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

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CE 4594: Soil and Groundwater Pollution

November 11, 1990
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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.
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 monomer 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).
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 groundwater 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,
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

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Adsorption (ug/L)</th>
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<tr>
<td></td>
<td>Teflon</td>
</tr>
<tr>
<td>Chloroform</td>
<td>10</td>
</tr>
<tr>
<td>Tetrachloroethylene</td>
<td>41</td>
</tr>
<tr>
<td>1,1,2,2-Tetrachloroethane</td>
<td>0</td>
</tr>
<tr>
<td>Hexachloroethane</td>
<td>4</td>
</tr>
<tr>
<td>Bromoform</td>
<td>0</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>11</strong></td>
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</table>

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
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.
Bibliography


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' 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...
been conducted.

One of the key questions that has been asked is: Do PVC and rigid, hardened PVC materials sorb or leach? PVC materials are known to sorb or leach 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 monomer (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 silting and grout contamination), development of a thorough understanding of site contamination, and the establishment of a thorough understanding of site contamination across the 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 geochmical 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 (as 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 in many instances, 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 cleanse the system of people who are not professionals who cannot exercise professional judgment an 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, we suggest we focus our attention on more serious issues than debating which casing material is best.
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. 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 pecked 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 could contaminate a monitoring well with such chemicals as hydrofuran, 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. Locarbon 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-
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, 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 a 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 water absorbed as a sponge. The process is not an immediate process, but will continue as long as there is a force pushing the molecules into the matrix and capacity exists in the substrate to absorb additional molecules.

In the case of organic molecules or aqueous solution in a monitoring well casing, the rate of adsorption 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 Waals's force) and are dependent on the structure of the molecule at 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 length 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 many molecules can be adsorbed at equilibrium.

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

The first is a paper by Barcelona (1983), which demonstrated the magnitude of adsorption of organics to various polymeric tubing materials associated with sampling equipment.

Barcelona's experiments involved only fresh LD 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. His experiments are valid for sample tubing material and conclusions that these materials (except Teflon) contain 50 percent foreign ingredients (plasticizers) indicated the formulation to produce the necessary flexibility.

The second experimental work performed by
the rigid PVC. If the chemical were trichloroethylene, the maximum sorbed by the rigid PVC would be 6 percent. None would be sorbed by 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 adsorption issue. This series of experiments address the absorption of organic solvent in 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 concentration. Because this new water is in contact with the already-saturated surface of the well casing for as short a time as one hour, and probably no longer than 24 hours, the key issue is how much sorption takes place under those conditions. In both cases, and for all materials exposed, net sorption is nominally zero. While admittedly this will be some experimental error associated with these results 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 stick
- 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 engineers, should not end up like Louis Agassiz, the 19th cent. 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.

References

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 these 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 situations. What are the waste materials that we’re dealing with? What is the ability of that particular casing material to work well in the environment that it’s going to be exposed to? If it doesn’t have long life for its intended purpose, why put it in? Why go out and put in another 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 selected facilities is more often than not we don’t have an adequate purging.

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

These are questions that are posed to me, the regulator.

The point that I’m making here is that in this situation the phthalates may be or may not be coming from 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 time.

Sometimes as much as seven casing volume been pumped out of a particular well, other times a very small casing volume. Phthalates show up at different concentrations, 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 material over the other, but I do have a strong opinion that we should always be looking at the most compatible casing material for a particular situation.

There’s another thing that causes some interest confusion at these particular locations. We’re only purging out these wells once every three months, on a very sampling basis.

Is the well purge adequate with that kind of residence time? With higher yield wells, the residence time probably isn’t going to be that long, even when we don’t go out...
purge the well except at three- and four-month intervals. In lower yield situations, the residence time could be a lot longer. What we're seeing is that the 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 correction program for 20 years longer...

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.

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 contami-
quidit~ s;~-z~ple q:cn if pizri~~~~~ .7Lk-..r--.

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're 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.
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. 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 supplies. 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. 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. 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. 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 discussion 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 the...
physical, chemical, and biological aspects of the subsurface environment are 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 p. 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 stability of volatile compounds and the chemical speciation of many dissolved chemical constituents. Pressure and temperature effects on the carbonate system may shift the pH and redox potentials and affect the chemistry of iron, manganese, sulfur, oxygen, and other mineral equilibria. Gibb et al. 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.

In addition to altering water chemistry and subsurface microbiology, sampling can influence the temperature and pressure. Water 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 studied three types of well casing exposed under water, static and pressure. Certain samples were covered with steel, polypropylene, other plastics and inert materials. Water-soiluble polymer additives or reagents may be used to avoid contamination. Surface porosity of the pipe material, the kind of leaching from the pipe, 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 routine sampled in response to regulatory requirements. Sampling taps are located at the well head and at various points through the distribution systems for obtaining samples from which to analyze the inorganic and bacterial constituent 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, chlorine, and chlorinated hydrocarbons.

Due to the possibility of 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 point throughout the distribution system. An attempt to develop a mass balance of organic compounds delivered to and obtained from a water distribution system would be desirable; however, the frequently used indicator of organic content, dissolved organic carbon (DOC), is not recommended. Most methodology for determining DOC do not include volatile constituents and rarely identify 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.

Surface 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...
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: "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, excess water can remain at dangerously low water levels for days or even months. Also, if the casing 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 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 one of 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 free 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 proven 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 seal (or mixtures that expand) cement is used. Solids in 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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p:rmps, and the sampling devices should be 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. Holz recently reported on the bias 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 cost 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 a 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 unnoticeable, 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.

References

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 (51 mm) I.D. by 2¾-inch (60 mm) O.D. The stainless steel was "Armo Welded 2-inch Type 316," 2½-inch (63 mm) I.D. by 2¾-inch (60 mm) O.D. The polytetrafluoroethylene (virgin PTFE) was 2½-inch (52 mm) I.D. by 2¾-inch (60 mm) O.D. All coupons were cut to a length of 55 mm, which produced a surface area of 100 cm² per coupon. Each coupon was then cut once lengthwise to allow placement into a 257 mL jar. The tube edges were not considered to be a factor in this study.

Exposure Jars: The exposure jars were "Quercia Clear with TFE-Lined" screw caps 25 mL capacity (actual 260 mL with no head space). These jars were...
obtained from Fisher Scientific, catalog #05-230-7D. All jars with liners were covered with foil to eliminate 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 (DCE), toluene and chlorobenzene at a concentration of 10 ppb each was prepared in distilled/deionized water. A second spiking solution was prepared containing 0.5 ppm trichloroethylene (TCE) in distilled/deionized water. This separate spike was prepared because of TCE'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 sterilized 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 aliquotted 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 reservation. 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 1.3 m x 2 mm, 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 LC-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:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>methylene chloride</td>
<td>133 ppb</td>
</tr>
<tr>
<td>1,2-dichloroethane</td>
<td>126</td>
</tr>
<tr>
<td>trans-1,2-dichloroethylene</td>
<td>128</td>
</tr>
<tr>
<td>trichloroethylene</td>
<td>147</td>
</tr>
<tr>
<td>toluene</td>
<td>87</td>
</tr>
<tr>
<td>chlorobenzene</td>
<td>110</td>
</tr>
</tbody>
</table>

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
Working standards were prepared from a stock of addition of the stock into pure water. The three-point curve was prepared initially at the beginning 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 showed 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. Analysis 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
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 ppm 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 ppm contaminated water for seven days and 24 hours.

Acknowledgment

This project was funded by Waste Management Inc. The authors wish to acknowledge C. Blackley, J. Lummls, N. Cole and T. Buedel for their assistance in conducting these experiments.

References


The authors are employed by Radiant Corp., P.O. Box 1300, Research Triangle Park, NC 27709.
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. Homola 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), polyethylene, and stainless steel well casing when exposed to dissolved volatile organic hydrocarbons of approximately 1000 ppm concentrations (Sykes 1986). The U.S. Environmental Protection Agency (EPA) 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 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 into two slots, as well as being cut at right angles to the slots. These sections were completely submerged in premium, unleaded regular, and leaded regular grades of 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, photograph 1 (premium gasoline), photograph 2 (unleaded regular), photograph 3 (leaded regular), and photograph 4 (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). The fragments on the "cut face" of each of the samples show no alteration from long-term exposure to 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.

Therefore, "The question is not what you see, it's what you don't see." The EPA and state agencies should recognize such confirmation data and not make unsubstantiated conclusions such as the deterioration of the use of PVC casing and screen in the presence of gasoline.

References


Biography Sketch

Gene J. Schmidt is director of Ground Water Management in the Environmental Affairs and Safety Department of the Anoco Corp. (P.O. Box 375, Stillwater, OK 74074).
Well Construction and Purging Effects on Ground-Water Samples

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Water Survey Division, Illinois Department of Energy and Natural Resources, Champaign, Illinois 61820-7407

Abstract

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 hydrocarbons, 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

1. 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 hydrocarbons, 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

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The effects of drilling fluids, grouts, or well casing interactions with the geologic formation or ground water are
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 (8) 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 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 alurry seals of 2–5 ft were placed in the bore holes above the sand pack of the site 1 wells. The alurry 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 inflow. 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 casing seal from the top of the heaving material to the land surface.

Table I. Field Installations Data

<table>
<thead>
<tr>
<th>location</th>
<th>material</th>
<th>depth of screened interval (below land surface), ft</th>
</tr>
</thead>
<tbody>
<tr>
<td>site 1 (upgradient)</td>
<td>PVC</td>
<td>36.5–38.5</td>
</tr>
<tr>
<td>site 1 (downgradient)</td>
<td>stainless steel (304)</td>
<td>34.5–35.5</td>
</tr>
<tr>
<td>site 1</td>
<td>PTFE</td>
<td>35.5–37.5</td>
</tr>
<tr>
<td>site 2 (upgradient)</td>
<td>stainless steel (304)</td>
<td>28.0–29.0</td>
</tr>
<tr>
<td>site 2</td>
<td>PTFE</td>
<td>28.0–29.0</td>
</tr>
<tr>
<td>site 2 (downgradient)</td>
<td>PVC</td>
<td>32.5–34.5</td>
</tr>
<tr>
<td>site 2</td>
<td>gas-drive sampler (Teflon/Al oxide)</td>
<td>30.75–32.0</td>
</tr>
<tr>
<td>site 2</td>
<td>PVC</td>
<td>40.5–42.5</td>
</tr>
<tr>
<td>site 2</td>
<td>stainless steel (304)</td>
<td>40.5–42.5</td>
</tr>
<tr>
<td>site 2</td>
<td>gas-drive sampler (Teflon/Al oxide)</td>
<td>41.25–42.5</td>
</tr>
</tbody>
</table>

*Materials used in the study were as follows: PVC, rigid polyvinyl chloride (vinyl chloride) schedule 40 NSF approved for potable water use; SS, 304 stainless steel; PTFE, poly(tetrafluoroethylene) (PTFE) (Teflon, Du Pont).
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 obtainable 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 the upgradient and downgradient ground locations. Improper well purging can obviously cause gross bias in ground-water monitoring results that far exceed those due to materials' 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 high salinity 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

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

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Dissolved Ferrous Iron, mg L−1</th>
<th>Dissolved Sulfide, mg L−1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upgradient</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVC</td>
<td>0.03</td>
<td>0.12</td>
</tr>
<tr>
<td>SS</td>
<td>0.02a</td>
<td>0.15</td>
</tr>
<tr>
<td>Downgradient</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVC</td>
<td>0.04</td>
<td>4.57</td>
</tr>
<tr>
<td>SS</td>
<td>1.23</td>
<td>4.37</td>
</tr>
</tbody>
</table>

*Method detection limit = 0.02 mg L−1 (accuracy 90% (−10% bias), precision ±15% r.s.d.). *Method detection limit = 0.010 mg L−1 (accuracy 80% (−20% bias), precision ±20% r.s.d.).

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 [S2−, 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, Eh, pH, 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), S2−) 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
The cement grouts should have been placed either after well 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 NaHCO₃ digestion of the aqueous samples prior to analysis (25). 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 affect 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 consistently showed high pH, alkalinity (>90% hydroxyl or caustic), Ω, and Ca²⁺ 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 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.

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

<table>
<thead>
<tr>
<th>Field Site</th>
<th>Upgradient</th>
<th>Laboratory</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH, pH units</td>
<td>12.7</td>
<td>&gt;13</td>
</tr>
<tr>
<td>Alkalinity (OH⁻), milliequiv-L⁻¹</td>
<td>2.6</td>
<td>167</td>
</tr>
<tr>
<td>Sulfate</td>
<td>19.0</td>
<td>1069</td>
</tr>
<tr>
<td>Calcium</td>
<td>2.21</td>
<td>578</td>
</tr>
<tr>
<td>Potassium</td>
<td>26.6</td>
<td>62</td>
</tr>
<tr>
<td>Silicate</td>
<td>5.84</td>
<td>0.7</td>
</tr>
<tr>
<td>Conductivity, μS</td>
<td>1975</td>
<td>11500</td>
</tr>
<tr>
<td>Other species</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.05</td>
<td>0.02</td>
</tr>
<tr>
<td>Aluminum</td>
<td>&lt;0.10</td>
<td>0.17</td>
</tr>
<tr>
<td>Chloride</td>
<td>1.10</td>
<td>1.04</td>
</tr>
<tr>
<td>Iron (total)</td>
<td>0.09</td>
<td>0.10</td>
</tr>
<tr>
<td>Manganese (total)</td>
<td>0.02</td>
<td>&lt;0.02</td>
</tr>
</tbody>
</table>

* Unless otherwise specified, units are mg-L⁻¹.
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 (ci2DCY) 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
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 (μg-L⁻³) range.

Acknowledgments

We thank Mark Sievers, Ed Garske, Mike O'Hearn, and Jim Gibb for their help with various aspects of the project.

Registry No. PTFE, 9002-84-0; PVC, 9002-86-2; SS, 12597-63-1; H₂O, 7732-18-5; Fe, 7440-18-5; S²⁻, 18496-25-8; C, 7440-44-0; 11DC, 75-34-3; C12DCY, 156-59-2.

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Received for review October 11, 1985. Revised manuscript received April 1, 1986. Accepted July 22, 1986. We appreciate the support of the USEPA-ESRL, Ada, OK, and USEPA-EMSL, Las Vegas, NV (CR8099690), and the Campus Research Board of the University of Illinois.
Sampling Tubing Effects on Groundwater Samples

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Volatile organic compound poses a challenge to groundwater sampling protocols, since they can be lost as a water sample extracts 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, trichloro-
chane, 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 CO₂ or N₂ 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 exposure are more difficult to evaluate. Matrix interferences (4), volatilization losses (5, 6), leaching (7–9), and sorptive (6, 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 (9). 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 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 "adsorbs" 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 (∼10 mL.m⁻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 cm 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 exposure. 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.mm⁻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 (4).

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 for a few days before being exposed to the atmosphere.

The analytical solvents used were ACS reagent grade or Distilled in Glass (Duracid and Jackson) and were used without further purification. Standards were made up in doubly distilled water or in 10⁻³ M NaHCO₃ 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) (PEG) (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...
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 (µg 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 3 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 CHCl₃ 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 ±5% relative standard deviation at ±5% accuracy achieved in the course of all of these experiments. The results demonstrate the rapid sorptive removal of CHCl₃ by both PVC and silicone tubing to the extent that 80% depletion of the dissolved compound 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 CHCl₃ 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 CHCl₃ into distilled water took place almost immediately. The amount desorbed constituted less than 10% of the total CHCl₃ 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 CHCl₃ sorbed (20–45% of maximum) in 5 min than did PVC and silicone. TFE, which sorbed the least amount of CHCl₃ 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 CHCl₃ 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 ex-
Table I. Leachable Organic Matter and PEG Sorption

<table>
<thead>
<tr>
<th>Material</th>
<th>Total Carbon, mg-C/m²</th>
<th>Volatile Carbon, % of Total</th>
<th>% PEG Sorbed of 10 ppm-C Spike</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIL</td>
<td>30.6</td>
<td>7.2</td>
<td>N.D.</td>
</tr>
<tr>
<td>PVC</td>
<td>33.2</td>
<td>20.0</td>
<td>N.D.</td>
</tr>
<tr>
<td>PE</td>
<td>20.6</td>
<td>5.7</td>
<td>N.D.</td>
</tr>
<tr>
<td>PP</td>
<td>23.5</td>
<td>8.6</td>
<td>N.D.</td>
</tr>
<tr>
<td>TFE</td>
<td>0.66</td>
<td>&lt;0.5</td>
<td>20</td>
</tr>
</tbody>
</table>

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

Table II. Sorption of CHCl₃ with Increased Organic Background

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>CHCl₃ Sorption, µg/m²</th>
<th>CHCl₃ Sorption, µg/m²</th>
<th>% of CHCl₃ Sorption</th>
<th>% Diff</th>
</tr>
</thead>
<tbody>
<tr>
<td>Teflon</td>
<td>40</td>
<td>42</td>
<td>26</td>
<td>+5</td>
</tr>
<tr>
<td>PP</td>
<td>61</td>
<td>52</td>
<td>44</td>
<td>-15</td>
</tr>
<tr>
<td>PE</td>
<td>71</td>
<td>52</td>
<td>50</td>
<td>-27</td>
</tr>
<tr>
<td>PVC</td>
<td>125</td>
<td>130</td>
<td>40</td>
<td>+45</td>
</tr>
<tr>
<td>SIL</td>
<td>139</td>
<td>133</td>
<td>97</td>
<td>+17</td>
</tr>
</tbody>
</table>

* 61-min exposure runs.  # Calculated on the basis of complete sorption of CHCl₃ from solution.

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

<table>
<thead>
<tr>
<th>Material</th>
<th>Low Carbon Background</th>
<th>High Carbon Background</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Max. Sorption, µg/m²</td>
<td>Max. % Desorbed, %</td>
</tr>
<tr>
<td>TFE</td>
<td>237</td>
<td>13</td>
</tr>
<tr>
<td>PP</td>
<td>354</td>
<td>17</td>
</tr>
<tr>
<td>PE</td>
<td>483</td>
<td>18</td>
</tr>
<tr>
<td>PVC</td>
<td>622</td>
<td>8</td>
</tr>
<tr>
<td>SIL</td>
<td>624</td>
<td>2</td>
</tr>
</tbody>
</table>

* Sorption of 400 ppb halocarbon mixtures from bicarbonate buffered distilled water background.  # 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 Harts (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.
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 sorption 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 dodecane 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 sorbates 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.

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

<table>
<thead>
<tr>
<th>tubing diameter, in.</th>
<th>TFE</th>
<th>PP</th>
<th>PE</th>
<th>PVC</th>
<th>SIL</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/4</td>
<td>4</td>
<td>6</td>
<td>10</td>
<td>14</td>
<td>15</td>
</tr>
<tr>
<td>(4)</td>
<td>(6)</td>
<td>(7)</td>
<td>(17)</td>
<td>(15)</td>
<td></td>
</tr>
<tr>
<td>3/8</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>(2)</td>
<td>(2)</td>
<td>(2)</td>
<td>(3)</td>
<td>(3)</td>
<td></td>
</tr>
<tr>
<td>1/2</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>(0.5)</td>
<td>(0.7)</td>
<td>(1)</td>
<td>(2)</td>
<td>(2)</td>
<td></td>
</tr>
</tbody>
</table>

* 40 ppb mixture of chloroform, trichloromethane, tetrachloroethylene, and tetrachloroethylene calculated on the basis of initial sorption rates on passage through 15 m of tubing at 100 mL/min. 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/min from a well bore to the land surface. Using conservative initial sorption rates from this study, of approximately 10 µg·m⁻²·min⁻¹, the percent sorptive loss of halocarbon mixtures in transport may be calculated. The calculated initial sorption rates ranged from 3 to 50 µg·m⁻²·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 1/2 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 1/2 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 as 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.

ACKNOWLEDGMENT

The authors appreciate the technical support of Greg George, Mark Brooks, and Pamela Reaners. The comments of James Pankow and Gary Miller were most helpful in preparing the paper. The information and support of various tubing material manufacturers are also appreciated.

LITERATURE CITED

The 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 $T/r$, 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.

The Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR or FTMS) (1-9) is a type of mass spectrometry 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, $\omega_0$,

$$\omega_0 = qB/m$$

or 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, $\omega_0$ (11).

$$F(t) = 2\pi K \exp(-t/r) \cos(\omega_0 t), 0 < t < T$$

In eq 2, $K$ is called (12) the scaling factor and is proportional to the number of ions, $N$, the cyclotron frequency, $\omega_0$, 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 (2, 15, 16) 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 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).

$$A(\omega) = \frac{K}{1 + \omega^2/\omega_0^2} \left[ 1 + \exp \left( -\frac{T}{r} \right) \right] \times$$

$$\left[ (\omega - \omega_0) \sin \left( (\omega - \omega_0)T \right) - \cos \left( (\omega - \omega_0)T \right) \right]$$

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 $T/r = 0$) to 2/T (when $T/r = \infty$) (17).

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

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Received for review September 10, 1984. Accepted November 13, 1984. This work was funded in part by the USEPA-NSERL under cooperative agreement No. CR809966-01 and by the Campus Research Board of the University of Illinois, Urbana-Champaign.
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 flown 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 macroporous resin beads contained in a small glass column. The sorbed organic compounds were then eluted with diethyl ether. 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 the 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), lipid 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 macroporous resin was obtained as 20-60 mesh beads from Rohm and Haas, 5000 Richmond St., Philadelphia, Pa. 19127. 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 5/8 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 x 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 ul 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 Vanaa 1200 gas chromatograph were employed with the Varian 1400 gas chromatograph interfaced to the Du Pont 21-90 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 to magnetic tape by the minicomputer. These programs were used to aid in the interpretation of each mass spectrum. A visual display of the mass spectrum on a cathode ray tube was used for inspecting line diagrams of each mass chromatogram to determine the 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 library.
Peak Index of Mass Spectra obtained 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, adapters, and valves are standard fittings except the upstream connection of the polymer tube to the valve's 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 IUD-2 resin into the glass column. A second glass wool plug is inserted near the stopcock 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 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 approximately 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 expedient 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.

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 N₂ 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,

\[
\frac{(P_i) \times (S) \times (V_i)}{(V_i) \times (V_{w})} = \frac{\mu g}{\text{liter}} = \text{ppb,}
\]

where

- \( P_i \) = peak area of the \( i \)th chromatographic peak in cm²,
- \( S \) = detector response factor in μg/cm²,
- \( V_i \) = volume of ether concentrate in μl,
- \( V_w \) = volume of water passed through the polymer tube in liters, and
- \( \text{ppb} \) = parts per billion by weight of the \( i \)th component in the water.

The total contamination equals \( \sum P_i \) ppb, 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 N₂ 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.
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.
high level of contamination from all polymers 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 patterns 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 most 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...
particular component cannot be iden. ced positively be.
cause of unresolved gc peaks, or a major contaminant
makes a minor component.

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

Static vs. Flowing Water. Interpretation of several ex-
perimental 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 obser-
vations, 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 valid-
ity 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 1/2-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 ex-
pended polymer surface area are held constant.

Previous investigations by others (29, 43, 44) have rel-
elated 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 * | Mass spectral data | Retention time, min | Concentration, ppb | % Total Concentration |
| 1 | I | 3.40 | 3.60 | 0.66 | 16.14 | Butylcyclohexanate |
| 2 | CL | 4.00 | 3.95 | 1.72 | 16.02 | 2-Ethylhexanol |
| 3 | CL | 4.50 | 4.52 | 4.62 | 43.01 | o-Cresol |
| 4 | CL | 5.45 | 5.40 | 0.24 | 2.23 | 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 | 1.76 | Unidentified |
| 11 | 8.40 | 0.40 | 1.02 | Unidentified |
| 12 | CM | 9.70 | 9.60 | 0.08 | 0.74 | Diethylphthalate |
| 13 | I | 10.00 | N | 1.45 | 13.49 | Butylcyclohexanate |
| 14 | CL | 11.50 | 11.80 | 0.08 | 0.74 | Diethylphthalate |
| 15 | CL | 12.50 | 12.40 | 0.05 | 0.46 | Diethylphthalate |

* See Figure 2. a 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. b Retention time of unknown gc peak. c Retention time of authentic sample. d Indicates that an authentic sample check was not made. e Concentration of the contaminant in the water in parts per billion. f Weight.

| Table II. Total Contamination and Identifications of Major Contaminants in Water Passed Through Various 25-Ft Lengths of 1/2-in. I.D. Polymer Tubes at 60 Mil/Min |
|-----------------|-----------------|-----------------|-----------------|
| Polymeric tube | Total contamination, ppb | Major contaminants (gc peak no.) |
| General chemical PVC | 11 | o-Cresol/3 | Naphthalene/4 | BOF/13 | 2-Ethylhexanol/2 | 2-Ethyl-l- methylphenoxy/3 |
| Laboratory grade PVC | 4 | 2-Ethyl hexanol/1 | Stearic acid/12 | DIBP/9 | BOF/6 | 3,4-Dimethoxy acetonaphthene/4 |
| Processed milk PVC | 6 | 2-Ethyl hexanol/2 | DIBP/9 | p-Nonyl phenol/10 | DEHP/11 | DEP/3 |
| 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 acetonaphthene/5 | Unkn, n | DIBP/8 | DBP/9 |
| Hospital-surgical PVC | 6 | 2-Ethyl hexanol/4 | Lauric acid/9 | DEHP/17 | DIBP/11 | Phthalic anhydride |
| Garden hose | 170 | Alcohol/2 | Alcohol/3 | Alcohol/4 | DBM/7 | DIBP/10 |
| Black latex | 26 | Decyl amine/2 | Unkn, n | Unkn, n | DIBP/7 | Butylchloroacetate |
| Polyethylene | 1 | Unkn, n | Unkn, n | Unkn, n | Unkn, n | Unkn, n |
| Polypropylene | 2 | Unkn, n | Unkn, n | Unkn, n | Unkn, n | Unkn, n |

* Abbreviations used for common contaminants: BOF = butylcyclohexanate; DIBP = diisobuty1phthalate; DEHP = di-ethylhexyl phthalate; CL = cl-ethylhexyl phthalate; BGBP = dibutylglycolylbutylphthalate; BOF = butylcyclohexanate; DIBP = diisobuty1phthalate. DIBP = diisobuty1phthalate. Refer to appropriate chromatograms in Figures 2-3. * Mass spectra and retention times used to tentatively identify unresolved gc peaks as a mixture of alcohols. * Insufficient water sampled to make any positive identifications.
DrsNo: CLEJ-00574 - 12.05-

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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 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 in 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 this apply 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 very simple and portable extraction column, accurate on-site sampling of a production solution is possible by connecting an extraction column parallel to the 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                  | GC  | LB  | PM  | FB  | FU  | HS  | GH  | BL  |
| 2-Ethylhexanol               | X   | X   | X   | X   | X   | X   | X   | X   | Impurity or transformation* |
| C10 satd. alcohol            |     |     |     |     | X   |     |     | X   | Possibly octanol           |
| Unkn. alcohols               |     |     |     |     |     |     |     | X   | Not present in PVC         |
| o-Cresol                     | X   |     |     |     |     |     |     |     | Suspected stabilizer        |
| p-Ethylphenol                | X   |     |     |     |     |     |     |     | Same                        |
| o-Phenylphenol               | X   |     |     |     |     |     |     |     | Same                        |
| 2-Ethyl-4-methylphenol       |     |     |     |     |     |     |     |     | Same                        |
| 2,4-Di-tert-butyl-4-methylphenol |   | X   |     |     |     |     |     |     | Same                        |
| 2,5-Di-tert-butyl-4-methylphenol | X |     | X   |     |     |     |     |     | Same                        |
| p-Nonylphenol                |     |     |     |     | X   |     |     |     | Same                        |
| p-Dodecylphenol              |     |     | X   |     |     |     |     |     | Same                        |
| p-BuButylphenol              |     |     |     |     | X   |     |     |     | Same                        |
| Ethyl acetate                |     |     |     |     | X   |     |     |     | Same                        |
| Butylchloroacetate           | X   | X   |     |     |     | X   |     |     | Suspected stabilizer        |
| Naphthalene                  | X   |     | X   |     |     |     |     |     | Highly toxic                |
| 2-Ethylhexanal               | X   |     |     |     |     |     | X   |     | Common impurity             |
| 2,4-Dimethoxyacetophenone    |     |     |     |     | X   |     |     |     | Same                        |
| Decylamine                   |     |     |     |     |     | X   |     |     | Transformation of Zn salt   |
| Stearic acid                 |     |     |     |     |     |     |     | X   | Same                        |
| Lauroic acid                 |     |     |     |     |     |     |     | X   | Same                        |
| Myristic acid                |     |     |     |     |     |     |     | X   | Same                        |
| Phthalic anhydride           | X   |     |     |     |     |     |     |     | Impurity or transformation* |
| Butylbenzoate                |     |     |     |     | X   |     |     |     | Known plasticizer          |
| Butylsuccinimide             |     |     |     |     |     |     |     | X   | Suspected plasticizer       |
| n-Butylmaleate               |     |     |     |     |     |     |     | X   | Same                        |
| Ethylglycolylisopropylphthalate |   |     |     |     |     |     |     | X   | Known plasticizer          |
| Butylglycolylisobutylphthalate |     |     |     |     |     |     |     | X   | Same                        |
| Dimethylphthalate            | X   |     |     |     |     |     |     |     | Same                        |
| Diethylphthalate             | X   | X   | X   |     |     |     |     |     | Same                        |
| Dibutylphthalate             | X   | X   |     |     | X   |     |     | X   | Same                        |
| Diisobutylphthalate          | X   | X   |     |     | X   |     |     | X   | Same                        |
| Di-2-ethylhexylphthalate     | X   | X   | X   |     |     |     |     | X   | Same                        |

*Abbreviations are: GC = general chemical PVC; LB = laboratory PVC; PM = processed milk PVC; FB = food-beverage PVC; FU = FDA-USDA |
| HS = hospital-surgical PVC; GH = garden hose plastic; BL = black latex tube. X indicates that the contaminant was found in the designated |
| 1Highly toxic refer to materials found in solvents, starting chemicals, and solubilizers 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 (8, 15, 37, 39); while little is known about cumulative toxicity and the synergistic effect of mixtures (3), some investigators (3, 32, 33) 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

The authors thank Neil G. Johansen, Perkin Elmer Corp., for providing high resolution SCOT column separations of two mixtures. The facilities for this research were generously provided by the Ames Laboratory of the USABC and Iowa State University Energy and Mineral Resources Research Institute, Ames, Iowa 50010.

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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 non-sterile conditions. The extent of loss was small, however, considering the length of the equilibration period. 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; Fayez 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), hexa-hydro-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; Fayez 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. 1977; 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 benzenes (PCBs) from water and waste water. PCBs are hydrophobic organic chemicals with large octanol-water partition coefficients ($K_{ow}$) in the 10$^5$ range (Velth et al. 1975). $K_{ow}$ values have been found to correlate with partitioning of organic chemicals between aqueous solution and the organic matter in soil and sediments (Raffelhoff 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.
recently, data were obtained at this laboratory on desorption of chloroform. in 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, 1,2,2-trichloroethane and tetrachloroethylene. Concentrations were in the 24 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 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, trichloroethylene, benzene, chloroform, 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 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 9 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 explo-

sires through PVC membrane filters. These results indicated that bonds were not adsorption, but are associated with PVC, whereas materials tested were found with cellulose acetate and polypropylene membranes. Legett, personal communication. Braunstein et al. observed hydrogen bonding of 2.4-DNT to tannins in lose, 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 Kₚₗ 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 1.36 for HMX. Based on previous work by this laboratory using PVC filter membranes and the Kₚₗ 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 or 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, cyclohexa-
none, 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 in low concentration (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 60 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
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 used to destroy HMX and RDX in solution, HgCl₂ (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 MgCl₂ and 175 mg/L CaCl₂ were added. To lower the dissolved oxygen content, samples were purged with N₂ gas for several minutes and were then placed in a glove box that was flushed several times with N₂ gas and purged with N₂ 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 small amount of each sample was chosen as a control. 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 leaked 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 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 O₂ 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 (66 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 was not statistically significant.

### Table 1

<table>
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<th>Sample</th>
<th>TNT Mean Initial</th>
<th>Final*</th>
<th>RDX Mean Initial</th>
<th>Final*</th>
<th>HMX Mean Initial</th>
<th>Final*</th>
<th>DNT Mean Initial</th>
<th>Final*</th>
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<td>Glass control</td>
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<td>511 ± 13</td>
<td>1977 ± 22</td>
<td>2011 ± 15</td>
<td>305 ± 28</td>
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<td>611 ± 29</td>
<td>612 ± 15</td>
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<td>404 ± 24</td>
<td>398 ± 27</td>
<td>412 ± 44</td>
<td>427 ± 20</td>
<td>441 ± 10</td>
<td>420 ± 17</td>
<td>544 ± 6</td>
<td>502 ± 4</td>
</tr>
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<td>427 ± 20</td>
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<td>420 ± 20</td>
<td>404 ± 15</td>
<td>402 ± 10</td>
<td>384 ± 7</td>
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*After 80 days incubation
was minimal. However, it is not clear what mechanism accounts for the increased loss of HMX 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 80 casing manufactured 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 analyses 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

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<th>Day of</th>
<th>PVC or</th>
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<th>Atmosphere</th>
<th>Initial pH</th>
<th>Salts</th>
<th>RDX (µg/L)</th>
<th>HMX (µg/L)</th>
<th>DNT (µg/L)</th>
<th>DO (mg/L)</th>
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Sterile = samples were incubated with bactericidal agent
Non-sterile = samples had no bactericidal agent added
AMB O₂ = samples were incubated in ambient atmosphere, in presence of O₂
LOW O₂ = samples were incubated in glove box flushed with N₂ gas
Salts - = no salts added
Salts + = MgCl₂ + CaCl₂ salt solution added
There was an average loss of 18.0 percent for TNT: the mean initial concentration was 637 μg/L and the mean final concentration was 53 μg/L. Analysis of variance of the 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 Cl. Analysis of variance also indicated that the interaction of PVC and sterility (the term DC) was significant. This 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 stabilizers).

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 HPLC. 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 50 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

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<th>F</th>
<th>Level of significance</th>
<th>Term</th>
<th>DF</th>
<th>Mean square</th>
<th>F</th>
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</table>

**S** = presence or absence of MgCl₂ and CaCl₂ 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 PI), oxygen content (the term O2), 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 2042 μg/L. Although the loss appears to be slightly less for the glass controls (X = 1953 μg/L or 6.1 percent less) than for the samples with PVC casing (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 no 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 (X = 544 μg/L) to day 25 (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 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 incremental 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. vited in these experiments should not limit the use of PVC for this application.

Long-term leaching studies using local groundwater 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 casing is acceptable for ground water monitoring for low levels of these munitions.

Acknowledgments

This project was funded by the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) under reimbursable project number 82-D-8. We wish to thank B.T. Foley for analytical assistance. Dr. J. Sando and Dr. L. Eng for assistance in formulating the scope of the project. Dr. H.C. Haggard, M. Stutz and D.C. Leggett for technical comments on this and the original manuscript. The contents of this report are not to be used for advertising or promotional purposes.

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