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Monitoring Soil Column Mobility of Cross-Linked and Soluble Polyacrylates Using Gel Permeation Chromatography

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The potential fate of polymeric materials in soils is important to environmental safety. This study validated high-performance gel permeation chromatography (HPGPC) to assess elution behavior of a commercially available, cross-linked, high molecular weight polyacrylate absorbent (PA) and a soluble low molecular mass (4500 Da), linear poly(acrylic acid) (LPA) in three types of columns prepared from sandy and loamy soils. HPGPC was used to monitor the elution of the soluble PA and LPA from the columns. The LPA represents the fraction (<4%) of the PA that is typically extractable in commercial PA material. Over 99% of the PA sample was found to be retained on a Borden sand test column. The amount that moved is probably related to the extractable polymer. A total of 92% of the non-cross-linked LPA was retained on a Borden sand column. Virtually all of the LPA was retained on the Fox loam column. PA mobility could not be studied on the Fox loam soil; however, the high clay content of this soil is expected to make the PA less mobile than in Borden sand. Londo loam soil yielded high levels of background interferents for PA and LPA, preventing acquisition of definitive mobility data. However, LPA and PA are expected to be less mobile on Londo loam than on Borden sand due to the higher organic matter/clay contents. These results indicate that typical consumer product-grade PAs would not move appreciably through common soil types in or near landfills. The results also support the use of LPA as a model for studying movement of the soluble portion of commercially available PA through soils and demonstrate that HPGPC is suitable for quantifying soluble polyacrylates in synthetic groundwater effluents.

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Introduction

Polyacrylate absorbents (PAs) are cross-linked acrylic polymers that can absorb and retain many times their weight of water or aqueous solutions. Commercial PAs are prepared by polymerizing a mixture of acrylic acid, sodium acrylate, and a multifunctional cross-linking agent (0.001−1 wt %) to form a three-dimensional network with virtually infinite molecular weight. Because of this cross-linked network, PAs are insoluble in water apart from a small amount of soluble materials (<10%). This soluble fraction contains primarily polyacrylates with a broad range of molecular mass, predominantly in the range of 10^3−10^6 Da.

The absorption properties of PAs make them well-suited for use in disposable hygiene products such as diapers, adult incontinence products, and feminine protection hygiene pads. These consumer products are typically disposed in municipal solid waste, about two-thirds of which is landfilled (*1*). A recent study has shown that high molecular weight PAs are not substantially degraded during composting with simulated municipal waste (*2*). This has led to considerable interest in studying the potential for movement of the long-lived PAs through a soil profile if they leach out of nonlined landfills. A number of publications have addressed either the movement of these materials through landfills and soils or the analytical methods available for quantifying PAs (*3*−*13*). However, most of these studies used laboratory-prepared, radiolabeled PA and determined that virtually all of this PA is immobile, even in sandy soils (*6*).

The primary objective of the present study was to determine if commercially available, nonradiolabeled PA material would exhibit the same immobile behavior as laboratory-prepared, radiolabeled PA in different soils. To accomplish that objective, the mobilities of commercial PA and a low molecular weight linear polyacrylate (LPA) were studied to represent both the realistic case and the worst case (if one assumes that the LPA is more likely to be mobile in soil). As it was necessary to be able to detect nonradiolabeled PA in groundwater, a secondary objective of this study was to validate a newly developed analytical method (*5*) for the determination of PA in leachates of different soils.

Monitoring the fate of PAs in environmental studies presents a challenge, given the required sensitivity and specificity to measure trace concentrations of PAs in complex environmental matrixes. The insoluble, cross-linked polymer network of PAs makes direct chromatographic procedures impossible. To characterize PAs with hydrolyzable ester cross-links, it is possible to first hydrolyze the cross-link network under heat and high pH and then use size exclusion chromatography to determine molecular weight distributions of PA samples (*14*). However, since not all commercial PAs have ester cross-links, broad utility of this method is limited.

For monitoring the fate of nonradiolabeled materials, several analytical methods have been developed that quantify PA in a sample by measuring the concentration of sodium present. A sodium ion selective electrode has been used successfully in measuring the concentration of sodium polyacrylates and their percent neutralization in certain matrixes, such as dust collected in manufacturing facilities and the absorbent core of diapers (*13*). A procedure was developed to quantify PA dust in air by measuring sodium using either atomic absorption or atomic emission spectroscopy (*15*). However, all of these procedures that rely on the measurement of sodium require close attention to sample collection, preparation, analysis, and data interpretation

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because of the potential for contamination by background environmental sodium. This potential for sodium interferences makes such methods unsuitable for soil column studies. Recently, a very sensitive and specific procedure to determine PA dust in air has been developed that utilizes the inherent ion exchange properties of PA and the sensitivity of neutron activation analysis (*16*). This procedure exchanges the sodium present in the PA for europium; hence, it reduces interferences from sodium and other background species. This technique was not evaluated for the present study because a research-scale nuclear reactor was not available in the laboratory facility where this work was performed. Finally, pyrolysis-gas chromatography coupled with detection by either mass spectrometry, flame ionization detection, or infrared spectroscopy has been successful in certain soil applications (*3*). However, pyrolysis of aqueous extracts from soil matrixes can produce interferences that make quantitation of the polyacrylate difficult, particularly at the trace concentrations encountered in soil column studies.

For the above-cited reasons, many previous environmental monitoring studies used laboratory-prepared, radiolabeled materials with the carbon-14 typically incorporated at the 2- and 3-carbon positions on the polymer backbone (*6*−*12*). The use of a radiotracer, coupled with sensitive radioanalytical techniques, has facilitated determination of the fate of PA in complex matrixes ranging from landfills to soil columns. Detection of $^{14}CO_2$ or $^{14}CH_4$ in gaseous emissions in several studies demonstrated some mineralization of low molecular weight oligomers. Radiotracer techniques were precluded from the present study because our objective was to perform soil column studies with a commercially available PA.

High-performance gel permeation chromatography with refractive index detection (HPGPC/RI) was also successfully used to quantify polyacrylates in aqueous extracts of sandy soil (*5*). Because HPGPC/RI appeared to be an attractive method for monitoring the movement of the lower molecular weight soluble portion of the PA through soil columns, it was applied in the present soil column studies. Validation data, including recovery, precision, and detection limits for various soil column effluents, were evaluated in this work.

Materials and Methods

Cross-Linked Polyacrylate Absorbent. The commercially available cross-linked PA test substance, provided by the Institute for Polyacrylate Absorbents (Washington, DC), is representative of materials used in consumer hygiene products. It is predominantly a high molecular weight, insoluble, cross-linked material that is approximately 65% neutralized and contains 3.6% of a water-soluble fraction. The weight-average molecular mass of this soluble fraction was 178 500 Da, based on GPC analyses with molecular mass ranging from approximately 1000 to 2.8 million Da.

Linear Polyacrylic Acid. The LPA reference substance was provided by Rohm & Haas Company (Spring House, PA) as a viscous, amber solution at a concentration of 44−46% in water (Acusol 445N) with a weight-average molecular mass of 4500 Da. Solid LPA material was isolated from the solution by freeze-drying and was partially neutralized as described elsewhere in this publication.

Soils. Three types of soils were selected for the study: Borden sand, Londo loam, and Fox loam. Table 1 summarizes the salient properties for each soil type. The Borden sand has been previously described (*6*). The soils were stored at ambient temperatures for the study duration.

Preparation of Synthetic Groundwater Solution. The synthetic groundwater solution used as an eluant for the soil column experiments was described previously (*18*). It was designed to be representative of dilute groundwater in a carbonate substratum under a landfill site in southern Ontario, Canada, where the Borden sand was collected. Composition was as follows (per liter): 51.0 mg of $CaCO_3$ and 9.6 mg of $CaSO_4$ (23.4 ppm Ca^{2+}), 7.9 mg of $MgSO_4$ (1.6 ppm Mg^{2+}), 2.6 mg of NaCl and 1.3 mg of Na_2SO_4 (1.4 ppm Na^+), and 0.4 mg of KCl (0.23 ppm K^+). Carbon dioxide was gently bubbled through the solution to adjust the pH to 8.2, and then the bottle was tightly capped. Calculated anion concentrations were 1.7 ppm Cl^-, 14.0 ppm SO_4^{2-}, and 30.6 ppm HCO_3^-. Ion concentrations used here were lower than for those reported for typical sandstone, shale, and limestone groundwaters (*19*, *20*), which minimizes the coprecipitation of PA. Therefore, the use of this synthetic groundwater is expected to solubilize more PA than typical groundwaters and therefore represents a worst-case medium for PA mobility.

TABLE 1. Soil Characterization Data

property	Borden sand	Fox loam	Londo loam
organic matter[a] (%)	1.75	0.55	2.49
sand (%)	97.9	75.8	35.7
silt and clay (%)	2.1	24.2	64.3
organic carbon (%)	1.01	0.32	1.45
permeability (cm/s)	7.0×10^{-3}	2.79×10^{-5}	2.14×10^{-3}
total cation exchange capacity (mequiv/100 g)	2.8	20.7	15.0
predominant soil type	sand	clay	loam
field capacity, 1/3 bar[b] (%)	1.05	22.13	9.76
witting point, 15 bar (%)	0.61	12.78	5.38
available moisture (%)	0.44	8.38	4.38

[a] Estimated by assuming the average C content of soil organic matter is 58%, as per Hausenbuiller (*16*). [b] Measured as per ASTM D3152.

Preparation of LPA Stock and Calibration Solutions. Stock solutions of LPA were prepared by dissolution into reagent-grade water and adding standardized 1 N NaOH to generate stoichiometrically a 65% neutralized material. The solution was allowed to stand overnight at room temperature and was then taken to final volume with synthetic groundwater solution. The resultant 10 mg/mL stock solution was stored in an amber, Teflon-lined, screw-top vial at 4 °C. Calibration standards of this LPA were prepared with concentrations of 0, 5, 20, 50, 100, and 300 μg/mL.

Preparation of Sample Diluent (5×) Solution. Sample diluent solution (5× solution) was used to dilute standards and samples before analysis by HPGPC. It was prepared by dissolving 8.78 g of NaCl and 24.14 g of Na_2HPO_4 in 100.0 mL of reagent water and stirring with mild heating (~40 °C) until dissolved. The pH was adjusted to 6.8 by dropwise addition of 85% H_3PO_4. The dilution scheme required the ratio of 1.25 mL of this 5× solution per 5 mL of sample or standard, which adjusted the sample to a pH and buffer concentration similar to the HPGPC mobile phase with no significant dilution of the sample.

Preparation of HPGPC Mobile Phase. A 0.23 M NaCl and 0.34 M Na_2HPO_4 solution was prepared using reagent-grade water. The pH was adjusted to 6.8 by dropwise addition of phosphoric acid. The solution was filtered through a 0.45-μm nylon filter, placed into the HPLC mobile phase reservoir, and sparged with helium for about 10 min.

Preparation of Soil Columns. Test soils and soil columns were prepared to conform to previously published guidelines (*21*). Soils were air-dried, finely ground with a mortar and pestle, and sieved through a no. 30 sieve into an aluminum pan. Glass chromatography columns, 30 cm in length × 5 cm i.d., fitted with adjustable flow adapters, were each filled with about 550 g of prepared soil. Each column was preconditioned by passing approximately 2 pore volumes of synthetic groundwater through the columns.

TABLE 2. Experimental Design for the Soil Column Study

test system	no. of unspiked (control) columns	no. of columns spiked with LPA	amt. of soluble LPA added, mg	no. of columns spiked with PA	amt. of PA added, mg
Londo loam soil	1	1	50	0	0
Fox loam soil	1	1	50	0	0
Borden sand	1	1	50	1	500

Determination of Soil Column Pore Volume. The weight of the column with the dry soil was measured and recorded as the "soil column dry weight". The bottom of the column was closed off, and then synthetic groundwater was slowly added to the top until the soil was saturated (i.e., a very slight pool of liquid, ~ 1 mL, remained on the surface of the soil). The wet column was then weighed and recorded as soil column wet weight. The soil column pore volume was then calculated by

$$\text{pore volume (mL)} = \frac{\text{wet weight (g)} - \text{dry weight (g)}}{d\ \text{(g/mL)}} \quad (1)$$

where $d = 1.0$ = density of synthetic groundwater solution.

Preparation of Fortified and Control Soil Columns. A total of seven soil columns were prepared for this study (Table 2). LPA-fortified (50 mg/column) soil columns were prepared for each of the three soil types. The column was fortified with LPA by injecting 5 mL of the 10 mg/mL LPA solution (containing 50 mg of LPA) and immediately stopping the flow for overnight equilibration.

One column of Borden sand was fortified with 500 mg of cross-linked PA material. The first 2−3 cm of the soil in the top of the preconditioned column was removed from the column, mixed with the PA, and left to equilibrate overnight in a covered container. After overnight equilibration, the soil/PA mixture was repacked into the Borden sand column.

Control columns were not fortified with any LPA or PA but were equilibrated in the same manner as the fortified columns. After overnight equilibration, synthetic groundwater flow was restarted for all of the columns and adjusted to a flow rate of 0.2 mL/min.

Fraction Collection. Flow was continued through the columns until the total volume of effluent fractions collected from each column was roughly equivalent to 30 pore volumes. For example, if the Borden Sand column had a measured pore volume of 155 mL, then column effluent collection continued until a total volume of at least 4650 mL was obtained.

Screw-top glass vials (capacity of 20 or 40 mL) were used in the fraction collectors to collect the column effluent. Multiple vials were therefore usually required to contain each pore volume fraction. The resulting fraction collection vials for each column were combined into the final pore volume fractions that were eventually analyzed by HPGPC/RI. The weight of each vial was recorded and used in compositing fraction collection vials into the final pore volume fraction samples.

Sample Preparation. A total of 10 mL of each pore volume fraction sample was centrifuged for approximately 30 min at a rotational centrifugal force of 3000*g*. No visible solid material was present in the supernatant after centrifugation. A 5-mL aliquot of each of the centrifuged samples was diluted by the addition of 1.25 mL of the 5× diluent solution. The diluted sample was mixed in a vortex mixer for about 1 min and then filtered through a 0.45-μm nylon syringe filter into an autosampler vial, capped tightly, and stored at approximately 4 °C until analysis. Samples were allowed to warm to ambient temperature before analysis by HPGPC/RI.

TABLE 3. HPGPC Analysis Parameters

pump	Waters 6000
flow rate	1.0 mL/min
injector	Rheodyne 7010 with Alcott 728
injection vol	100 μL
detector	Waters model 410 refractive index detector
detector parameters	range: 5 × 10−6 RIUFS, temp: 35 °C
column	300 mm × 7.8 mm i.d., TosoHaas TSK−Gel G1000-PW
column temp	35 °C
mobile phase	0.23 M NaCl, 0.34 M Na_2HPO_4 adjusted to pH 6.8 with H_3PO_4

Analytical Method Validation. The recovery, precision, and detection limits of the HPGPC/RI method were determined by spiking effluents from Borden sand, Fox loam, and Londo loam soil columns with known amounts of LPA solution described above. Additionally, the precision of the calibration procedure was evaluated by periodic injections of standards throughout the soil column studies. The method recovery and precision were evaluated by analyzing triplicate samples of effluents from each type of soil column spiked with LPA at 0, 5, 50, and 100 μg/mL. Seven replicate samples of each type of soil column effluent spiked at 10 μg/mL also were analyzed to evaluate precision and recovery and to estimate the method detection limit (MDL). This latter concentration was chosen to be between two and five times the estimated instrument detection limit (IDL), which was 4.4 μg/mL, to facilitate a statistical calculation of the MDL, as described in more detail below. Each sample was prepared for HPGPC instrumental analysis and injected in duplicate. The experimental data were used to calculate the values for the method recovery, method precision, and MDL. To minimize the level of soil interferences present in the spiked samples, late eluting soil column fractions (such as pore volume fraction no. 30) were selected from each type of soil column.

The value for the method precision at 10 μg/mL was used to calculate the MDL using standard U.S. EPA methodology (*22*). Validation of the calibration curve for the HPGPC of LPA was conducted by analyzing the calibration standards in triplicate and calculating the slope, *y*-intercept, instrumental precision, and correlation coefficient.

HPGPC/RI Analysis. A TosoHaas TSK-Gel G-1000 PW high-performance gel permeation column was used to determine the LPA in the soil column fractions. System parameters are described in Table 3. The TSK Gel G-1000 PW columns are intended to exclude any polymer with a molecular mass higher than 1000 Da, allowing for the polymer to travel through the column as a narrow band increasing the sensitivity and allowing for trace determination (about 5 ppm).

The TSK Gel G-1000 PW column was selected to separate LPA and higher molecular weight polymers from soil matrix interferences, many of which have molecular mass below 1000 Da (e.g., humic substances). Monomers, oligomers, and other materials with molecular mass of less than 1000 Da will be separated from the higher molecular mass polymer and are not determined by this method. Of course, other materials with a molecular mass of greater than 1000 will

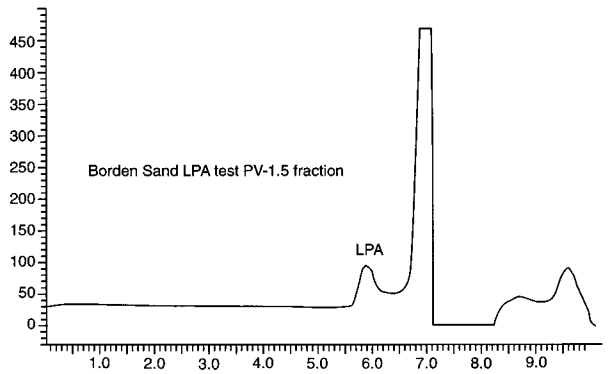

FIGURE 1. HPGPC chromatogram for LPA spiked in the 1.5 pore volume fraction (PV-1.5) of Bordon sand leachate.

elute at the same time as the PA, interfering with the analysis. The LPA or PA components were detected with a refractive index detector and were identified by comparing chromatographic peak elution times to those obtained from analyses of the LPA calibration standards. The concentrations of the eluting components were determined by use of an external calibration curve.

The HPGPC was calibrated by injecting LPA standards at the following concentrations: 0, 5, 20, and 100 μg/mL to establish a calibration curve. Single injections were used for all analyses of the soil column pore fraction samples.

Quality Control Samples. Quality control (QC) samples included instrument method blanks (e.g., synthetic groundwater, prepared for analysis in the same manner as the calibration standards and samples), matrix spikes (e.g., soil column fraction, spiked with a level of LPA within the calibration range), method spikes (e.g., synthetic groundwater fortified with LPA at a concentration within the instrument calibration range), and a calibration verifier standard (i.e., after approximately every 10 samples, a 20 μg/mL LPA standard was analyzed to verify instrument calibration).

Instrument Detection Limit. The IDL was calculated by graphically estimating the signal-to-noise ratio (S/N) for a 5 μg/mL standard and extrapolating to the concentration that would provide an S/N ratio of 3:1. Duplicate determinations of the IDL yielded estimates of 4.8 and 4.0 μg/mL.

Results and Discussion

Method Validation. The HPGPC/RI method was demonstrated to be capable of detecting the LPA in each of the soil columns at levels below 5 μg/mL. For the Borden sand, the retention window for LPA was clear of interferences (Figure 1). However, for the Fox loam and Londo loam soils, there were interfering peaks in GPC that were primarily present in the early pore volumes from the soil columns that could not be readily resolved from the LPA. These interferences are thought to be organic materials of molecular mass 1000 or higher leaching from the loamy soils. Nonetheless, it was possible to use the control column data to compare with the test column to provide adequate validation results.

The method recovery (see Table 4) was suitably quantitative for samples spiked in the range of 5−100 μg/mL for each of the three soil matrixes. The MDLs, as determined from analyzing the 10 μg/mL level, ranged from 0.9 μg/mL for Borden sand to 3.5 μg/mL for the Londo loam. The fact that the Londo loam and Fox loam MDLs are higher than those for the synthetic groundwater and the Borden sand appears to be a direct result of the GPC interference peak that elutes in the LPA retention window for those two matrixes. Nonetheless, because the interference obtained for the loamy soils was consistent, it was possible to correct for interferences to obtain recovery data for the LPA in these soils.

TABLE 4. Method Validation and Method Detection Limit Results

LPA added (μg/mL)	N[a]	LPA found (μg/mL)	mean %RSD[b]	mean % recovery	MDL[c] (μg/mL)
		Synthetic Groundwater			
0.0	3	nd[d]	–[e]	–	–
5.0	3	5.8	3.0	116	–
10.0	7	10.3	5.2	103	1.6
50.0	3	48.0	3.8	95	–
100.0	3	99.6	3.1	100	–
		Borden Sand Control			
0.0	3	nd	–	–	–
5.0	3	5.4	4.6	108	–
10.0	7	10.4	2.8	105	0.9
50.0	3	48.9	2.1	98	–
100.0	3	99.3	0.7	99	–
		Fox Loam Control			
0.0	3	nd	–	–	–
5.0	3	6.9	5.5	138	–
10.0	7	11.3	6.5	113	2.3
50.0	3	50.9	2.0	102	–
100.0	3	102.6	1.01	102	–
		Londo Loam Control			
0.0	3	(8.2)[f]	–	–	–
5.0	3	6.0	15.9	120	–
10.0	7	10.9	10.0	109	3.5
50.0	3	62.8	7.5	109	–
100.0	3	110.2	5.5	110	–

[a] *N*, number of determinations. [b] %RSD, percent relative standard deviation. [c] MDL, method detection limit calculated from the 10 μg/mL spike. [d] nd, not detected. [e] –, not applicable. [f] Value represents an interference peak that eluted near the LPA retention time.

Quality Control Results. The QA/QC procedures for this study included the use of initial calibration, daily calibration, blanks, method spikes, and matrix spikes. Initial calibration of the HPGPC/RI system was performed prior to all sample analyses. In each case, the initial calibration curves yielded correlation coefficients greater than 0.999, and the back-calculated accuracy for individual standards ranged 93−105% across the calibration range of 5−100 mg/mL. Criterion for successful initial calibration was a correlation coefficient of >0.995.

On those days in which an initial calibration curve was not generated, a daily initial calibration verifier (ICV) at 20 μg/mL was analyzed to verify the established calibration curve. The 20 μg/mL standard also was analyzed approximately every 10 injections to measure and document the calibration drift during each analysis sequence. For the analysis of the daily ICV, the mean accuracy was 98% with a standard deviation (σ) of 5% over the duration of the entire study. The criterion for the ICV was 80−120% accuracy relative to the initial calibration curve.

QC samples were prepared and analyzed with each set of soil column test samples. QC samples consisted of method spikes (LPA-fortified synthetic groundwater), matrix spikes (LPA-fortified soil column pore fraction samples), and method blanks (synthetic groundwater). Each QC sample was taken through the entire sample preparation procedure in the same manner as the soil column pore volumes samples, ensuring that the entire analytical procedure was evaluated.

No peaks corresponding to LPA were observed in the instrument or method blanks. Recoveries of the matrix spikes and the method spikes are given in Table 5. The mean recoveries for all spiked samples ranged 94−106%. The Fox loam and Londo loam control columns contained matrix interferences that eluted in the GPC retention time window for LPA. Therefore, the concentration of the LPA in matrix-spiked samples was corrected for the interference present in the unspiked sample.

TABLE 5. Matrix Spike Recovery and Precision

sample[a]	N[b]	% recovery mean	% RSD[c]
method spike	7	98	6.6
Borden sand control	6	94	9.6
Borden sand PA test	3	98	3.2
Borden sand LPA test	6	102	15.5
Londo loam control	6	101	24.8
Londo loam LPA test	6	106	7.2
Fox loam control	2	104	9.3
Fox loam LPA test	2	101	12.9

[a] All samples spiked at 20 μg/mL with LPA. [b] *N*, number of determinations. [c] %RSD, percent relative standard deviation.

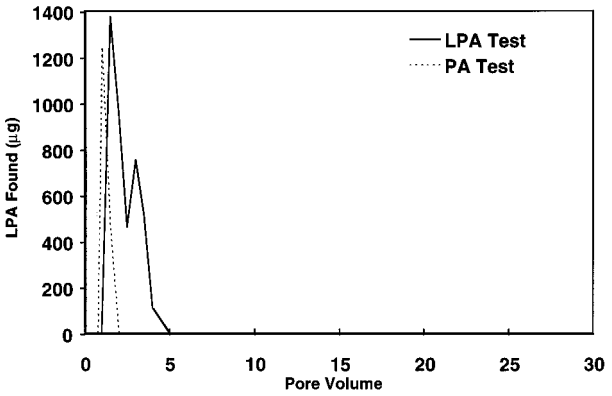

FIGURE 2. Elution profile of Bordon sand PA and LPA test.

Soil Column Results. The results for the determination of LPA mobility in the three soils and PA mobility in the Borden sand are shown in Figures 2−4. For the PA-fortified Borden sand test column, 1.7 mg of the PA, or 0.34% of the initial 500-mg charge, eluted within the first two pore volumes (see Figure 2). The remainder of the PA (99.7%) was apparently highly retained by the sand since no further materials were detected in the eluant fractions throughout 30 pore volumes. Less than 0.04% of the PA below a molecular mass of 1000 was not analyzed by the GPC analytical method. The portion of the PA that moved through the sand column was most likely the soluble portion. Since the PA contained 3.6%, or 18 mg, of soluble materials (saline extractables), then (1.7 mg/18 mg) × 100%, or 9% of these extractables appear to have moved through the sand column. It can be estimated by difference that about 91% of the soluble portion of the PA was retained by the Borden sand test column, a result consistent with a previous study using radiolabeled PA (*7*).

As shown in Figure 2, a portion of the LPA also moved through the sand column eluting within five pore volumes. This portion corresponded to 4.2 mg of the LPA or 8% of the initial 50-mg charge. The remainder of the LPA was apparently highly retained by the sand since no further materials were detected in the eluant fractions throughout 30 pore volumes. By difference, it can be estimated that 92% of the LPA was retained by the Borden sand test column. As with the PA, a small amount of LPA components below a molecular mass of 1000 was not detected by the GPC analytical method and was not considered in this study. The 92% retention of the LPA compares favorably with the 91% retention of the soluble fraction of the PA, indicating that the LPA is a suitable model for studying the movement of PA through soils.

In summary, the results for the sand columns indicate that even for this soil, with worst-case mobility, more than 99% of the PA is retained by the soil after the passage of 30 pore volumes of synthetic groundwater. Even in the case of the soluble portion of the PA, or of the soluble LPA, both of which would be expected to be more mobile than the cross-linked, insoluble portion of the PA, more than 90% remains on the sand column after passage of 30 pore volumes. These results, which indicate that these materials are highly retained by sand, support those found previously using a laboratory-prepared radiolabeled PA (*6*).

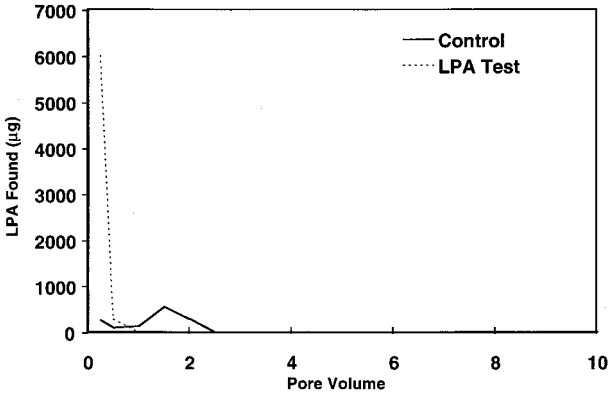

FIGURE 3. Elution profile of Fox loam test and control columns.

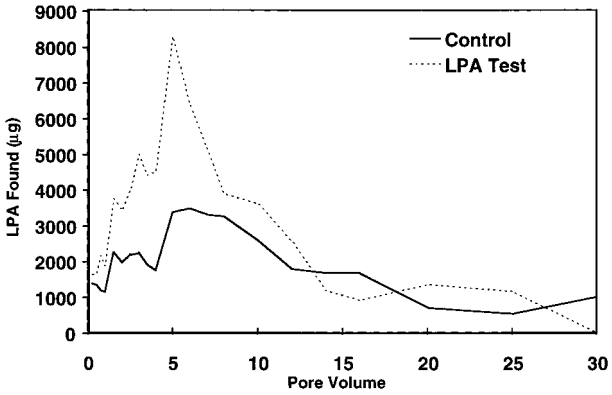

FIGURE 4. Elution profile of Londo loam test and control columns.

Since our experience indicated that PA tends to block the flow of eluant through high organic matter or clay types of soils, such as Londo loam and Fox loam, mobility through these soils was studied with the LPA only. The elution profiles for the control and test columns for Fox loam and Londo loam columns are shown in Figures 3 and 4. For the Fox loam LPA column, a large peak was detected in the 0.25 pore volume fraction. Considering basic column theory, it is not possible that LPA would be found prior to elution of at least one pore volume. Therefore, this peak is likely to consist of organic matter of molecular mass 1000 or higher leaching from the soil. The Fox loam control column showed smaller amounts of material (274 μg) eluting at 1.5 pore volume. This also was probably due to organic material leaching from the control column. There was no detectable material eluting from the test column beyond 1.0 pore volume, indicating that virtually all of the LPA was retained on the Fox loam soil. Although we were not able to study PA mobility on Fox loam, it is expected that, due to the higher clay content, PA would be less mobile in this soil than observed for the Borden sand.

Matrix interferences also were detected in all the Londo loam column pore volumes for both the test and control columns. This interference coeluted with the LPA peak in the GPC analysis, effectively raising the detection limit for LPA in these pore volumes. When the data from corresponding fractions in the test and control columns are compared, the Londo loam LPA test column consistently shows a higher level of material eluting throughout the 30 pore volumes of eluant. However, the high background level

of interferent from both of these columns prevents a reliable interpretation of the Londo loam column studies. Nevertheless, due to higher organic matter and clay content, the LPA and PA would be expected to be less mobile on the Londo loam column than on the Borden sand column.

The primary objective of the present study was to determine if nonradiolabeled, commercially available PA material would exhibit the same immobile behavior as radiolabeled, laboratory-prepared PA in different soils. On the basis of the results of the soil column studies, it can be concluded that typical commercial PAs used in contemporary consumer products would not move to any appreciable extent through soil types that might be found in, beneath, or adjacent to landfills into the groundwater supply.

With regard to the validation of the HPGPC method, it was realized from the beginning of this study that a method that requires sensitivities to determine polymer at the low ppm level in very complex matrixes would have limitations. Also the use of a refractive index detector does not help in the characterization of the materials under investigation. The conditions used within the limitations imposed by the analysis are optimal. It also was known that the use of radiolabeled materials in previous studies had limitations. The purpose of the current study was to attempt to elucidate questions raised by the use of the radiolabeled materials. Some of the questions were related to the movement of polymer through soils since the previous studies did not use size exclusion chromatography to identify the mobile radiolabeled materials as polymer. As a result, the mobile material could have been ^{14}C-tagged monomers, oligomers, or very low molecular weight polymers, or even excess reactants moving through the soils.

The HPGPC/RI method has been shown to have good recovery, precision, selectivity, and a sufficiently low detection limit for performing soil column studies of commercially available polyacrylates on Borden sand and Fox loam columns. It is less useful for high organic content soils such as Londo loam due to interferences that leach off from this soil. This method also should be suitable for studying the movement of other polymers through Borden sand, Fox loam, or soils with similar characteristics (see Table 1). It is particularly attractive for general use because it does not require the use of radiolabeled polymer.

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