SOIL COLUMN STUDIES WITH A FIBER-OPTIC LASER SPECTROMETER

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April 1994

Final Technical Report for Period June 1993 - August 1993

[redacted]

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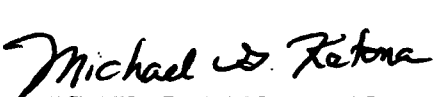

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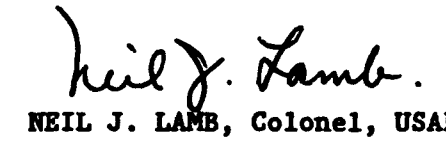

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	April 1994	Final Jun-Aug 93

4. TITLE AND SUBTITLE

Soil Column Studies with a Fiber-optic Laser Spectrometer

5. FUNDING NUMBERS

6. AUTHOR(S)

Brian S. Vogt

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Armstrong Laboratory Environics Directorate (AL/EQ)
Tyndall Air Force Base, Florida, 32403

8. PERFORMING ORGANIZATION REPORT NUMBER

AL/EQ-TR-1994-0011

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

Summer Faculty Report AL/EQ Project Officer/ Bruce Nielsen DSN 523-6227

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for Public Release. Distribution Unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

A fiber-Optic laser spectrometer was used in soil column experiments to study transport of contaminants through soils. A unique fiber-optic laser probe was adapted into a modular stainless-steel column so that the probe could be used to study the transport of fluorescent contaminants through soils in the column. It was verified that the probe performed well when sealed inside a soft column. Retention characteristics of napthalene and amino G acid (7-amino-1.3 napthalene disulfonic acid) on washed sand in columns were determined: amino G acid passed through the column quickly, while napthaline was retained for a significant period. A procedure for ensuring accurate calibration of the laser spectrometer was delineated. It was found that low levels of suspended solids do not interfere significantly with the fluorescence of amino G acid. Moderate levels of suspended solids were compensated for by using turbidity measurements made with the laser probe.

14. SUBJECT TERMS	15. NUMBER OF PAGES
Fiber-optic Laser Spectrometer Transport of Fluorescent Contaminants Soil Retention of Amino G Acid	32
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	Unlimited

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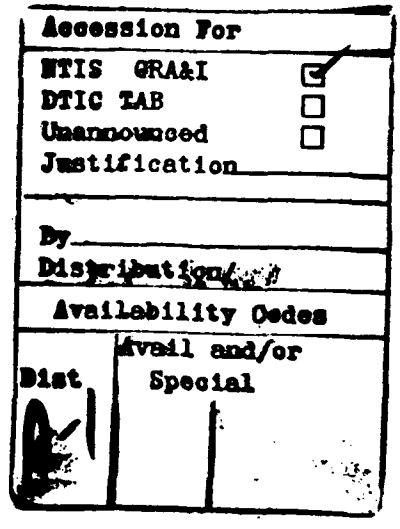
PREFACE

This report was orginally prepared by Universal Energy Systems, Inc., under Contract number F49620-85-C-0013 for the Air Force Office of Scientific Research, Bolling Air Force Base, Washington D.C. It contains results of summer faculty research spons ' by the Armstrong Laboratory Environics Directorate (AL/EQ) 139 Barne drive, Tyndall Air Force Base, Florida 32403-5323.

This report covers research performed by Dr. Brian S. Vogt of Bob Jones University between June and August 1993. The report is being reprinted and submitted to Defense Technical Information nter because of its widespread interest to the DOD Engineering and Servi s c unity. The AL/EQW Mentor was Mr. Bruce Nielsen. The AL/EQ Summer Faculty Coordinator was Mary E. Reynolds.



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INTRODUCTION

The Environics Directorate of Armstrong Laboratory (AL/EQ) conducts research dealing with many environmental issues. Among these is the development of new technology to monitor and remediate contaminated Air Force sites. Another area of research at AL/EQ is the use of model aquifers to study the fate and transport of contaminant plumes. Data from model aquifers are mathematically modeled, permitting a better understanding of how contaminants are distributed when released into the environment. The research reported in this paper involves both monitoring technology (fiber-optic laser fluorescence spectroscopy) and fate and transport research (soil column studies).

Traditional site evaulation entails collecting soil and groundwater samples from wells drilled into the soil and then analyzing those samples in a laboratory with methods such as liquid chromatography (LC), gas chromatography (GC), or liquid scintillation counting (LSC). The acquisition, transport, and analysis of samples by these methods are moderately time-consuming. Fiber-optic laser fluorescence spectroscopy is an alternative method of analysis that permits rapid *in situ* measurements of fluorescence coming from aromatic hydrocarbons, which are components of many fuels and solvents. This method relies on optical fibers to convey excitation light from a laser to a sample. Analyte fluorescence induced by the laser light is carried from the sample back to optics and electronics for analysis and display. Analysis of toluene in monitoring wells at Tinker AFB, OK, has been performed with a transportable fiber-optic spectrometer using a tunable dye laser as an excitation source[1]. Results of the fluorescence analysis in that study compared favorably to results of samples analyzed by GC.

Additional time and cost savings in site evaluation can be realized by using cone penetrometry. The SCAPS (Site Characterization and Analysis Penetrometer System) program is a collaborative effort of the Air Force, Army, and Navy initiated to develop efficient site characterization methods. A cone penetrometer is a truck-mounted system that hydraulically pushes a hardened steel tube into the ground at a rate typically on the order of one meter per minute. The tube contains a variety of sensors or soil and groundwater sampling tools. Adaptation of a fiber-optic probe into a cone penetrometer permits rapid spectroscopic characterization of a contaminated site without drilling monitoring wells. Results of field measurements with fiber optics configured in cone penetrometers using a nitrogen laser[2] or a Nd:YAG-pumped dye laser[3] for fluorescence excitation have been reported. A comparison of instruments of these types was recently made[4]. The nitrogen system is somewhat less expensive, but its single output wavelength of 337 nm cannot be used to excite the BTEX (benzene, toluene, ethyl benzene, and xylenes) or naphthalene components in fuels because

those components do not absorb 337 nm light. The Nd:YAG pumped dye system offers greater sensitivity and a flexible range of excitation wavelengths. The temporal characteristics of fluoreacence measured with that system were used in combination with wavelength information to construct wavelength-time matrices, which can be used to characterize the type of fuel the fluorescence originated from. It was concluded that, as far as site evaluation is concerned, the measurement of fluorescence from fuels should be used as a screening technique at this point in time.

Five things were accomplished this Summer. First, a procedure for ensuring accurate instrument calibration was delineated. Second, a unique fiber-optic laser probe was adapted into a modular stainless-steel column system so that the probe could be used to study the retention of fluorescent contaminants by soils in the column. Third, it was verified that the probe performed well when sealed inside a soil column. This is significant because the column approximates the conditions found in model and real aquifers. Column studies were used in preference to model aquifer studies because columns are easily configured and the experiments are comparatively brief. Fourth, the retention characteristics of two fluorescent tracer molecules on washed sand in columns were determined. This was done in anticipation of a model aquifer study to be undertaken with the same sand and fluorophores. Fifth, the effects of suspended solids on fluorescence signals were investigated. It was found that low levels of suspended solids do not interfere significantly with the fluorescence of amino G acid (7-amino-1,3-naphthalene disulfonic acid). Moderate levels of suspended solids were compensated for by using turbidity measurements made with the laser probe. This is significant because samples taken from model and real aquifers often contain suspended solids.

APPARATUS

The laser system was designed and installed at AL/EQ by G.D. Gillipsie and his research group[5]. The principles of operation have been described elsewhere[6]. In summary, the 1064 nm output of a 20 Hz Nd:YAG laser (Continuum Surelite Series 20) is frequency doubled to 532 nm, which is used to pump a dye laser containing rhodamine 590 laser dye (Exciton). The laser output from this dye may be tuned to any nominal wavelength over the 548-580 nm range, which is in turn frequency doubled to give a nominal ultraviolet (UV) output wavelength in the 274-290 nm range. Frequency doubling was performed because UV light is required to excite fluorescence from the compounds being studied. The UV output is directed to the solution being analyzed through a single 600 μm diameter launch fiber (Fiberguide Industries). Fluorescence excited by the UV light is isotropically scattered in the solution. One or more fibers are used to collect a fraction of the fluorescence and transmit it to

a computer-controlled monochromator (Chromex 500 IS/SM) for dispersion into its component wavelengths. The fluorescence decay profile at a wavelength selected by the monochromator is detected by a photomultiplier tube powered at 2000 volts by a digital power supply (Stanford Research Systems PS325). The fluorescence profile is displayed on and quantified with a digital storage oscilloscope (Tektronix 2440).

Figure 1 is a cut-away view of the end of the probe showing how it is constructed[7]. This probe is a modification of that designed and tested during the Summer of 1992[8]. In summary, one end of a five-meter bundle of seven fibers is glued inside a foot-long stainless-steel tube for support. The other end of the bundle is interfaced to laser and monochromator optics. The probe is inserted into a sample to be analyzed. Laser light enters the solution from the central fiber in the bundle and excites fluorescence from the analyte in the solution. Five of the surrounding fibers are used to collect fluorescence and transmit it to the monochromator.

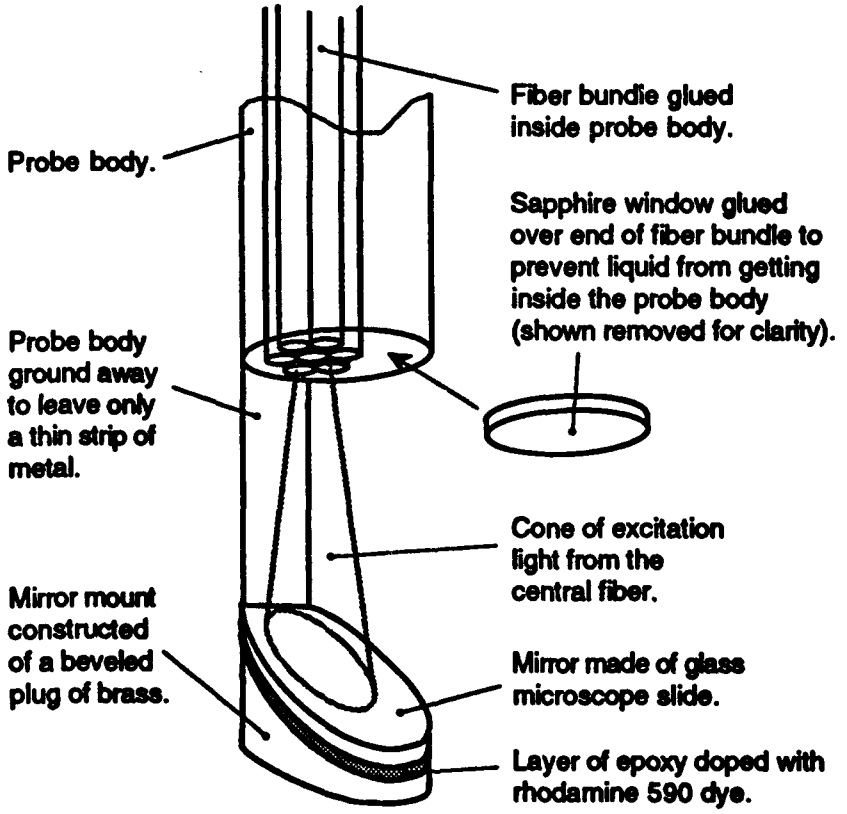

Figure 1. Construction of the Fiber-Optic Probe.

Without the mirror attached to the probe end it was found that some of the light signals measured were sensitive to the position of the probe inside the vessel containing the sample. This phenomenon was attributed to the reflection of light off the walls of the container. The

mirror presents a constant, controlled optical view to the collection fibers and minimizes problems due to light scattering and reflection. The mirror is constructed of microscope slide glass and is angled to reflect UV laser light out of the view of the collection fibers. UV light that is neither absorbed by the sample nor reflected by the mirror enters into the mirror glass. Most of the light that enters the mirror is absorbed instead of being reflected back into the optical path. Current work employs UV light with a wavelength of 287 nm for excitation.

Water in monitoring wells in both real and model aquifers often contains suspended solids that render the water turbid. Turbid solutions can scatter both excitation light and analyte fluorescence. Light scattering leads to erroneously low signals. It is necessary, therefore, to quantify sample turbidity and make signal corrections. Ideally, measurements of both fluorescence and turbidity measurments would be made with a single probe. This is easily accomplished with the probe used in this study. Only five of the fibers surrounding the central fiber are used for collection of analyte fluorescence. The remaining surrounding fiber is used to tramsit a portion of the visible light from the Nd:YAG laser (532 nm) to the probe end, where it passes through the solution and glass mirror. Once the visible 532 nm light travels through the mirror, it excites fluorescence from the rhodamine 590 dye embedded in the epoxy. Some of this fluorescence is scattered into the collection fibers. Any solids suspended in the sample will attenuate both the amount of excitation light reaching the rhodamine 590 and the amount of rhodamine 590 fluorescence reaching the collection fibers. The greater the turbidity, the lower the rhodamine 590 fluorescence signal detected will be. A solution with no suspended solids is used as a reference. This approach assumes that the suspended solids act as a neutral density light filter. As will be seen, it appears that this assumption was valid in these experiments.

Figure 2 illustrates how the probe is used to measure analyte fluorescence alone. UV light from the dye laser is transmitted through the central fiber to the solution, where it excites analyte fluorescence. As already discussed, any UV excitation light that is not absorbed by the

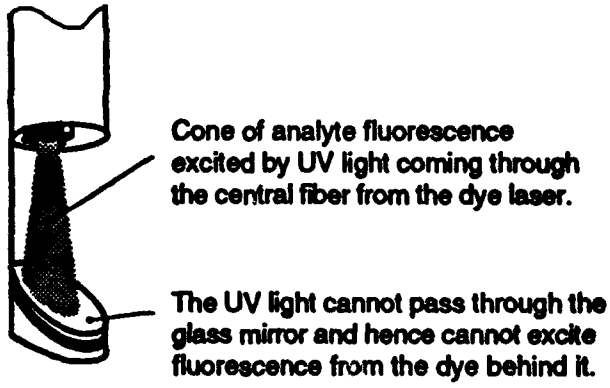

Figure 2. Use of the Probe to Measure Analyte Fluorescence.

analyte in the solution is either reflected or absorbed by the mirror and hence cannot excite fluorescence from the rhodamine 590 dye embedded in the epoxy behind the mirror. This is advantageous because fluorescence from the rhodamine dye could interfere with measurements of fluorescence from some analytes. Furthermore, during the analyte fluorescence measurement a shutter was inserted in part of the optical path to prevent visible light (532 nm) from the Nd:YAG laser from entering the probe. This was done because the intensity of 532 nm light scattered back into the collection fibers was great enough to interfere with measurement of the analyte fluorescence. The shutter also prevents the 532 nm light from exciting rhodamine fluorescence, which has already been seen to be a potential interference. With the shutter inserted only fluorescence from the analyte is observed.

Figure 3 illustrates how the probe is used to measure fluorescence from the embedded rhodamine 590 dye. Visible light (532 nm) from the Nd:YAG laser is transmitted through a noncentral fiber to the solution. Because neither the analyte nor the glass mirror absorb visible light, it travels through them and excites the dye behind the mirror. The fluorescence thus excited is collected for analysis by the same five fibers that collect analyte fluorescence. During this process 287 nm light continues to enter the solution through the central fiber and

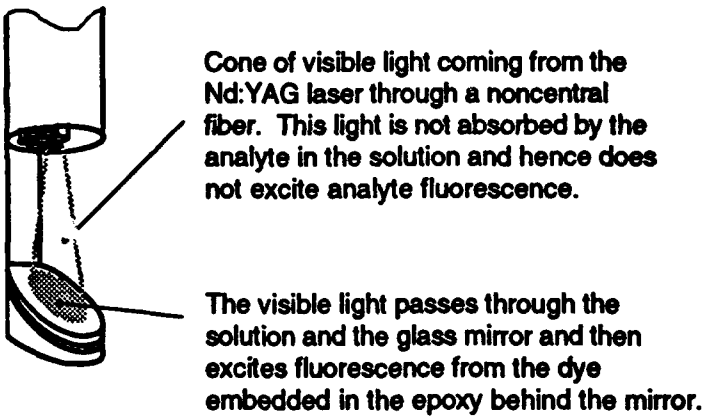

Figure 3. Use of the Probe to Measure Embedded Dye Fluorescence.

thus excites fluorescence from the analytes. The analytes studied in this research were naphthalene (Aldrich Chemical Company, purified by sublimation[9]) and 7-amino-1,3-naphthalene disulfonic acid (monopotassium salt) (Eastman Fine Chemicals, used as received). The latter is sometimes called amino G acid (abbreviated AGA hereafter). Naphthalene exhibits UV fluorescence and was monitored at 335 nm instead of its peak maximum of 323 nm[10] to avoid a water Raman signal. AGA exhibits blue fluorescence and was monitored at 445 nm, which corresponds to the maximum in its fluorescence spectrum[11]. Rhodamine 590 was monitored at 590 nm. The spectra of the analytes were so different from the spectrum of

rhodamine 590 that analyte fluorescence did not pose any significant interference in the measurement of rhodamine 590 fluorescence. If such an interference had been a problem, it could have been easily eliminated by inserting a shutter into the optical path to prevent 287 nm UV excitation light from entering the probe and exciting the analytes. Changing excitation wavelengths with the dye laser used in this study is accomplished by rotating a mirror on a mechanical stage. The dye laser remained tuned at 287 nm for both AGA and naphthalene excitation. This gave adequate results and eliminated the need to change dye laser output wavelengths.

Figure 4 shows how the probe was adapted into a stainless-steel column and pump apparatus. Two LC pumps (Waters 510) were connected to the inlet end of the column with a six-port LC sample loop injector (Valco C6U). One pump was used to pump background solution through the column; the other was used to pump contaminant plumes. The pumps and column were connected to the sample loop injector in such a way that the flow from one pump was directed to waste while the flow from the other was directed to the column. Not shown in Figure 4 is the liquid handler (Gilson 212B) that was connected to the effluent end of the column to permit fractionation of the effluent for subsequent analysis. The background solution consisted of distilled water containing 0.005 M $CaSO_4$ (calcium sulfate) and 0.02 w/w % NaN_3 (sodium azide). The $CaSO_4$ serves to raise the ionic strength of the solution; the NaN_3 was added to prevent microbial and algal growth. This mixture has been used successfully in batch, column, and model aquifer sorption studies[12]. All calibration standards and contaminant plumes were made up in background solution.

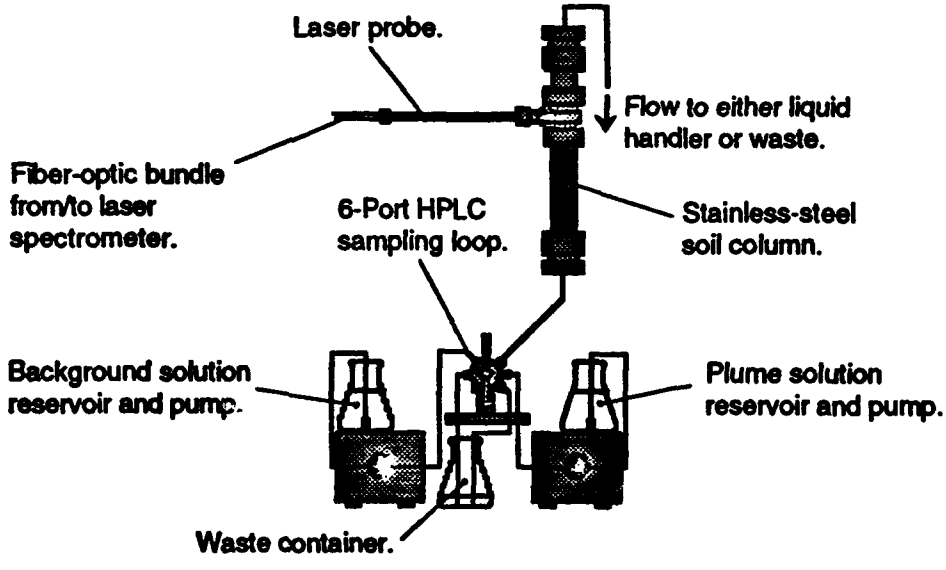

Figure 4. Laser Probe, Column, and Pump Configuration.

Initial attempts to adapt the probe into a glass column were abandoned because the glass was too fragile. It was undertaken to use a stainless-steel column instead. Figures 5 and 6 show details of the soil column and how the laser probe was adapted into it. The probe was sealed into a Swagelok fitting with a Teflon ferrule, which made the seal liquid-tight without damaging the probe body. Different columns lengths were easily achieved simply by replacing the upper and lower column sections with tubing of different length. The length of the upper column section was 7.5 cm in all experiments. The time required for any given experiment was a function of both column length and pump rate. Initially the length of the lower section was 47.8 cm. It was, however, cut to 15.0 cm and then 7.5 cm to shorten experiment times. The column was filled with a slurry of washed sand in background solution. While being filled, the

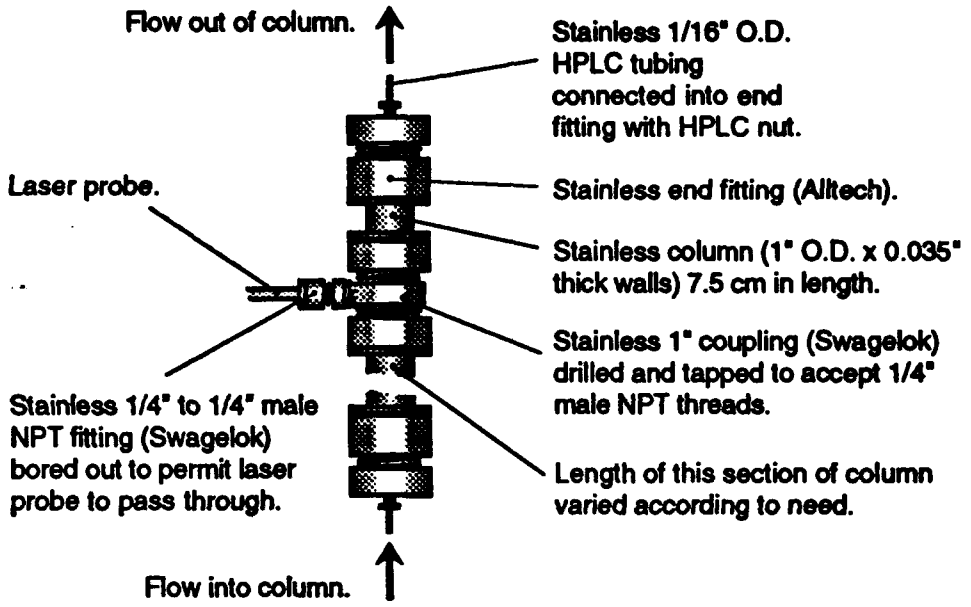

Figure 5. Construction of the Soil Column and the Laser Probe Interface.

column was attached to the pump system with all tubing and the bottom of the column filled with background solution in order to avoid bubble entrapment in the system. Depending upon what the probe was to be used for, it was either adapted into or removed from the column. When doing either of these, the column was oriented horizontally (with the probe adapter fitting aimed up) and the effluent end blocked to prevent loss of liquid from and introduction of bubbles into the column. Furthermore, a gentle flow of liquid through the column and out the probe adapter fitting was maintained so as to not introduce any bubbles into the screen cylinder. When adapting the probe into the column, the probe was rotated on its long axis so that the metal strip connecting the probe body to the glass mirror mount was oriented vertically. This was done so that if a bubble got into the column inadvertently it would not get

trapped in the optical path of the probe. When the laser probe was not adapted in the column, it was replaced with a short length of stainless-steel tubing sealed shut on one end with an end cap. This was done to avoid drying the column out between experiments.

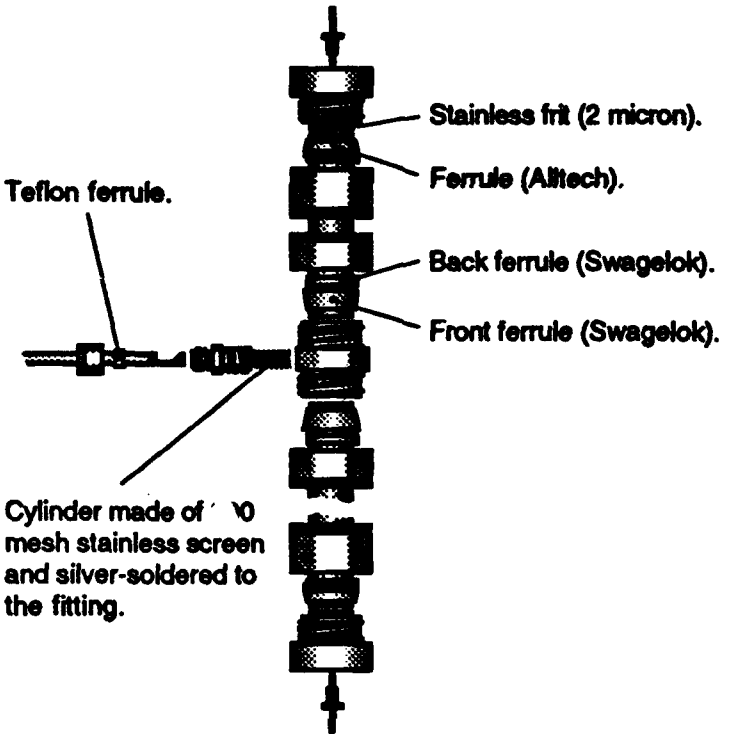

Figure 6. Exploded View of the Soil Column and the Laser Probe Interface.

RESULTS

It has been reported[13] that the fluorescence of a given concentration of AGA is constant between pH 6.3 and 9.4. The effect of sand on the pH of water was checked. It was observed that addition of 15 g of unwashed sand to 60 mL of distilled water changed the pH to about 6.2 after stirring for two minutes. Monitoring the pH for approximately 35 minutes while continuing to stir showed that the pH gradually rose to about 6.5. It was unknown whether the pH of the background solution would remain between 6.3 and 9.4 during column studies. The pH of a solution of AGA was varied between pH 5.3 and 8.9. The fluorescence of this solution was monitored with the laser probe and found to be constant. Consequently, it was decided that buffering the background solution was unnecessary.

The dye laser used to excite fluorescence in this study exhibited some variation in output power with respect to time. Fluorescence intensity is a function of excitation power. Consequently, the fluorescence signal from any given solution varied with time. A photodiode was positioned in the optical system to monitor the amount of UV light scattered off the face of the laser probe excitation fiber. The signal from the photodiode was recorded whenever a fluorescence measurement was made. Each fluorescence signal was subsequently corrected by normalizing to a photodiode signal of 50 mV. A value of 50 mV was chosen because it was typical of photodiode signals. All fluorescence readings, including those from calibration standards, were corrected in this fashion. It was initially assumed that the photodiode signals were sufficiently reproducible from day to day so that daily calibration would be unnecessary. However, after several experiments it was found that AGA calibration behavior exhibited some variation from day to day that could not be corrected for with photodiode readings. It was suspected that the AGA standards were decaying, but spectrophotometer absorbance measurements indicated that this was not so. At one point, however, the photodiode had to be replaced because its signal had degraded so far as to give inadequate response. It is believed that the UV light incident upon the photodiode was damaging it, causing its response to a given level of dye laser power to change over moderate periods of time. It is felt that the normalization of fluorescence signals based on photodiode signals in this experimentation was effective during a given day but not necessarily from day to day. It is also possible that the spatial characteristics of the excitation beam varied. This may have changed the effective volume of the cone of light entering the solution from the laser probe, which in turn would change the amount of AGA excited. Consequently, it was decided that calibration would be performed every day the laser was used for analysis.

Typical calibration data for AGA are shown in Figure 7. These data were broken down into two sections with a linear fit for the low concentration data and a second-order polynomial fit for the high concentration data. This gave greater accuracy when estimating AGA concentrations from signal measurements than using a single equation for all the calibration data because no single equation describes all of the data adequately. The limit of detection was estimated using the IUPAC method[14] and found to be 0.17 ppb AGA in this experiment.

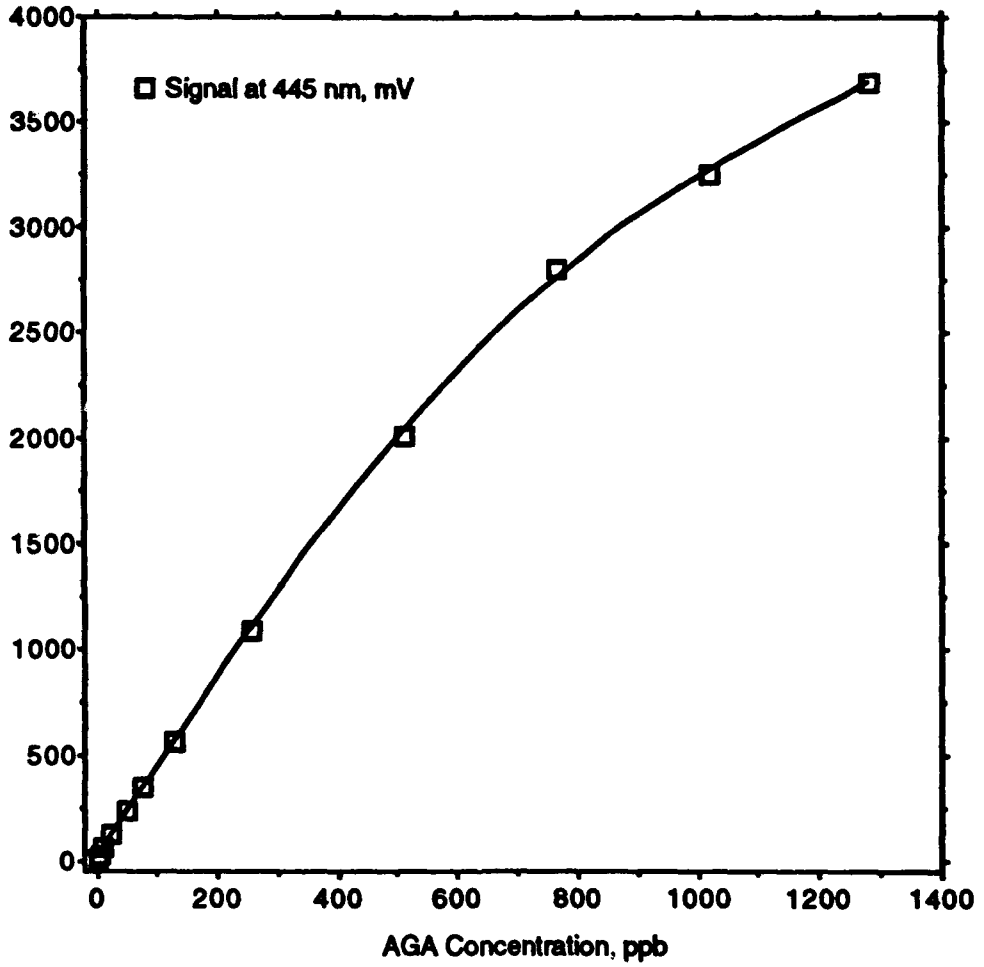

Figure 7. Typical AGA Calibration Data.

Figure 8 shows breakthrough curves for AGA on a sand column with a 47.8 cm lower column section. Pumping rate was 1 mL/min. The contaminant plume was a 19.8 mL pulse of 1200 ppb AGA. The left-hand, lower-volume profile in Figure 8 represents AGA concentrations detected by the probe while it was embedded in the column. Each point on the other profile is the concentration of AGA detected in a vial containing effluent dispensed into it by the liquid handler. The probe was then removed from the column to perform analysis on the vial

contents. The vial profile occurs at higher volume (later in time) than the column profile because the contaminant plume must travel past the probe and through the upper 7.5 cm column section before reaching the vials.

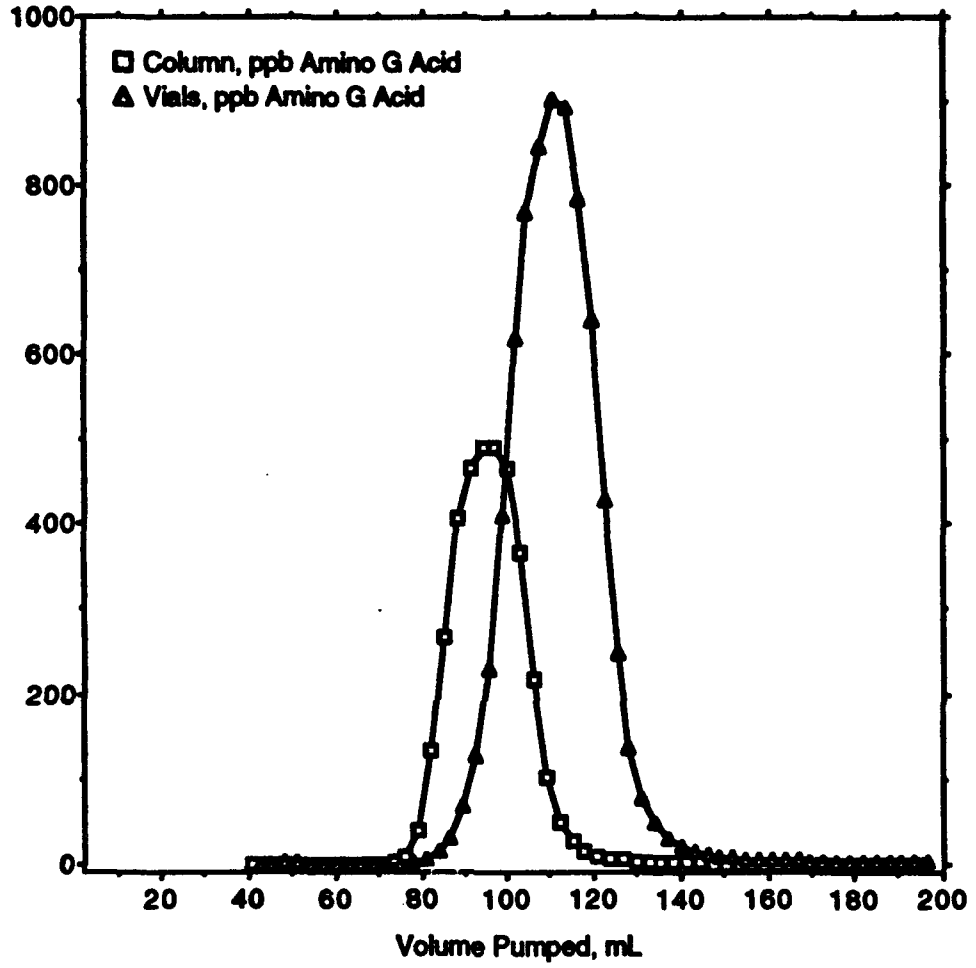

Figure 8. Breakthrough of AGA on Sand (1 mL/min Pump Rate).

The mass of AGA recovered in each vial was calculated by multiplying the AGA concentration by the volume of effluent in the vial. The sum of the masses recovered in all vials was 22.1 μg, which is 93.1% of the 23.8 μg in the plume. This experiment was performed before it was known that daily calibration would be required. Consequently, the AGA concentrations in this experiment were estimated from calibration data acquired on a different day. Inaccuracy in AGA concentrations may account for the less than 100% recovery. Trapezoidal integration of the column profile gave an area of only 10.6 μg, or only 44.7% recovery of the mass contained in the plume. A simple hypothesis was constructed to account for this. The cylinder housing the end of the probe in the column consists of very fine, 200

mesh stainless steel (see Figure 6). It is conceivable that the highly fractured edges of the sand particles blocked some of the openings in the screen. At high pump rates, one would expect partial blockage to present a great enough resistance to liquid flow that some channeling around the mesh cylinder would occur. In that event not all of the analyte would pass through the optical path of the probe and the concentrations detected by it would be low, giving the behavior evident in Figure 8. To test this hypothesis, the sand was removed from the column and replaced with a mixture of relatively large glass beads (4-6 mm in diameter). The lower column section was shortened to 150 mm in order to shorten experiment time. The experiment was repeated with a 4.98 mL plume of 1200 ppb AGA and a pump rate of 1 mL/min. The resulting profiles are shown in Figure 9.

Analysis of the vial contents indicated a recovery of 5.81 µg, or 97.9% recovery. This recovery was better than in the previous run because a single-point calibration of the 1200 ppb plume was used to correct the calibration data of a previous day. This correction was not

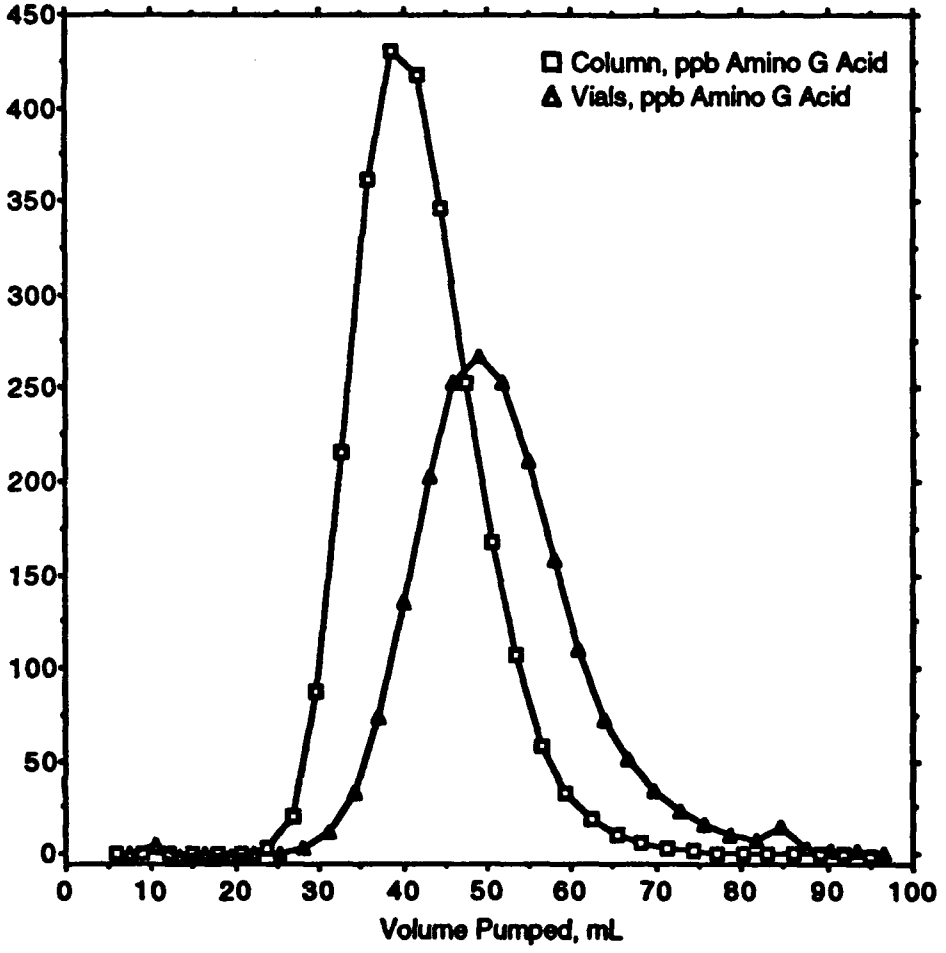

Figure 9. Breakthrough of AGA on Glass Beads (1 mL/min Pump Rate).

entirely effective because correcting a nonlinear calibration plot with a single point is subject to a moderate amount of error. Integration of the column profile in Figure 9 gave 7.57 µg of AGA, or 127% recovery. The fact that the recovery was not low supports the idea that channeling occurred in the previous experiment. This led to lower pump rates in subsequent experiments. That the recovery was signficantly higher than 100% merits some explanation. Putting large particles in a column results in higher porosity at the column walls than in the column center because particles are packed more tightly in the center. Consequently, fluid flow is radially heterogeneous. In this experiment it appears that the AGA concentration was also radially heterogeneous. Higher AGA concentrations at the center of the column than at the edges would explain the behavior observed in Figure 9.

Figure 10 presents the results of an AGA column experiment performed with a low pump rate (0.2 mL/min) to determine whether channeling around the screen cylinder could be avoided. This and all subsequent column experiments were performed with a 7.5 cm lower

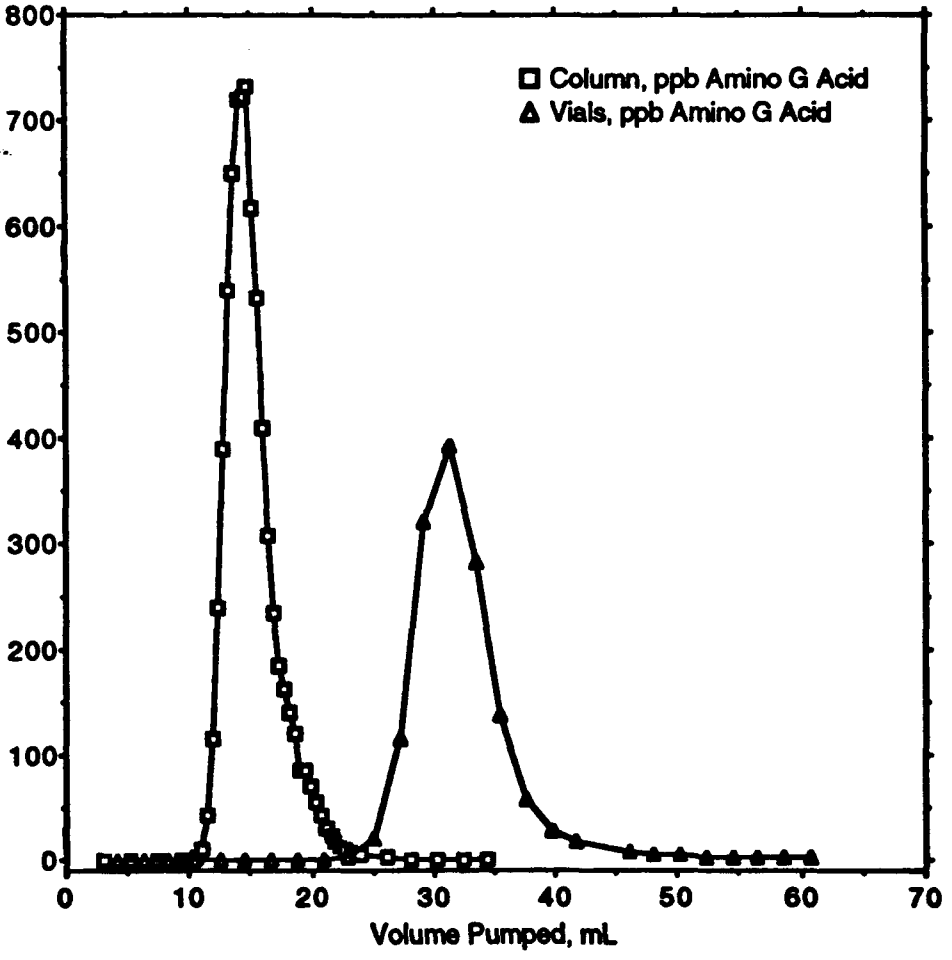

Figure 10. Breakthrough of AGA on Sand (0.2 mL/min Pump Rate).

column section. A 2.82 mL plume of 1020 ppb AGA was used. Recovery in the vials was 2.94 μg, which is 102% of the mass in the plume.

Integration of the column profile yielded an area of 3.09 μg (107% recovery). These recoveries are good. The deviation from 100% is not hard to explain. The value of the volume for any given point in the breakthrough curves presented is calculated from the pump rate and the time of pumping. For this experiment the flow rate was 0.21 mL/min. If it had been 0.20 mL/min instead, the column recovery would come out to 102% and the vial recovery 97.3%. Consequently, a small amount of inaccuracy in the pump rate determination explains all of the error. In this and prior experiments the flow rate was obtained by dividing the volume of effluent collected in a 5 mL graduated cylinder by the time it took to collect it. In subsequent experiments the volume collected was calculated by weighing the effluent collected in a given period of time and dividing it by the density of the effluent, which was taken to be the density of the background solution. The density (0.9971 g/mL) was determined by weighing 50 mL of solution in a volumetric flask. Error in timing and any inaccuracy inherent to the analysis will also affect calculated recoveries.

The fact that the areas of the two curves in Figure 10 are essentially identical suggests that no channeling was occurring around the laser probe. Clearly, the probe performs well in the soil column environment. It should be straightforward to fit a screen cylinder around the end of the probe to permit measurements to be made with the probe embedded in model or real aquifers. One would expect fluorescence measurements from such environments to be representative of actual analyte concentrations only if the rate of water flow is comparable to or lower than the 0.2 mL/min pump rate used in this experiment. Estimates of groundwater flow rates are often reported as linear velocities, which are in units of distance/time rather than volume/time. The estimation of linear velocity in this experiment was made as follows. First, it was assumed that AGA was not adsorbed to any appreciable extent on the sand. One study reported that losses of AGA due to adsorption on soil ranged from only 0.5% up to 80%, depending on soil type[15]. Second, it was assumed that the pore volume of the lower column section was 15 mL, which is the volume corresponding to the maximum of the column profile in Figure 10. At a flow rate of 0.2 mL/min, the contaminant plume would reach the laser probe in (15 mL)/(0.2 mL/min) or 75 min. In the 75 mm column that was used, this translates to a linear flow velocity of 1 mm/min or 1.4 m/d. Making different assumptions in this estimation would result in a value higher than 1.4 m/d. Reported average linear groundwater velocities for a sand aquifer in Ontario, Canada, vary between 0.076 m/d and 0.091 m/d, depending on the method of estimation used[16]. The linear groundwater velocity at Columbus Air Force Base, Mississippi, USA, can be estimated to be no greater than 0.4 m/d by using published tritium plume data[17]. These groundwater velocities are significantly lower than those employed in these column studies. This suggests that, barring other complications, fluorescence measurements made with a screen-protected laser probe embedded in soils could

be used to reliably estimate contaminant concentrations. The same pertains to model aquifer studies employing appropriate flow conditions.

In another effort to shorten experiment time, the experiment represented by Figure 10 was repeated with a 2.937 mL plume of 1020 ppb AGA and a background pump rate of 0.3 mL/min. The results are shown in Figure 11. Recoveries were 2.99 mg (99.8% recovery) for the column and 2.98 mg (99.5% recovery) for the vials. Comparison of Figures 10 and 11 shows that the results from the two experiments are essentially identical, indicating that 0.3 mL/min was low enough to prevent channeling around the laser probe. Consequently, all subsequent experiments were performed with a pump rate of 0.3 mL/min.

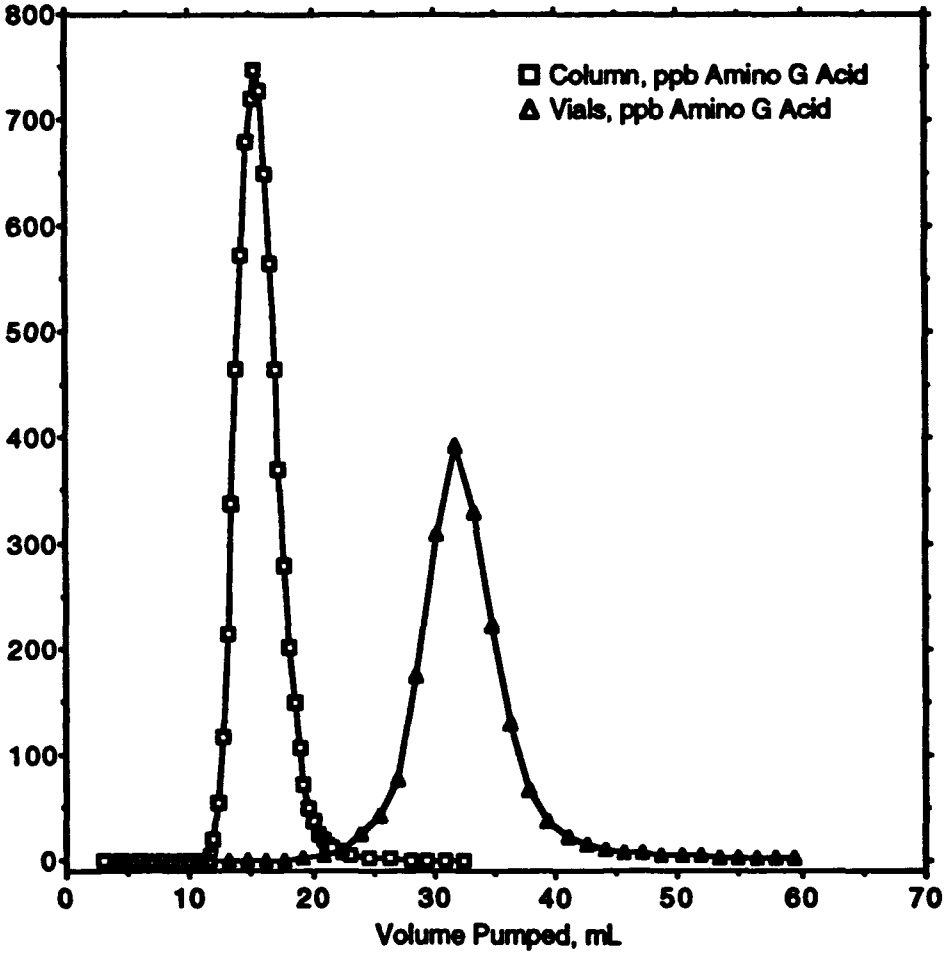

Figure 11. Breakthrough of AGA on Sand (0.3 mL/min Pump Rate).

Naphthalene is of interest in the monitoring of Air Force sites because it is a key component of jet fuels. Several experiments involving naphthalene were performed. Figure 12

shows typical naphthalene calibration data. The limit of detection in this experiment was estimated to be 5.63 ppb.

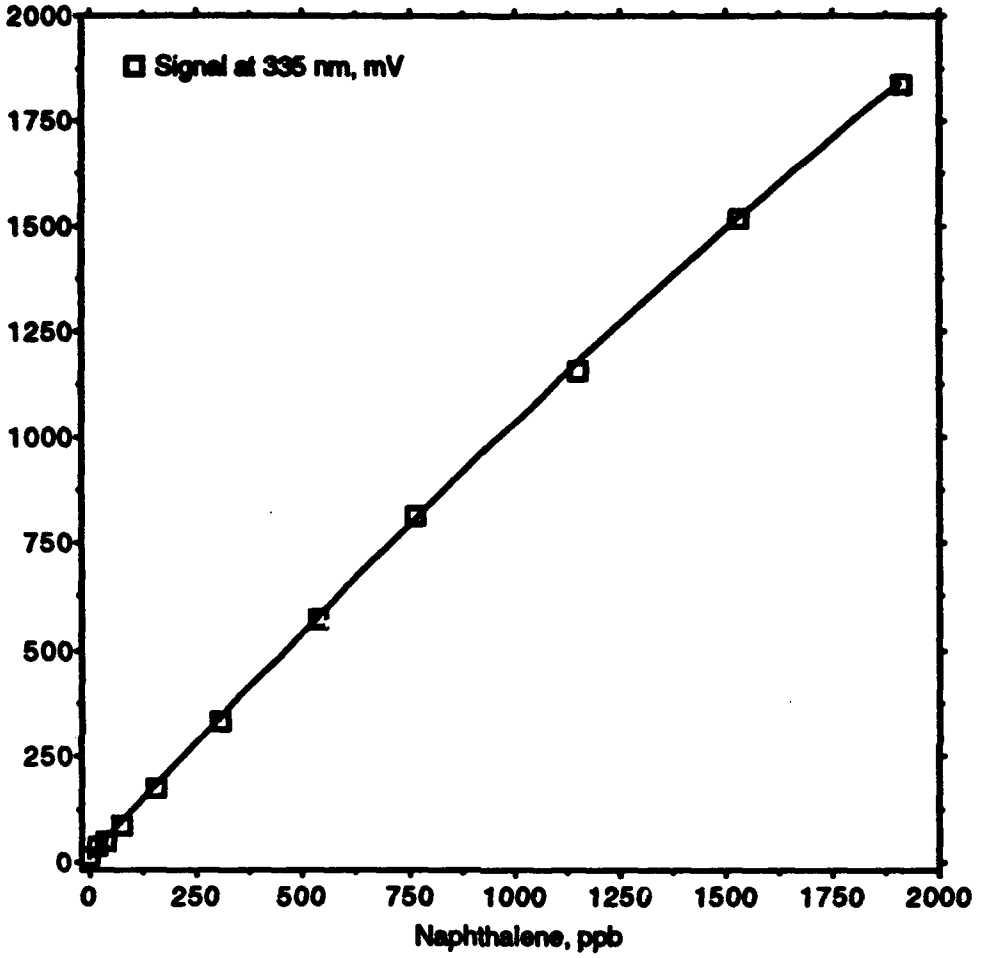

Figure 12. Typical Naphthalene Calibration Data.

Figure 13 shows the results of a column experiment performed with a 2.944 mL plume of 1530 ppb naphthalene. Integration of the profile gave an area of 4.24 μg (94.1% recovery of the mass in the plume). Fractionation of the effluent into many vials was not performed in this or subsequent experiments because the AGA experiments demonstrated that integration of the column and effluent profiles gives identical results when experimental conditions are properly controlled. However, the effluent was collected in flasks for analysis to check naphthalene mass balance. Analysis of the effluent showed a recovery of 4.34 μg of naphthalene (96.4% recovery), which agrees well with the the profile integration.

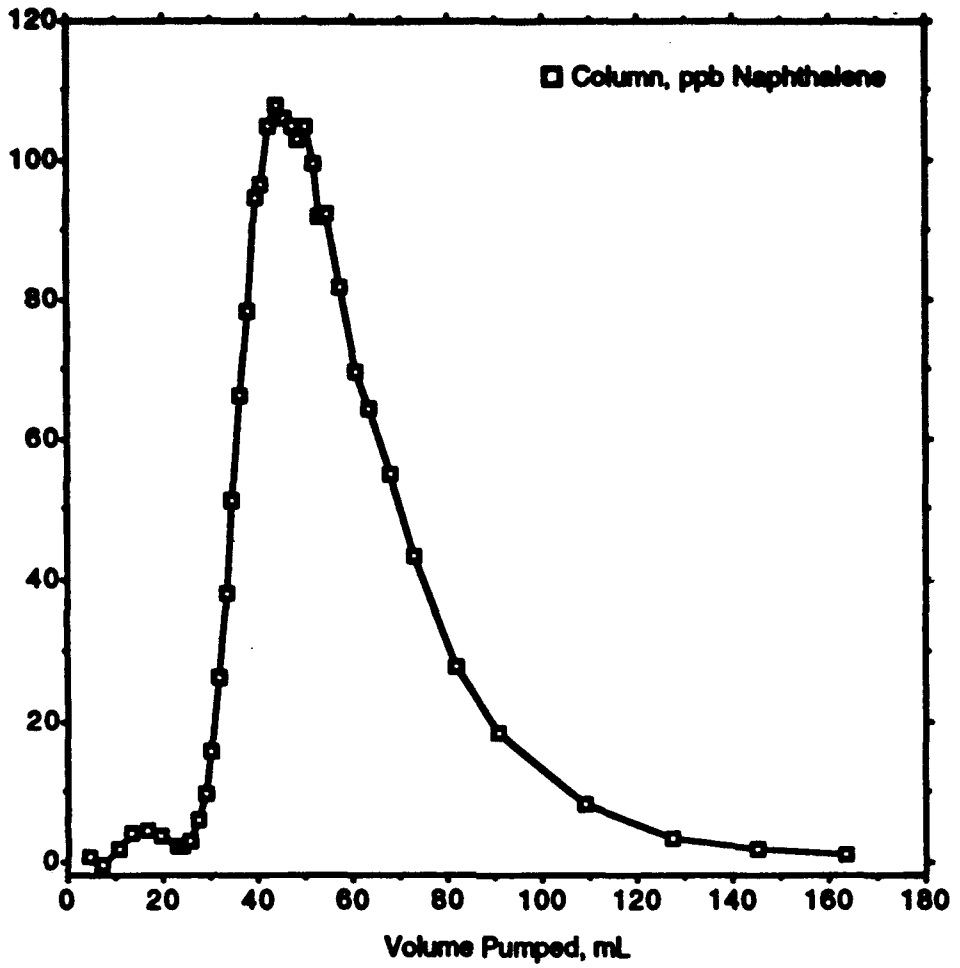

Figure 13. Breakthrough of Naphthalene on Sand (0.3 mL/min Pump Rate).

The last column experiment was performed with 2.958 mL of contaminant plume containing 1030 ppb AGA and 1530 ppb naphthalene. Fluorescence measurements at the analytical wavelengths for both were taken alternately as a function of time. The results are shown in Figure 14. Recovery estimated by integration of the profiles was 4.64 µg (103% recovery) for naphthalene and 3.04 µg (99.6% recovery) for AGA. The effluent was collected in three flasks and analyzed. Recovery was 2.90 µg of AGA (95.1% recovery) and 3.75 µg of naphthalene (82.8% recovery). All of the 3.75 µg of naphthalene recovered was present in the same effluent recovery flask. Assuming that the remainder of the naphthalene was present in the following flask, calculations show that it would have been present at a concentration below the limit of detection. This explains why it appears that some naphthalene is missing.

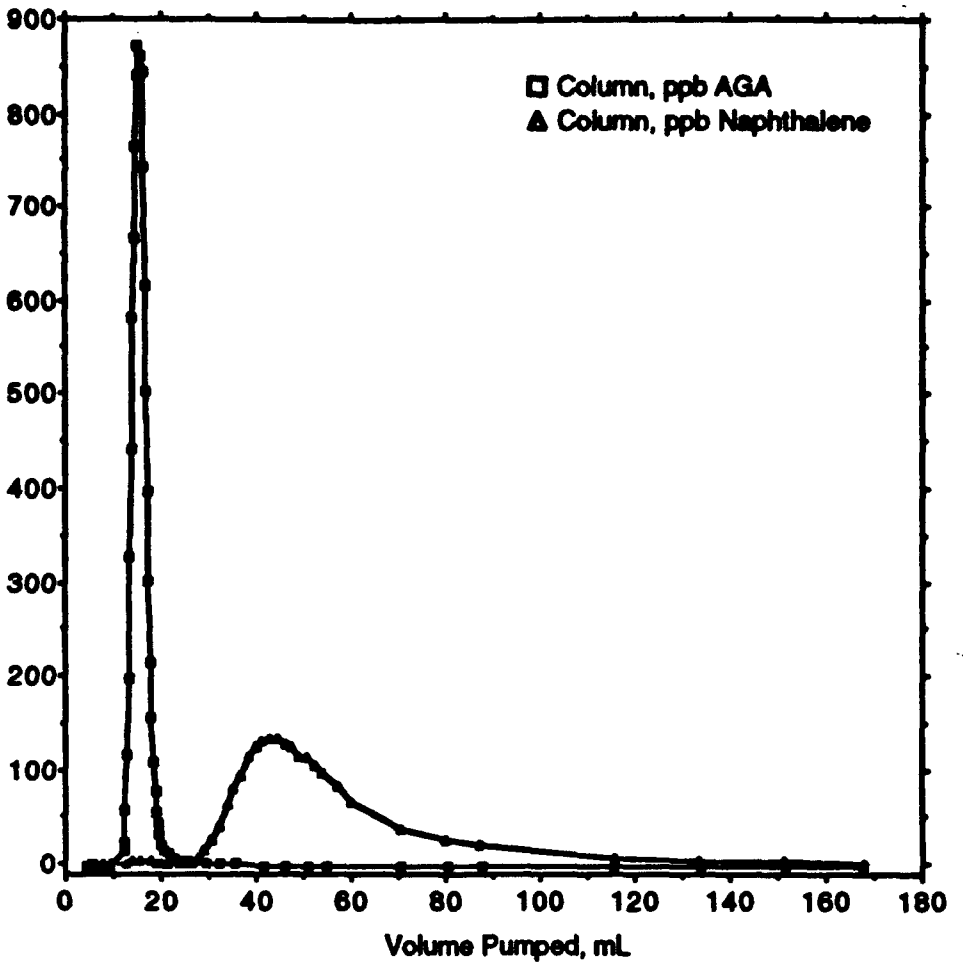

Figure 14. Breakthrough of AGA & Naphthalene on Sand (0.3 mL/min Pump Rate).

Sorption coefficients are constants that describe the distribution of a contaminant (AGA or naphthalene) between the liquid phase (background solution) and the solid phase (sand). They are used in characterizing the interaction between contaminants and soils. The sorption coefficient has the same form as an equilibrium constant. Apparent sorption coefficients may be estimated even in systems that do not reach equilibrium. At sufficiently high sorption rates, the adsorption process does appear to reach equilibrium even in flowing systems[18]. The determination of sorption coefficients in columns depends upon comparing the volume pumped when the solvent in the contaminant plume passes a given point in the column to the volume pumped when the contaminant passes that same point. Consider the naphthalene profile in Figure 14. The long tail indicates that naphthalene travel through the column is somewhat retarded by the sand. This is qualitatively similar to previously observed naphthalene behavior[19]. However, the water in the contaminant solution is not retarded by the sand. If one could follow the progress of that water through the column, one would observe it passing the

laser probe much sooner than the naphthalene does. One could then estimate the sorption coefficient of naphthalene on the sand by comparing the breakthrough behavior of naphthalene to that of water. Monitoring the contaminant plume water is possible when collecting the effluent in fractions. One can add tritiated water to the plume and analyze the effluent for it with LSC. That process, however, introduces additional sample handling and analysis time. It would be much more convenient to be able to monitor the contaminant solvent plume with the laser probe instead of having to collect samples for separate analysis. The AGA profile passes the laser probe at a relatively low volume and is comparatively sharp and symmetrical, indicating that it is retarded by the sand minimally or not at all. If it is completely unretarded by the sand, AGA could be used to monitor the contaminant solvent plume fluorimetrically instead of by LSC with tritiated water, thus permitting complete characterization of the adsorption process by *in situ* fluorescence measurements. Although they have yet to be performed for AGA on sand, batch equilibration studies can be used to determine the degree of adsorption on any given matrix. Even if AGA is adsorbed to some extent, one could perform a preliminary experiment with tritiated water and AGA to determine by how much the AGA profile is displaced from the profile of the tritiated water. Subsequent experiments could then rapidly determine the relationship of various contaminants to AGA, and by using a combination of the data determine sorption coefficients. This would provide a signficant time and cost savings if several column experiments were performed.

As previously mentioned, samples from model and real aquifers often contain suspended solids. For this reason the effect of suspended solids on AGA fluorescence was investigated. A slurry of unwashed sand in background solution was made. The large solids were permitted to settle out and the supernatant, which was turbid due to the solids it contained, was poured off. 10 mL aliquots of this turbid suspension were evaporated in an oven and the residues weighed to determine the mass of dissolved and suspended solids contained in the aliquots. The same was done with 10 mL aliquots of background solution. Subtraction indicated that the sand suspension contained 550 mg/L of suspended solids. A normal set of AGA calibration standards in background solution was prepared in volumetric flasks. A duplicate set, identical to the first except that a fixed volume of suspension was added to each flask, was also prepared. The suspension was maintained during the preparation of these solutions by stirring with a magnetic spin vane. Each pair of solutions was then titrated together to obtain fluorescence readings for a fixed concentration of AGA with varying amounts of suspended solids. For example, a normal 25.7 ppb AGA solution was titrated with a 25.7 ppb AGA solution containing suspended solids. These solutions were stirred with magnetic spin vanes throughout the process. The resulting data are presented in Figure 15. Each curve represents a calibration curve for AGA in the presence of a fixed amount of suspended solids. The trend is not surprising: AGA fluorescence drops as turbidity increases. Visual comparison of the 200 mg/L solution to photographs of solutions obtained

from monitoring wells at Tinker Air Force Base suggested that the turbidity of the 200 mg/L solution used in this study approximated a worst case scenario from a real site.

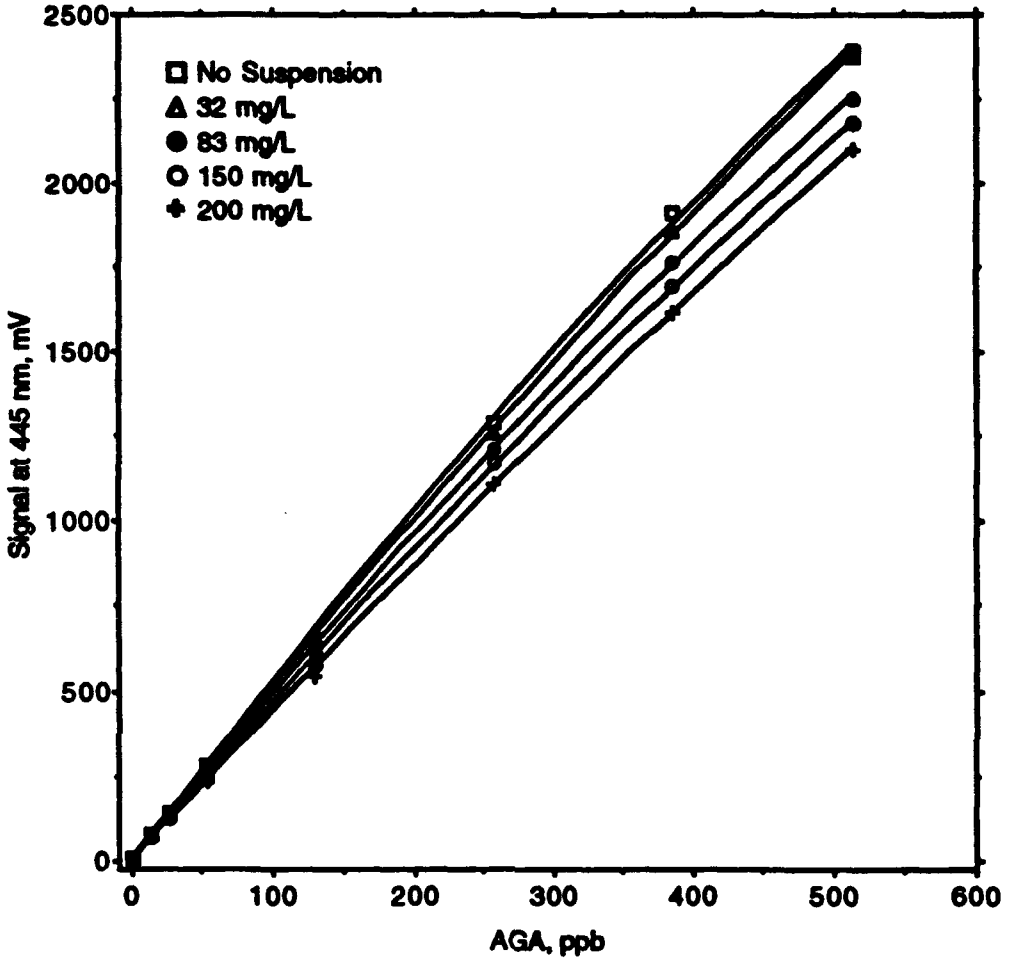

Figure 15. Affect of Turbidity on AGA Fluorescence.

The fluorescence signal from the rhodamine 590 was measured at 590 nm immediately after each 445 nm AGA measurement. Each AGA fluorescence measurement was corrected by dividing it by the fraction of rhodamine signal left in the turbid solution. For example, if the rhodamine signal in the turbid solution was 90% of what it was in the corresponding solution with no suspended solids, the AGA fluorescence signal was corrected by dividing it by 0.90. Figure 16 shows the results of these corrections for the 150 mg/L suspensions. The corrected 150 mg/L calibration curve is essentially collinear with that corresponding to the solutions with zero suspended solids, indicating that the correction worked well. It also suggests that 445 nm light and 590 nm light were scattered to the same extent by the suspended solids used in this experiment. This is not necessarily true with solids from other sources, such as clay-

containing soils. Experiments need to be performed with other fluorophores and soil types to determine the scope of applicability of the process used in this study. The idea of being able to make *in situ* fluorescence measurements and correct them for turbidity in the sample by making measurements with the same probe at essentially the same time is very attractive.

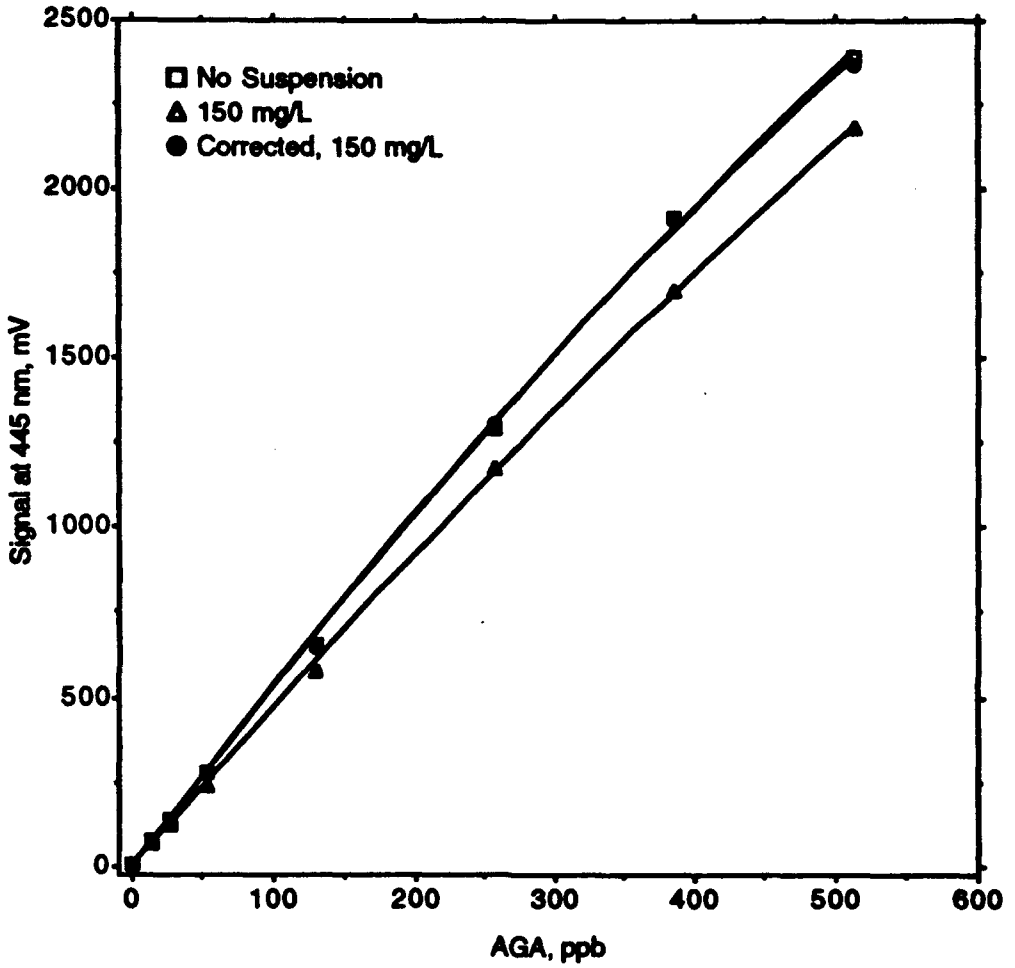

Figure 16. Correction of AGA Fluorescence Data for Turbidity.

The samples containing 150 mg/L of suspended solids were also treated as unknowns. The concentration of AGA was estimated first from the uncorrected fluorescence readings and then from the corrected readings. Figure 17 shows a plot of calculated *versus* actual AGA concentration. This plot would have a slope of one if the calculated and actual values were identical. The uncorrected data have a slope of 0.892; that for the corrected data is 0.994. Slopes and values of r^2 for similar plots at all four suspension concentrations studied are given in Table 1. All of the slopes for the corrected data are close to one. The data in Table 2 illustrate the level of accuracy achieved for a 129 ppb AGA solution with and without the

turbidity correction. The concentrations calculated with the correction are all between 123 and 128 ppb, as opposed to values between 103 and 124 ppb when no correction was applied. Table 3 shows percent errors for all the solutions measured at the different levels of turbidity.

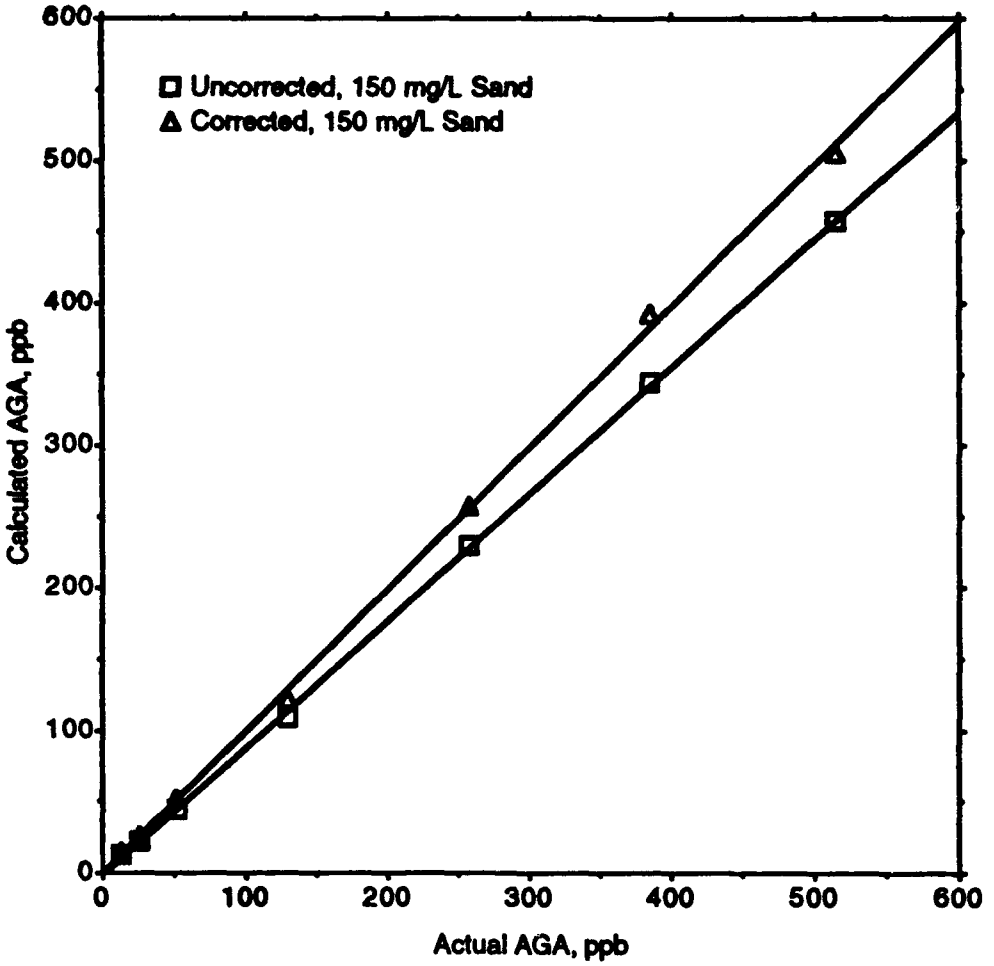

Figure 17. Calculated Versus Actual AGA Concentrations.

A limitation of the turbidity-correction process used in this study has to do with the relationship of the analyte fluorescence spectrum to that of the dye embedded in the probe. It was possible to correct for the effects of suspended solids in this study because the fluorescence spectra of AGA and rhodamine 590 do not overlap at their respective analytical wavelengths. Of course, even if the fluorescence spectra did overlap it would be possible to selectively excite the analyte or embedded dye as long as their absorption spectra were significantly different and the laser could be quickly and reproducibly tuned to the appropriate excitation wavelengths. Another possible way to distinguish between signals from the analyte

and embedded dye would be to rely on time discrimination. If the fluorescence lifetimes of the two were sufficiently different, it would be possible to deconvolute their respective contributions to the overall fluorescence decay profile at a single wavelength. These capabilities will be phased into the apparatus as soon as the proper computer hardware and software are installed. Another potential problem would be background fluorescence from naturally occurring fluorophores. Background fluorescence of various degrees has been reported to occur in the 400-600 nm range[20]. Obviously, the extent of this problem would vary from site to site. It would be a relatively easy matter to quantify the problem in model aquifer studies. Perhaps a combination of time and wavelength discrimination could be used to work around it in real aquifer measurements, but that has yet to be realized.

Table 1. Linear Fit Data from Plots of Calculated Versus Actual AGA Concentrations With and Without Turbidity Correction.

	Sand, mg/L			
	32	83	150	200
Slope Without Turbidity Correction	0.988	0.927	0.892	0.851
r^2	0.9999	0.9999	0.9998	0.9997
Slope With Turbidity Correction	1.018	0.9852	0.994	0.9585
r^2	0.9995	0.9995	0.9993	0.9995

Table 2. Error in Calculated AGA for a 129 ppb AGA solution.

	Sand, mg/L			
	32	83	150	200
Concentration Calculated Without Turbidity Correction, ppb	124	117	109	103
Percent Error	-3.9	-9.3	-16	-20
Concentration Calculated With Turbidity Correction, ppb	127	128	123	123
Percent Error	-1.6	-0.8	-4.7	-4.7

Table 3. Average Errors in Calculated AGA Concentrations.

Sand, mg/L	Average Percent Error Without Turbidity Correction	Average Percent Error With Turbidity Correction
32	2.8	2.4
83	6.6	2.6
150	11	2.8
200	13	4.2

The last problem encountered in the correction for suspended solids was that rhodamine 590 dye embedded in the laser probe was photochemically degraded as a function of time. Work is currently underway to find a photochemically stable combination of turbidity-correction dye and probe configuration.

CONCLUSION

The soil column experiments performed in this research demonstrate not only the feasibility of using a fiber-optic laser spectrometer for such studies, but also show that such an approach is accurate. Measurements made with the probe adapted into the column permit rapid, *in situ* analysis to be performed, obviating the need to collect samples for subsequent analysis. The practicality of making both fluorescence and turbidity measurements with a single probe has not only been demonstrated, but shown to be highly successful.

Work currently in progress centers on several areas. First, the probe is being miniaturized from one-fourth inch in diameter to one-eighth inch in diameter. This will require the use of a maximum of two fibers in the bundle. Second, efforts are being made to make the probe more durable. The susceptibility of the embedded rhodamine dye to photolysis has already be referred to. Use of silica-clad fiber instead of plastic-clad fiber will result in longer probe life due to the higher UV transmittance. Current probes are slowly degraded because the plastic fiber cladding does absorb some UV light. It is also hoped that adapters can be fitted onto the end of the probe to permit them to be inserted directly into loose soil matrices without damage. The third area of current effort is probe multiplexing. It is hoped that a computer-driven microcontroller can be used to connect several probes to a single optical system. This will be done so that model aquifers can be studied with multiple probes embedded in the soil matrix, permitting rapid and relatively noninvasive continuous monitoring to be performed. It

will also provide a logical step to transitioning this technology to Air Force field sites, where multiplexed probes could provide almost simultaneous monitoring of ground water at multiple locations. Last, it is now possible for a model aquifer study to be done as soon as the apparatus for such a study is ready.

REFERENCES

1. G.D. Gillispie and R.W. St. Germain, "In-Situ Tunable Laser Fluorescence Analysis of Hydrocarbons," *Environmental and Process Monitoring Technologies*, Tuan Vo-Dinh, Editor, *Proc. SPIE 1637*, 151-162 (1992).
2. S.H. Lieberman, G.A. Theriault, S.S. Cooper, P.G. Malone, R.S. Olsen, and P.W. Lurk, "Rapid, Subsurface, In Situ Field Screening of Petroleum Hydrocarbon Contamination Using Laser Induced Fluorescence Over Optical Fibers," *Proceedings of the Second International Symposium on Field Screening Methods for Hazardous Wastes and Toxic Chemicals*, 57-63 (1991).
3. W.L. Bratton, J.D. Shinn, S.M. Timian, G.D. Gillispie, and R. St. Germain, "The Air Force Site Characterization and Analysis Penetrometer System (AFSCAPS); Laser Induced Fluorescence Cone Penetrometer. Volume I-System Development and Evaluation," Air Force technical report AL/EQ-TR-1993-0009 (1993).
4. G.D. Gillispie, R.W. St. Germain, and J.L. Klingfus, "Subsurface Optical Probes: Current Status and Future Prospects," *Proceedings of the Third International Symposium on Field Screening Methods for Hazardous Wastes and Toxic Chemicals*, in press (1993).
5. G.D. Gillispie, North Dakota State University, Department of Chemistry, Ladd Hall, Fargo, ND 58105-5516.
6. G.D. Gillispie and R.W. St. Germain, "In-Situ Tunable Laser Fluorescence Analysis of Hydrocarbons," *Environmental and Process Monitoring Technologies*, Tuan Vo-Dinh, Editor, *Proc. SPIE 1637*, 151-162 (1992).
7. The probe used in this study was constructed by Dr. Terence Tipton, AL/EQC, 139 Barnes Drive, Suite 2, Tyndall AFB, FL 32403-5323 PO Stop 37. The author appreciates the probe construction and optical configuring and tweaking performed by Dr. Tipton.
8. B.S. Vogt, "Application of Fiber-Optic Laser Fluorescence Spectroscopy to Environmental Monitoring," *USAF Summer Research Program--1992, Summer Faculty Research Program (SFRP) Reports, 6*, Air Force technical report AFOSR-TR-93-0116 (1992) (NTIS accession number AD-A261 994/8/XAB). The changes made by Dr.

Tipton include switching from a two-fiber bundle to a seven-fiber bundle, adding the sapphire window, using a metal backing plug to support the glass mirror, and using a narrow support to attach the mirror to the probe body to permit easy solution flow through the optical path. The last difference-using a fluorophore in the optical path as a means of monitoring sample turbidity-was discussed during the Summer of 1992 but incorporated only recently. The rhodamine 590 doped into the expoxy behind the mirror serves this function.

9. This purification was performed by C1C Anthony L. Mitchell, who was involved in this research for several weeks due to his participation in the Air Force Academy Cadet Summer Research Program. The author appreciates Cadet Mitchell's assistance during his visit to Tyndall AFB.
10. Determined by Dr. Tipton.
11. P.L. Smart and I.M.S. Laidlaw, "An Evaluation of Some Fluorescent Dyes for Water Tracing," *Water Resources Research, 13*, 15-33 (1977).
12. W.G. MacIntyre, T.B. Stauffer, and C.P. Antworth, "A Comparison of Sorption Coefficients Determined by Batch, Column, and Box Methods on a Low Organic Carbon Aquifer Material," *Ground Water, 29*, 908-913 (1991).
13. P.L. Smart and I.M.S. Laidlaw, *op cit.*, Figure 4.
14. J.D. Winefordner and G.L. Long, "Limit of Detection: A Closer Look at the IUPAC Definition," *Analytical Chemistry, 55*, 712A-724A (1983).
15. S.T. Trudgill, "Soil Water Dye Tracing, with Special Reference to the Use of Rhodamine WT, Lissamine FF, and Amino G Acid," *Hydrological Processes, 1*, 149-170 (1987).
16. D.M. Mackay, D.L. Freyberg, and P.V. Roberts, "A Natural Gradient Experiment on Solute Transport in a Sand Aquifer: 1. Approach and Overview of Plume Movement," *Water Resources Research, 22*, 2017-2029 (1986).
17. J.M. Boggs, L.M. Beard, W.R. Waldrop, T.B. Stauffer, W.G. MacIntyre, and C.P. Antworth, *Transport of Tritium and Four Organic Compounds during a Natural-Gradient Experiment (MADE-2)*, Electric Power Research Institute technical report TR-101998 (project 2485-05), 5-7 (1993)
18. W.G. MacIntyre, T.B. Stauffer, and C.P. Antworth, *op cit.*
19. *Ibid.*
20. See P.L. Smart and I.M.S. Laidlaw, *op cit.*, and S.T. Trudgill, *op cit.*