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***In-situ* Soil Solution Extraction with Polyacrylonitrile Hollow-Fibers.**

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ABSTRACT

Hollow-fiber samplers permit the non-destructive extraction of the soil solution from the soil matrix. Samplers constructed from polyacrylonitrile filter elements were successfully used to extract solution from a range of soil types. Preliminary testing showed that the filter elements did not retain any of the major anions or cations present in soil solution. Inorganic ions capable of specific adsorption (PO_4 and Cu) were not retained, but phytate concentration was reduced by passage through the filter. Comparison with centrifuge drainage extraction showed that soil solution obtained from hollow-fiber samplers had a higher pH, as a result of CO_2 degassing, and lower elemental concentrations. It was concluded that the hollow-fiber samplers were preferentially extracting solution from the larger pores, and that this solution may better represent that extracted by plants.

INTRODUCTION

Soil solution composition has become a widely used tool in understanding the bioavailability of elements and their interaction with the soil solid phase. Unfortunately, extraction of unaltered soil solution from the solid matrix of the soil is problematic (Wolt, 1994). Extraction procedures based on displacement (Adams *et al.* 1980), compression (Ross and Bartlett, 1990), centrifuge drainage at low (Gillman 1976) and high (Davies and Davies, 1963) speeds, immiscible liquid displacement (Mubarak and Olsen, 1976) and extraction through ceramic cups (Grassmann and Udluft, 1991) have all been widely used. Displacement and low speed centrifuge drainage are generally considered reference methods against which other approaches are evaluated.

A hollow-fiber extraction method using bundles of 0.25 mm diameter cellulose-acetate filter elements was proposed by Jackson and co-workers (Jackson *et al.*, 1976, Levin and Jackson, 1977), but has not been widely adopted. More recently the use of larger diameter polyvinyl alcohol (Yanai *et al.*, 1993) and polysulfone (Jones and Edwards, 1993) hollow-fiber soil solution extractors has been reported. These samplers offer the advantages of non-destructive soil solution sampling.

The objectives of this study were to evaluate polyacrylonitrile filter elements for use in hollow-fiber solution extractors, and to compare the solution obtained from a range of soils by these extractors with that obtained by centrifuge drainage.

MATERIALS AND METHOD

Hollow-Fiber Solution Sampler Construction

Hollow-fiber soil solution extractors were constructed from Asahi Chemical Industry Co. Microza AP series polyacrylonitrile ultrafiltration fibres (50000 dalton molecular weight cutoff), purchased as a filtration module from Pall Australia. The fiber elements have an outside diameter of 1.4 mm and internal bore of 0.8 mm and were removed from the filter module in 18 cm lengths. One end of the fibre was sealed with nylon fishing line (0.8 mm OD) secured with isocyanurate cement (Supa-glue) while the other was connected to a PTFE tube (1.6 mm OD) using a Tygon tubing joiner (1.14 mm ID). Vacuum was applied by connecting an evacuated 10 mL blood collection tube to the sampler using a 20G multi-sample needle.

Prior to use the samplers were pre leached for 2 h with deionized water (approximately 10 mL). The sampler pore volume was 0.42 mL, consisting of 0.22 mL in the 18 cm hollow-fiber element and 0.20 mL in 30 cm of PTFE tube.

Conformation of the Hollow-Fiber Extraction Zone.

The conformation of the soil volume from which hollow-fiber samplers extract soil solution was determined by placing a sampler in the center of a 25 mm diameter cylinder of soil (Soil D, Table 1) at field capacity. Vacuum was applied to the sampler and 7 mL of soil solution extracted. The soil column was then split longitudinally, and divided into 2 cm sections for the determination of gravimetric moisture content. The process was repeated, but using a longer extraction period to obtain 15 mL of soil solution.

Evaluation of Hollow-Fiber Effects on Solution Composition.

The potential for vitiative effects of the hollow-fiber filter elements on solutions was evaluated in several ways

- by analyzing synthetic solutions, with comparable composition to soil solution, before and after passage through a hollow-fiber filter element
- by analyzing soil solution before and after passage through a hollow-fiber filter element
- by comparison of the composition of soil solution extracted by hollow-fiber samplers with that obtained by centrifuge drainage.

Synthetic soil solution.

A synthetic soil solution of approximately 1.5 mM NaCl, 0.5 mM K₂SO₄ and 1.0 mM CaCl₂ and containing approximately 5 μM P as orthophosphate, 5 μM P as phytate (inositol hexaphosphate), and 10 μM Ni, Cu and Zn was prepared ensuring a slightly acid matrix was maintained (≈ pH 4). Portions of this solution were then adjusted to pH values of approximately 7 and 8.2 by the addition of NaOH. Equilibrium with atmospheric CO₂ was achieved by bubbling with air for 16 h. Portions of these solutions were then passed through hollow-fiber samplers using vacuum applied from a blood sampling vial. Solution pH was determined immediately following filtration. Control samples were filtered to 0.025 μm (Millipore VSWP) (Menzies *et al.*, 1991) prior to elemental analysis to minimize errors resulting from the presence of microparticulates. Three replications were made of each treatment, and data for hollow-fiber filtered and control samples compared using Student's t-test (Cochran and Cox, 1957). The three pH solutions were treated as different experiments.

Extracted soil solution

The effect of hollow-fiber filtration on extracted soil solution was evaluated on soil solution extracted from soils A, C and D by centrifuge drainage (Gillman, 1976). Soil solution was drawn through hollow-fiber filters using vacuum applied from an evacuated blood sampling vial and at low tension using a syphon effect. Solution pH was determined immediately following filtration. Control samples were filtered to 0.025 μm (Millipore VSWP) (Menzies *et al.*, 1991) prior to elemental analysis. Three replications were made of each treatment, and analysis of variance performed using SAS programs (SAS, 1996).

Comparison of hollow-fiber and centrifuge drainage extraction.

To compare soil solution extracted by hollow-fiber samplers and that obtained by centrifuge drainage a set of five soils of widely differing chemical and physical characteristics was selected (Table 1). For each soil, pots of approximately 1 kg of air-dry soil were prepared for soil solution extraction by adding sufficient de-ionized water to obtain a moisture content equal to that at 10 kPa suction. Where soil solution was to be obtained by hollow-fiber extraction, two 18 cm long fibers were placed into the air-dry soil prior to wetting up. Pots were covered with a plastic mulch to minimize evaporation and allowed to incubate for several weeks.

Soil solution was obtained from hollow-fiber samplers by attaching an evacuated 10 mL blood sampling vial. This vacuum was generally sufficient to obtain a 7 to 8 mL sample over an 8 h period. Following extraction, pots were adjusted to weight with de-ionized water, allowed to equilibrate for 1 day, and solution extraction repeated (soils A, B and C only). A total of three

extractions were made from each sampler. The centrifuge drainage procedure employed was essentially that of Gillman (1976), where 300 g samples of incubated soil were extracted at 700 g relative centrifugal force for a period of 40 min. Solution pH and EC were measured and bicarbonate concentration determined by potentiometric titration (APHA, 1992) on all samples immediately following extraction. Solutions obtained by centrifuge drainage were then filtered to 0.025 μm (Millipore VSWP) (Menzies *et al.*, 1991) prior to elemental analysis.

Three replications were made of each treatment, and the composition of hollow-fiber and centrifuge drainage solutions compared using Student's t-test (Cochran and Cox, 1957). Samples produced by repeated sampling were compared using a one way analysis of variance (SAS, 1996). Each soil was considered as a separate experiment.

Solution Analysis

Control and hollow-fiber filtered solutions were analyzed by inductively coupled plasma atomic emission spectroscopy (ICPAES) for Na, P, S, K, Ca, Ni, Cu and Zn. Orthophosphate was determined colorimetrically using malachite green (Motomizu *et al.*, 1983), and Cl determined using mercuric thiocyanate (APHA, 1992). Soil solution C concentration was determined by ICPAES following acidification and N_2 sparging (Oweczkin *et al.*, 1995).

RESULTS AND DISCUSSION

Conformation of the Hollow-Fiber Extraction Zone.

As hollow-fiber filter elements can be used to extract soil solution without disrupting the soil, they can be employed to repeatedly sample an experimental system. This provides a means of studying dynamic systems, such as plant uptake (Yanai *et al.*, 1996) or fertilizer dissolution effects on soil solution composition. To fully exploit this capability, the zone from which solution is extracted by a hollow-fiber sampler needs to be defined. As the soil matrix and filter element of the hollow-fiber present a greater constraint to the movement of solution than the inner pore of the sampler, it was anticipated that a cylindrical extraction zone would be produced. This was confirmed by the experimental data (Figure 1), the gravimetric moisture content being decreased uniformly along the length of the extraction fiber (fitted linear regression slope was not significantly different to zero, $P < 0.05$). This result confirms one of the assumptions made by Yanai *et al.* (1993) in calculating the soil volume from which solution was sampled.

Evaluation of Hollow-Fiber Effects on Solution Composition

Synthetic soil solution and extracted soil solution.

The synthetic test solutions were intended to evaluate the influence of the polyacrylonitrile filter elements, used to construct hollow-fiber samplers for this study, on a number of analytes, viz.

- The major cations typically present in soil solution (Ca, Mg, Na, and K)
- Micronutrient cations with the potential to be specifically adsorbed (Zn, Ni and Cu)
- The major anions typically present in soil solution (Cl and SO_4)
- Specifically adsorbing anions (PO_4)
- Organic phosphates (phytate)
- Soil solution pH

Filtration through the hollow-fiber sampler did not significantly ($P < 0.05$) alter the solution pH or the concentration of any of the inorganic anions (Table 2). However, the concentration of phytate in the solution was significantly ($P < 0.05$) reduced. Similarly, soil solutions passed through the filter elements, either under vacuum or low tension, were not significantly ($P < 0.05$) altered, other than the significant reduction in organic phosphorus and organic C (Table 3).

These tests demonstrate that inorganic anions are not retained in detectable quantities by the polyacrylonitrile filter elements. Similar results have also been reported for polyvinyl alcohol (Yanai *et al.*, 1993) and polysulfone (Jones and Edwards, 1993) hollow-fiber filter elements.

Comparison of hollow-fiber and centrifuge drainage extraction

While the preceding experiments demonstrate that soil solution can pass through the filter element unaltered, the soil solutions produced by hollow-fiber samplers and that obtained by centrifuge drainage differ markedly. In general, soil solutions obtained by hollow-fiber extraction had a higher pH and lower elemental concentrations than those obtained by centrifuge drainage (Table 4).

Application of suction to the hollow-fiber samplers causes degassing of CO_2 from the extracted soil solution, and results in a pH increase (Suarez, 1986, 1987; Zabowski and Sletten, 1991). Gas bubbles were noted emerging from the hollow-fiber samplers and, as the suction applied was well below the filter's bubble-pressure, were attributed to degassing following passage of solution through the filter membrane. As degassing occurred after the solution was separated from the soil matrix, CO_2 loss will have resulted in an increase in pH without alteration of the

concentration of other ions. This situation contrasts with that produced where CO₂ degasses from solution within the soil matrix and pH is maintained by exchange buffering (Dahlgren *et al.*, 1997). The pH of the highly acidic soils solution obtained from soil sample C did not differ significantly ($P < 0.05$) between the two extraction procedures (Table 4).

While hollow-fiber extraction raised the pH of solutions obtained from the soil, the pH of previously extracted soil solution was not significantly ($P < 0.05$) altered by passage through the hollow-fiber element (Table 3). We attribute these conflicting results to two effects. Firstly, it should be noted that the pH of all three soil solutions used in this test was higher than that recorded immediately following extraction (Table 4). Exposure to atmospheric CO₂ conditions, both in the head-space of the storage vial and while the solution was exposed during the conduct of the experiment, resulted in CO₂ loss from the solution and a consequent increase in pH. Secondly, the period of exposure to vacuum needed to draw a 5 mL sample of previously extracted soil solution through the filter element (approx 20 min) was shorter than that required to extract solution from within the soil matrix (8 h).

The concentration of the major cations and anions was significantly ($P < 0.05$) lower in solutions obtained by hollow-fiber extraction than those produced by centrifuge drainage (Table 4). Concentration differences were generally most apparent for K, Na and S, in some instances solutions produced by centrifuge drainage were twice the concentration of hollow-fiber extracted solutions. Differences between extraction methods were less marked, and less consistent, for the trace elements.

For four of the five soils used, soil solutions extracted by hollow-fiber samplers contained significantly ($P < 0.05$) lower organic C concentrations than centrifuge drainage solutions (Table 4). This difference can in part be attributed to retention of high molecular weight humic and fulvic acids by the hollow-fiber filter element (Gaffney *et al.*, 1996), as observed for previously extracted soil solution (Table 3). These organic acids would fall into the molecular weight range 5×10^4 to 10^6 dalton; the nominal cutoff values for the hollow-fiber and $0.025 \mu\text{m}$ membrane filter elements. However, this effect can not entirely account for the differences between extraction methods. Soil solution extracted by centrifuge drainage from soil A contained 146 mg L^{-1} organic C, of which 127 mg L^{-1} was able to pass through the hollow-fiber, while soil solution extracted from this soil by the hollow-fiber contained only 33.4 mg L^{-1} .

In view of the ability of previously extracted soil solution to pass through the filter elements unaltered, we attribute this difference in solution composition to the hollow-fiber yielding a “selective” sample of the soil solution. We propose that the hollow-fiber sampler preferentially extracts the energetically more available solution from within the largest pores, and that this solution contains lower solute concentrations than solution closer to the soil colloids. This pattern of extraction is likely to provide a better representation of the soil solution utilized by plants. However, soil solution obtained by centrifuge drainage may more accurately represent solution in equilibrium with the soil solid phase, and as such would be more applicable to studies dealing with soil chemical processes (e.g. mineral dissolution studies).

Hollow-fiber samplers in soils A, B and C were sampled on 3 occasions, extracted solution being replaced with deionized water and the soil re-equilibrated for one day before re-sampling. The

period of one day between samplings was sufficient for redistribution of solution within the soil matrix, and a similar sample flow rate and volume was obtained on each occasion. Over the period, a total of > 20 mL of solution (approx 100 filter element pore volumes) passed through each sampler. Repeated sampling of the hollow-fiber extractors in soils A, B and C yielded solutions of comparable composition (Table 5), indicating that the samplers do not need a stabilizing or preconditioning phase as is suggested for ceramic cup samplers (Grossmann and Udluft, 1991).

CONCLUSIONS

Hollow-fiber extraction provides a simple means of non-destructively sampling the soil solution. From soil at field capacity, a single extractor is capable of yielding, over an 8 h sampling period, sufficient solution (8 mL) for a comprehensive elemental analysis. The polyacrylonitrile filter elements are resistant to biodegradation, and have yielded soil solution after installation in soil for up to 4 months. Filtration of solutions through the hollow-fiber elements used in this study did not alter the concentration of any inorganic ions. However, phytate was adsorbed by the filter element, and large molecular weight organic ligands excluded by the filter.

The soil solution sample obtained from soil by hollow-fiber extraction differs from that produced by centrifuge drainage. We propose that the sampler is yielding the energetically most available solution, from within larger pores, and as such may be a better representation of the solution taken up by plant roots.

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TABLE 1. The classification and selected characteristics of the soils used.

Soil	Classification		pH	EC mS cm ⁻¹	Ca	Mg	Na	K	Al	PSD ^c %	MC ^d %
	U.S. Taxonomy ^a	Australian ^b									
A	Aridic Haplustert	Black Vertosol	7.78	0.75	34.2	15.8	1.9	1.5	<0.1	27 / 24 / 49	46 / 25
B	Aridic Haplustert	Black Vertosol	7.68	0.36	22.9	26.0	2.4	1.2	<0.1	22 / 14 / 64	60 / 31
C	Oxyaquic Hapludalf	Yellow Kurosol	4.18	0.43	1.5	2.7	0.6	0.3	4.6	66 / 29 / 6	27 / 8
D	Typic Haplustox	Red Ferrosol	5.13	0.38	5.5	4.6	0.1	1.8	1.2	28 / 33 / 39	31 / 14
E	Oxyaquic Hapludalf	Yellow Kurosol	4.89	0.06	0.3	1.6	0.2	0.2	4.2	63 / 25 / 12	37 / 16

a Soil Survey Staff (1996)

b Isbell (1996)

c Particle size distribution (PSD) (sand / silt / clay) determined by pipette method (Gee and Bauder, 1986)

d Moisture characteristics (MC) (field capacity -10 kPa / wilting point -1500 kPa) by pressure plate method (Klute 1986)

TABLE 2. The pH and elemental composition of “synthetic” soil solutions in an unfiltered state (U) and having been passed through a hollow-fiber filter element (H).

Treat	pH	Ca ----- mM -----	K ----- mM -----	Na	Al ----- μM -----	Zn ----- μM -----	Cu ----- μM -----	Cl ----- mM -----	S ----- mM -----	P _t ----- μM -----	P _i
Solution 1											
U	4.02	1.02	0.48	1.48	12.7	11.5	8.6	5.1	0.24	11.0	5.8
H	4.08	0.92	0.48	1.46	11.6	12.6	11.7	5.1	0.24	7.2* ^a	5.3
Solution 2											
U	7.05	0.85	0.45	1.33	<0.1	6.5	2.7	3.9	0.24	13.2	6.0
H	7.04	0.86	0.50	1.34	<0.1	6.3	2.6	4.0	0.24	6.7*	5.4
Solution 3											
U	8.42	0.92	0.48	3.32	<0.1	2.8	0.7	4.6	0.27	10.3	4.4
H	8.40	0.93	0.49	3.33	<0.1	2.4	0.6	4.7	0.26	6.3*	4.4

a For values identified with an asterisk the concentration is significantly different (P<0.05) to the untreated solution.

TABLE 3 The pH and chemical composition of soil solutions extracted from three soils by centrifuge drainage (U), and these solutions following filtration through a hollow-fiber element under vacuum (HV) or low tension (HL). Superscripts indicate that a significant different ($P>0.05$) exists between values followed by different letters.

Treat.	pH	Ca	K	Mg	Na	Al	Fe	Zn	Cu	Cl	S	P _t	P _i	Si	C
		----- mM -----				----- μM -----				----- mM -----		----- μM -----		----- mg L ⁻¹ -----	
Soil A															
U	7.23	3.44	0.96	14.0	21.1	32.8	0.5	2.5	0.8	13.5	3.1	20.0 ^a	12	8.8	147 ^a
HV	7.29	3.56	0.98	12.6	22.3	45.8	0.5	4.4	0.8	12.2	2.6	16.4 ^b	13	8.4	127 ^b
HL	7.22	3.45	1.03	12.5	25.2	34.0	0.6	1.2	1.2	12.0	3.0	15.0 ^b	10	9.2	n.d.
Soil D															
U	4.52	1.19	6.78	8.09	1.9	1460	0.8	54	1.4	1.7	0.4	2.5 ^a	0.7	24.1	15.7 ^a
HV	4.51	1.18	6.66	8.03	1.9	1440	0.8	55	1.5	1.6	0.4	2.0 ^b	0.7	23.9	10.0 ^b
HL	4.52	1.21	6.82	8.16	1.9	1480	1.3	56	1.6	2.1	0.4	2.7 ^a	0.4	24.3	n.d.
Soil E															
U	4.52	0.01	0.26	0.80	1.4	100	115	1.7	2.5	2.9	1.2	6.2 ^a	0.6	12.1	352
HV	4.55	0.01	0.23	0.75	1.4	109	95	3.2	2.7	2.9	1.1	3.6 ^b	0.6	11.9	323
HL	4.56	0.01	0.23	0.80	1.5	113	93	4.0	3.2	3.1	1.2	3.8 ^b	0.3	12.4	n.d.

TABLE 4. The pH, electrical conductivity (EC) and chemical composition of soil solutions extracted from five soils by centrifuge drainage (C) and hollow-fiber extraction (H).

Treat.	pH	EC S m ⁻¹	Ca ----- mM	Mg ----- mM	K ----- mM	Na ----- mM	Al ----- μM	Fe ----- μM	Zn ----- μM	Cu ----- μM	Cl ----- mM	S ----- mM	P _t ----- μM	P _i ----- μM	Si ----- mg L ⁻¹	C ----- mg L ⁻¹
Soil A																
C	7.12	0.913	3.44	14.0	0.96	21.1	32.8	0.5	2.5	0.8	13.5	3.08	27.0	12.0	8.8	146
H	7.56*	0.755*	2.45*	9.45*	0.66*	15.7*	25.0*	1.3	0.5	0.5	11.8	1.41*	16.9*	13.7	7.2*	33.4*
Soil B																
C	6.42	0.209	0.30	3.24	0.28	8.4	6.0	0.4	4.5	1.1	10.1	1.39	10.8	5.2	6.9	16.9
H	6.98*	0.165*	0.20*	2.12*	0.17*	6.0*	3.7*	0.3	1.1*	1.0	8.8*	0.39*	10.3	5.2	5.2*	2.2*
Soil C																
C	3.63	0.348	0.32	6.83	1.27	10.6	91.5	8.2	16.3	1.0	12.8	2.40	17.5	5.8	19.7	80.8
H	3.68	0.214*	0.21*	4.68*	0.57*	5.7*	69.6	5.9*	5.9*	0.7*	8.5*	0.92*	11.8	7.6	15.1*	29.1*
Soil D																
C	4.18	0.612	1.32	10.1	8.01	2.1	1577	0.9	58.2	1.5	1.8	0.59	3.4	1.1	24.5	14.1
H	4.83*	0.303*	0.74*	5.57	1.97*	1.3*	995*	1.0	44.1*	1.8*	0.2*	0.18	1.5	0.4	22.3*	9.5*
Soil E																
C	4.34	0.051	0.01	0.85	0.28	1.5	111	95.4	1.8	2.5	2.9	1.33	6.4	3.6*	12.5	350
H	4.77*	0.034*	0.01	0.48*	0.17*	1.2*	83.0	66.0	11.5*	2.6	2.6	0.57*	6.5	1.6	10.0*	324

a For values identified with an asterisk the concentration is significantly different (P<0.05) to the centrifuge drainage solution.

TABLE 5. The pH, electrical conductivity (EC) and chemical composition of three sequential extractions from hollow-fiber samplers.

Time	pH	EC S m ⁻¹	Ca ----- mM	K mM	Mg ----- mM	Na ----- mM	Al ----- μM	Cl mM	P μM	S mM	Si mg L ⁻¹
Soil A											
1	0.756	7.55	2.45	0.66	9.45	15.7	25.0	16.9	11.8	1.41	7.2
2	0.760	7.22	2.49	0.68	9.58	15.8	25.1	19.0	11.2	1.58	8.0
3	0.754	7.04	2.41	0.72	9.25	15.7	25.1	19.9	11.0	1.98	8.2
Soil B											
1	0.698	1.65	0.20	0.17	2.12	6.0	3.7	10.3	8.8	0.39	5.2
2	0.701	1.60	0.22	0.18	2.32	6.4	4.1	10.4	8.8	0.52	5.4
3	0.702	1.64	0.23	0.19	2.45	6.6	4.3	10.4	8.8	0.69	6.0
Soil C											
1	0.415	2.14	0.21	0.57	4.68	5.7	69.6	11.8	8.5	0.92	15.1
2	0.411	2.09	0.22	0.63	4.70	5.8	73.0	11.4	8.3	0.91	15.5
3	0.424	1.98	0.21	0.68	4.37	5.6	67.8	11.4	8.0	0.95	16.0

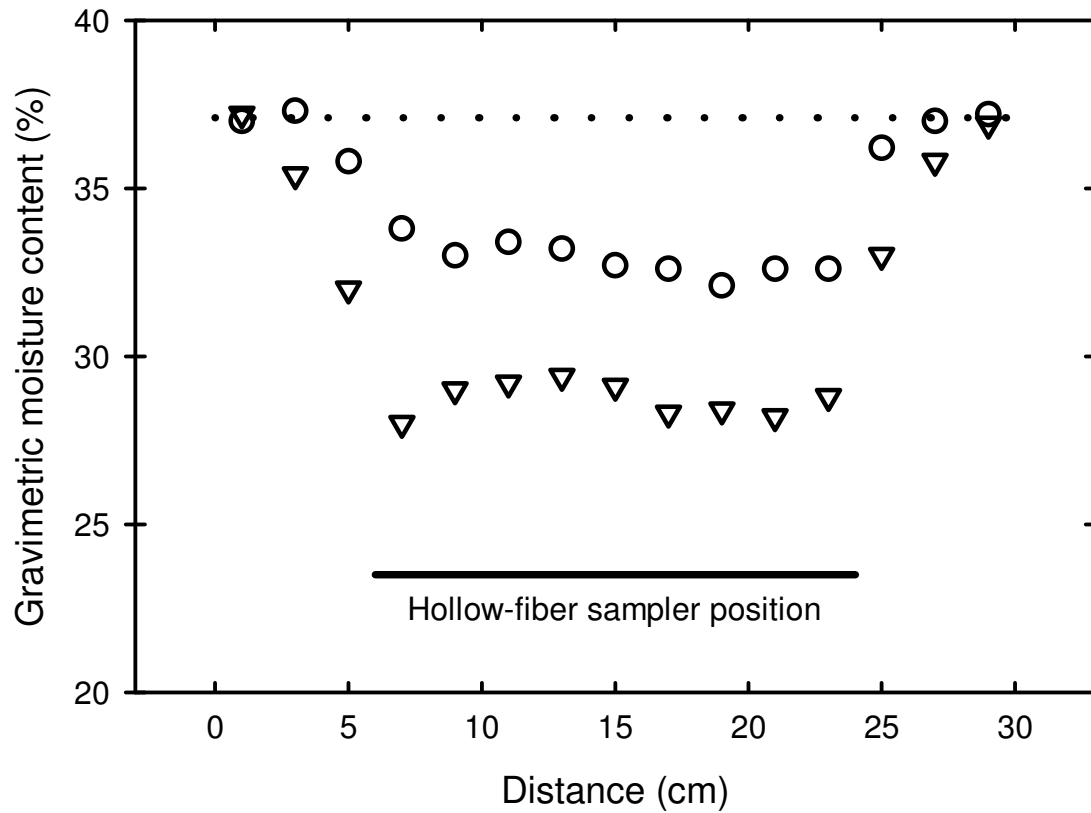


FIGURE 1. The gravimetric moisture content of a 2.5 cm diameter cylinder of soil following extraction of 7 mL of water (●) or 15 mL of water (▼). The initial water content (field capacity) is indicated by the dotted line, and the position of the sampler indicated by the solid bar.