



## Project Summary

# Efficiency of Soil Core and Soil-Pore Water Sampling Systems

K. W. Brown

Laboratory column and field lysimeter studies were conducted to evaluate the efficiency of soil core and soil-pore water samples to detect migrating organic components of land treated wastes. In the laboratory, column leaching studies were performed by packing sieved soil into 35 cm  $\times$  4.6 ID glass columns. Bastrop clay, Norwood silt loam, or Padina loamy sand soils were amended with an API separator sludge (API), a solvent recovery sludge (SRS) or a wood preserving waste (WPW). A total of 10 pore volumes of leachate were collected from the columns and analyzed for bromide and selected organic chemicals. For both the Bastrop clay and Padina loamy sand amended with the API waste, breakthrough of hydrocarbons having 16 to 29 carbon atoms occurred in the leachate from the columns at 1 to 2 pore volumes. Break through of isophorone from the loam and clay soils amended with the SRS waste occurred between 3 and 5 pore volumes with a maximum concentration of 28  $\mu\text{g}\cdot\text{L}^{-1}$  detected in the leachate from the clay columns.

Pentachlorophenol and 2,4-dimethylphenol were the only two compounds from the WPW amended columns that were detected in high concentrations in the leachate. The concentration of pentachlorophenol in the leachate reached peak concentrations between 5 and 8 pore volumes while the 2,4-dimethylphenol reached a peak concentration between 2 and 3 pore volumes. Results from the laboratory column study indicate that chemical structure and soil texture will have a

major influence on the mobility of organic chemicals in soil. Long chain alkanes were leached rapidly through the soil but appeared in low concentrations while pentachlorophenol leached more slowly but was detected in higher concentrations.

For the field lysimeter study, large undisturbed monoliths of the Bastrop, Norwood, and Padina soils were collected and equipped with an under-drain system. Porous ceramic cups were installed at three depths in the monoliths. Soil core and soil-pore water samples collected periodically were monitored for 11 chemicals in the WPW amended soils, 8 chemicals in the SRS amended soils, and 19 chemicals in the API waste amended soils. Polynuclear aromatic hydrocarbons (PNA), as well as alkanes with greater than about 10 carbons and pentachlorophenol were preferentially adsorbed to the soil which made soil core samples most efficient for detecting these chemicals. Phenols, chlorinated and nitrogenated phenols, cresols, and aromatics were all weakly adsorbed by all three soils and thus were fairly randomly sampled by either the soil-pore water or soil core samples. Generally, for the aromatic constituents of the SRS waste, a higher percentage of samples had these constituents in the soil-pore water samples than in the soil core samples. Thus, for chemicals with octanol water partition coefficients ( $\log K_{ow}$ ) of four or larger, soil-pore water samples will be ineffective in detecting these chemicals. Chemicals having  $\log K_{ow}$  values of three or less are generally found in soil-pore water samples, and the probab-

ity of detecting transition chemicals (log  $K_{ow}$ 's between three and four) by soil core or soil-pore water sampling techniques is about equal.

**This Project Summary was developed by EPA's Robert S. Kerr Environmental Research Laboratory, Ada, OK, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).**

## Introduction

Unsaturated zone monitoring systems are currently required at hazardous waste land treatment facilities to determine if pollutants are moving beneath the treatment zone. Soil-pore water samples are taken to detect the movement of "fast moving" chemicals while soil-core samples are used to detect "slow moving" chemicals. While there is considerable information on the proper procedures to follow in obtaining a soil-pore water or soil-core sample, there is a lack of information on the efficiency of these two techniques in detecting chemicals, particularly organic chemicals, as they move through the unsaturated zone.

Because of ease of installation and operation porous ceramic cups are the soil-pore water sampler of choice. While much data have been collected using porous cups, most of it pertains to inorganic ion concentrations and little information is available on their effectiveness in measuring organic concentrations. Data by Tsai *et al.* (1980) and Smith and Carsel (1986) indicate that porous ceramic cups may have a significant capacity to adsorb and effectively screen out certain organic compounds; however, the magnitude of the problem is unclear. An additional problem with using these samplers is that the applied vacuum may vaporize some or all of the organic compound of interest (Barbee and Brown 1986).

The physical properties of organic chemicals often differ drastically from that of water and may cause them to move through the unsaturated zone as a separate, immiscible phase, probably as thin films floating on water. Barbee and Brown (1986) documented the rapid movement of xylene through macropores in well-structured soils. Thus, much heterogeneity exists in the soil solution but the ability of the porous ceramic cup to sample such a non-uniform solution is unknown now. Because the volume of soil from which a

porous cup extracts a water sample is dependent on the soil moisture content, soil texture, gradient applied, and possibly other factors, this phenomenon is further complicated.

Soil samples are thought to be best suited for sampling for constituents such as heavy metals and polar organic compounds which are adsorbed to the soil surfaces. The ability of a soil sample to accurately measure the chemical concentration of a constituent which is moving rapidly through the macropores of a well-structured soil is also unknown. Since both soil and water are present, soil-core sample analysis is further complicated. A high concentration of a given constituent in a small quantity of water may be masked by the large volume of soil which could have a low constituent concentration. Other unknowns include the number and size of samples to collect, how to sample on the scale of soil peds, how to sample heterogeneous areas, and how to sample liquid moving between peds.

Thus, both sampling systems are quite limited when monitoring the potential movement of organic constituents through unsaturated soil. The objective of this project was to determine the efficiency of soil-pore water and soil-core sampling systems for sampling and detecting organic chemicals which migrate beneath the zone of waste incorporation.

## Materials and Methods

A two-phased approach, consisting of laboratory soil columns and field barrel lysimeters containing undisturbed soil monoliths, was used. The laboratory soil column phase was conducted to determine the waste constituent movement rate as a function of pore volumes of water leached through the soil column. This data provided the means for designing the sampling schedule for the field barrel lysimeters.

The field barrel lysimeter study included 36 lysimeters, 12 each from profiles of the three soils used in the laboratory study. The three wastes used in the laboratory study were applied to the barrels so that three barrels of each soil received one waste with the remaining three barrels of each soil serving as controls. Soil-pore water and soil-core samples were taken on a time schedule according to the number of pore volumes of leachate collected from the bottom of the barrels. Thus, the soils could be sampled at the optimum time to catch the peak concentration of chemicals at a

particular depth. Likewise, the laboratory and field data could be compared through the number of pore volumes of leachate collected.

The same soils were used in both phases of the study and included Bastrop clay (Udic Paleustalf), Norwalk silt loam (Typic Udifluent), and Paducah loamy sand (Grossarenic Paleustalf). The three wastes selected for use included an API separator sludge (A) from the petroleum refining industry, solvent recovery sludge (SRS) produced from reclaiming nonhalogenated solvent-containing wastes, and a chlorinated wood preserving waste (WP) from a pine wood treatment plant. The major chemical constituents in each waste were identified initially by using a Hewlett-Packard Model 5970 Mass Spectrometer (MS) interfaced with a Model 5880 Gas Chromatograph (GC). Laboratory column studies were performed by packing 28 cm of nonsterilized sieved soil into 35 by 4.6 cm glass columns plugged with solvent washed glass wool. Five percent (by weight) of the dry soil was removed from the top of each column, wetted and mixed with waste at a rate of 5 percent (w/w) of the entire soil column. The soil remaining in the column was saturated, the waste amended soil was placed in the top of the column, and a 3-cm head of water containing 150 mg L<sup>-1</sup> bromide was applied. Leachate samples were collected in 0.1-pore volume increments for the first pore volume and 0.2-pore volume increments thereafter until 10-pore volumes were collected.

Leachate samples from the laboratory columns were analyzed for bromide and organics. Bromide analysis was done by specific ion electrode. Samples for organic analysis were extracted by the procedure of Giam *et al.* (1980). Chemicals were identified by GC-MS and quantified by a Tracor Model 51 Gas Chromatograph.

Field barrel lysimeters were collected using the procedure of Brown *et al.* (1985). To install the side wall flow barrels, 15 cm of soil was removed from the surface of each lysimeter. Five cm of soil were replaced and porous ceramic cups 6.2-cm long by 4.8-cm diameter were installed vertically at depths of 24, 41, and 61 cm below the original soil surface. One hundred ml of soil slurry followed by finely sieved soil was used to backfill the small gap between the porous cup sampler and the soil. A plastic collar was added to help prevent

sidewall flow along the sampler. All soils were tested with a bromide solution before waste application to assure that there was no sidewall flow. After testing, the remaining 10 cm of soil which had been removed from each barrel was mixed with waste and returned to the barrel. Waste application rates were 5 percent (w/w) for the API and SRS wastes and 1.5 percent for the NPW waste.

Soil core samples were taken using a 1.8-cm diameter Oakfield hollow cylinder tube sampler. Special care was taken to assure that loose contaminated soil did not fall down the hole and contaminate deeper samples. Each time the sampler came in contact with the soil it was washed sequentially with tap water, acetone, and distilled water to prevent any potential cross contamination. Sample holes were plugged with an appropriate length of stoppered PVC pipe. Sampling intervals were 20 to 30 cm, 36 to 46 cm, and 53 to 64 cm which corresponded to the 25, 41, and 61-cm deep soil-pore water samples. Soil samples were stored in solvent washed soil moisture cans, sealed with duct tape, and stored in a freezer. The soil samples were extracted using slightly modified Method 3540 (USEPA, 1982). Organic constituents were identified and quantified as previously described.

## Results and Discussion

The bromide breakthrough curves from the laboratory soil columns were consistent between the various soil-waste treatments with the effluent bromide concentration (C) reaching the influent bromide concentration ( $C_0$ ) typically at 1.4 pore volumes. Early bromide breakthrough was not observed on any of the columns which indicated that there was no preferential sidewall flow. The dispersion transport characteristics were evaluated by fitting the breakthrough data to the chromatographic equation for one-dimensional transport of a conserved anion as suggested by Goerlitz (1984). According to Goerlitz (1984), the dispersion coefficients for the soils were within the anticipated range. All the fitted curves pass very near  $C/C_0$  of 0.5 at 1-pore volume, which according to theoretical calculations, indicates that the soils behaved like homogenous porous media.

Peak concentrations of alkanes from API waste amended sand and clay soils in laboratory soil columns occurred after 2-pore volumes of leachate passed through the soil. It was estimated that

only 0.02% of the total amount of alkanes applied to the sand soil were leached through the column after 10-pore volumes of flow. PNA compounds began appearing in the leachate from all soils at about 3-pore volumes. For the SRS waste amended soil columns, isophorone was the major waste constituent. Peak isophorone concentrations occurred at about 2-pore volumes in the sand soil and 4-pore volumes in the loam and clay textured soils. Measurable quantities of pentachlorophenol began appearing in the leachate from all three soils in the laboratory columns after 3.5-pore volumes of leachate passed. In the loam soil a definite peak was observed at 6.5-pore volumes while in the sand and clay soils the concentrations continued to steadily rise through the 10-pore volumes collected. Concentrations of 2,4 dimethylphenol, a related compound, peaked at 3-pore volumes for all soils.

Of the field barrel lysimeters treated with API waste, the sand lysimeters had the largest number of samples containing waste constituents. This shows that the waste was most mobile in this soil. Waste constituents were generally detected in either the pore-water or core sample but rarely in both samples taken at the same time and location (Table 1). Lightweight alkanes such as nonane and decane with low octanol water partition coefficients were best sampled by taking a soil-pore water sample while heavier alkanes such as pentadecane were best sampled by taking a soil-core sample. Regression analysis comparing the soil-core data to the soil-pore data generally showed little correlation. Both the soil-pore and core data were highly variable and the standard deviations often equalled or exceeded the means.

PNA compounds leaching from the API waste amended soils were detected almost exclusively in soil-core samples with phenanthrene as a single exception. In the sand lysimeters, concentrations of acenaphthylene, acenaphthene, fluorene, fluoranthene and pyrene were significantly higher in the soil-core samples. In the loam textured soil, concentrations of acenaphthylene, anthracene, and chrysene were significantly greater in the soil-core samples. In the clay soil, only concentrations of acenaphthene and anthracene were significantly greater in the soil-core samples. Again, the variability in the data was very high resulting in large standard deviations and a lack of correlation between the soil-pore and core samples. The PNA

compounds had log  $K_{ow}$  values ranging from 3.92 to 5.79 and based on this would be expected to be partitioned onto the soil fraction. It is, therefore, reasonable that the soil-core samples were more efficient than soil-pore water samples for detecting PNAs.

Mobile constituents from the WPW-treated lysimeters were detected in both the soil-core and pore-water samples (Table 2). By arranging these chemicals according to their log  $K_{ow}$  values, it appears that those compounds with log  $K_{ow}$  values in the 1.5 to 3.4 range were weakly adsorbed to the soil and thus are fairly randomly sampled by both soil core and soil-pore water techniques. Pentachlorophenol tended to be more strongly adsorbed to the soil, and thus appeared to be sampled better by taking a soil core sample, while p-chloro-m-cresol was only detected in soil-pore samples. SRS waste constituents were weakly adsorbed to the soils and moved rapidly through all three soils. Generally, the greatest percentage of samples containing measurable quantities of constituents occurred in the soil-pore water samples (Table 3). The log  $K_{ow}$  values for this group of chemicals range from about 1.5 to 3.4 which further indicates that they are only weakly adsorbed to the soil and significant amounts may remain partitioned in the aqueous phase. Statistical analysis of the data showed that there was no significant difference between the two sampling systems and a correlation analysis of paired data failed to show any significant correlation between the systems. Perhaps the large variability in the data caused this. To reduce the variability of the data, any sampling system will require many samples.

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**Table 1.** The Percentage of Samples From Three Soils Having a Measurable Quantity of Each Alkane that Occurred in Either the Soil Core Sample Only, Pore Water Sample Only, or Both

Chemical	Log K <sub>ow</sub>	Soil Core -----	Pore Water (%) -----	Both
Nonane	4.51	17	83	0
Decane	5.01	11	89	0
Undecane	5.58	55	40	5
Dodecane	6.10	31	54	15
Tridecane	6.65	50	29	21
Tetradecane	7.20	75	25	0
Pentadecane	7.72	87	9	4
Heptadecane	8.25	96	0	4
Nonadecane	8.79	94	3	3
Tricosane	12.00	100	0	0
Tetracosane	12.53	91	9	0

**Table 2.** The Percentage of Samples From Three Soils Having a Measurable Quantity of Each WPW Constituent that Occurred in Either the Soil Core Sample Only, Pore Water Sample Only, or Both

Chemical	Log K <sub>ow</sub>	Soil Core -----	Pore Water (%) -----	Both
Phenol	1.46	50	50	0
2,4 dinitrophenol	1.53	75	25	0
2-nitrophenol	1.76	50	50	0
4-nitrophenol	1.91	0	0	0
2-chlorophenol	2.17	0	0	0
2,4 dimethylphenol	2.5	67	33	0
2,4 dichlorophenol	2.75	100	0	0
4,6 dinitro-o-cresol	2.85	88	6	6
p-chloro-m-cresol	2.95	0	100	0
2,4,6 trichlorophenol	3.38	14	86	0
Pentachlorophenol	5.01	75	25	0

**Table 3.** The Percentage of Samples From Three Soils Having a Measurable Quantity of Each SRS Constituent that Occurred in Either the Soil Core Sample Only, Pore Water Sample Only, or Both

Chemical	Log K <sub>ow</sub>	Soil Core -----	Pore Water (%) -----	Both
Ethylbenzene	3.13	44	32	24
Xylene	3.17	26	67	7
2-butoxyethanol		39	26	35
1,2,4-trimethylbenzene		27	69	4
Acetophenone	1.58	15	72	13
2-phenyl-2-propanol		31	44	25
Isophorone	1.70	31	30	39
Naphthalene	3.35	12	88	0

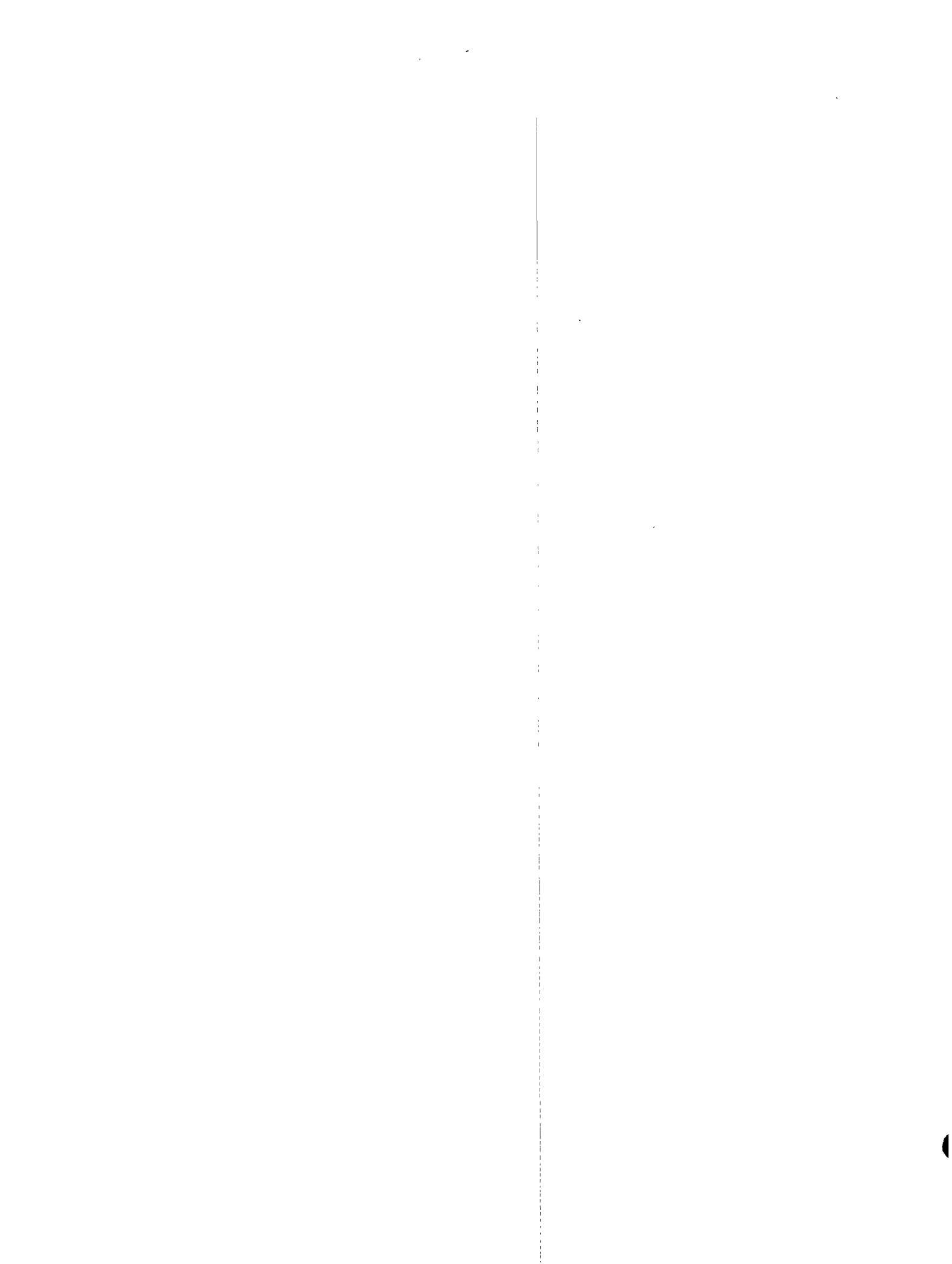
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*K. W. Brown is with Texas Agricultural Experiment Station, Texas A&M University, College Station, TX 77843.*

*Fred M. Pfeiffer is the EPA Project Officer (see below).*

*The complete report, entitled "Efficiency of Soil-Core and Soil-Pore Water Sampling Systems," (Order No. PB 87-106 100/AS; Cost: \$16.95, subject to change) will be available only from:*

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*The EPA Project Officer can be contacted at:*

*Robert S. Kerr Environmental Research Laboratory  
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P.O. Box 1198  
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