CRITERIA FOR SELECTING MONITORING DEVICES AND INDICATOR
PARAMETERS FOR DIRECT PORE-LIQUID SAMPLING OF PETROLEUM
HYDROCARBON CONTAMINATED SITES

by

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U.S. ENVIRONMENTAL PROTECTION AGENCY

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NOTICE

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INTRODUCTION

In recent years, there have been increasing requirements for
vadose zone monitoring.

Vadose zone monitoring devices in use include a variety of in
situ samplers to collect pore-liquids under saturated or
unsaturated conditions. Pore-liquid samples containing petroleum
hydrocarbons are generally considered as direct evidence of
contaminant migration; pore-liquid sampling is required by
regulation for land treatment units. This report describes these
samplers together with their advantages and disadvantages. It
also describes the application of indicator parameters and tracer
chemicals to monitoring petroleum hydrocarbon contaminated soils.

THE VADOSE ZONE

The vadose zone is the hydrogeological region extending from the
ground surface to the principle water table. Other commonly used
terms for this region are the "unsaturated zone" and the "zone of
aeration." These other terms do not suggest the existence of
locally saturated conditions above the principle water table.
Saturated or near-saturated conditions can develop when pore-
liquids collect on low permeability lenses that are often called
perching layers. Most pore-liquid flow through the vadose zone
is under unsaturated conditions and is primarily controlled by

negative pore-liquid pressure gradients
(negative pore-liquid pressures are referred to as pore-liquid tensions).

Chemical species released at or near the land surface generally migrate to some degree through the vadose zone. Analyses of vadose zone liquids and gases can provide an early warning of potential ground-water pollution from such releases. This early warning can provide a means to mitigate potential problems prior to ground-water degradation (1,2)

PORE-LIQUID SAMPLERS

Vadose zone liquids from soil samples are usually extracted in the laboratory. Alternatively, the mobile pore-liquids may be sampled directly and repeatedly from "undisturbed" soils using permanently installed in situ pore-liquid samplers. The most obvious difference between these two techniques is that soil sampling is a destructive process which prevents repetitive sampling from the same location. More importantly, the two techniques do not sample the same types of liquid (3,4). In situ samplers are capable only of sampling pore-liquids held at tensions of up to about 60 centibars (cb) (5). Soil sampling with subsequent pore-liquid extraction provides liquids which may be held at tensions of up to several bars, depending on the extraction technique. Extraction under several bars of pressure

may strip off cations preferentially sorbed in electrical double layers, sorbed organics, and even components of the soil. These species may not be present in the same concentrations (absolute or relative) in samples provided by in situ pore-liquid samplers. In situ pore-liquid samplers are "point samplers" and can be effectively used to indicate relative changes in the amount of solute flux. Caution must be exercised when quantitative results are desired since the variability of these measurements must be appropriately established.

INDICATOR PARAMETERS

The concept of using indicator parameters to identify complex systems with simple but representative elements has been in practice for a long time. For example, pH measurements of water samples can indicate the presence of an acid or a base while specific conductance measurements can indicate the presence of ionized salts in a water sample. More recently, phenanthrene has been used as a indicator for the presence of creosote contamination in investigations at past and current sites of wood treating facilities. It is the single most abundant chemical in creosote and the most water soluble, and, therefore, the most mobile.

The indicator parameter itself can vary depending on the needs or goals of a particular program. As an example, in California,

when a site is suspected to be contaminated, the initial site investigation typically samples and analyzes the site soils for ten or more Title 22 (California Code of Regulations) metals. These metals are then used as indicator parameters to determine if the site soils are contaminated. If, as a consequence of these findings, remedial action (particularly excavation and removal), is found to be warranted, then as few as three of these metals can be used as indicator parameters for evaluating potential work health and safety hazards and for identifying requirements that would assure adequate worker protection.

Indicator parameters have been powerful tools for assisting in the measuring of complex systems using simple techniques. It is, therefore, natural to identify their potential usefulness for monitoring recently recognized environmental issues, such as the complex petroleum hydrocarbon contaminated sites.

Reviewing the definitions of the terms "indicator" and "parameter" in the precise dictionary sense will assist in understanding the factors which must be considered in selecting a chemical or group of chemicals that can properly be termed "indicator parameters." Webster's defines an "indicator" as a substance that is so strictly associated with particular conditions that its presence is a direct indication of the presence of these conditions. The term "parameter" is defined as a characteristic element or constant factor which describes a

particular population. Thus, an indicator parameter is a substance, a chemical or group of chemicals, with characteristics indicative of the presence of a particular population. In simple terms, where the indicator parameters are found, then a particular population is known to be present. These definitions help to clarify what determines an indicator parameter. However, numerous factors must be considered in selecting indicator parameters appropriate for direct pore-liquid sampling applications.

This report reviews various in situ samplers and includes relevant literature citations. Some of the described samplers are not commercially available at this time. However, they may have been available in the past and may be found at sites with established vadose zone monitoring programs. Some of the samplers can be fabricated. There are numerous qualifiers, hints, and warnings which should accompany the description of each sampler. We depend on the reader to review cited references to obtain complete descriptions of the covered samplers. The applications and limitations of many of the samplers presented here were described in a series of articles by Everett (6), Everett et al. (7), Wilson (7), Wilson (8), Everett et al. (9), and Everett and McMillion (5). This report extends and updates these articles.

SELECTING PORE-LIQUID SAMPLERS

This report also presents a discussion of factors that affect
selection of indicator parameters and tracer chemicals. The
concepts developed and explained are intended to aid in selecting
and identifying chemicals that can be used as indicator
parameters for monitoring petroleum hydrocarbon contaminated
sites.

IN SITU PORE-LIQUID SAMPLER CATEGORIES

In situ samplers extract liquids from saturated and unsaturated
soils. Most samplers designed to sample from unsaturated soils
also sample from saturated soils. This is useful in areas where
the water table fluctuates, resulting in alternating saturated
and unsaturated conditions. In contrast, samplers designed for
sampling from saturated soils cannot be used in unsaturated
conditions. This is because the negative pore-liquid pressures
in unsaturated soils prevent liquid from moving into air-filled
cavities at atmospheric pressures (Richard's Outflow Principle).
Also, the openings in saturated samplers are too large to prevent
air from entering the samplers when suctions are applied. Using
this distinction, the types of pore-liquid samplers have been
categorized as follows:

- suction samplers (unsaturated/saturated sampling)

- experimental suction samplers (unsaturated/saturated sampling)

- experimental absorption samplers (unsaturated/saturated sampling)

- free drainage samplers (saturated sampling)

- perched ground-water samplers (saturated sampling).

The term "pore-liquid" could be applicable to any liquid residing in porous media, both saturated and unsaturated, ranging from aqueous pore-liquids to oil. However, all of the samplers described in this report were designed to sample aqueous pore-liquids only. The abilities of these samplers to collect other pore-liquids may be quite different than those described.

CRITERIA FOR SELECTION OF PORE-LIQUID SAMPLERS

The choice of appropriate sampling devices for a particular location is dependent on various criteria (see Table 1). Well-structured soils have two distinct flow regions including macropores (e.g. interpedal openings, cracks, burrows, and root traces) and micropores (e.g. interpedal openings between soil

grains). Under saturated conditions, liquids move more rapidly

through macropores than through micropores. Because of this,

contaminants transported by free drainage may bypass the finer

pores. Consequently, pore-liquids in macropores may have

different chemistries than those in micropores (10). This

difference can be attributed to the fact that oxygen contents of

macropores can change in a matter of hours during an infiltration

event, whereas micropores may remain suboxic regardless of flow

conditions (11). In addition, micropores are less susceptible to

leaching than macropores (2, 12, 13, 14). Because of these

differences, sample chemistry can vary widely from location to

location and from time to time depending on the amount of liquid

drawn from these two flow systems. Therefore, it is prudent to

consider using both unsaturated and free drainage samplers in a

sampling program, depending on site characteristics.

Table 1. Criteria for Selecting Pore-Liquid Samplers

---

1. Required sampling depths
2. Required sampling volumes
3. Soil characteristics
4. Chemistry and biology of the liquids to be sampled
5. Moisture flow regimes
6. Required durability of the samplers
7. Required reliability of the samplers
8. Climate
9. Installation requirements of the samplers
10. Operational requirements of the samplers
11. Commercial availability
12. Costs

Specific guidelines for designing vadose zone pore-liquid
monitoring networks have been discussed by Wilson (1), Wilson
(15), Everett (7), Wilson (8), Everett et al. (7), Morrison (2),
Wilson (16), Everett et al. (9), Robbins and Gemmel (17), Merry
and Palmer (18), U.S. Environmental Protection Agency (19), and
Ball and Coley (20).

SUCTION SAMPLERS (UNSATURATED/SATURATED SAMPLING)

Table 2 presents suction samplers and some of their operational
constraints. In general, a suction sampler consists of a hollow,
porous section attached to a sample vessel or a body tube (see
Figure 1). Samples are obtained by applying a vacuum within the
sampler and collecting pore-liquid in the body tube. Samples are
retrieved by a variety of methods.

The principles of suction sampler operation are as follows.
Unsaturated portions of the vadose zone consist of
interconnecting soil particles, interconnecting air spaces, and
interconnecting liquid films. Liquid films in the soil provide
hydraulic contact between the saturated porous section of the
sampler and the soil (see Figure 1). When a vacuum greater than
the pore-liquid tension is applied within the sampler, a
pressure-potential gradient is created toward the sampler. If
meniscuses of the liquid in the porous segment are able to
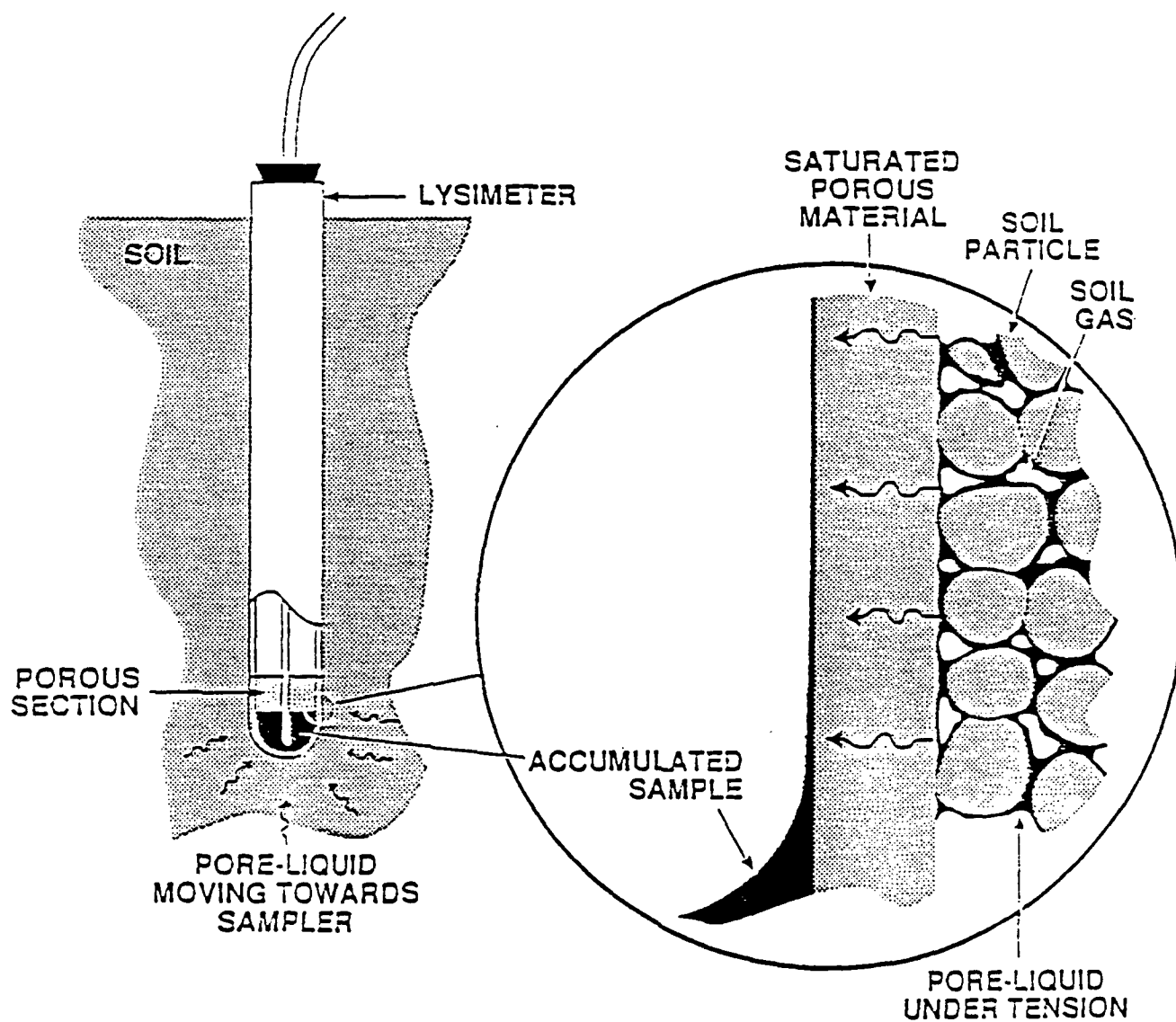
Figure 1. Hydraulic contact between saturated porous
element of a vacuum lysimeter and soil

withstand the applied suction, liquid moves into the sampler.
The ability of the meniscuses to withstand a suction decreases
with increasing pore size and also with increasing hydrophobicity
of the porous segment. This relationship is defined by the
capillary rise equation (21). If the maximum pore sizes are too
large, and/or they are hydrophobic, the meniscuses are not able
to withstand the applied suction. As a result, they break down,
hydraulic contact is lost, and only air enters the sampler.

The ability of a sampler to withstand applied suctions is gaged
by its bubbling pressure (19, 22). The bubbling pressure is
measured by saturating the porous segment, immersing it in water,
and pressurizing the inside of the porous segment with air. The
pressure at which air starts bubbling through the porous segment
into the surrounding water is the bubbling pressure. The
magnitude of the bubbling pressure is equal to the magnitude of
the maximum suction which can be applied to the sampler before
air entry occurs (see air entry values in Table 2). Because the
bubbling pressure is a direct measure of how a sampler will
perform, it is more useful than measurement of pore size
distributions.

As soil pore-liquid tensions increase (low soil-liquid contents),
pressure gradients toward the sampler decrease. Also, the soil
hydraulic conductivity decreases exponentially. These result in
increasingly lower flow rates into the sampler. At pore-liquid

tensions above about 60 cb (for coarse grained soils) to 80 cb (for fine-grained soils), the flow rates are effectively zero and samples cannot be collected (Everett and McMillion) (5). Samplers which have air entry values exceeding the 60-80 cb range are preferred (see Table 2).

Porous samplers with the appropriate air entry values suitable for pore liquid sampling are typically hydrophilic. In situations where aqueous and nonaqueous liquid phases are present, water will be preferentially drawn into (along with dissolved components) the pores of the porous element because of its polarity and relatively high surface tension. Field collection of nonaqueous phase organic liquids using water saturated suction samplers is not possible. However, suction samplers can provide representative samples of the aqueous phase, including dissolved components.

As demonstrated by Neary and Tomassini (23), new samplers may be contaminated with water-soluble cations during manufacturing. In order to reduce chemical interferences from these and other substances on the porous sections, a variety of pre-installation procedures have been developed, including acid flushing (24, 25, 26, 27, 28, 29) Debyle et al. (27) recommend discarding the first one or two sample volumes when sampling dilute solutions with newly acid-flushed, installed samplers. This allows cation exchange between the porous segment and the

TABLE 2. SUCTION SAMPLER SUMMARY

Sampler Type	Porous Section Material	Max. Pore Size (μm)	Air Entry Value (kPa)	Wetting Characteristic	Operational Suction Range (kPa)	Max. Operational Depth (m)

Commercially Available Suction Samplers

Sampler Type	Porous Section Material	Max. Pore Size (μm)	Air Entry Value (kPa)	Wetting Characteristic	Operational Suction Range (kPa)	Max. Operational Depth (m)
Vacuum Lysimeters	Ceramic PTFE Stainless Steel	1.2-3.0 15-30 7	>100 5-10 20	HL HB HL	<60-80 <5-10 <20	<7.5 <7.5 <7.5
Pressure Vacuum Lysimeters	Ceramic PTFE Stainless Steel	1.2-3.0 15-30 7	>100 5-10 20	HL HB HL	<60-80 <5-10 <20	<15 <15 <15
High-Pressure Vacuum Lysimeters	Ceramic PTFE Stainless Steel	1.2-3.0 15-30 7	>100 5-10 20	HL HB HL	<60-80 <5-10 <20	<90 <90 <90
Filter Tip Samplers	Ceramic	1.2-3.0	>100	HL	NA	Unlimited

Experimental Suction Samplers

Sampler Type	Porous Section Material	Max. Pore Size (μm)	Air Entry Value (kPa)	Wetting Characteristic	Operational Suction Range (kPa)	Max. Operational Depth (m)
Cellulose Acetate	Cellulose Acetate	<2.8	>100	HL	<60-80	<7.5
Hollow Fiber Samplers	Noncellulose Polymer	<2.8	>100	HB	<60-80	<7.5
Membrane Filter Samplers	Cellulose Acetate PTFE	<2.8 PTFE	>100 5-10	HL HB	<60-80 NA	<7.5 <7.5
Vacuum Plate Samplers	Alundum Ceramic Fritted Glass Stainless Steel	7 1.2-3.0 4-5.5 7	20 >100 50 20	HL HL HL HL	<20 <60-80 50 <20	<7.5 <7.5 <7.5 <7.5

NA = Not Available
HB = Hydrophobic
HL = Hydrophilic

pore-liquid to equilibrate following acid flushing. Sintered stainless steel samplers used in virus studies are chlorinated and rinsed with a 10% solution of sodium thiosulfate to neutralize free chlorine (30). Other pre-installation procedures (e.g. pressure testing) are described by Everett and McMillion (5) and Timco (31).

Suction sampler installation and sampling procedures are described by U.S. Environmental Protection Agency (19), Soilmoisture (22), Timco (31), Linden (32), Rhoades and Oster (33) Klute (34), Brose et al. (35), Morrison (2), Cole et al. (36), Wengel and Griffen (37), Brown et al. (38), and Chow (39).

Vacuum Lysimeters[1]

Vacuum lysimeters generally consist of a porous cup mounted on the end of a tube, similar to a tensiometer (see Figure 2). A stopper is inserted into the upper end of the body tube and fastened in the same manner as the porous cup or, in the case of rubber stoppers, inserted tightly (19).

A variety of materials have been used for the porous segment including nylon mesh (40), fritted glass (41), sintered glass (42), Alundum®, stainless steel (43), polytetrafluorethylene

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[1]A device used to measure the flux of water within a soil monolith, usually undisturbed; or to collect percolating water for analyses.

HAND SUCTION PUMP

SUCTION LINE

WATER SAMPLE

VACUUM

STOPPER

SAMPLE FLASK

BODY TUBE

POROUS CUP
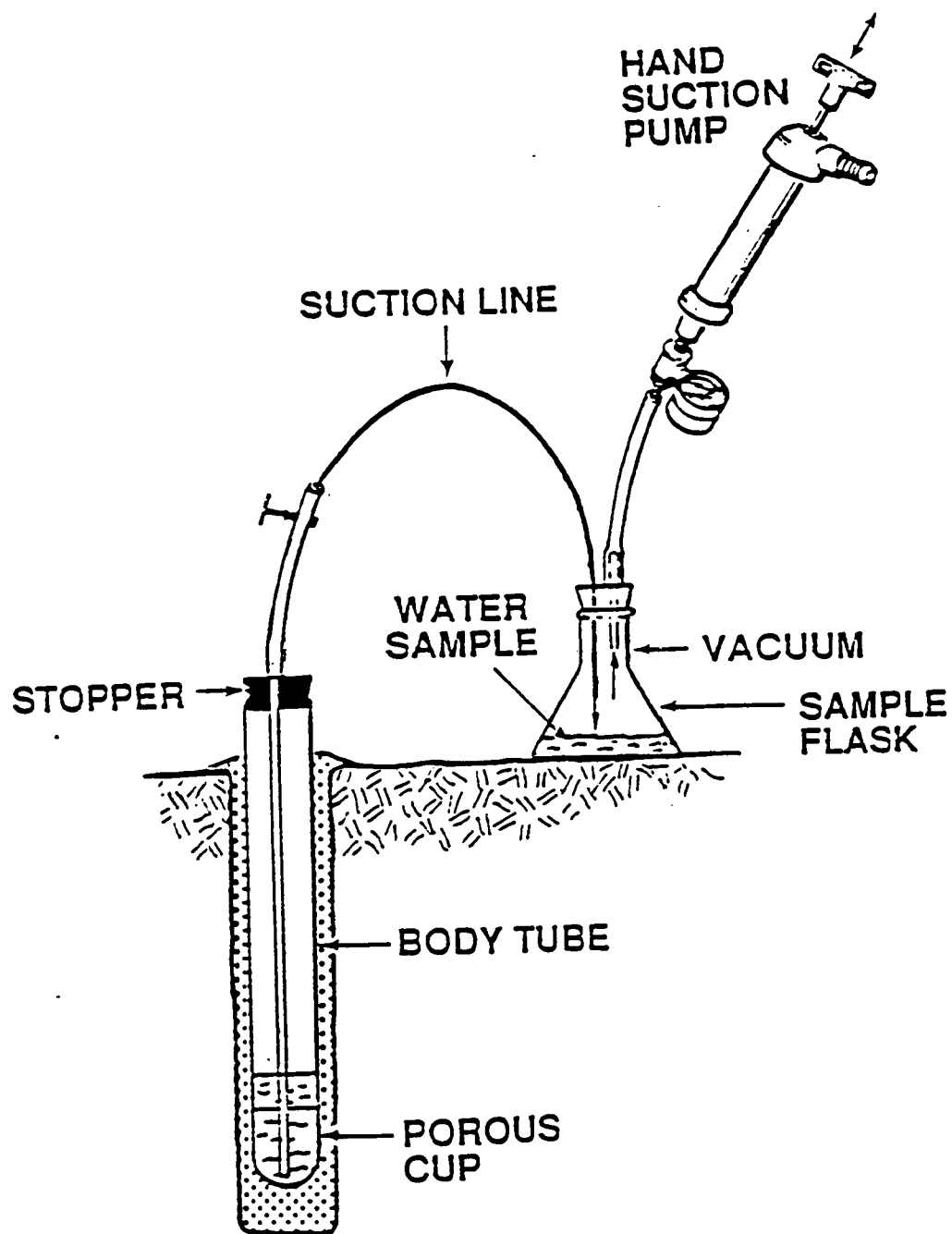
Figure 2. Vacuum Lysimeter (Courtesy, Soilmoisture Equipment Corp., 1981).

(PTFE) (31), and ceramics (22). The sampler body tube has been made with PVC, ABS, acrylic, stainless steel (44) and PTFE (31). The stopper is typically made of rubber (19), neoprene, or PTFE. The outlet lines are commonly polycarbonate, PTFE, rubber, polyethylene, polypropylene, Tygon®, nylon, stainless steel, and historically, copper. Fittings and valves are available in brass, stainless steel, PVC, and PTFE.

Vacuum lysimeters transfer samples directly to the surface via a suction line. Because the maximum suction lift of water is about 7.5 m, these samplers cannot be operated below this depth. In practice, suction lifts of even 7.5 m may be difficult to attain.

PRESSURE-VACUUM LYSIMETERS

These samplers, depicted in Figure 3, were developed by Parizek and Lane (45) for sampling pollutants moving in the vadose zone beyond the reach of vacuum lysimeters. Again, the porous segment is usually a porous cup at the bottom of a body tube. Two lines are forced through a two-hole stopper sealed into the upper end of the body tube. The discharge line extends to the base of the sampler and the pressure-vacuum line terminates a short distance below the stopper. At the surface, the discharge line connects to a sample bottle and the pressure-vacuum line connects to a pressure-vacuum pump. The sampler and its components are commonly made out of the same materials used for vacuum
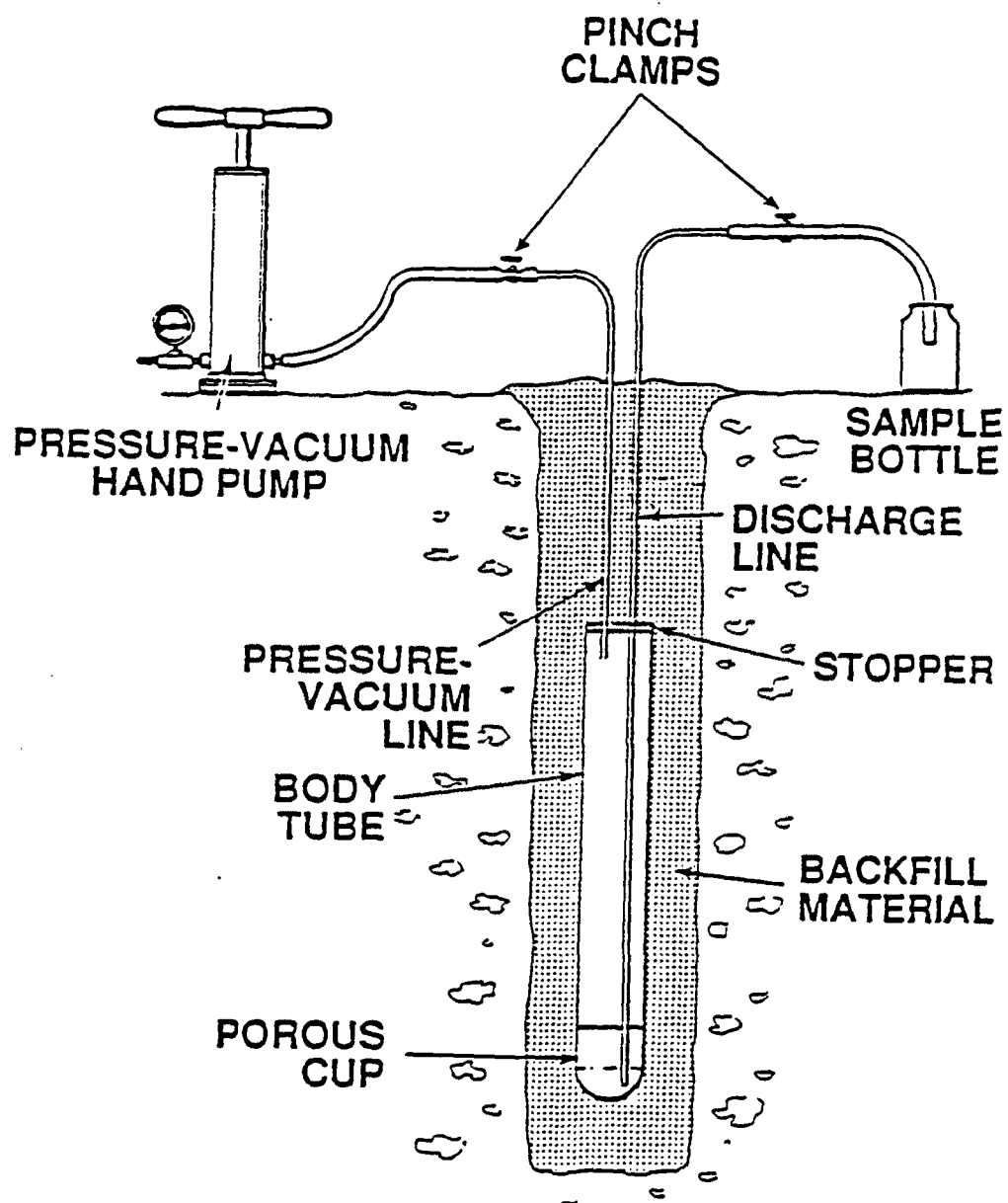
Figure 3. Pressure-Vacuum Lysimeter (Courtesy, Soilmoisture Equipment Corp., 1989).

lysimeters. Pressure-vacuum lysimeters first collect pore-liquid in the body tube by application of vacuum through the pressure-vacuum line. The sample is then retrieved by pressurizing the sampler through the same line; this pushes the sample up to the surface through the discharge line (see Figure 3).

Because samples are retrieved under pressure, these samplers can be used below 7.5 m. However, when positive pressure is applied for sample retrieval, some of the sample may be forced back out of the cup. At depths of over about 15 m, the volume of sample lost in this manner may be significant. In addition, pressures required to bring the sample to the surface from depths greater than 15 m may be high enough to damage the cup or to reduce its hydraulic contact with the soil (46, 47). Rapid pressurization causes similar problems. Morrison and Tsai (48) developed a tube lysimeter with the porous section located midway up the body tube instead of at the bottom (see Figure 4). This design mitigates the problem of sample being forced back through the cup. However, it does not prevent problems with porous segment damage due to over pressurization or rapid pressurization. The sleeve lysimeter (which is not presently available commercially) was a modification of this design for use with a monitoring well (2). Another modification is the casing lysimeter which consists of several tube lysimeters threaded into one unit (see Figure 5). This arrangement allows precise spacing between units (31).

PRESSURE-
VACUUM LINE

THREADED
COUPLING

PVC BODY
TUBE

DISCHARGE
LINE

POROUS
SECTION

THREADED
COUPLING

PVC WELL
POINT
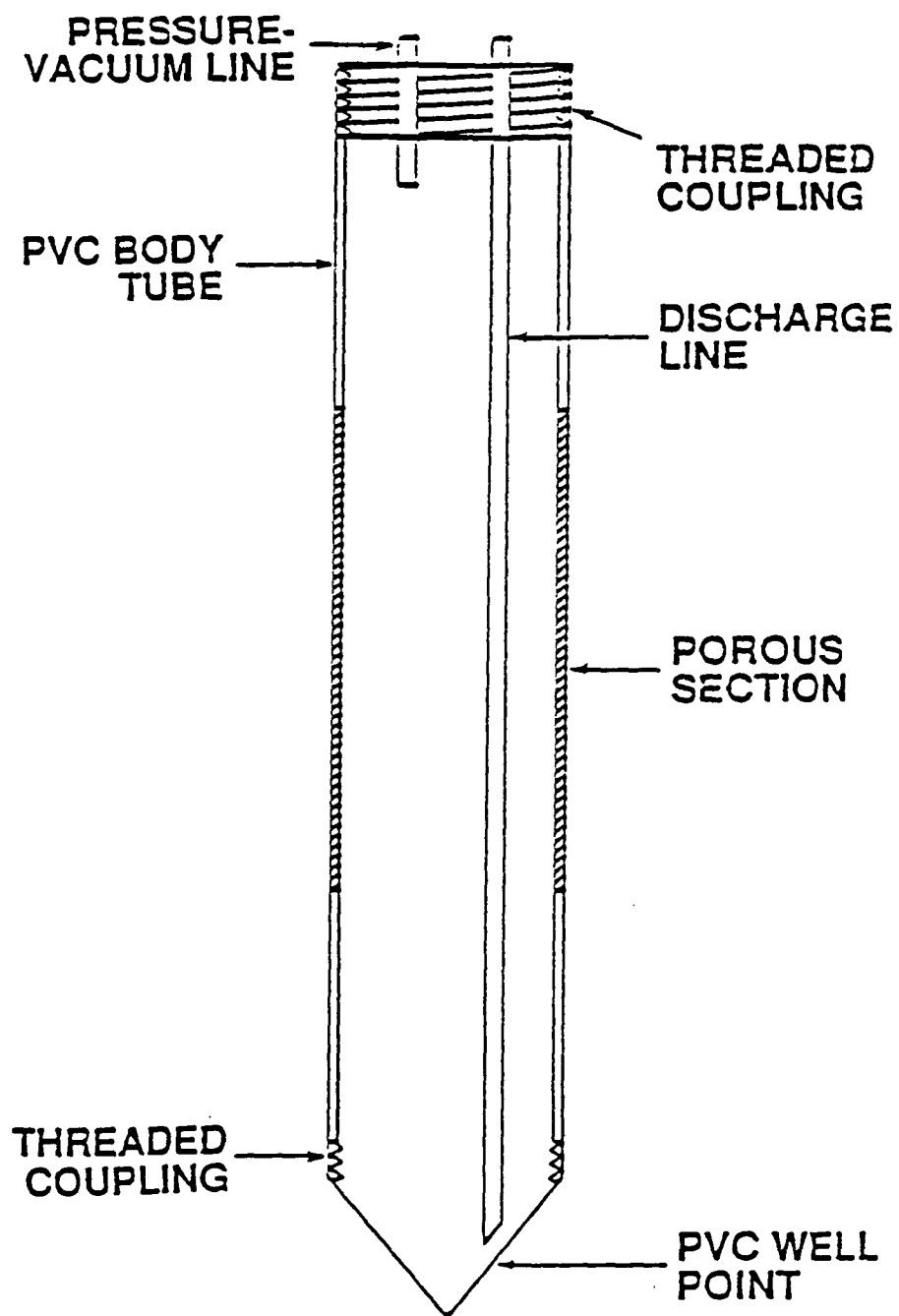
Figure 4. Tube Pressure-Vacuum Lysimeter (Morrison and Tsai, 1981).

FLUSH THREADED CASING

DISCHARGE LINES

PRESSURE-VACUUM LINES

GROUND SURFACE

BENTONITE SEAL

BLANK TUBE

SILICA PACK

LYSIMETER

POROUS SECTION

BENTONITE SEAL

BLANK TUBE

SILICA PACK

LYSIMETER

FLUSH THREADED CASING
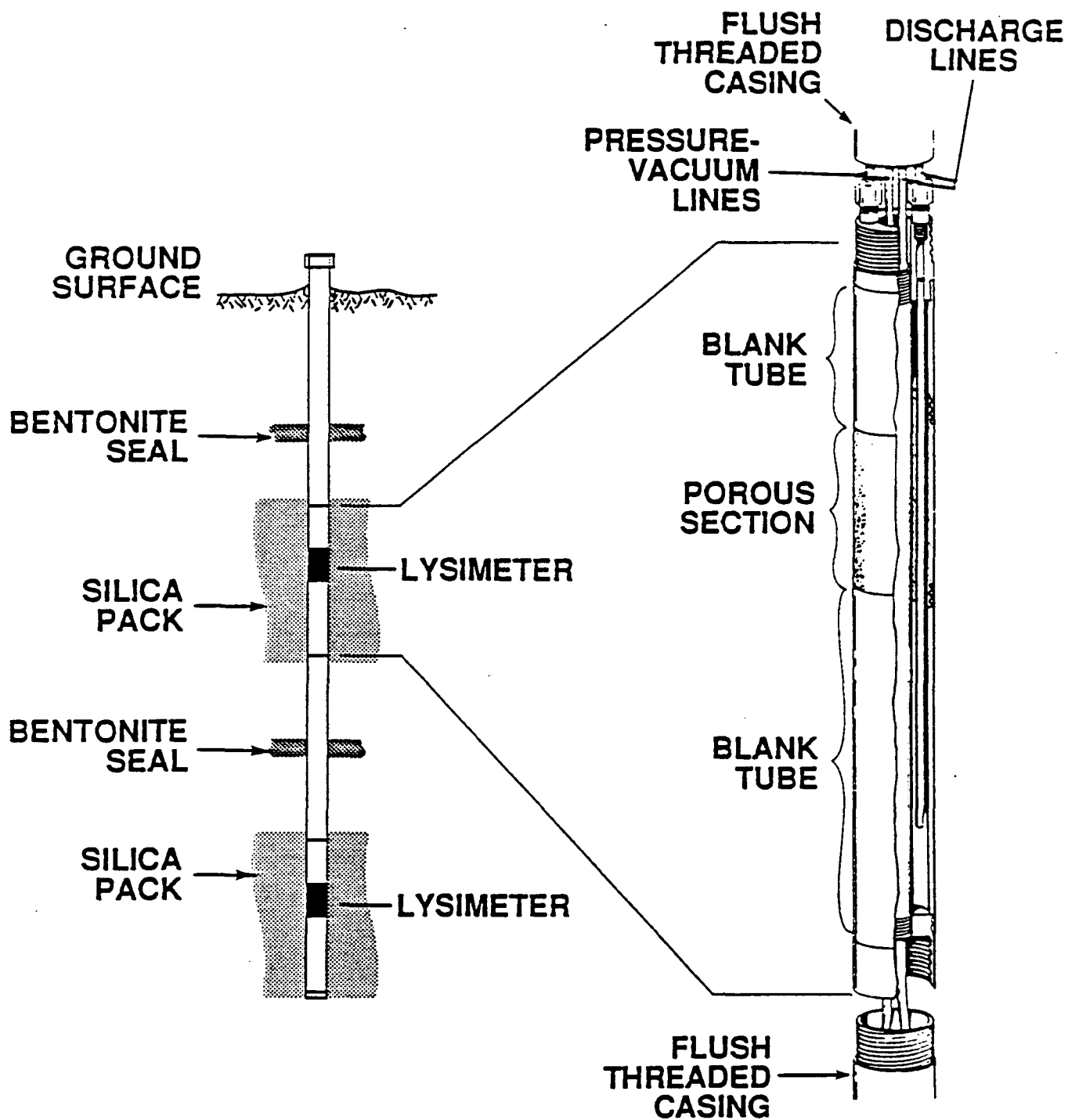
Figure 5   Casing Lysimeter (Courtesy, Timco Mfg., Inc., 1989)

Nightingale et al. (49) described a design which allows incoming samples to flow into a chamber not in contact with the basal, porous ceramic cup (see Figure 6). The ceramic cup is wedged into the body tube without adhesives or threading. The sampler was used to sample the vadose zone, the capillary fringe and the fluctuating water table in a recharge area. Knighton and Streblow (50) reported a sampler with the porous cup mounted on the top of a chamber (see Figure 7). These designs also allow pressurization for sample retrieval without significant liquid loss. However, because the porous cups are exposed to pressure, possible damage due to over pressurization or rapid pressurization remains a problem.

HIGH-PRESSURE VACUUM LYSIMETERS

High-pressure vacuum lysimeters operate in the same manner as pressure-vacuum lysimeters. However, they include one-way check valves and a transfer vessel or chamber between the sampler and the surface (see Figure 8). These accessories prevent sample loss through the porous section during pressurization, and possible cup damage due to over pressurization. The samplers are manufactured generally using the same materials as vacuum lysimeters (22, 31).
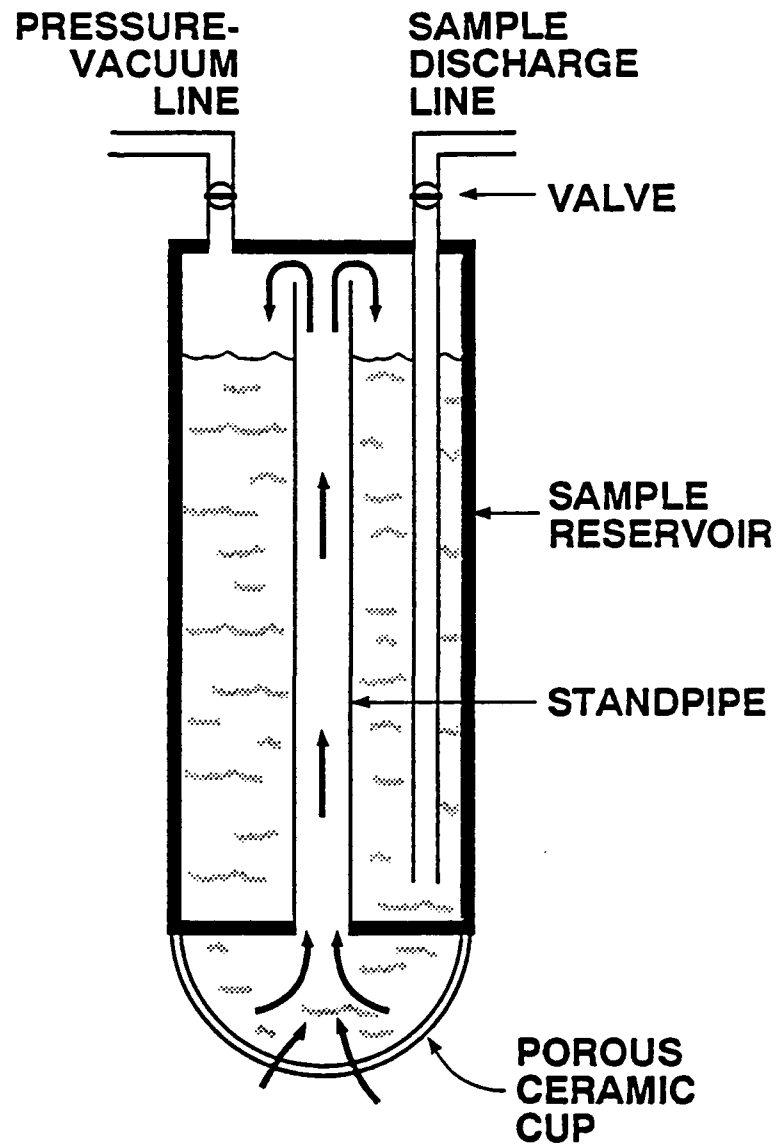
Figure 6. Modified pressure-vacuum lysimeter (Nightingale, et al, 1985).
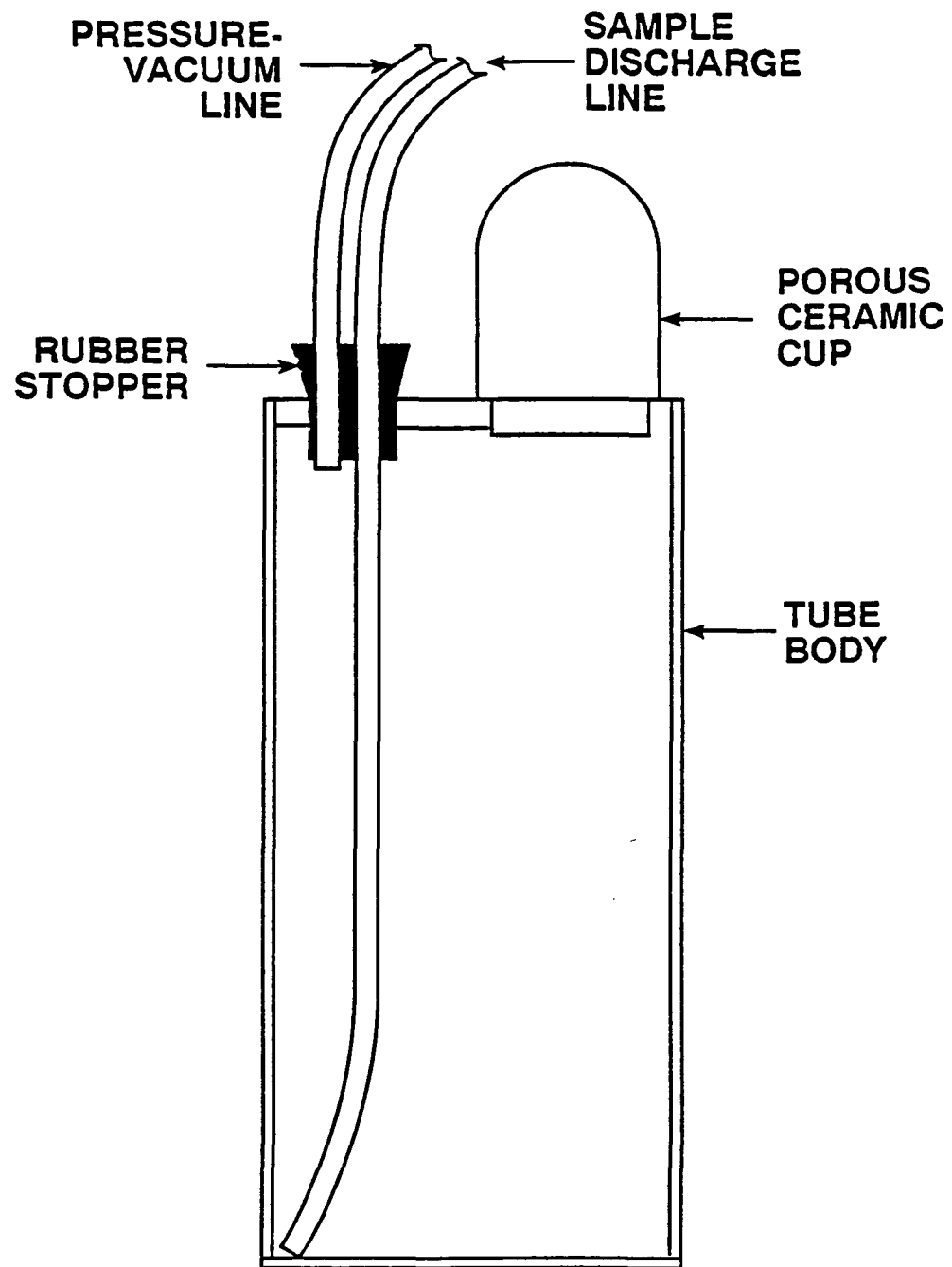
Figure 7. Knighton and Streblow-type vacuum lysimeter (Knighton and Streblow, 1981).
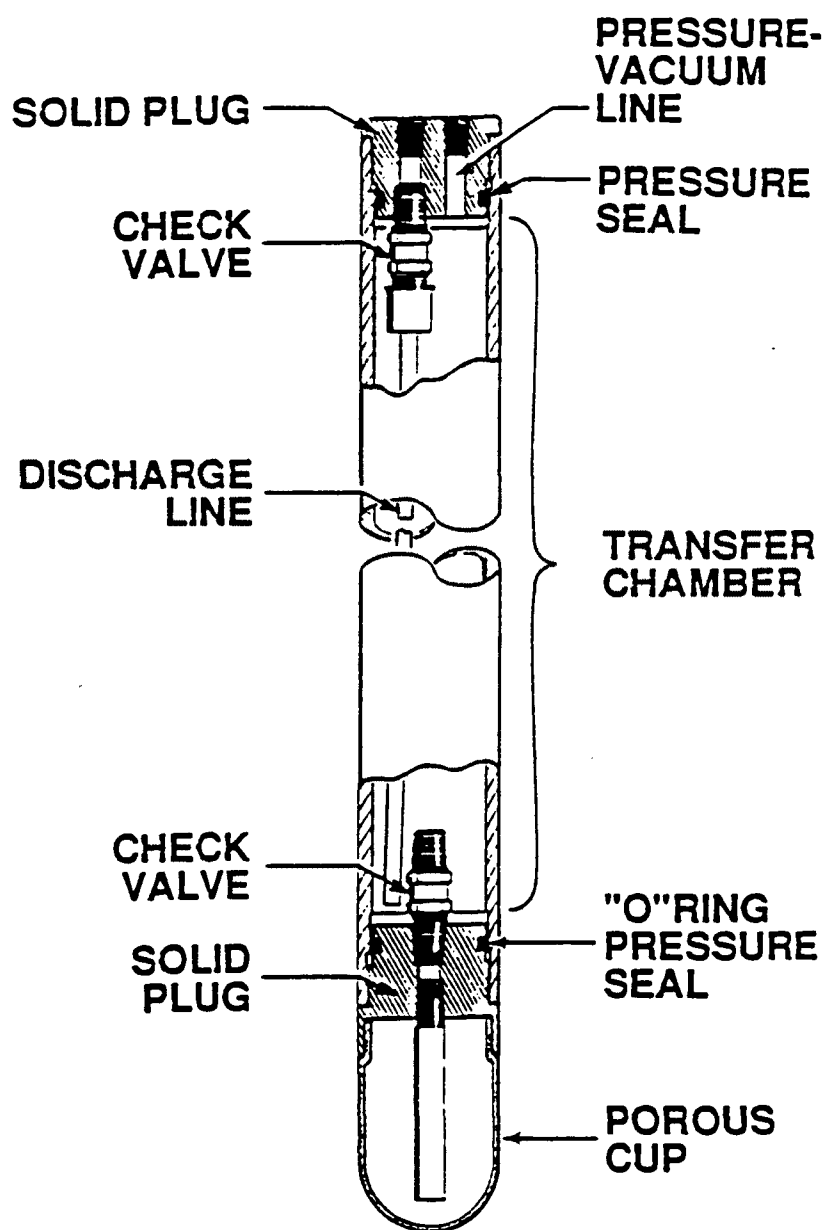
Figure 8   High Pressure-Vacuum Lysimeter (Courtesy, Soilmoisture Equipment Corp., 1989)

FILTER TIP SAMPLERS

Filter tip samplers consist of two components: a permanently installed filter tip, and a mechanically-retrievable glass sample vial (see Figure 9). The filter tip includes a pointed end to help with installation, a porous section, a nozzle, and a septum. The tip is threaded onto riser pipes which terminate at the surface. The sample vial includes a second septum. When in use, the vial is seated in an adaptor which includes a disposable hypodermic needle to penetrate both the septa, allowing sample to flow from the porous segment into the vial.

The body of the filter tip is constructed from a variety of materials, including thermoplastic, stainless steel, or brass. The attached porous section is available in high density polyethylene, porous ceramic, or sintered stainless steel. The septum is made of natural rubber, nitrile rubber, or fluororubber (51, 52).

A sample is collected from a filter tip sampler by lowering an evacuated sample vial down the access tube to the porous tip. The vial is coupled with the porous tip via the hypodermic needle and sample flows through the porous section into the vial. Once full, the vial is mechanically retrieved (see Figure 9).
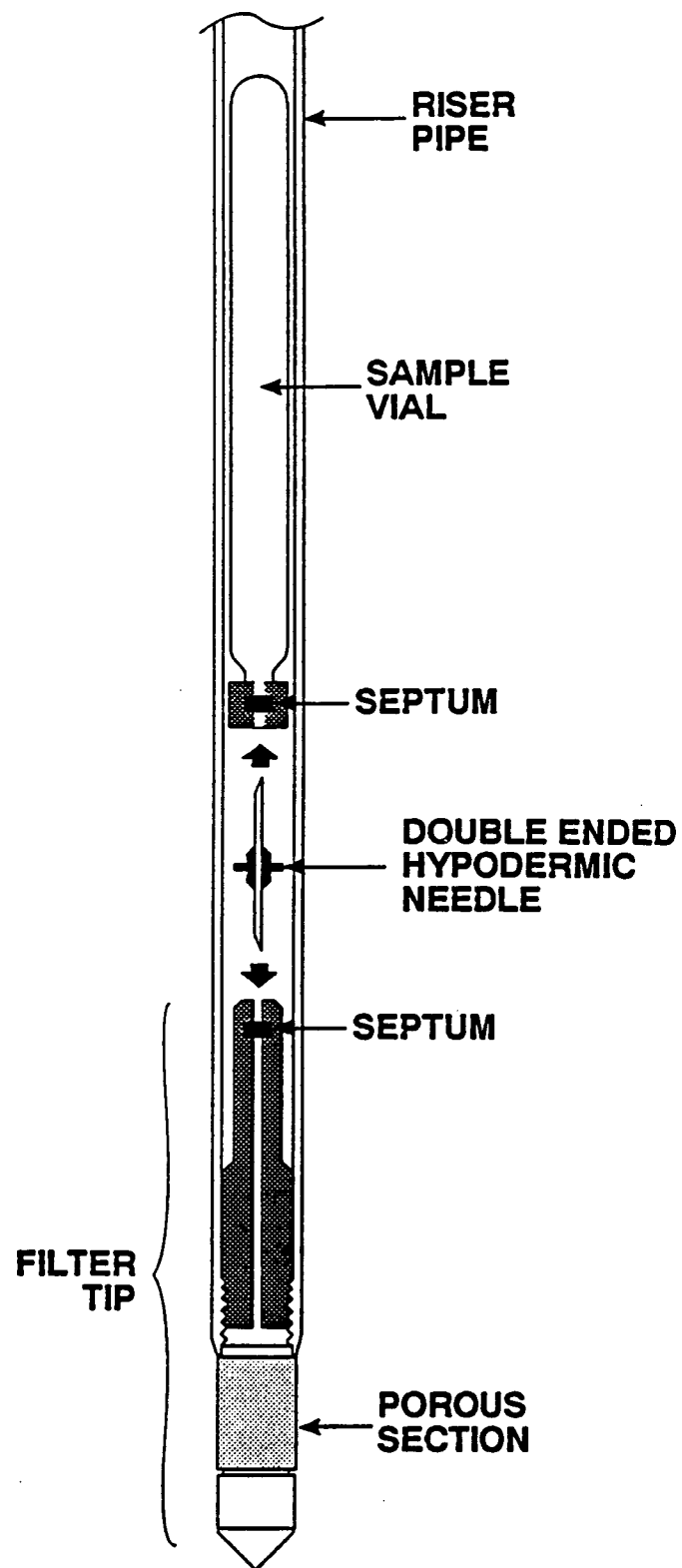
Figure 9. Filter tip sampler (BAT Envitech Inc., 1988).

EXPERIMENTAL SUCTION SAMPLERS (UNSATURATED/SATURATED SAMPLING)

Experimental samplers, described in the literature, are usually limited to research applications because of their fragility. For the most part, these samplers are not commercially available. However, most of these samplers may be easily fabricated. Experimental suction samplers operate on the same principles as vacuum lysimeters, and are also limited to depths of less than 7.5 m (see Table 2).

CELLULOSE-ACETATE, HOLLOW-FIBER SAMPLERS

These samplers consist of a bundle of cellulose-acetate hollow fibers (see Figure 10). The bundle of flexible fibers is pinched shut at one end and attached to a suction line at the other end. The suction line leads to the surface and attaches to a sample bottle and source of suction in the same manner as a vacuum lysimeter. Levin and Jackson (53) described similar fibers made from a noncellulosic polymer solution.

MEMBRANE FILTER SAMPLERS

Membrane filter samplers were described by Morrison (2), U.S. Environmental Protection Agency (19) and Stevenson (54). Figure 11 shows that a sampler consists of a membrane filter of polycarbonate, cellulose acetate, cellulose nitrate or PTFE

SUCTION
LINE

CELLULOSE-
ACETATE HOLLOW-
FIBER BUNDLE

SEALED
END
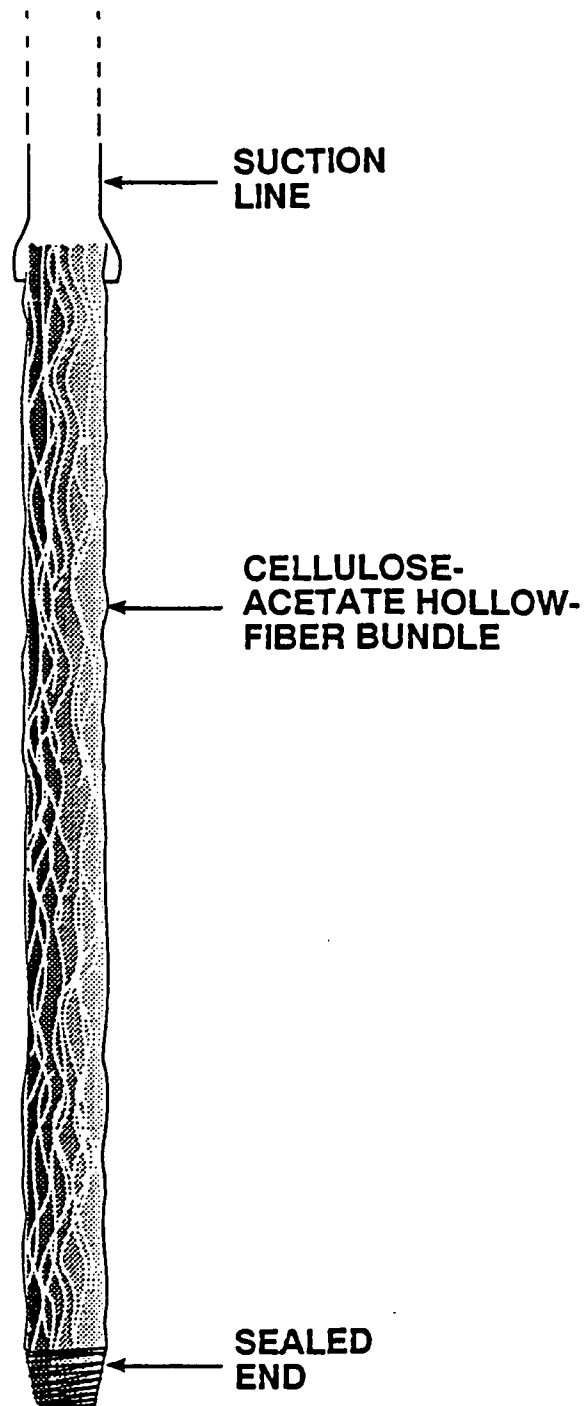
Figure 10.   Cellulose-acetate hollow-fiber sampler.

mounted in a "swinnex" Type filter holder (54, 55, 56). The filter rests on a glass fiber prefilter. The prefilter rests on a glass fiber "wick" which in turn sits on a glass fiber collector. The collector is in hydraulic contact with the soil, extending the sampling area of the small diameter filter (see Figure 11). A suction line leads from the filter holder to the surface. At the surface, the suction line is attached to a sample bottle and suction source in a manner similar to vacuum lysimeters.

BARREL LYSIMETER

There are two limitations with suction samplers. First, they may not sample from macropores (unless the macropores are directly intercepted). Second, their results cannot be used in quantitative mass balance studies. Horby et al. (57) described an installation which could be used to surmount these problems (see Figure 4). A barrel-sized casing (e.g., 57 cm outside diameter by 85.7 cm high) is placed in a support device and gently pushed into the soil with a backhoe. As the casing is pushed, soil is excavated around it to help with insertion. The process results in an encased monolith of undisturbed soil. The monolith is then rotated and lifted, pressure-vacuum lysimeters are placed in its base, and the bottom is sealed. Subsequently the assembly is placed back into the ground at the monitoring site (see Figure 12). All fluid draining through the monolith is
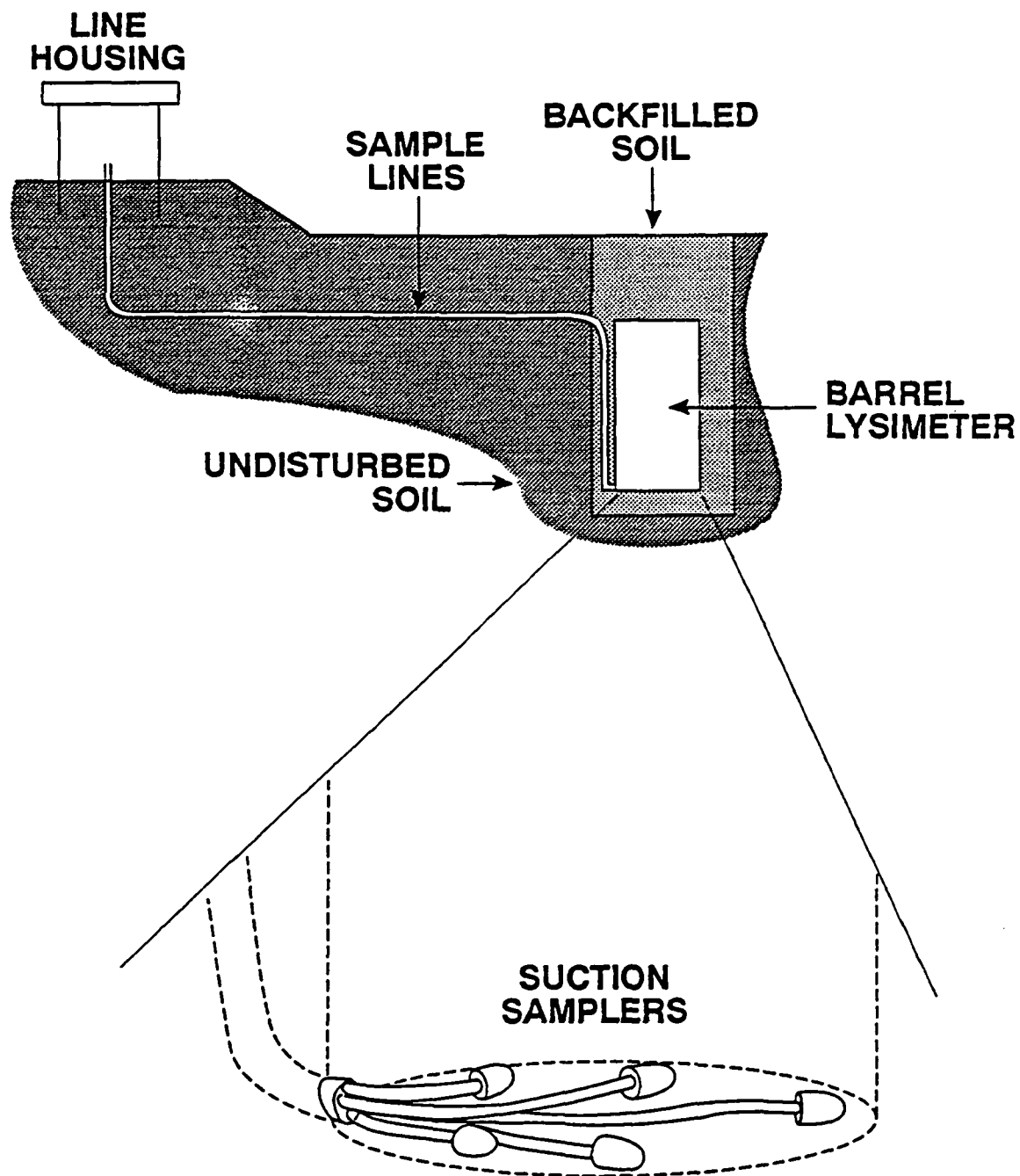
Figure 12. Barrel lysimeter (after Hornby et al, 1986).
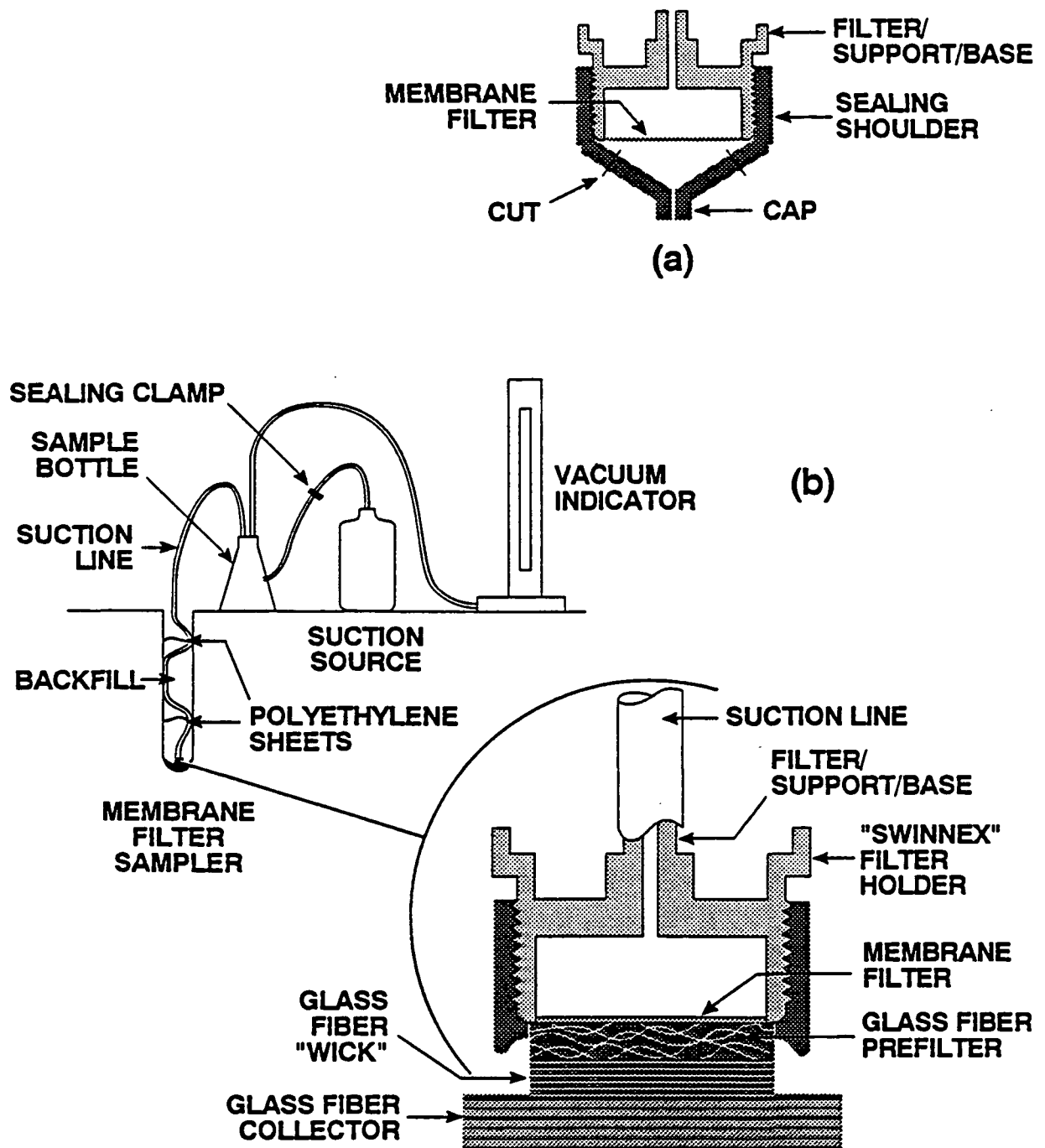
Figure 11. Membrane filter sampler (Stevenson, 1978):
a) Preparation of filter sampler,
b) Installation of filter sampler.
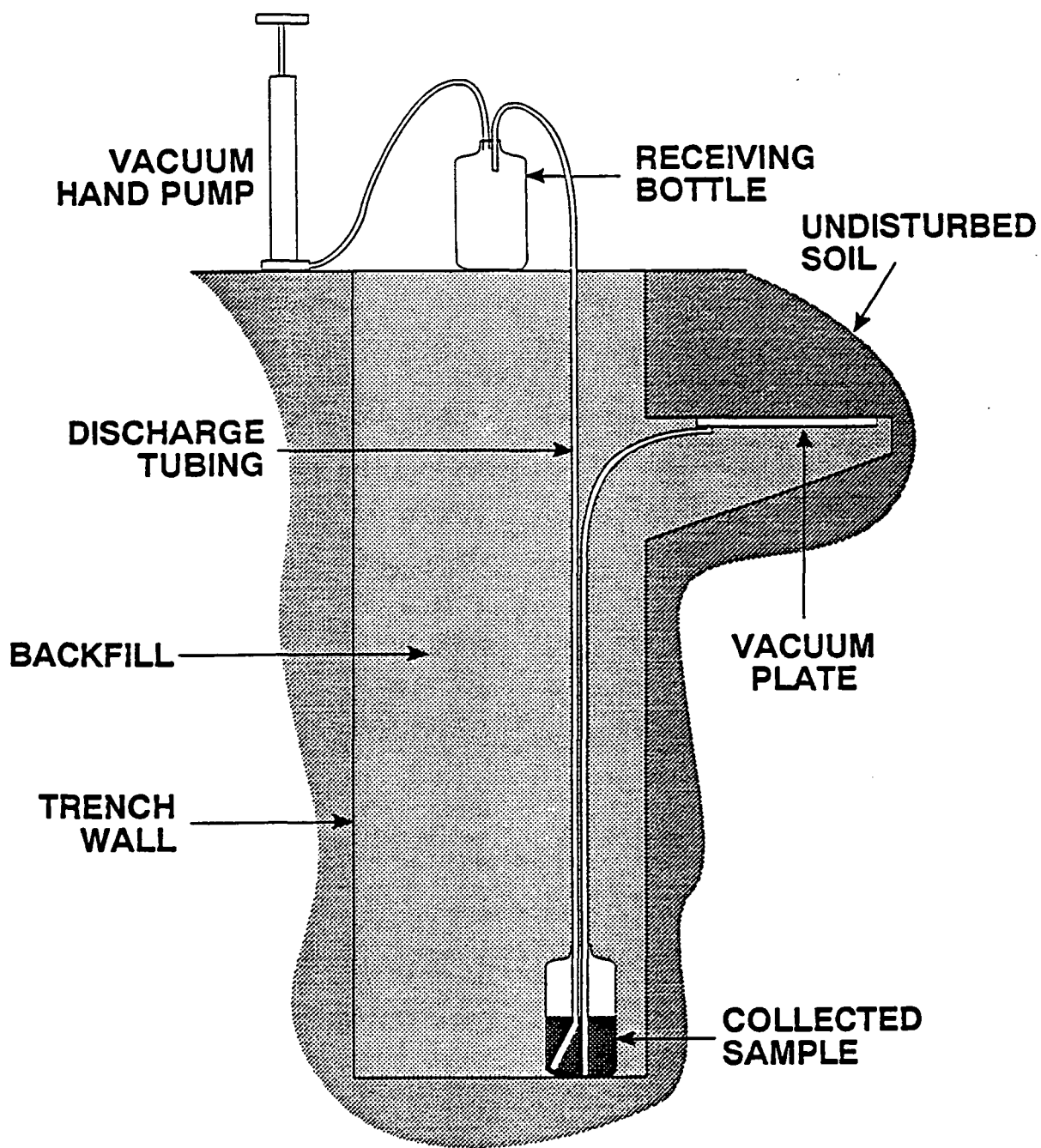
Figure 13.   Vacuum plate sampler installation (after Cole, 1958).

collected by the samplers. Inasmuch as the boundaries of the system are sealed, the flux of liquid through the system requires maintaining a vertical downward hydraulic gradient by applying continual suction to the samplers.

VACUUM PLATE SAMPLERS

A vacuum plate sampler consists of a flat porous disk fitted with a nonporous backing attached to a suction line which leads to the surface (see Figure 13). Plates are available in diameters ranging from 4.3 to 25.4 cm and custom designs are easily arranged (2, 22). Plates are available in Alundum®, porous stainless steel (43), ceramic (1.2 to 3.0 μm maximum pore size) or fritted glass (4 to 5.5 μm maximum pore size) (59, 22, 60, 61, 36, 63, 64). The nonpermeable backing can be of fiberglass resin, glass, plastic, or butyl rubber.

OPERATIONAL CONSTRAINTS OF SUCTION LYSIMETERS

The inherent heterogeneities of unsaturated pore-liquid movement and chemistry limit the degree to which samples from suction samplers can be considered representative. This is because the small cross-sectional areas of suction samplers may not adequately integrate for spatial variabilities in liquid movement rates and chemistries (27, 65, 66, 67). Biggar and Nielsen (67) suggested that results of chemical analyses from suction sampler

	TABLE 3a.	POROUS MATERIAL INTERACTIONS*			
	Absorbs Species	Desorbs Species	Screens Species	No Signif. Inter-aciton	No Inter-action
Al[b]		[c]C(2)[d]		C(16)	-
Alkali-nity				SF(11)	
Ca		C(1,2,18) CAF(18) A(14)		C(3,6,10, 11,25) PTFE(3) A(3) FG(18,22) CAF(10)	
C		FG(22)			
CO$_3$		C(2)			
HCO$_3$		C(2)			
Cd	C(11)			C(3) PTFE(3) A(3)	
Cl				C(11,25) SF(11)	PTFE(13)
Cr	C(19)	C(3) PTFE(3) A(3)			
Cu	C(11)	C(3) PTFE(3)		A(3)	
Fe	C(11)	PTFE(3) A(3)		C(3,25)	PTFE(13)
H				SF(11)	
K	C(5,6,15)	C(18)[e] A(14)		C(1,25) CAF(18) FG(18,22)	

samples are good for qualitative but not quantitative comparisons, unless the variabilities of the parameters involved are established. Law (3) came to similar conclusions, stating that results from suction sampling could not be used for quantitative mass-balance studies.

Chemical interactions between porous segments and the liquids which pass through them affect the validity of pore-liquid samples collected with suction samplers (68). Potential interactions can include sorption, desorption, cation exchange, precipitation, and screening (69). These interactions can also occur with all other parts of the samplers which liquids contact. However, the much higher surface area within the pores of porous segments makes them the most critical element chemically. Table 3 presents the results of a literature review for porous section/pore-liquid interactions. An attempt has been made to document the pertinent features of the listed studies. However, the reader should refer to the original papers to determine if experimental techniques are applicable to the situation of interest. The absence of entries for a constituent relative to a material does not infer absence of interactions.

EXPERIMENTAL ABSORPTION SAMPLERS (UNSATURATED/SATURATED SAMPLING)

Absorbent samplers depend on the ability of a material to absorb pore-liquids (2). Samples are collected by placing the sampler

	Absorbs Species	Desorbs Species	Screens Species	No Signif. Inter-aciton	No Inter-action
Pb					PTFE(13)
SiO$_2$		C(2)			
Si				C(4) PTFE(4)	
SO$_4$				C(11)	
Sr		C(11)			
Zn		C(11)			PTFE(13)
High Molec. Wt. Cmpds.			C(17,21) CAF(10)		
4-nitro-phenol	PTFE(23)				
Chlori-nated Hydro-carbons	PTFE(23, 24)				
Diethyl Phthal-ate				PTFE(23)	
Naph-thalene	PTFE(23)				
Acenaph-thene	PTFE(23)				

TABLE 3a.   POROUS MATERIAL INTERACTIONS* (Continued)

* NOTES ON Table 3a:
  a: Comparisons of materials based on this table should be made cautiously. Differing experimental techniques should be considered as a source of differing conclusions. Undocumented factors often include material age and sampling history.
  b: Valence states are often not reported in studies.

	Absorbs Species	Desorbs Species	Screens Species	No Signif. Inter- aciton	No Inter- action
Mg	C(6)	C(2,3,11, 18) A(3,14) CAF(18)		C(10,25) PTFE(3) CAF(10) FG(18,22)	PTFE(13)
Mn	C(11)	A(3)		C(3) PTFE(3) A(14)	PTFE(13)
Na	C(6)	C(12,18) A(14) CAF(18) FG(18,22)		C(1,11, 25)	PTFE(13)
NH$_4$	C(4,12)			PTFE(4)	
N		FG(22)			
NO$_2$				C(4,5) PTFE(4)	
NO$_3$			CAF(10)	C(4,8) PTFE(4)	
NO$_3$-N			C(10) CAF(10)		
(NO$_2$+ NO$_3$)-N				C(5)	
P	C(1,5,8, 15,18)			CAF(18) FG(18)	
PO$_4$	C(4,5,7)			PTFE(4) CAF(10)	
PO$_4$-P				C(10) CAF(10)	

TABLE 3b. REFERENCES AND NOTES ON EXPERIMENTAL TECHNIQUES (a)

Reference Number in Table	Citation Number in Text	Porous Section was washed	Results are a Function of Several Factors	Dilute Solutions were Tested	Tests performed on non-porous materials
1	108	X			
2	24	X			
3	106	X			
4	109	X			
5	110		X		
6	27	X	X		
7	28	X			
8	69	X			
9	33				
10	53	X			
11	29				
12	111	X			
13	2	X			
14	23	X	X	X	
15	112				
16	68		X		
17	3	X			
18	113		X		
19	11		X		
20	114				
21	34				
22	56	X	X		
23	115		X	X	X
24	116		X	X	X
25	105	X	X		

(a)   Absence of information on experimental techniques means that the techniques were not specified in the citation.

NOTES ON TABLE 3a (Continued)

c: Abbreviations:
    1. C = porous ceramic
    2. PTFE = porous   polytetrafluoroethylene
    3. A = porous Alundum
    4. CAF = cellulose acetate fibers
    5. FG = fritted glass or glass fibers
    6. SF = silica flour

d: Numbers in parenthesis refer to references in Table 3b

e: Example: Reference 18 in Table 3b (i.e., citation number
    113 in text) found that there is no significant
    interaction of cellulose acetate fibers with potassium in
    solution. The porous section was washed prior to testing
    and results were found to be a function of several
    factors.

CERAMIC ROD SAMPLERS

These samplers consist of solid, tapered ceramic rods. Prior to installation, the rods are boiled in distilled water, dried, and weighed. The rods are simply installed by driving them into the soil. After a period of time, the rods are withdrawn, weighed, and again boiled in distilled water. The water is then analyzed (71).

PROBLEMS WITH EXPERIMENTAL ABSORPTION SAMPLERS

As with other samplers, there are problems with chemical absorption, desorption, precipitation, cation exchange and screening of various pore-liquid components as a function of the sampler materials. Tadros and McGarity (70) discussed these concerns in relation to sponge samplers. Shimshi (71) provided a good discussion of the limitations of sampling for nitrate with ceramic rod samplers.

FREE DRAINAGE SAMPLERS (SATURATED SAMPLING)

A free drainage sampler consists of some sort of collection chamber which is placed in the soil. Pore-liquid in excess of field capacity is free to drain through soil (usually through macropores) under the influence of gravity. Hence, these samplers collect liquid from those portions of the vadose zone

in contact with soil. Liquid is allowed to absorb into the sampler material over time. The sampler is then removed, and liquid is extracted for analyses. The simplicity of these samplers have made them attractive to some investigators.

Physically, absorbent methods are limited to soils approaching saturation. Sampling requires removing the device and bringing it to the surface. Because of this requirement, repeat sampling at the same location is difficult. Although the sampler may be placed back at its original location, identical hydraulic contact with the soil cannot be guaranteed.

SPONGE SAMPLERS

This sampler includes a cellulose-nylon sponge seated in a galvanized iron trough (70). Samples are collected by pressing the dry sponge against a soil surface with a series of lever hinges. The sponge is left in place until a sufficient volume of pore-liquid has been collected for analyses. Theoretically, there is no maximum sampling depth for sponge samplers. However, because access trenches are required for operation, installations are restricted to shallow depths dictated by excavation equipment and safety considerations.

- Pan Lysimeter

- Glass Block Lysimeters

- Caisson Lysimeters

- Wicking Soil Pore-Liquid Samplers

- Trough Lysimeters

- Vacuum Trough Lysimeters

- Sand-Filled Funnel Samplers

PAN LYSIMETERS

A pan lysimeter generally consists of a galvanized, metal pan of
varying dimensions (see Figure 14). A copper tube is soldered to
a raised edge of the pan. Plastic or Tygon tubing connects the
copper tube to a collection vessel. Any liquid that accumulates
on the pan drains through the tubing into the vessel (19, 45).

GLASS BLOCK LYSIMETERS

Barbee and Brown (72) developed free drainage samplers made from
hollow-glass bricks (see Figure 15). These glass bricks, which
are produced as ornamental masonry, have dimensions of 30 by 30
by 10 cm and have a capacity of 5.5L. To build a sampler, nine
holes, 0.47 cm in diameter, are drilled along the perimeter of
one of the square surfaces of a brick. Nylon tubing is inserted
into one of the holes to allow for sample removal. The

which are intermittently saturated due to events such as rainfall, flooding, or irrigation. This gravity drainage creates a slightly positive pressure at the soil-sampler interface causing fluid to drip into the sampler. Some free drainage samplers apply a small suction in order to break the initial surface tension at the soil-sampler interface. Samples are retrieved either by accessing the samplers at depth or by drawing samples to the surface through a suction line.

Suction samplers can also be used to sample free drainage flow. However, the small area of those samplers compared to the spacing of macropores limits their usefulness for this application. In addition, suction must be applied to suction samplers to collect samples, even under saturated conditions. Free drainage samplers are passive collectors which automatically collect the percolating liquids.

Free drainage samplers are classified differently by various authors, depending on the installation methods. Many free drainage samplers are installed in the side walls of trenches and are referred to as trench lysimeters. However, free drainage samplers are also installed in the walls of vertical caissons. The principle behind each of the samplers is essentially the same. However, the materials and construction differ. Free drainage samplers include the following:

SUCTION
LINE
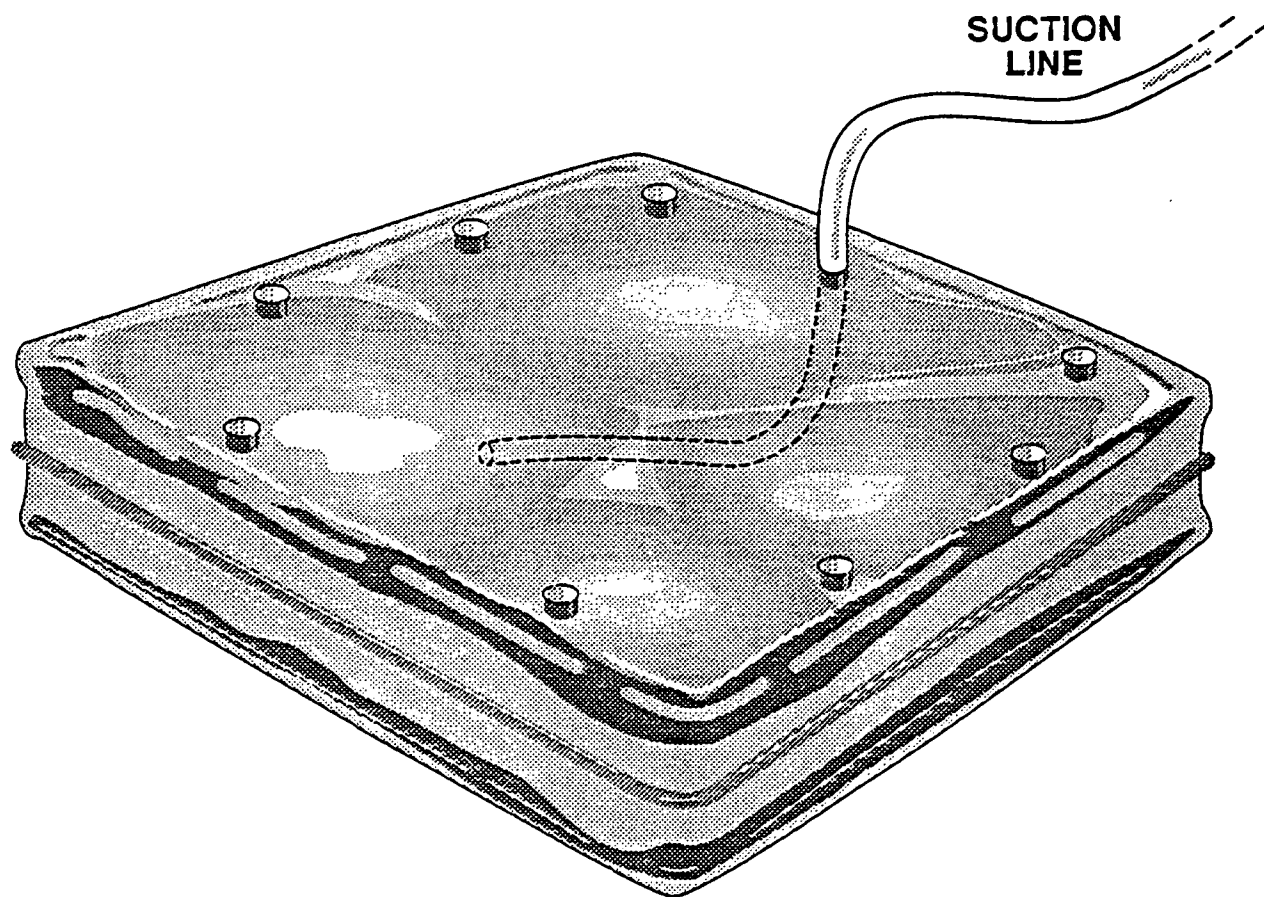
Figure 15.   Glass block lysimeter (after EPA, 1986).

SIDE VIEW

12 IN
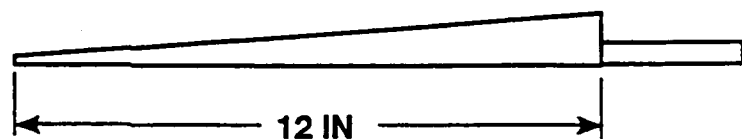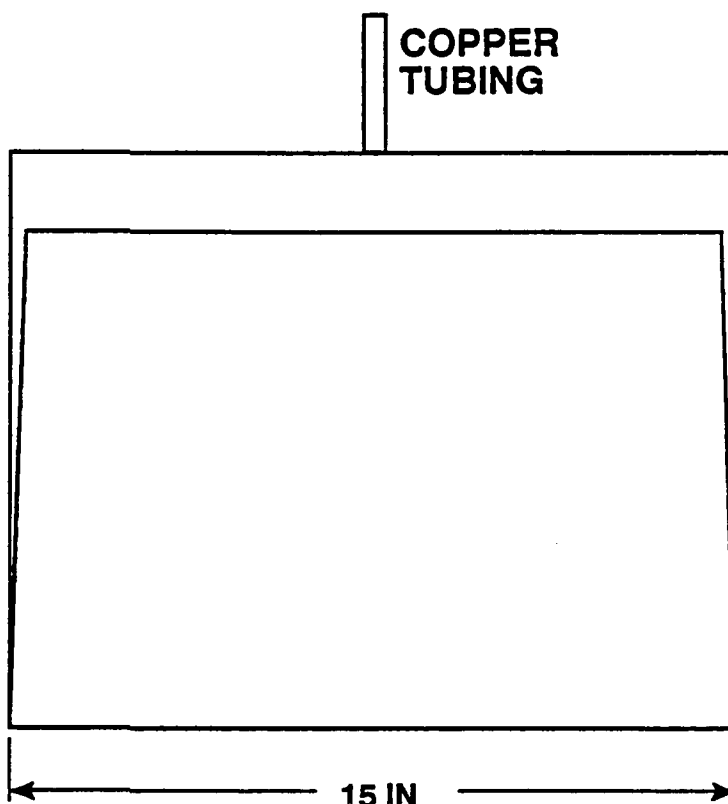
COPPER
TUBING

GALVANIZED
16 GAGE
METAL PAN

15 IN

PLAN VIEW

Figure 14.   Example of a pan lysimeter (EPA, 1986).
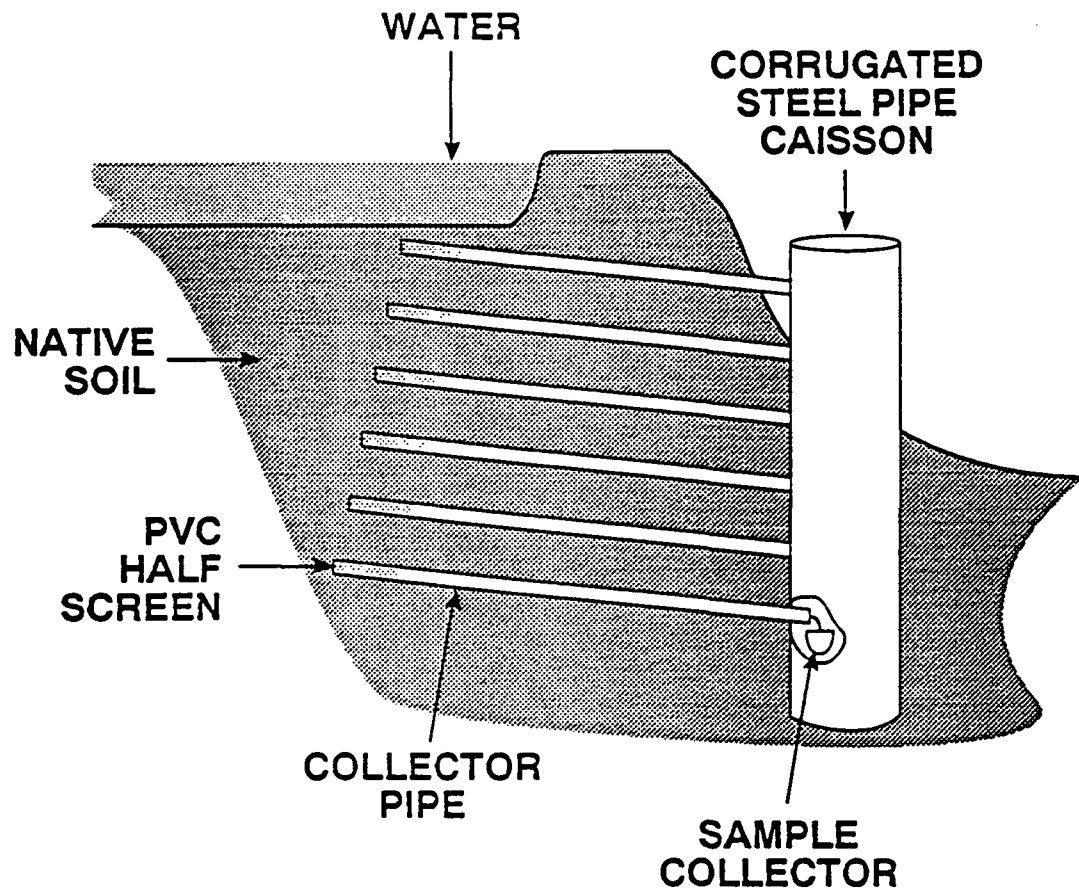
Figure 16. Example of a caisson lysimeter (Schmidt and Clements, 1978).

collecting surface is fitted with a fiber glass sheet to improve contact with the soil. Pore-liquid collection is enhanced by a raised lip along the edge of the surface.

Level blocks are critical for retrieving the bulk of the sample. However, the inside glass surface is uneven and has low spots ("dead spots") where residual sample collects between sampling cycles. This leads to cross-contamination of samples.

CAISSON LYSIMETERS

A caisson lysimeter consists of collector pipes, radiating from a vertical chamber (2). A design used by Schmidt and Clements (73) consists of a nearly horizontal, half-screened PVC casing (see Figure 16). Schneider et al. (74) designed a similar system consisting of the following components: (1) a stainless steel tube extending diagonally upward through the caisson wall into the native soil, (2) a screened plate assembly within the tube to retain the soil, (3) a purging system used to redevelop the sampler when it becomes clogged, (4) an airtight cap that prevents exchange between the air in the caisson and the soil air.

WICKING SOIL PORE-LIQUID SAMPLERS

Hornby et al. (58) described a wicking sampler (see Figure 17),

which combines the attributes of free drainage samplers and pressure-vacuum lysimeters. The sampler collects both free drainage liquid and liquid held at tensions to about 4 cb. A standing "Hurculon" fibrous column acts as a wick to exert a tension on the soil pores in contact with a geotextile fiber which serves as a plate covering a 30.5 by 30.5 by 1.3 cm pan. The terminus of the fibrous column is sealed into the cap of a tubular chamber. This chamber also contains an inlet pressure-vacuum line and a sample collection tube. Materials for the sample collection tube depend on the constituents being sampled. Glass and PTFE were recommended materials when sampling for organics (58).

TROUGH LYSIMETERS

Trough lysimeters, also known as Abermayer lysimeters, rely on a trough or pail to collect pore-liquid. A fiberglass screen is suspended inside the trough to maintain a firm contact with the edges of the sampler and the soil. The screen is lined with glass wool and covered with soil until the soil is even with the top of the trough (75).

Morrison (2) reported a trough lysimeter in which two parallel metal rods are inside the trough, in contact with the bottom side of the screen, and bent toward the collection tube (see Figure 18). Liquid that enters the trough migrates along these
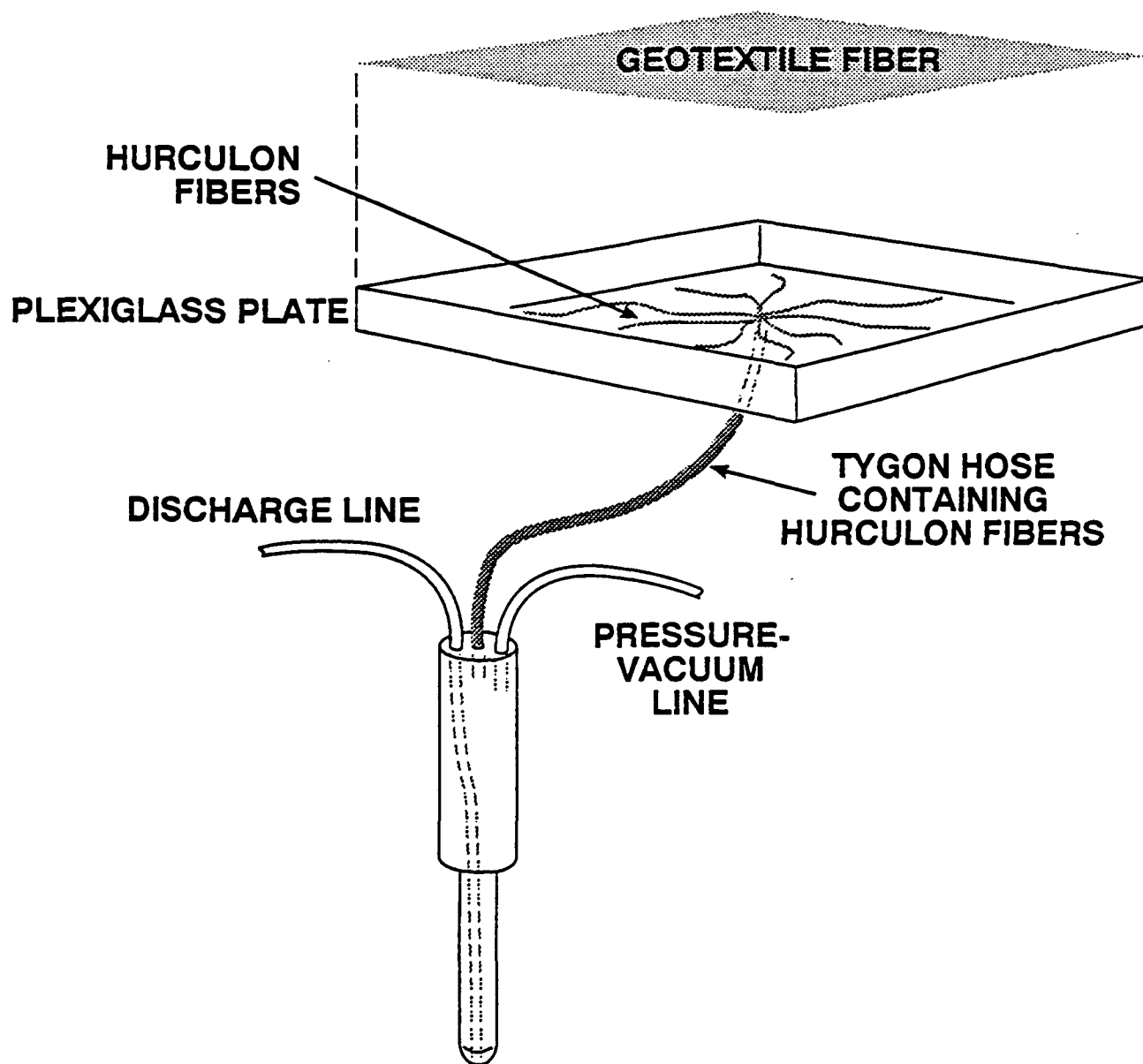
Figure 17.   Wicking type soil pore-liquid sampler (Hornby et al, 1986).

rods towards the collection tube in response to capillary forces. A modification of this design consists of a metal trough with a length of perforated PVC pipe mounted inside. The trough is filled with graded gravel so that coarse material is immediately adjacent to the PVC pipe and fine sand is at the edges and the top of the trough. The pipe is capped at one end while the other end is connected to a sample container via a drainage tube (2).

VACUUM TROUGH LYSIMETERS

Montgomery et al. (76) described a vacuum trough lysimeter consisting of a metal trough equipped with two independent strings of ceramic pipe, each 13 mm in diameter. The primary purpose of this design is to sample free drainage. However, the device also apparently allows extraction of samples under applied suctions of up to 50 cb. The ceramic pipes act as a vacuum system, and samples are extracted through a suction line.

SAND-FILLED FUNNEL SAMPLERS

Brown and Associates (77) discussed a sand-filled funnel for collecting freely draining liquid (see Figure 19). The funnel is filled with clean sand and inserted into the sidewall of a trench. The funnel is connected through tubing to a collection bottle. Application of suction to a separate collection tube pulls the sample to ground surface.

FIBERGLASS
SCREEN

METAL RODS

SAMPLE LINE
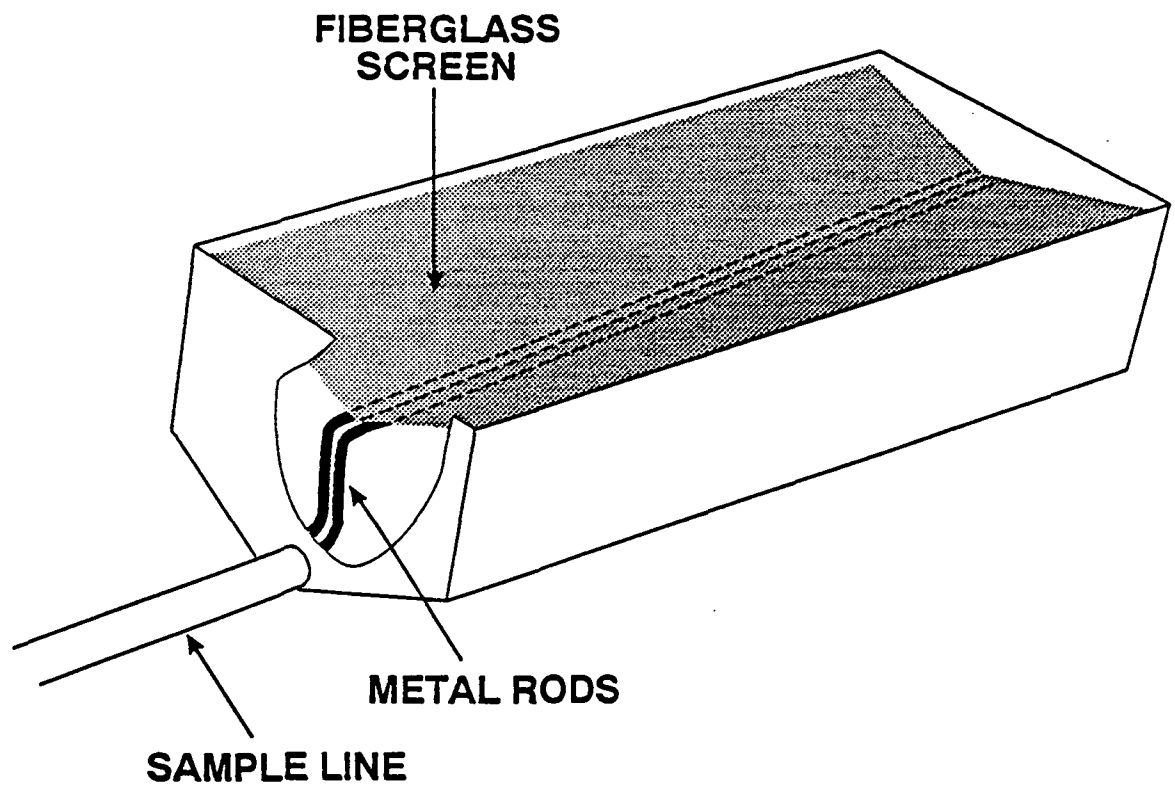
Figure 18.   Trough lysimeter (after Jordan, 1968).

PERCHED GROUND-WATER SAMPLING (SATURATED SAMPLING)

Perched water occurs where varying permeability layers in the vadose zone retard downward movement of liquid. Over time, liquid collects above lower permeability layers and moisture content may increase to saturated (78, 9). Once soil becomes saturated, wells and other devices normally installed below the water table can be used to collect samples.

Sampling perched liquid is attractive because the perching layer collects liquid over a large area. Such integrated samples are more representative of areal conditions than suction samples (78). This also allows the sampler to potentially detect contaminants which may not be moving downward immediately adjacent to the sampler. In addition, larger sample volumes can be collected than those which can be obtained by suction samplers. Everett et al. (7, 9) discussed the incorporation of perched ground-water sampling into monitoring programs.

Perched water systems can be difficult to find and delineate. Surface and borehole geophysical methods (e.g. neutron logging) and video logging of existing wells are often used. Also, perched systems tend to be ephemeral. Therefore, suction samplers are sometimes required as backups. As with all samplers, potential chemical interactions between sampler materials and the constituents of interest should be considered.
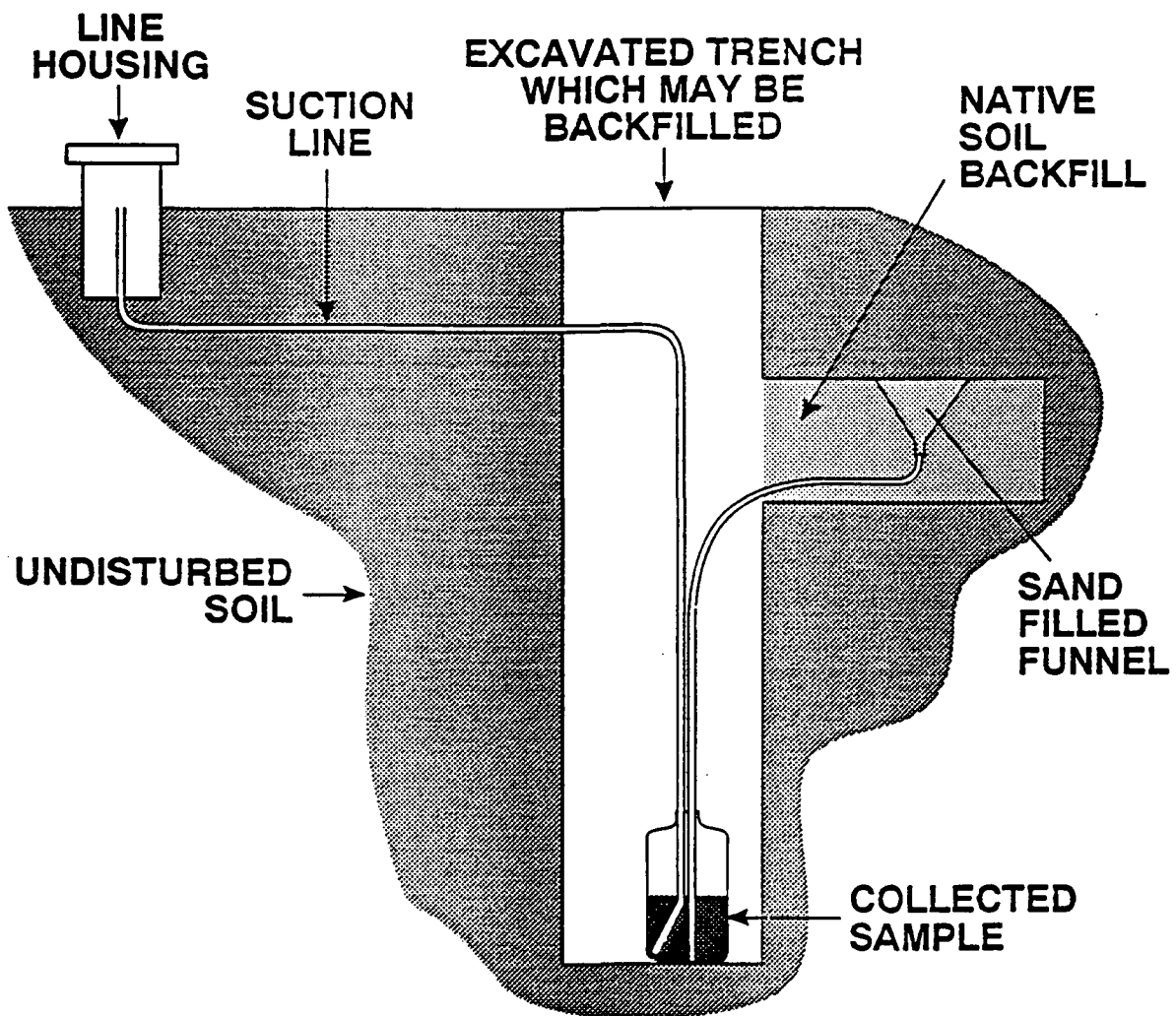
Figure 19. Sand filled funnel sampler installation (EPA, 1986).
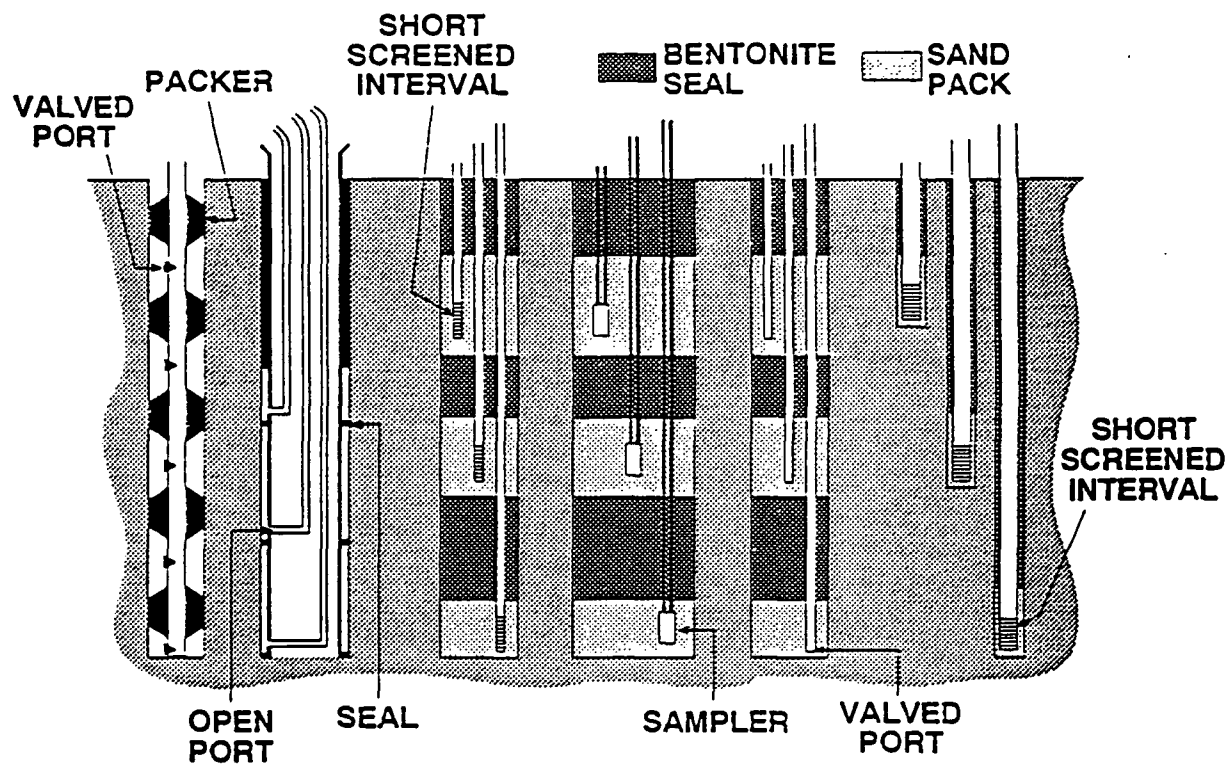
Figure 20. Examples of point sampling systems (after Patton and Smith, 1988).

Because these samplers are usually installed for other purposes, incompatibility of materials with monitoring objectives is often a problem. Everett et al. (9), Dunlay (79), and U.S. Environmental Protection Agency (80) discussed this topic.

Following are some of the methods for sampling perched groundwater:

- Point samplers
- Wells
- Cascading water samplers
- Drainage samplers

POINT SAMPLERS

Point samplers are open ended pipes or tubes, such as piezometers or wells with short-screened intervals, installed for the purpose of collecting samples from a discrete location in saturated material (see Figure 20). Samples are collected by bringing liquid which flows freely into the device to the surface by one of a variety of methods. Figure 20 presents various point sampler configurations which have been used (2, 9, 19, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96).

LOCKABLE
PROTECTIVE COVER

WELL CAP

CONCRETE
SURFACE
SEAL

CASING

SURFACE
CASING

SURFACE
CASING SEAL

POTENTIO-
METRIC
SURFACE "A"

BACKFILL

ZONE
OF LOW
PERMEABILITY

POTENTIO-
METRIC
SURFACE "B"

SEAL

WELL
SCREEN

FILTER

DENSE PHASE
SAMPLING CUP
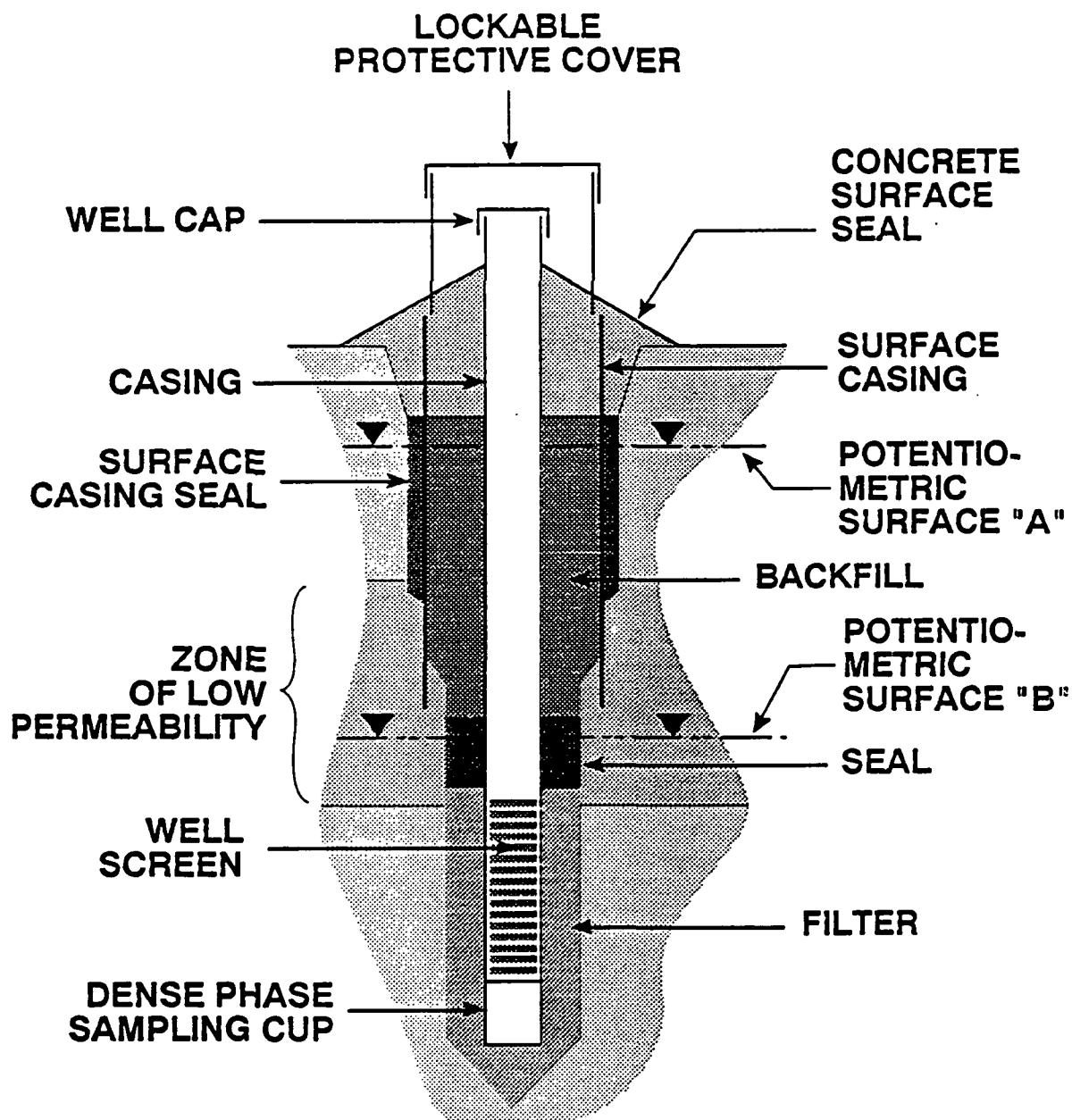
Figure 22. A monitoring well installed to sample from the lower of two
ground-water zones (after Riggs and Hatheway, 1988).
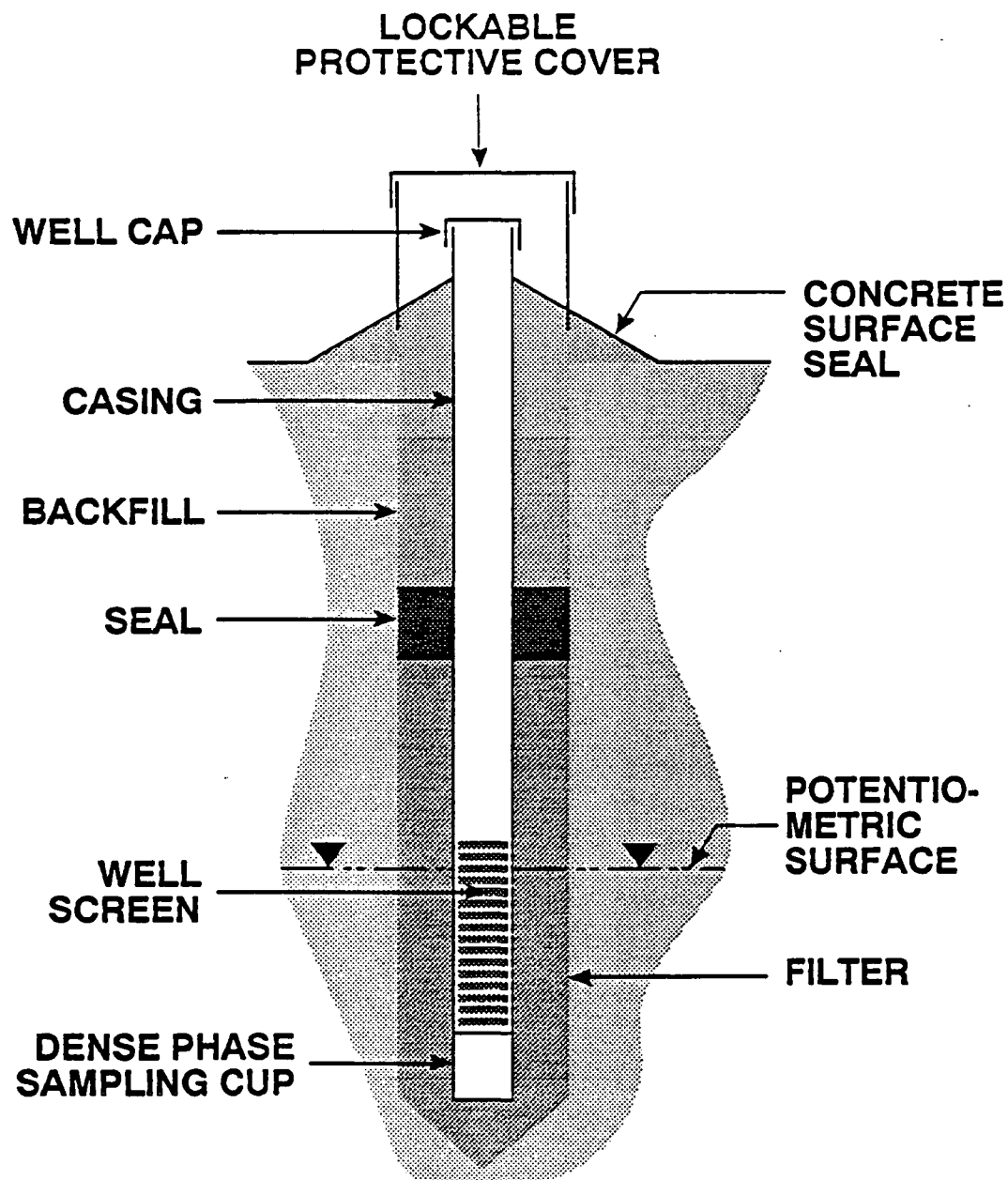
Figure 21. A monitoring well with the uppermost ground-water level intersecting the slotted well screen (after Riggs and Hatheway, 1988).
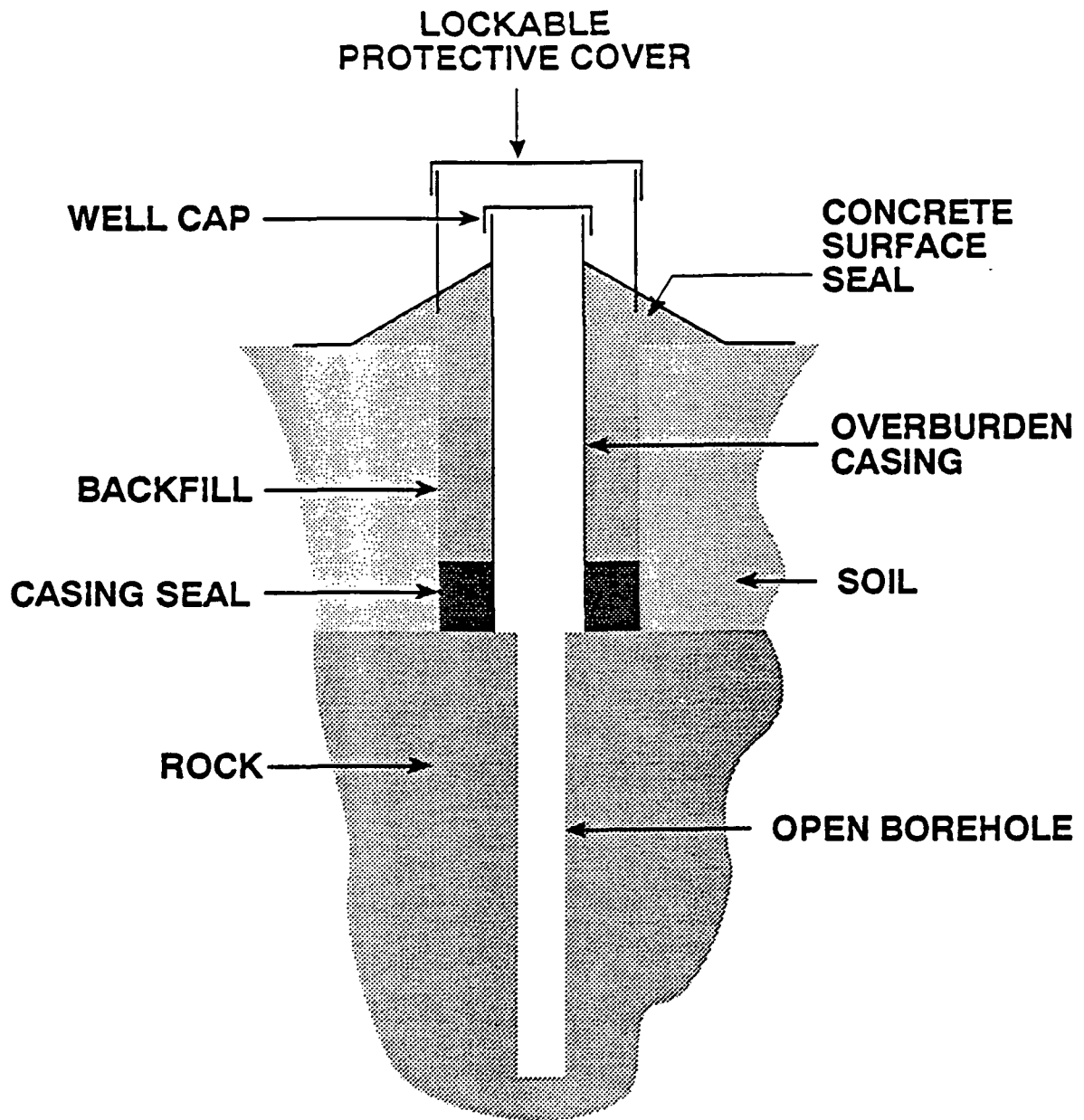
Figure 23.   An open-hole ground-water monitoring well in rock (after Riggs and Hatheway, 1988).

CASCADING WATER SAMPLERS

Cascading water occurs when a well is screened throughout a perched layer and the underlying water table (see Figure 24) or when water leaks through casing joints at the perched layer. Because the water table is lower than the perched layer, water flows into the well in the portion open to the perched layer, and cascades downward to the water table. This situation is common in some areas where the practice has been to install water wells with large screened intervals (44). Samples are collected by capturing liquid flowing into the well from the perched layer before it cascades down to the water table (78). Alternatively, water samples pumped from a well that has been shut down for a period of time represent ground water that has been influenced by cascading water (see Figure 24).

DRAINAGE SAMPLERS

Shallow perched systems may spread contamination, cause problems with structures, or interfere with agriculture. Drainage systems are installed to alleviate these problems. These systems cause gravity flow of perched ground water to a ditch or sump from which it is pumped out. This outflow can be sampled. Typical drainage systems include tile lines, half perforated pipes,

synthetic sheeting, or even layers of gravel and sand. Depending
on the design of the system, it may be possible to sample
outflows which drain different areas.

Schilfgaarde (96) contains numerous papers on the design and
construction of drainage systems. Donnan and Schwab (97)
described sampling from agricultural drainage systems. Gilliam
et al. (99), Gambrell et al. (100), Eccles and Gruenberg (101)
and Gilliam et al. (102) described sampling from tile drainage
lines. Gilliam et al. (99) and Jacobs and Gilliam (103)
described sampling from drainage ditches. Wilson and Small (104)
described a lateral drain sampler installed beneath a new
sanitary landfill.
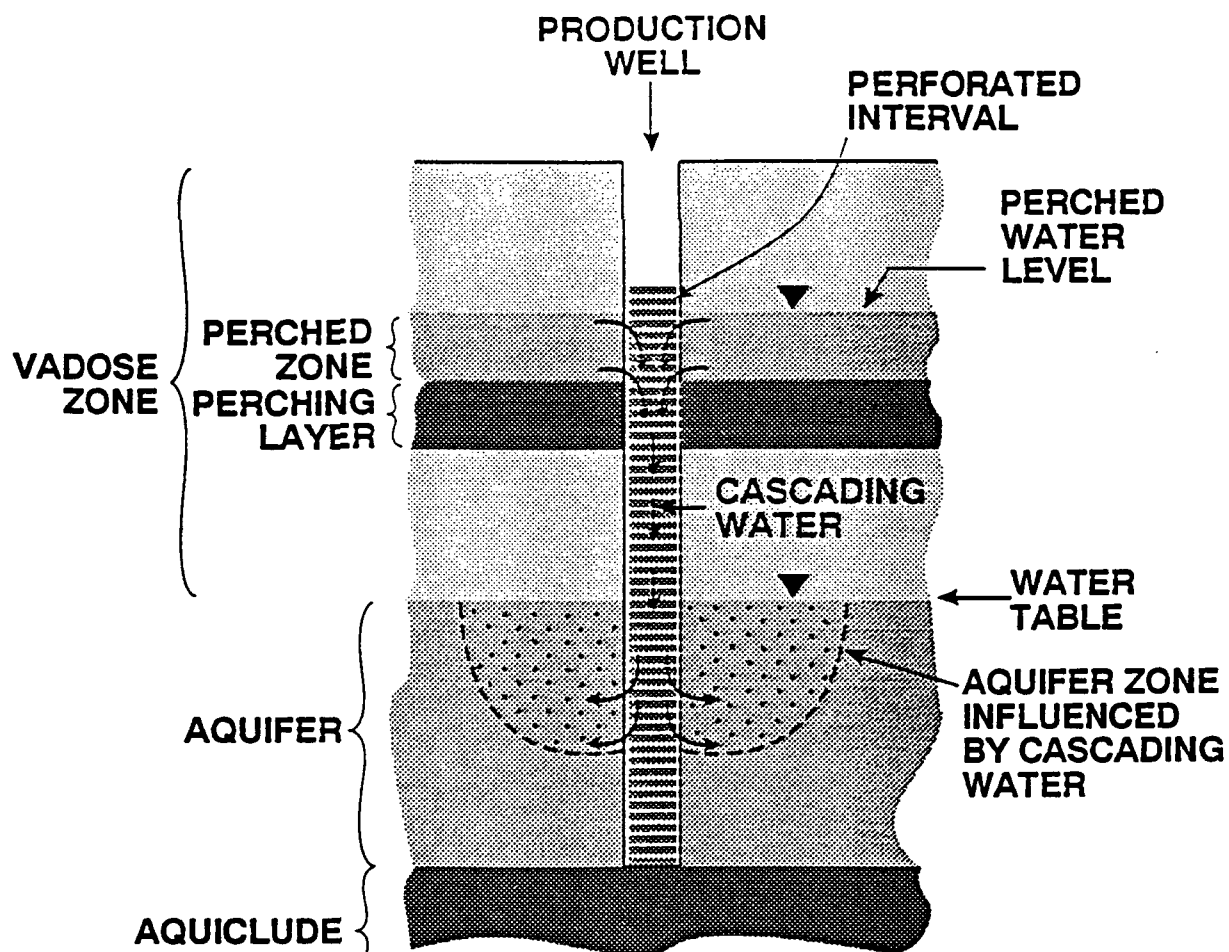
Figure 24. Conceptualized cross section of a well showing cascading water from perched zone (after Wilson and Schmidt, 1979).

tracer chemical should also be conservative. That is, in the case of an organic compound, the tracer chemical should not be reactive and it should not interact with the environment, for example, by adsorption on to the materials of the media being monitored.

As might be expected even when the final indicator parameters for RCRA ground-water monitoring were selected (pH, specific conductivity, total organic carbon, and total organic halogens), it became apparent quickly that many uncertainties associated with these indicators were still present when they were compared with the properties for an ideal indicator parameter. As a result, one of the conclusions reached in the RCRA ground-water monitoring program was the need to develop guidance for selecting and using indicator parameters by specifying conditions such as type of operations or hydrologic situations under which valid correlations could be expected. Unfortunately, ground-water regimes being examined would not be expected to be readily comparable with the varieties of conditions which actually exist in the vadose zone. In addition, site-specific differences between aquifers and vadose zone sediments in different regions of the country could in some cases invalidate the use of the same indicator parameters.

In the vadose zone, therefore, it appears more reasonable to select a series of indicators that would be consistently valid

SELECTING INDICATOR PARAMETERS FOR PORE-LIQUID SAMPLING OF

PETROLEUM HYDROCARBON CONTAMINATED SITES

One of several original concepts used by the Environmental Protection Agency (EPA) in its ground-water monitoring program developed under the Resource Conservation and Recovery Act (RCRA) was the selection of indicator parameters and tracer chemicals for the detection/monitoring phase. The purpose of these measurements was to provide an initial indication of whether migration of hazardous constituents in the ground-water regime had occurred. This concept can also be applied to contaminant migration monitoring in the vadose zone.

Among the key factors to be considered in selecting any indicator parameter is to find a compound that is naturally absent from the overall system to be monitored, and yet is related to the compounds that are in the source being monitored. The indicator parameter(s) should be selected from the broad range of compounds stored in the UST since they will behave in a similar manner in the environment. Also, analytical sensitivity, precision, accuracy and costs of the monitoring procedures should be reasonable. If a tracer that is exotic by definition and absent from the system being monitored cannot be found, then the next best choice might be an indicator parameter which provides a measure of relative change rather than indicating only the presence or absence of this particular compound. An effective

C8) (cracking) range and produce a high percentage of branched (reforming) chains, both of which increase the octane rating.

Petroleum products make up a family of related organic products. Gasoline contains a mixture of low-boiling hydrocarbons typically made up of branched-chain alkanes, alkenes, and cycloalkenes (aromatic hydrocarbons). In general, the chain lengths are between C4 to C8.

Aviation jet fuels are generally composed of light petroleum distillates consisting of mixtures of gasoline and kerosene with kerosene containing carbon chains from about C9 to C14, and having a somewhat higher octane rating than automotive gasoline since it contains a large fraction of aromatic hydrocarbons. Diesel fuels are generally composed of carbon chains ranging rom C11 to C20 and contain very small quantities of aromatic hydrocarbons.

Another category of petroleum products consists of lubricating oils. They contain higher molecular weight hydrocarbons with carbon chains ranging from C20 to C28 and contain very low concentrations of aromatic hydrocarbons. Waste oils may contain some additional products generated by thermal decomposition of the lubricating oil during its use.

for similar situations within the realm of vadose zone monitoring applications, and which would also be compatible with and be representative of the various types of materials which represent typical contaminant sources. The family of indicator parameters for this purpose will likely be considerably larger than for ground-water monitoring programs. By understanding the various environments which can exist and the various petroleum hydrocarbons which are stored and represent contaminant sources, an indicator parameter system can be selected to be somewhat more dependent on site-specific conditions than the indicator parameters typically used for ground-water monitoring programs.

CHEMISTRY OF PETROLEUM PRODUCTS

Petroleum products are complex substances made up of many chemical compounds generally produced from petroleum crude oil. Petroleum crude oil is subjected to fractional distillation which separates a number of individual hydrocarbon products based on their boiling point. In addition to distillation, the organics are also subjected to catalytic cracking and catalytic reforming. Cracking refers to the breaking of long carbon chains to form shorter carbon chains with lower molecular weights. Reforming refers to transforming straight-chain hydrocarbons into branched-chain hydrocarbons. The purpose is to produce a hydrocarbon fraction (gasoline) which is in the four and eight carbon (C4 to

the chemicals that have been used by the major petroleum companies to specifically identify their products. Since they vary from manufacturer to manufacturer, they are not likely to be candidates for indicator parameters. However, if a site has multiple potential sources of leaks, they might be useful in identifying which source is the contributor.

Physical and chemical information of petroleum hydrocarbon compounds typically found in gasoline are summarized in Table 4. This information includes water solubility of hydrocarbons, boiling points of individual compounds, and vapor pressures. The list of gasoline components was selected from the California Leaking Underground Fuel Tank (LUFT) Field Manual.

Each of these individual compounds in this complex mixture of chemicals have their own chemical and physical properties which will determine how they behave in the particular subsurface environment into which they are introduced. Since most of the components are of lower molecular weight, they normally have high vapor pressures, and, therefore, will be present in the vapor phase. In addition, these lower molecular weight compounds all have some solubility in water ranging from several thousands parts per million to a few parts per million. As a result, in pore liquids, these organics will be present as two distinct phases in the environment. The water soluble portion of the organic is known as the water phase. The water insoluble,

Prior to the introduction of the higher octane gasolines (unleaded and super unleaded gasolines), compounds like tetramethyl lead and tetraethyl lead had been added to the lower octane gasolines to reduce knocking and increase or boost the octane ratings. Other organic compounds, such as ethylene dibromide (EDB) or ethylene dichloride (EDC), have also been added to leaded gas primarily because of their ability to remove lead from the engine. With the gradual phasing out of leaded gasoline, and, as a consequence, phasing out the use of organic lead compounds and EDB and EDC as additives, large amounts of aromatic hydrocarbons such as benzene and toluene are being added to boost gasoline octane ratings for increased engine performance and to prevent knocking.

In recent years, methanol and ethanol have also been added to gasoline to make products referred to as "gasahol." The alcohols are also used primarily to boost the octane, and, as a secondary benefit, reduce the effect of water in the gasoline. Another gasoline additive that has been used recently to boost octane ratings is methyl tertiary butyl ether.

Another category of compounds is made up of gasoline additives. Some of these additives, while they represent a very small fraction in gasoline, are chemical compounds with markedly different properties from the branched chain and aromatic hydrocarbons which contain only carbon and hydrogen. These are

immiscible portion is known as the non-aqueous phase. Since non-halogenated hydrocarbons have densities less than water, they will float in the water phase. If the hydrocarbons are halogenated, i.e, contain bromine and chlorine, like EDB and EDC, their densities are greater than water, and any immiscible portions of these compounds will sink to the bottom of the water phase. This is further complicated by the fact that most organic compounds are subject to biodegradation, and some of the degradation products from microbial processes can also be present in either phase.

FACTORS AND CONSIDERATIONS THAT AFFECT THE SELECTION OF INDICATOR PARAMETERS

As a first step in selecting indicator parameters, it is necessary to define, in general, the products to be monitored. Petroleum hydrocarbon compounds can be divided into several major categories that can be further defined by products stored in tanks. It is also helpful to further divide some of the major products stored in tanks. It is also helpful to further divide some of the major products into subcategories. The major product categories can be defined as complex multi-component systems, simple multi-component systems, and single component systems.

TABLE 4. SELECTED PHYSICAL AND CHEMICAL PROPERTIES FOR MAJOR COMPONENTS FOUND IN A TYPICAL GASOLINE MIXTURE					
	Solubility (ppm)	Boiling Point (°C)	Vapor Pressure (mm Hg)	Henry's Law Constant (atm-m^3/mole)	Specific Density[A]
Benzene	1791	80.1	95.19	5.48×10^{-3}	.8765
Toluene	550	110.6	22.0	6.74×10^{-3}	.8669
Ethylbenzene	152	136.2	10.0	$6.44.10^{-3}$	.8670
m-Xylene	146	139.1	8.3	6.3×10^{-3}	.8642
o-Xylene	175	144.4	6.6	5.1×10^{-3}	.8610
p-Xylene	198	138.3	8.76	7×10^{-3}	.8610
n-Butane	61[B]	-.5	1823	.947	.6012
n-Pentane	35	36.1	430[B]	1.23	.6262
n-Hexane	13[B]	69	120[B]	1.68	.6603
Ethylene dibromide (EDB)	250	131.6	11[B]	N/A	2.701
Ethylene dichloride (EDC)	8650	83.7	8%	9.8×10^{-4}	1.2351
Tetraethyl Lead	N/A[C]	110	.15[B]	N/A	1.659
Tetramethyl Lead	N/A[C]	110	22.5[B]	N/A	1.99

[A]Based on compound at 20°C and water at 4°C

[B]At 20°C

[C]Decomposes in water, ultimately to Pb^{++}

Note: Unless otherwise noted, physical properties listed at 25°C

Sources: 1) Montogomery, J.H, and Welkom, L.M. 1990. Groundwater Chemicals Desk Reference. Lewis Publishers. Chelsea, MI.
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suited as an indicator parameter. Since the simplest examples are those tanks containing single component products stored as raw materials or finished products, the choice of an indicator parameter for this case will also be the simplest.

The two subcategories which exist in a single component system are organic and inorganic liquids. The inorganic chemicals are most likely strong acids or strong bases, or highly concentrated solutions of inorganic salts which are water soluble. The organic chemicals are single chemical products such as benzene, acetone, or chlorobenzene. In these cases, the logical indicator parameter to identify for single component systems is the particular organic or inorganic chemical which is stored in a potential contaminant source. Inorganic products can be monitored using generic indicator parameters such as electrical conductivity and/or pH, while the organic products can be monitored using a sensor for specifically detecting the presence of that organic compound.

Storage tanks containing simple multi-component systems consisting of simple mixtures of organic chemicals are also relatively simple to monitor. Indicator parameters can most likely be selected from the organic component present in the tanks that has the highest concentration provided its physical and chemical properties lend themselves to measurement in the field. In general, simple multi-component systems contain less

The largest single product category under multi-component systems would be petroleum products. The category of petroleum products can be further divided into subcategories, ie., automotive fuel, aviation fuel, diesel fuel, and other petroleum products such as lubricating oils, waste oils, etc. As examples of simple multi-component systems, two subcategories would be mixtures of compatible chemicals stored for recycling and mixtures of compatible hazardous wastes. Examples of single component systems would be tanks storing either a raw material or finished product. These substances, as well as any other substance in a single component system can be further separated into two general subcategories - organic materials and inorganic materials. Indicator parameters that will eventually be selected as representative of a particular petroleum hydrocarbon compound will most likely be chosen from each one of these various subcategories wherever possible. While the three generic divisions and the major categories within them are convenient for describing petroleum hydrocarbon compounds, the subcategories represent that particular population which contains the characteristic element(s) that can be utilized as the indicator.

The next step in selecting indicator parameters is to determine the chemical components which are present in each one of these subcategories. Their chemical and physical properties are then used to assist in selecting those chemical(s) which are best

be affected by the subsurface depending on their chemical and their physical properties which differ from component to component. Without a thorough understanding of these chemical and physical properties and how these properties govern the behavior in the vadose zone, it is difficult to make any determination of what component or group of components should be selected as an indicator parameter(s).

Finally, the selection is made more difficult by the fact, as noted earlier, that the vadose zone is also a multicomponent system. It is composed of three separate phases: solids, liquids and gases. Each phase may also consist of several different substances. For example, the solid phase, soils, is typically a variable mixture of coarse to fine-textured particles.

The analytical method selected to measure an indicator parameter is an important consideration. Some products may lend themselves in particular to simple analytical measurements such as pH or conductivity which can be made in the field, while other products would require more sophisticated laboratory analytical techniques.

Any attempt to deal with early detection monitoring of leaks in the vadose zone requires an understanding of the nature of the product which has been released and its behavior in the

than four to five individual chemicals and all of the materials are typically chemically compatible. For example, one typical storage unit might contain only hydrocarbons with similar boiling points and vapor pressures being stored prior to recycling, while another typical unit could contain chlorinated hydrocarbons to be incinerated. Since the organic compounds within each tank would have to be compatible for safety requirements, it is quite likely they would have similar boiling points and vapor pressures. Therefore, in most instances, it is relatively straightforward to select an indicator parameter for tanks containing simple multi-component systems.

Of all three divisions, the complex multi-component system is the most difficult one to select a chemical from that would be a suitable indicator parameter since, by definition, there are many individual chemical substances present in varying amounts. This division is unique since, for all practical purposes, the only substances that make up the division are petroleum products. As discussed earlier, there are several different petroleum products, e.g, jet fuel, gasoline, kerosene, and other examples. The differences are small, however, such as lower or higher molecular weight fractions or percentages of aromatic hydrocarbons. All are basically the same complex multi-component mixtures of hydrocarbons. The presence of all of these chemical compounds greatly complicates the behavior of the mixture when they are released into the environment as they will interact and

In any monitoring system, false positives or false negatives can occur. A false positive will lead to the conclusion that a release has occurred when no release, in fact, has occurred. A false negative will lead to the conclusion that no release has occurred when, in fact, a release has occurred. Therefore, an ideal indicator parameter system would prevent the occurrence of false negatives and false positives. For example, if two or more indicator parameters are identified to be present in an established ratio in the source mixture, then the detection of only one of these components would not conclusively indicate that a new leak is occurring. Further, detecting one of these components could suggest that: 1) an "old" or "aged" leak which has been subjected to biodegradation has occurred or, 2) a new leak has occurred and the sampled liquid may not contain both indicator parameters due to contaminant partitioning at the sampler porous membrane or in the soil prior to reaching the pore liquid sampler.

All of this information would seem to indicate that although indicator parameters can be selected to monitor and identify contaminant releases, it is unlikely at this time that any single indicator parameter can be selected for all systems that must be monitored. In fact, it would appear that, specific indicator parameters are typically used for specific types of materials stored in the underground environment. The goal, therefore, is to define those indicator parameters which can be used

subsurface environment. Consequently, a knowledge of (1) the physical and chemical properties of products which are potential contaminants, (2) the mechanisms responsible for contaminant releases, and (3) knowledge of the environment into which the chemicals are leaking, is necessary. Only with this understanding can any comprehensive program provide early warning for detecting leakage prior to its introduction into the ground-water regime.

The fact that the vadose zone is made up of a series of totally different and unique environments varying substantially from site to site, which are almost never homogeneous, is likely the most difficult problem to address. The vadose zone is a complex environment consisting of components of both saturated and unsaturated zones. The capillary fringe zone is the next deeper zone normally encountered and is underlain by the aquifer or the saturated zone. The migration of hazardous constituents from leaking petroleum hydrocarbon contaminant sources is even more complex since the mechanism for migration is different within each of these zones. Therefore, the fundamental understanding of the migration of hazardous constituents must include an awareness of all of the hydrogeologic complications which can exist in each zone and must consider as a consequence the multi-dimensional interactions which can occur.

affecting migration of liquids from a leaking tank and their

affects on monitoring methodologies, parameters relating to each

process controlling transport and fate, and monitoring

methodologies showing the interaction of the processes with

monitoring technology, are summarized in several tables. For the

purposes of this report, it is useful to modify and expand these

tables to include the concept of indicator parameters. A brief

discussion of each indicator parameter's physical and chemical

properties has been included to assist in understanding how they

will control migration of liquids.

In selecting indicator parameters for monitoring the release of

petroleum hydrocarbon liquids, it is necessary to understand the

processes controlling subsurface migration or transport of these

liquids and to recognize that there will most likely be three

components present affecting transport or migration: (1) the

stored product, (2) the product vapor, and (3) the water. The

processes which govern product and vapor mobility and migration

are, in general, very poorly understood.

Two distinct aspects of the migration process can typically be

identified: transport processes and fate processes. Transport

processes are those responsible for the actual movement or

migration of the constituents through the soils in the

subsurface, while fate processes are those responsible for

transformation or retardation of the constituents which of course

unequivocally. Furthermore, the goal should be to provide families of specific indicator parameters which are likely to indicate that any potential release source with its associated system is leaking so that this system can be used until another more general approach becomes apparent. This approach will then accommodate both those single component and simple multi-component systems as well as the complex, multi-component products, which represent the single largest percent of petroleum hydrocarbons.

As has been pointed out previously, the vadose zone is extremely complex and any attempt to select indicator parameters without making some simplifying assumptions would not be successful. If some generalities are used to simplify the conditions in the underground environment, then indicator parameters can be selected to monitor for leaks until a better understanding of transport and fate processes are provided by continued research efforts. In addition, by collecting information from indicator parameters used for monitoring, a database can be acquired which would lead to areas where future research efforts could best be concentrated.

FATE AND TRANSPORT CHARACTERISTICS OF INDICATOR PARAMETERS

In a recent report entitled "Processes Affecting Subsurface Transport of Leaking Underground Tank Fluids" (117), processes

Each of the fixed parameters of a liquid, which are its chemical and physical properties, are discussed separately in the report. Solubility is a key parameter which influences persistence, transport, and the ultimate fate of the leaking liquid in the natural underground environment. Adsorption, dispersion, diffusion, volatilization, degradation, toxicity, and other similar properties are functions of the solubility of the liquid and its concentration in water. Density of the liquid influences migration. For example, those liquids with densities less than that of water "float" on the water layer, while those which are denser than water sink to the bottom of the water layer. The viscosity of a liquid affects its flow velocity or its ability to transport, migrate within the subsurface environment.

The surface tension of the liquid is responsible for the capillary effects and the wetting of the soil particle surfaces in the underground, and the dielectric constant, which is a measure of the dipole moment of the liquid, influences its ability to adsorb on the soil particles. A liquid with a high dielectric constant has a high dipole moment and would adsorb strongly on an ionic solid (soil grains with charged particles on their surface, such as clay). In a mixture of water and an organic compound, water adsorbs preferentially since it has the highest dielectric constant. Vapor pressure and the boiling point of a fluid have an affect on what portions of the fluid will be in the vapor phase of the subsurface environment within

has an effect on migration. By understanding these aspects of the migration process, suitable indicator parameters for monitoring tank leakage can be selected. Transport can occur by both liquid and vapor migration; soil surface and interface properties between the various phases in the unsaturated zone and biological degradation can affect the fate or distribution in the environment.

Major attenuation mechanisms for organic chemicals are biodegradation, adsorption, and volatilization, all of which will be determined by the physical/chemical properties of the fluid. Although biodegradation is important in the attenuation of organics, it is specific to organics rather than all chemicals in general and not generally applicable to every chemical. Excluding mercury, volatilization is also unique to organic chemicals and is governed by their fixed properties such as vapor pressure, boiling point, and Henry's law constant, but also by the variable properties of the environment such as the air-filled porosity, pore size and shape, and temperature.

Adsorption is determined by the fixed properties of the liquid, its molecular structure, dielectric constant, solubility, and viscosity as well as the variable properties of the environment such as the soil organic content, the volumetric water content, and surface area of soil particles. Adsorption occurs to some extent for all chemicals.

Another major attenuation mechanism for organics is volatilization. Although detecting the presence of a leak through monitoring for vapor release is very cost effective, there are problems associated with this approach because of the many complications which can occur as a result of the subsurface environment. To simplify these complexities, indicator parameters can be identified by considering only the physical/chemical properties of the liquids, and ignoring the interactions which can occur in the subsurface. Using this approach, vapor monitoring can be considered as an adjunct for monitoring the leak. For example, vapor monitoring can be considered an early warning system that would indicate the possibility of a problem in the subsurface. Such an approach should be supplemented by appropriate monitoring for pore liquids. This approach could prove useful particularly in those instances where it is not feasible either technically or economically to monitor continuously for liquids, but where an early alert would be desirable.

SELECTION OF INDICATOR PARAMETERS

As discussed in earlier sections, selection of indicator parameters for single component systems and even simple multi-component systems is straightforward. The complex multi-component system consists essentially of petroleum products in the system for which it is more difficult to select indicator

the vadose zone. Vapor phase hydrocarbons can exhibit enhanced mobility in vadose zone pore spaces not occupied by liquid, potentially migrating extended distances to redissolve into pore water at some remote location.

Adsorption and volatilization can be discussed in terms of how the physical/chemical properties affect interaction of the liquids in the underground environment with the variable characteristics of the unsaturated zone and to what extent site environmental factors have on their behavior. Adsorption is applicable only to liquids which are organic substances. It is responsible for the attenuation mechanisms which remove organics through adsorption. The moisture content and organic content of the soil, the soil surface area, and the pore/water chemistry all influence adsorption processes and determine the transport and fate of the liquid.

The physical/chemical properties of liquids in the subsurface environment cannot be altered except through biodegradation. In addition, variable conditions in the subsurface environment are responsible for surface chemical affects that influence transport and fate. It follows that chemical constituents under consideration as indicator parameters should be selected based on the properties of the subsurface environment; consequently, it is more suitable to select several sets of environmental indicator parameters for different sets of conditions.

Because so many previous studies have included three other alkyl benzenes - toluene, ethyl benzene, and total xylenes, they will also be included in this list of candidates. Other criteria such as the chemical/physical properties of petroleum products, rather than concentrations as the sole criteria, can be used to screen indicator parameters from the list of potential candidates.

Brief descriptions of these 10 organic compounds, presented below, provide a summary of chemical and physical properties which will assist in the selection of the most appropriate indicator parameter(s).

Benzene is a clear, colorless, highly flammable liquid. It is the simplest of the aromatic hydrocarbons and has the highest water solubility of all of the potential indicator parameters.

Toluene or methyl benzene, an aromatic hydrocarbon, is a flammable liquid very slightly soluble in water and has been used as a gasoline additive for blending in the preparation of unleaded gasolines.

Ethyl benzene, also an aromatic hydrocarbon, is a derivative of benzene with one of the hydrogens on the ring substituted with an ethyl group. It is a colorless, flammable liquid that is essentially insoluble in water. It is a product of the cracking and reforming catalysis from crude petroleum oil.

parameters. However, by using the assumptions made in previous
sections, some reasonable choices can now be made.

There are thousands of individual organic chemical compounds in
the many commercial petroleum products. Consideration of only
those hydrocarbons appreciably ubiquitous at potential sources of
petroleum hydrocarbon release reduces the number to under 15 –
three straight-chain alkanes, six branched-chain alkanes, and six
alkyl benzenes. One of the elements, lead (Pb), is present at a
concentration significantly higher than any of the others, and
two non-petroleum organics, ethylene dibromide and ethylene
dichloride, account for the majority of the additives although
they are only present in a few parts per million (approximately
100 ppm to 300 ppm).

The 15 petroleum organics can be further reduced in number by
considering only the five elements that represent 60 percent of
those present in appreciable quantities. Including the element
lead and the additives EDB and EDC, eight potential choices that
can be used as indicators for the presence of a gasoline leak can
be identified as follows:

2	straight-chain alkanes
2	branched-chain alkanes
1	alkyl benzene
1	element
2	additives

area soils (117) and may not be seen in pore-water samples above
the detection limit.

Ethylene dichloride (EDC) or 1, 2-dichloroethane is similar to
EDB with chlorine substituted for bromine. It is a liquid with a
density greater than water and very high water solubility. Both
of these compounds are used as scavengers for lead in engines
that use leaded gasoline.

Tetraethyl lead is an organo-metallic compound that is used as a
gasoline additive to prevent knocking in automotive engines. It
is used only in leaded gasolines. It is essentially insoluble in
water, but is soluble in benzene, gasoline and other similar
organic compounds.

Each of these chemical and physical properties will be important
in determining the chemical's behavior in the subsurface
environment. For example, benzene has a relatively high vapor
pressure, a specific gravity less than water, a viscosity
slightly less than water, and a high water solubility. These
properties can now be used to predict how this compound will be
distributed in the subsurface - the solid phase, the liquid
phase, and the vapor phase. It will dissolve in water to the
extent of its equilibrium solubility and will then form a
separate phase which is immiscible in water but will float on the

water table since it has a specific gravity less than water. Its high vapor pressure will allow a portion of it to vaporize and enter the vapor phase and its relatively low viscosity will allow it to migrate readily through the soil.

One need in particular is to differentiate between "old" leaks and "new" leaks. In many instances for existing installations, past operations will have released some amount of product prior to when the requirements for monitoring were recognized. When a monitoring system is installed, background values of organic compounds may be high enough that if the tank now begins to leak, it will not be recognized because of the high background. In particular, this will be the case when the parameters that are being used to monitor leaks are the more volatile aromatic hydrocarbons commonly used; such as benzene, toluene and xylene, and if attention is given exclusively to the individual concentrations of each organic compound.

Comparison of the relative ratios of leaked organic liquid constituents to the relative ratios of the constituents found in automotive gasoline may provide a possible means to differentiate between an "old" leak and a "new" leak. Over time, the various reactions and interactions within the soil environment which have been discussed earlier (differences in adsorption, chemical and biological degradation, volatilization, vapor transport and dissolution, and partitioning in soil pore-liquid between the

various organic components) will all begin to change the relative ratios of the leaked gasoline in the soil environment from that in the original leak source. Thus, over time, the "old" or aged leaked gasoline organic component ratios will be different from the "new" leaked gasoline organic component ratios. While background concentrations of the leaked residual "old" gasoline components will alter the concentrations of the "new" leaked gasoline components to some extent, the ratios should still be close. By obtaining data from existing old leaking tank installations and comparing these ratios to the new product ratios, the validity of this method of differentiating an "old" leak from a "new" leak can be established. The effectiveness of this approach is dependent upon the recognition that changes in gasoline product blends and source crudes occur with time.

CONCLUSION

A review of the cited literature reveals that it is difficult, and perhaps impossible, to obtain pore-liquid samples which are not altered by the sampling process (this concept is roughly analogous to Heisenberg's Uncertainty Principle for quantum mechanics). Investigators should choose sampling devices and methods which provide the least altered samples. However, cost considerations will dictate a point at which increased sample representativeness is not practical. At this point, it is the investigator's responsibility to document the types of alteration

caused by the sampling process. The research necessary to quantify these alterations has increased in recent years as vadose zone monitoring concepts have matured.

Early warning monitoring of contaminant movement in the vadose zone requires knowledge of potential release sources, an understanding of the chemical and physical properties of the potential contaminant, and familiarity with its behavior in the subsurface environment. The vadose zone is a widely varied and typically nonhomogeneous environment which includes regimes of both unsaturated and saturated flow. No one single indicator parameter can currently be identified for use in all systems that must be monitored. Specific indicator parameters must be identified for use in monitoring each specific potential contaminant material and application. Ideal properties of an indicator parameter are dictated by the factors identified in this report.

Liquid alterations caused by the sampling process are important. Probably, however, alterations of non-dilute solutions are generally less significant than the inherent, spatial variabilities of pore-liquid chemistries. Such variabilities are caused by preferential flow and physical heterogeneities (105, 106, 107). As a result, even an unaltered pore-liquid sample should only be viewed as representing temporally the sample location and not representing spatially any other point. This

limitation does not detract, however, from the value of vadose

zone monitoring systems in a comprehensive ground-water

monitoring and protection program. The primary purpose of

installing such systems is early warning and detection of

pollutants moving from a release source.

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SPS E.P. Meier
Eugene P. Meier, Director, AMD

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SUBJECT: Transmittal of Deliverable Report (89-0889A), "Criteria for
Selecting Monitoring Devices and Indicator Parameters for Direct
Pore-Liquid Sampling of Petroleum Hydrocarbon Contaminated Sites"
(USER'S GUIDE)

FROM: Robert N. Snelling
Acting Director

TO: Sylvia K. Lowrance
Director, Office of Solid Waste (OS-300)

The subject report is a user's guide for selecting pore-liquid
sampling equipment for vadose zone monitoring. This is one of a series of
outputs produced through a cooperative agreement with the University of
California at Santa Barbara entitled, "Vadose Zone Equipment Specifications
and Monitoring Strategies Development". The guidance in this document is
largely supported with guidance provided in the new ASTM standard guide for
pore-liquid sampling that also was produced through the same cooperative
agreement. Both guides will support an upcoming comprehensive OSW guidance
manual needed to implement upcoming regulations for extended vadose zone
monitoring requirements at hazardous waste sites. The OSW contact for this
report is Neal Durant.

The purpose of this document is to provide assistance to investigators
in developing approaches to pore-liquid sampling tailored to their individual
vadose zone monitoring requirements. Highlights of the subject guide follow:

1. Describes features and operating principles of pore-liquid
sampling devices.

2. Discusses suction samplers, free drainage samplers,
and perched groundwater samplers.

3. Describes criteria used in selecting sampling devices for
specific monitoring objectives.

4. Distinguishes between sampling for aqueous and non-aqueous pore-
liquids.

5. Details operational constraints of sampling devices.

6. Describes potential chemical interactions between sampling device
and various indicator analytes.

7. Provides approach to indicator selection and data interpretation.

8. Discusses factors relevant to sampling for petroleum products.

9. Explains importance of fate and transport considerations in selecting indicators.

10. Guides development of QA/QC plans.

The concept of monitoring pore-liquids is the most certain approach to identifying the migration of contaminants. Representative pore-liquid samples provide direct evidence of the presence or absence of contaminants, whereas other available techniques do not; e.g., soil gas sampling and neutron logging. The research supporting the preparation of this document focused on evaluating the performance and potential utility of available pore-liquid sampling equipment. The underlying research also indicates that there are significant limitations with available pore-liquid sampling equipment. We identified many of the limitations several years ago and have been working on the development of new equipment to improve our pore-liquid sampling capabilities. Presently, pore-liquid sampling needs to be used in conjunction with other techniques, such as soil gas sampling and neutron logging, for an effective monitoring network; i.e., pore-liquid sampling alone is not intended to provide all of the information needed to determine the probable migration of all contaminants. The objective in preparing this guide is to assist investigators in determining where pore-liquid sampling fits into their monitoring networks.

This output meets its intent of contributing to the acceleration and acceptance of vadose zone monitoring techniques. The EPA requires vadose zone monitoring for land treatment and has determined that it should be included in monitoring strategies for other types of regulated facilities. In California, vadose zone monitoring already is required for most types of operating and closed hazardous and solid waste facilities. California regulations make reference to official EPA guidance, EPA/530SW86040, "Permit Guidance Manual on Unsaturated Zone Monitoring for Hazardous Waste Land Treatment Units," and rely heavily on other EPA publications for implementing their vadose zone monitoring strategy. In addition, this document will provide an essential reference for a new official OSW guidance document for vadose zone monitoring.

Attachment

cc (w/attachment):
Neal Durant, OSW (OS-321)
Tom Baugh, OMMSQA (RD-680)
Margaret Hawkins, OMMSQA (RD-680)

cc (w/o attachment)
Rick Linthurst, OMMSQA (RD-680)
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