacturer were placed in contact with low concentrations of aqueous solutions of TNT, RDX, HMX and 2,4-DNT for 80 days. Analysis indicated that there was more loss of TNT and HMX with the PVC casing than with the glass controls, but that the amount lost was, for the most part, equivalent among different types. A second experiment was performed to determine if these losses were due to sorption or if biodegradation was involved. Several different ground water conditions were simulated by varying salinity, initial pH and dissolved oxygen content. The only case where there was an increased loss of any substance due to the presence of PVC casing was with the TNT solution under nonsterile conditions. The extent of loss was small, however, considering the length of the equilibration period. This increased loss is thought to be associated with increased microbial degradation rather than sorption. Several samples of PVC casing were also leached with ground water for 80 days. No detectable interferences were found by reversed-phase high performance liquid chromatography (HPLC) analysis. Therefore, it is concluded that PVC well casings are suitable for monitoring ground water for the presence of these munitions.

Introduction

Polyvinyl chloride (PVC) is commonly used to fabricate casings for ground water monitoring wells because of its strength, corrosion resistance, weatherability, weight and cost. However, it has not been determined whether this material is acceptable for many ground water monitoring applications. Several researchers have found evidence that some contaminants may sorb to PVC, thereby lowering their concentrations (Lawrence and Tosine 1976, Miller 1982, Barcelona et al. 1985). Other substances have been shown to leach from various types of PVC and these substances could interfere with some methods of chemical analysis (Jaeger and Ruben 1970, 1972; Junk et al. 1974; Christensen et al. 1976; Banzer 1977; Fayz et al. 1977; Dressman and McFarren 1978). Specifically, the purpose of this study was to determine if PVC well casing was acceptable for use in monitoring low levels of the explosives 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro 1,3,5,7-tetrazocine (HMX), and 2,4-dinitrotoluene (DNT), which is found as a contaminant in TNT manufacture.

A number of substances have been found to leach from various types of PVC. These include: vinyl chloride monomer (VCM), plasticizers (phthalate esters), stabilizers, impurities and transformation products (Jaeger and Ruben 1970; Junk et al. 1974, Christensen et al. 1976, Banzer 1977, Fayz et al. 1977, Dressman and McFarren 1978). However, for the rigid PVC that is used for well casing, National Sanitation Foundation (NSF) standards are set at a maximum limit of residual vinyl chloride monomer concentration of 10 ppm (NSF 1980). Also, the plasticizer content in rigid PVC products, such as pipe, is very low when compared with more flexible products such as tubing (Roff et al. 1971, ASTM 1980, Barcelona et al. 1984).

The literature contains evidence that some organic substances are strongly adsorbed by PVC. Lawrence and Tosine (1976) found that PVC chips were quite efficient at removing polychlorinated biphenyls (PCBs) from water and waste water. PCBs are hydrophobic organic chemicals with large octanol-water partition coefficients (K_{ow}) in the 10^5 range (Veith et al. 1979). K_{ow} values have been found to correlate with partitioning of organic chemicals between aqueous solutions and the organic matter in soil and sediments (Karickhoff et al. 1979). These coefficients might be useful in predicting the partitioning that can occur between aqueous solutions and a PVC surface as well. Values as high as those for PCB indicate a very strong tendency

partition into an organic phase although surface energies also play an important role in determining its distribution. It is not surprising, given the K_{ow} for TNT, that significant sorption on PVC was found.

More recently, Miller (1982) tested three types of well casing materials—including schedule 40 PVC, polyethylene, and polypropylene—for the sorption of volatile organic pollutants. The organics tested included bromoform, trichlorofluoromethane, trichloroethylene, 1,1,1-trichloroethane, 1,1,2-trichloroethane and tetrachloroethylene. Concentrations were in the 2-4 ppb range except for trichloroethane where the concentration was 14 ppb. After six weeks they found that PVC well casing material was superior to the other two materials and did not sorb or leach five of the six organics tested. Tetrachloroethylene, on the other hand, was substantially lost from solution in contact with PVC. Miller (1982) attributes this loss to adsorption, but does not explain its anomalous behavior compared to the other organic volatiles of similar structure, such as trichloroethylene and trichloroethane. In a desorption study well casings were exposed to the contaminants for four weeks and then to fresh water for four weeks. Only a small amount of tetrachloroethylene was desorbed. The bulk of the original material lost was not recovered. Whether specific adsorption accounts for the observed loss or some other mechanism does, such as enhanced biodegradation in the presence of PVC or penetration into the polymer due to the planar geometry of tetrachloroethylene, is not clear.

Curran and Tomson (1983) tested five types of plastic for adsorption of trace levels (0.5 ppb) of naphthalene and p-dichlorobenzene. The plastics tested were: Teflon®, polyethylene, polypropylene, Tygon tubing, and glued and non-glued PVC pipe. Twenty liters of solution were pumped through the tubing at a rate of 30 mL/min^{-1} (for a contact time of approximately 11 hours). They estimate that they recovered 80 to 100 percent of these organics from all of the plastics, with the exception of Tygon. They also tested the plastics for contaminant leaching and found that Teflon showed the least amount of leaching, with rigid non-glued PVC a very close second. Tygon again had the poorest performance. They believed the reason that non-glued, rigid PVC exhibited very little leaching was because of the low level of plasticizers used in its formulation.

Barcelona et al. (1985) found a substantial increase (2x) in sorption of low molecular weight, halogenated hydrocarbons (chloroform, trichloroethylene, trichloroethane, tetrachloroethylene) by flexible tubings made of PVC, polyethylene and polypropylene when compared with the sorption found by Miller (1982) for rigid well casings made of the same materials. They hypothesized that sorption of these chlorinated solvents is by absorption into the polymer matrix and that the flexible materials would present a virtual sink for the chlorinated solvent sorbates. Although they found 80 to 90 percent of the desorption of chloroform occurred almost immediately (within the first five minutes), the amount desorbed represented 3 percent or less of the total chloroform sorbed. These results are consistent with surface sorption followed by diffusion into the polymer matrix. Once diffusion into the matrix occurs the substance would not be easily desorbed.

Recently, data were obtained at this laboratory on the filtration of waters containing low levels of explosives through PVC membrane filters. These results indicated that [illegible] were no adsorptive [illegible] associated with PVC, whereas measurable losses were found with cellulose acetate nitrate membranes (Leggett, personal communication). Broadman et al. [illegible] observed hydrogen bonding of 2,4-DNT to nitrocellulose, which might account for the results obtained by Leggett; hydrogen bonding is not expected with PVC because of the lack of these sites in this polymer.

The K_{ow} values for the substances used in this study are lower than any of the organics tested by Miller (1982), Curran and Tomson (1983), and Lawrence and Tosine (1976) and ranged from 75.2 for DNT to 1.38 for HMX. Based on previous work by this laboratory using PVC filter membranes and the K_{ow} values of these analytes, significant sorptive losses are not expected. However, absorption or specific binding, such as that which may have occurred with tetrachloroethylene, is possible. It is also possible that substances such as the metallic components of stabilizers that leach at low levels from PVC may catalyze the decomposition of these munitions.

Materials and Methods

Threaded PVC well casing and screen, which was NSF-approved and met ASTM standards, was used in this study. Two manufacturers were selected. Threaded pipe was selected to circumvent leaching problems associated with solvent bonded joints. Boettner et al. (1981) have documented that leaching of the solvents used to join PVC pipe can be significant. However, tests performed with aqueous standards of four common bonding solvents (tetrahydrofuran, cyclohexanone, methylethylketone and methylisobutylketone) indicated these substances did not interfere with the method of analysis used in this study (Jenkins et al. 1984). After the pieces of casings and screen were cut they were rinsed with well water and dried using a clean paper towel to remove any shavings that may have been left after cutting.

Solutions used in these experiments were prepared by dissolving a combination of known amounts of TNT, RDX, HMX and DNT in fresh, local unfiltered ground water taken from a deep aquifer. This ground water was found to be very low in total organic carbon (0.7 mg/L) and showed no detectable interferences with the analytical procedure used in this report. All sample solutions were kept in glass beakers that were covered with glass to prevent evaporative loss, and were maintained in the dark at 10 C—an "average" ground water temperature in the United States.

The first experiment was performed to determine if there was any difference in the adsorptivity of different kinds of PVC casing or screen. Casings were selected that differed in diameter, schedule (or thickness), and manufacturer. Duplicate samples of 2-inch inside diameter schedule 40 and 80 casing, 2-inch diameter schedule 40 slotted well screen (with a filter area of 2.1 in.^{2}/lin. ft), 4-inch diameter schedule 80 casing, manufactured by one company (Company A) and 2-inch diameter schedule 40 casing from a second manufacturer (Company B) were tested. Four-inch long sample sections of the 2-inch diameter casing were placed in 1,000 mL glass beakers containing 750 mL of sample solution and 4-inch long sample sections of the 4-inch diameter casing were placed in 2,000 mL beakers containing 1,500 mL of sample solution. This gave an equivalent surface-area-to-sample volume ratio for all

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beakers that contained test solution but no casing served as controls. The initial concentrations of the analytes in the test solution were 624 μg/L TNT, 1977 μg/L RDX, 305 μg/L HMX and 611 μg/L DNT. Samples were analyzed in duplicate on days 0, 14 and 80.

In the second experiment, 4-inch long sections of both brands of 2-inch diameter schedule 40 casing were compared with glass controls, which contained no well casing, to determine if any substances were leached into fresh ground water that could interfere with HPLC analyses for the four munitions. Duplicate samples of each type of casing were tested in 1,000 mL beakers containing 750 mL of ground water. No munitions were added to the ground water, and the pH, dissolved oxygen content, and salinity of the water were not changed. The solutions were analyzed on days 0, 14 and 80.

The final experiment was designed to test whether biodegradation or the presence of PVC pipe, or both, affected the stability of low concentrations of the four munitions under a variety of conditions that simulated natural ground water. The variables used to simulate different ground water conditions included pH, dissolved oxygen content, and salinity. Therefore, the effect of sterility, presence of PVC, pH, dissolved oxygen content, and salinity were tested using a complete 2^5 factorial design. Once again, 4-inch long sections of 2-inch diameter schedule 40 pipe (Company A) were placed in 1,000 mL glass beakers containing 750 mL of the sample solution. The concentrations of analytes used in this sample solution were very similar to the concentrations used in the first experiment. The initial concentrations were 637 μg/L of TNT, 2081 μg/L of RDX, 252 μg/L of HMX and 544 μg/L of DNT. Glass control samples contained the same amount of solution without any casing. Since autoclaving was found to destroy HMX and RDX in solution, $HgCl_2$ (40 mg/L) was added to those portions of the solutions used to study the effect of sterility (USGS 1977). The pH of the sample solution was adjusted to an initial value of either six or eight with dilute solutions of HCl or NaOH. In those samples where the salinity was modified, 175 mg/L $MgCl_2$ and 175 mg/L $CaCl_2$ were added. To lower the dissolved oxygen content, samples were purged with N_2 gas for several minutes and were then placed in a glove box that was flushed several times with N_2 gas and purged with N_2 at a low rate for the duration of the experiment. The other (high dissolved oxygen) samples were incubated in the presence of air. Samples were analyzed on days 0 and 25. Only a single analysis of each sample was performed because of the large number of samples.

For all the experiments, aqueous concentrations of TNT, RDX, HMX and DNT were determined by reverse phase HPLC using a Perkin Elmer Series 3 High Performance Liquid Chromatograph (HPLC) equipped with a LC-65T variable wavelength detector, set at 254 nm, and an LC-8 column (Jenkins et al. 1986). Analytical stock standards were prepared for TNT, RDX, HMX and DNT by dissolving weighed quantities of Standard Analytical Reference Materials (obtained from the U.S. Army Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, MD 21010) for each substance in separate 100 mL volumetric flasks with HPLC grade methanol. Working standards were prepared by dilution of these stocks with 50:50 methanol/water (HPLC grade methanol and water).

The analytical precision of this HPLC method is ±2 percent for HMX and RDX and ±4 percent for TNT and DNT in the concentration range studied here (Jenkins et al. 1986). Quantitative recovery of DNT and RDX and a 5 percent loss of TNT and HMX were found when this method was tested in nine different laboratories (Bauer et al. 1986).

Dissolved oxygen was determined using the membrane electrode method (APHA-AWWA-WPCF 1980) on a Markson Selectro Mark Analyzer with an Orion O_2 electrode. The pH and conductivity were determined on an Orion 811 pH meter and a resistivity bridge, respectively, according to standard methods.

Results and Discussion

In the first experiment there was very little loss of RDX, HMX and DNT after 80 days for all casings tested, whereas there was a relatively large loss of TNT (Table 1). For TNT the mean concentration of the control samples was 511 μg/L (18 percent loss) while the mean concentration for the samples with PVC ranged from 464 μg/L (26 percent loss) for the 2-inch diameter schedule 40 pipe manufactured by B, to 398 μg/L (36 percent) for the same type of casing manufactured by A. Analysis of variance indicated that there were significant differences among treatments at the 95 percent confidence level. A least significant difference test indicated that all PVC casings, with the exception of those with the schedule 40 casing manufactured by B, had significantly lower concentrations than the glass control. None of the casing samples that were significantly lower than the glass control were significantly different from each other. Therefore, variation in amount of TNT lost between different types of casing

Table 1
Losses of Analytes Due to Exposure to Different Types of Casing and Well Screen (Concentration in μg/L)

Sample	TNT Mean Initial	TNT Mean Final*	RDX Mean Initial	RDX Mean Final*	HMX Mean Initial	HMX Mean Final*	DNT Mean Initial	DNT Mean Final*
Glass control	624 ± 25	511 ± 13	1977 ± 22	2011 ± 15	305 ± 28	346 ± 31	611 ± 29	612 ± 13
Company B 2-in. sch 40		464 ± 4		2062 ± 5		335 ± 15		618 ± 12
Company A 2-in. sch 40		398 ± 27		2004 ± 20		309 ± 9		612 ± 12
Company A 2-in. sch 40 well screen		412 ± 44		2005 ± 20		288 ± 13		613 ± 37
Company A 2-in. sch 80		441 ± 10		2003 ± 10		348 ± 26		606 ± 12
Company A 4-in. sch 80		427 ± 20		2026 ± 17		257 ± 29		600 ± 7

*After 80 days incubation

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was minimal. However, it is not c what mechanism accounts for the increased loss o NT in the presence of PVC. Losses may be due to sorption, chemical reaction, biodegradation or some combination of these factors.

After 80 days there was no statistically significant difference in the concentration of RDX in any of the samples with the exception of the sample containing the schedule 40 casing, manufactured by B, which was found to be significantly higher in concentration than the other samples, including the glass control. This may be due to the leaching of a substance from the casing that interfered with analyses.

Analysis of variance of the HMX indicated that there were some statistically significant differences between the samples. According to least significant difference calculations, two of the casing samples were not significantly different from the glass control (schedule 80 casing manufactured by A and schedule 40 casing manu ured by B). The remaining three samples were significantly lower in concentration than the glass control and were similar in concentration only to their neighbors.

The DNT data after 80 days showed very little variation between samples or loss with time. Mean concentrations for the different samples ranged from 606 to 618 μg/L. These differences were not statistically significant.

Some of the casing samples did differ from the glass controls in the amount of HMX and TNT lost. While it is not known what the mechanism for this loss was, it is interesting that there was not a statistically significant loss for any of the analytes in the samples containing well screen. If sorption was responsible for the loss, one would expect to find more sorption with the well screen since the surface area was almost exactly twice that of the regular casing. The final experiment attempts to provide more information

Table 2
Results of Factorial Experiment Which Tested the Effect of Sterility and the Presence of PVC Casing

Day of analysis	PVC or glass	Sample sterility	Atmosphere	Initial pH	Salts	Sample concentration (μg/L) TNT	RDX	HMX	DNT	DO (mg/L)	Final pH	Conductivity (μmhos/cm)
0						637±9	2081±15	252±22	544±11			
25	Glass	non-sterile	AMB O_2	6	-	541	1969	259	510	10.2	8.1	443
					+	551	1975	244	536	9.8	6.9	1267
				8	-	557	1976	262	514	10.3	8.2	380
					+	516	2000	274	515	10.2	8.1	1266
			LOW O_2	6	-	532	1959	270	488	1.6	8.6	435
					+	519	1932	253	470	1.6	8.4	1221
				8	-	576	1972	238	534	1.5	8.4	326
					+	488	1872	280	471	1.4	8.0	1169
		sterile	AMB O_2	6	-	575	1975	243	529	10.3	7.9	468
					+	589	1972	232	520	9.7	6.8	1268
				8	-	530	1985	239	578	10.4	8.2	441
					+	546	1995	234	523	10.2	8.2	1266
			LOW O_2	6	-	527	1905	243	515	1.6	8.2	454
					+	551	1938	242	519	1.9	8.2	1221
				8	-	419	1919	270	523	1.6	8.7	419
					+	495	1904	247	507	1.5	8.5	120[illegible]
	PVC	non-sterile	AMB O_2	6	-	436	1934	261	482	10.4	8.0	39[illegible]
					+	515	1992	258	472	9.6	6.9	1266
				8	-	509	2005	260	486	10.4	8.1	348
					+	502	1989	265	592	9.5	7.9	1250
			LOW O_2	6	-	462	1844	274	481	1.8	8.4	443
					+	494	2016	264	479	1.6	8.0	1264
				8	-	499	1935	260	492	11.4	8.2	306
					+	492	1949	216	502	1.2	8.1	1198
		sterile	AMB O_2	6	-	592	1891	221	505	10.9	7.8	479
					+	570	1921	253	487	10.0	6.7	1270
				8	-	518	1935	281	506	10.6	8.2	432
					+	552	1998	245	527	10.1	7.8	1250
			LOW O_2	6	-	526	1881	243	556	1.6	8.3	467
					+	544	1879	252	494	1.6	8.2	755
				8	-	462	1884	284	526	1.5	8.6	412
					+	451	1833	246	502	1.3	8.4	1187

Sterile = samples were incubated with bactericidal agent
Non-sterile = samples had no bactericidal agent added
AMB O_2 = samples were incubated in ambient atmosphere, in presence of O_2
LOW O_2 = samples were incubated in glove box flushed with N_2 gas
Salts – = no salts added
Salts + = $MgCL_2 + CaCL_2$ salt solution added

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There was an average loss of 18.5 percent for TNT: the mean initial concentration [illegible] 637 μg/L and the mean final concentration was [illegible] μg/L. Analysis of variance of the TNT data showed that the loss of TNT was significantly less for the glass controls than for the samples exposed to PVC (Table 3, the term G). Analysis of variance also indicated that the interaction of PVC and sterility (the term DG) was significant. The significance of this interaction is explained by the fact that the losses were equivalent for all the samples except for the non-sterile sample with PVC casing where loss was the greatest. The mean concentrations were: 529 μg/L in the sterile control samples, 527 μg/L in the sterile PVC samples, 535 μg/L in the non-sterile control samples and 489 μg/L in the non-sterile PVC samples. Since the losses were equivalent for the sterile control samples and the sterile PVC samples, loss is not attributed to sorption by the PVC or chemical reaction with either the casing or some leachate from the casing. The increased loss is apparently attributable to microbial activity and may be due to either the activity of microorganisms initially present on the PVC casing, the increased surface area for colonization due to the presence of PVC pipe, a stronger affinity of microorganisms for adhesion to a plastic surface, or it may be that the casing leaches some nutrient or growth factor (such as the metals present in stabiliz-

In the second experiment, 2-inch diameter schedule 40 casings manufactured by both companies were tested to determine if any substances were leached from the pipe that would interfere with reversed-phase sives. The unusually high RDX values for the casing manufactured b[illegible] that were observed in the previous experiment could have been caused by the leaching of some substance that co-eluted with RDX and absorbed at the wavelength used for analysis. However, after 60 days no spurious peaks were detected in any of the samples using the HPLC method described earlier. Some substances could have been leached that were not detectable using this analytical technique, such as stabilizers. However, Boettner et al. (1981) found that most of the commercial stabilizers used in the manufacture of PVC pipe showed only minor absorption at the wavelength used in these experiments (254 nm) and their elution characteristics are unknown.

The final experiment was designed to determine whether biodegradation or sorption by PVC (presence of PVC) caused losses of munitions from solution. This test was performed under a variety of conditions that simulated different ground water conditions by varying the pH, dissolved oxygen content and salinity. Therefore, this experiment utilized a full factorial design to test the effect of sterility, salinity, pH, dissolved oxygen, and presence of PVC pipe on the loss of TNT, DNT, HMX and RDX from solution. The analyses of the samples initially (Day 0) and after 25 days incubation are given in Table 2. Because results presented in Table 2 are complex, an analysis of variance was performed on the data set for each analyte. The TNT and RDX data had significant effects, which are presented in Table 3. For the HMX and DNT data there were no significant effects.

Table 3
Analysis of Variance of TNT and RDX Data from Table 2

		TNT			RDX		
Term	DF	Mean square	F	Level of significance	Mean square	F	Level of significance
S	1	406.1	<1	NS	1200.5	1.02	NS
P	1	5304.5	7.50	0.025	882.0	<1	NS
SP	1	903.1	1.28	NS	3570.1	3.04	NS
D	1	2080.1	2.94	NS	7938.0	6.76	0.025
SD	1	1058.0	1.50	NS	136.1	<1	NS
PD	1	10878.1	15.37	0.001*	6.1	<1	NS
O	1	9870.1	13.97	0.001*	24753.1	21.06	0.005*
SO	1	84.5	<1	NS	684.5	<1	NS
PO	1	561.1	<1	NS	3612.5	3.07	NS
OD	1	5832.0	8.24	0.025	882.0	<1	NS
G	1	4704.5	6.65	0.025	4095.1	3.48	NS
SG	1	435.1	<1	NS	3612.5	3.07	NS
PG	1	338.0	<1	NS	924.5	<1	NS
DG	1	3916.1	5.53	0.050	4512.5	3.84	NS
OG	1	36.1	<1	NS	0.1	<1	NS
Error	16	707.6			1175.1		

S = presence or absence of $MgCl_2$ and $CaCl_2$ salts
P = pH, pH = 6 or 8
D = microbial degradation — presence or absence of bactericidal agent
O = dissolved oxygen, high or low
G = glass vs. PVC
* = highly significant
NS = not significant

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ers) that increases the growth or rate of biodegradation.

The analysis of variance (Table 3) also indicated several other significant terms for TNT including pH (the term P), oxygen content (the term O), the interactions of pH and sterility (the term PD), and of the interaction of dissolved oxygen and sterility (the term OD). However, while these effects are important in considering the long-term stability of an aqueous solution of TNT, they are not important to the discussion of the suitability of PVC pipe for monitoring TNT. A more complete discussion of these effects is given by Parker et al. (1985).

There was a mean loss of 6.7 percent RDX over the 25-day study. The mean initial concentration was 2081 μg/L and the mean final concentration was 1942 μg/L. Although the loss appears to be slightly less for the glass controls ($\bar{x}$ = 1953 μg/L or 6.1 percent less) than for the samples with PVC casing ($\bar{x}$ = 1930 μg/L or 7.3 percent loss), this difference is not significant at the 95 percent confidence level (according to a paired t-test and analysis of variance). The analysis of variance did indicate that the interaction of sterility and dissolved oxygen content significantly affects the concentration of RDX. Again, however, this effect is not relevant to the discussion of the suitability of PVC pipe.

There was no loss of HMX over the 25-day incubation, even under non-sterile conditions, and thus there were no statistically significant differences using either the paired t-test or analysis of variance. The mean initial concentration was 252 μg/L and the mean final concentration was 253 μg/L. According to McCormick et al. (1981) the rate of biotransformation of HMX is slower than that for RDX and TNT, which may explain, in part, why there were not any losses observed. There were some differences between PVC samples and the control in the first experiment, but the exposure period was more than three times longer for that experiment.

The loss of DNT from day 0 ($\bar{x}$ = 544 μg/L) to day 25 ($\bar{x}$ = 511 μg/L) is relatively low—6.1 percent. The loss in the PVC samples was not significantly different from the glass controls at the 95 percent confidence level using either a paired t-test or analysis of variance.

Summary and Conclusions

A long-term study (80 days) was conducted under non-sterile conditions to determine if the presence of different types of PVC well casing and screen affected the concentration of low levels of TNT, RDX, HMX and DNT in aqueous solution. Results indicated that there is a statistically significant loss of TNT and, to a lesser extent, HMX in the presence of PVC casing. For the most part, the losses of these munitions were equivalent regardless of manufacturer, schedule or diameter of pipe. Well screens showed similar trends. In a short-term follow-up study (25 days) to determine whether these losses were due to biodegradation or sorption, or both, there was a statistically significant loss of TNT but no loss of HMX. This loss was not attributed to adsorption but seems to be associated with increased microbial degradation in the presence of PVC. While this loss was statistically significant, the increased loss relative to glass was only 6 percent after 25 days. Since the purging of stagnant water from the well prior to sampling should ensure a relatively short contact time between the sample and the well casing, the degree of loss e. oited in these experiments should not limit the use of PVC for this application.

Long-term leaching studies using local ground water with two different brands of PVC casing indicated that nothing was leached at sufficient concentrations to interfere with reversed-phase HPLC analysis for low levels of TNT, RDX, HMX or DNT in ground water.

Therefore, the authors conclude that the use of PVC well casings is acceptable for ground water monitoring for low levels of these munitions.

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