Bull. Environ. Contam. Toxicol. (1984) 32: 37–44

Bulletin of Environmental Contamination and Toxicology

A Column Technique for Determining Sorption of Organic Solutes on the Lithological Structure of Aquifers

D. F. Goerlitz

U.S. Geological Survey, 345 Middlefield Road, Menlo Park, CA 94025

In recent years the problem of ground-water contamination by organic substances of anthropogenic origin and the fate of these solutes has received increased attention. It has been estimated that presently some 6.5 billion cubic meters of contaminated liquids infiltrate our ground water each year. Waste dumps and chemical impoundments are primary contributors to the contamination. The fate of organics in aquifer systems was addressed in recent studies at St. Louis Park, Minnesota, and Visalia, California, where ground water is contaminated with organic wood preservatives (U.S. Environmental Protection Agency, 1980, Hult and Schoenberg, 1981, Ehrlich et al. 1982). The wood preservatives creosote and pentachlorophenol (PCP) are the largest volume pesticides produces in the United States (American Chemical Society, 1978, Cirelli, 1978). Creosote is obtained from the distillation of coal tar. Approximately 80-90 percent of the distillate is composed of polynuclear aromatic hydrocarbons (PAH, e.g., naphthalene, anthracene, phenanthrene), from 2-17 percent tar acids (e.g., phenol, methylphenol, naphthol) and the remainder is heterocycles, including some nitrogen compounds (U.S. Forest Products Lab., 1974). The individual compounds have widely differing solubilities in water, from grams per liter down to a few micrograms per liter.

Such contaminants in an aquifer system may be transported in solution, sorbed by sediments, volatilized, altered chemically or metabolized by organisms. The quantitative aspects of these physical, chemical, and biological factors must be determined to understand adequately the fate of the contaminants in the system. The sorption of these organic contaminants on the lithological framework is addressed in this paper as well as the development of a technique to prepare solutions of sparingly soluble compounds.

The time-honored method for determining sorption of solutes on sediment is by generation of sorption isotherms. These static, batch or individual flask experiments are laborious and time consuming and the experimental hiatus increases the chance of bacterial degradation. Further, sparingly soluble compounds are extremely difficult to dissolve in water and tend to sorb on any exposed organic surface.

Recently, a number of investigations have sought a less direct approach and have found correlations relating other sorbate-sorbent properties (Lambert, 1967, 1968, Briggs, 1974). They determined that sorption was a function of organic content of sediment and related that to the octanol-water partition coefficient or the sorbate. Karickhoff, et al., 1979, stated that reasonable estimation (within a factor of 2) of the sorption behavior of hydrophobic pollutants can be made from a knowledge of the particle size distribution and associated organic carbon content of the sediment and the octanol-water distribution coefficient of the pollutant. Unfortunately, octanol-water partition coefficients listed in the literature commonly vary over several orders of magnitude. Further, the organic carbon content of most aquifer sediments is less than 0.5 percent making accurate determination difficult, especially in carbonate sediments (Suzuki, et al., 1983). Mingelgrin and Gerstl, 1983, recently reevaluated partitioning as a mechanism of nonionic chemical adsorption in soils. They critically determined that correlation between soil uptake and low water solubility is expected but the complexity of the surface interaction, both on clays and organic matter, can result in large deviations from any proposed fit.

Because there are apparent problems of the batch sorption determination and uncertainties of the indirect octanol-water partition, organic-carbon method, the alternative sediment-column technique was investigated. Readily available high performance liquid chromatography (HPLC) equipment was used to conduct these studies, thus permitting automation of the elution and effluent monitoring. This method was found to be convenient, reproducible and closely resembles ground water-transport mechanism.

MATERIALS AND METHODS

The HPLC apparatus consisted of two constant flow chromatography pumps, Model 6000A, a variable wavelength detector, Model 450 and a refractive index detector, Model R401, all manufactured by Water Associates, * Milford, Massachusetts. A Model 1200 fraction collector and water jacketed, glass chromatography column obtained from Instrumentation Specialties Co., Lincoln, Nebraska, completed the chromatographic apparatus. An Omniscribe strip-chart recorder from Houston Instruments, Austin, Texas, was also used. The dimensions of the chromatography column used for the sediment sorption experiments were 15 mm ID x 300 mm L. A "saturator" column was fabricated from 4 mm ID x 300 mm L stainless steel tubing and end fittings having sintered stainless steel frits to retain the packing.

All chemicals used were of reagent grade quality. The organic compounds naphthalene, PCP, and phenol were checked for purity by reverse phase HPLC. The identities were confirmed by gas

---

The use of the brand names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

chromatography-mass spectrometry. The 0.01M and 0.015M $CaCl_2$ solutions were prepared in distilled water that was previously degassed by boiling. The pH of these solutions was adjusted to 7.0, near that of the ground water, using 0.01N NaOH and finally the solutions were filtered through 0.2 m polycarbonate membrane filters (Nuclepore Corp., Dublin, CA) into heat sterilized filtration flasks.

Aquifer sediment samples were obtained by coring at or near the ground-water table. The sediments were air dried then seived through 1.0-mm screen. The seived material was remoistened with a minimum amount of water, to the point of aggregation, so the fine material clung to the coarser particles. The damp, well mixed sediment was then transferred to the glass column in small amounts, increments of 1-3 mm in column depth, then packed down firmly using a teflon tipped tamper, of the same diameter as the inside of the column. The packing process was continued until the column was filled.

The packed column was assembled and autoclaved, the air was removed by aspirator vacuum then the column was connected to the chromatography pump and 0.01M $CaCl_2$ solution was pumped through the column bed at 1.0 mL/min. This step is completed (1-4 hours) when no gas bubbles are visible in the column.

Solutions for testing were introduced to the sediment columns at a fixed concentration. The difficulty soluble naphthalene was introduced by directing the eluant through a "saturator" column which was constructed from stainless steel tubing, as described above. The "saturator" column was packed with 60-80 mesh Chromosorb W coated 10 percent by weight with the selected PAH. It has been shown that exposure of such a large area, 2-3 m^2 for this substrate, to water quickly brings about saturation with respect to the coating (May et al., 1978). By use of two chromatography pumps, solutions at any desired concentration were produced as needed by adjusting the flow of the second pump to dilute the "saturator" column effluent. Figure 1 is a pictorial diagram of the apparatus. Soluble substances, such as phenol and PCP were mixed directly with the eluant in the reservoir and only one pump was used for these experiments.

RESULTS AND DISCUSSIONS

Initially the 0.01M $CaCl_2$ eluant was pumped through the sediment in the column until instrumental stability was observed on both the ultraviolet and refractive index detectors. To start the experiment, the feed solution was abruptly changed for the test solution at the head of the column. Figure 2 is a replot of the elution experiments for the solutes indicated and shows the solute concentration as a function of elution volume. The replots were prepared for illustration only and in practice the actual strip charts were used for evaluation. The $CaCl_2$ elution curve was generated by changing the solution concentration from 0.01M to 0.015M at the start of the elution experiment.

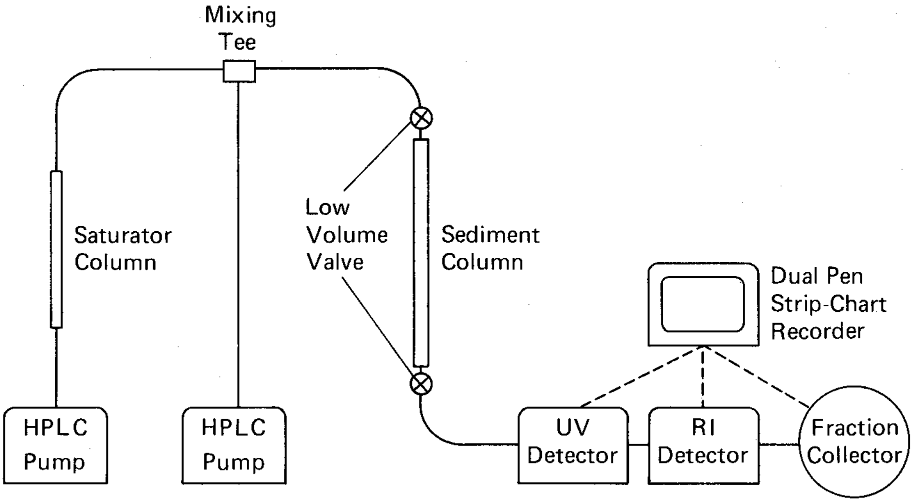

Figure 1. Sediment Column Elution Diagram

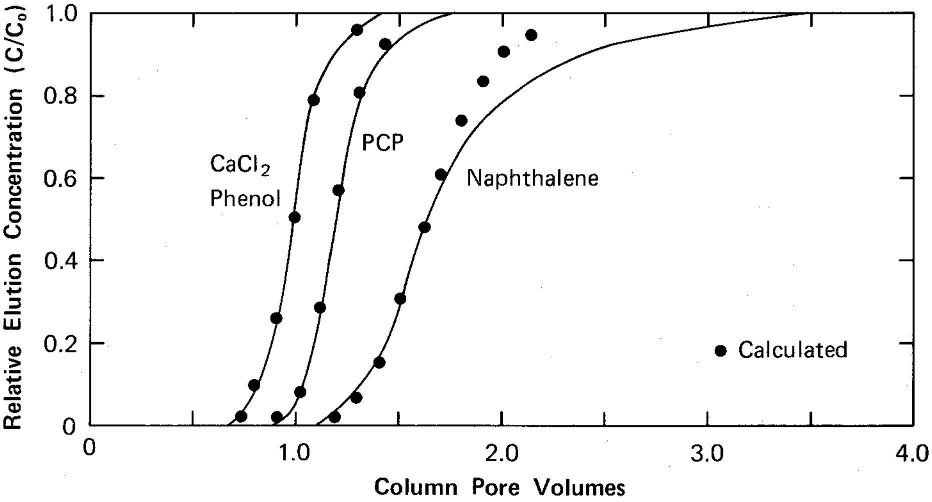

Figure 2. Comparison of Actual and Calculated Elution of organic compounds through columns of aquifer material from St. Louis Park, Minnesota

The elution profile for $CaCl_2$ is symmetrical and the inflection point occurs at one pore volume. This indicates that the $CaCl_2$ solute is not significantly sorbed by the aquifer sediment. The curve for phenol is superimposed over that of the conservative $CaCl_2$, again indicating no significant sorption reaction. PCP is retained somewhat and the naphthalene even more so. The shape of the elution curves, if symmetrical, indicate whether equilibrium is maintained over the concentration gradient and the retention indicates that sorption is occurring.

The method described by Wood (1978), was followed to determine the coefficient of partition or sorption for a sorbent-sorbate pair. First, the basic equation for transport in one dimension of a conservative, nonreactive solute having a constant density in an isotropic, saturated, porous medium is solved to obtain the system dispersion. Then the term for reaction or sorption, that is storage on the solid, is included in the equation which in turn is solved to obtain the partition coefficient. The one-dimensional equation describing the unreactive transport from storage in a solution-filled porous medium is written as:

$$\Theta \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - q \frac{\partial c}{\partial x} \qquad (1)$$

where Θ = porosity,
t = time of transport or elapsed time T,
c = concentration of solute M/L^3,
q = water flux $(L^3/L^2)/T$,
D = effective dispersion coefficient, which includes molecular diffusion plus the dispersivity constant multiplied by the flux $L \cdot L/T$, and
x = spatial coordinate L.

The analytical solution of this equation after dividing through by porosity (Ogata and Banks, 1961) is given by:

$$\frac{C}{C_o} = \tfrac{1}{2} \operatorname{erfc} \left[\frac{L-(q/\Theta)t}{2\sqrt{(D/\Theta)t}}\right] + \tfrac{1}{2} \exp \left(\frac{(q/\Theta)L}{D/\Theta}\right) \operatorname{erfc} \left[\frac{L+(q/\Theta)t}{2\sqrt{(D/\Theta)t}}\right] \qquad (2)$$

where C = concentration of output, m/cm^3,
C_o = concentration of input, m/cm^3,
D = dispersion coefficient, cm^2/sec,
erfc = complimentary error function, (1-erf),
exp = exponent, base e,
q = water flux, cm/sec,
L = length of column, cm,
Θ = porosity, and
t = time, sec.

Rearranging,

$$\frac{C}{C_o} = \tfrac{1}{2}\,\mathrm{erfc}\left(\frac{\Theta L-qt}{2\sqrt{D\Theta t}}\right) + \tfrac{1}{2}\exp\left(\frac{qL}{D}\right)\mathrm{erfc}\left(\frac{\Theta L+qt}{2\sqrt{D\Theta t}}\right). \tag{3}$$

The only unknown in this equation is D. For sorption on the solid the argument is:

Solute + Solid = Sorbed Solute, which is expressed by

$$\bar{c} = kc \tag{4}$$

where $\bar{c}$ = concentration of sorbed solute M/L^3.

Including the storage term on the solid in the transport equation, the result is:

$$\Theta \frac{\partial c}{\partial t} + \rho \frac{\partial \bar{c}}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - q \frac{\partial c}{\partial x} \tag{5}$$

where, ρ = bulk density (g dry solid/cm^3 column).

Partial differentiation of Equation 4 yields

$$\frac{\partial \bar{c}}{\partial t} = k \frac{\partial c}{\partial t} \tag{6}$$

then combining Equation 5 with Equation 6 gives

$$\Theta \frac{\partial c}{\partial t} + \rho k \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - q \frac{\partial c}{\partial x} \tag{7}$$

and simplifying,

$$(\Theta + \rho k) \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - q \frac{\partial c}{\partial x}\,. \tag{8}$$

The analytical solution to Equation 8 after dividing through by $\Theta + \rho k$ is:

$$\frac{C}{C_o} = \tfrac{1}{2}\,\mathrm{erfc}\left(\frac{(\Theta+\rho k)L-qt}{2\sqrt{D(\Theta+\rho k)t}}\right) + \tfrac{1}{2}\exp\left(\frac{qL}{D}\right)\mathrm{erfc}\left(\frac{(\Theta+\rho k)L+qt}{2\sqrt{D(\Theta+\rho k)t}}\right) \tag{9}$$

where k = partition coefficient, and
ρ = bulk density, g/cm^3.

The only unknown in this expression is k, the partition coefficient.

Arrays of fitted calculated points obtained by use of the transport equation are shown on Figure 2. The dispersion coefficient for the sediment column being tested was obtained by trial and error determinations of the D value giving best agreement between the experimental and calculated elution of $CaCl_2$ solution. This was obtained from Equation 3. Knowing the D value for the system, the partition coefficient k was found by trial and error from the solution of Equation 9, again by obtaining the best fit to the experimental values. The fit for the naphthalene elution was not as good as for phenol or PCP. This may be because the flux through the sediment was relatively too high, the "reaction" rate too slow, or because of a mixed sorption mechanism. These considerations will be the subject of another paper. Table 1 is a compilation of the pertinent experimental data. Repetitive tests using naphthalene on the same sediment (St. Louis Park, Minnesota) under similar conditions yielded dispersion and partition coefficients ranging within a factor of 2 through a four-experiment history.

Table 1. Column elution experimental data

Sediment (<2 mm):	Glacial till, St. Louis Park, MN
Column length:	26.6 cm
Column diameter:	1.50 cm
Volume:	47.0 cm^3
Dry weight, sediment	79.65 g
Bulk density (ρ):	1.695
Pore volume (gravimetric):	17.35 cm^3
Pore volume (elution inflection):	17.35 cm^3
Porosity (Θ):	0.3687
Flow rate:	0.1025 cm^3/min
Column-detector dead volume:	0.524 cm^3
Dispersion:	0.0008 cm^2/s
k PCP =	0.485
k naphthalene =	0.756

The slowest pumping rate of the HPLC pumps used in these experiments was 0.1 mL/min, the lower limit of the apparatus. More realistic, slower flow rates may be attained by use of syringe pumps such as manufactured by Instrumentation Specialties Co., Lincoln, Nebraska. Lower flow improves the overall dispersion and permits a wider range of experimental conditions necessary to study the reaction kinetics such as indicated by the assymmetric elution of naphthalene.

The sorption behavior of organic solutes in aquifer material can be readily determined by evaluation of the elution histories of sediment columns. This heretofor difficult technique has been made practical by use of modern HPLC technology. Additionally, the ability to select a solution concentration of a difficulty soluble compound by moderating the flow from the "saturator" column to the sediment test column permits wide flexibility for evaluation. The need for minimum of attention during the experiment is also a valuable feature of this technique.

REFERENCES

American Chemical Society (1978) Government concentrates. Chem Eng News 56 (43): 15

Briggs, GG (1974) A simple relationship between soil adsorption of organic chemicals and their octanol/water partition coefficients. Proc. 7th Br Insect Fungic Conf 1973. Brighton p83-86, The Boots Co Ltd, Nottingham

Cirelli DP (1978) Patterns of pentachlorophenol usage in the United States of America-an overview. In: Roa K (ed) Pentachlorophenol. Plenum Press, New York, p 13-18

Ehrlich GG, Goerlitz, DF, Godsy, EM, Hult MF (1982) Degradation of pehnolic contaminants in ground water by anaerobic bacteria: St Louis Park, Minnesota. Ground Water 20: 703-710

Hult MF, Schoenberg ME (1981) Preliminary evaluation of ground water contamination by coal-tar deriviatives, St Louis Park area, Minnesota. U S Geol Survey Open-File Rept 81-72

Karickhoff SW, Brown DS, Scott TA (1979) Sorption of hydrophobic pollutants on natural sediments. Water Res 13: 241-248

Lambert SM (1967) Functional relationship between sorption in soil and chemical structure. J Agric Food Chem 15: 572-576

Lambert SM (1968) Omega a useful index of soil sorption equilibria. J Agric Food Chem 16: 340-343

May WE, Wasik SP, Freeman DH (1978) Determination of the aqueous solubility of polunuclear aromatic hydrocarbons by a coupled column liquid chromatographic technique. Anal Chem 50: 175-179

Mingelgrin U, Gerstl Z (1963) Reevaluation of partitioning as a mechanism of nonionic chemicals adsorption in soils. J Environm Qual 12: 1-11

Ogata A, Banks RB (1961) A solution of the differential equation of longitudinal dispersion in porous media. U S Geol Survey Prof Paper 411-A

Suzuki J, Yokoyama Y, Unno Y, Suzuki S (1983) A sensitive method for measuring organic carbon in sediment. Water Res 17: 431-434

U S Environmental Protection Agency (1980) Damages and threats caused by hazardous materials sites. EPA-430/9-80/004 Washington, D C

U S Forest Products Laboratory (1974) Characterization of wood-preserving creosote by physical and chemical methods of analysis. USDA Forest Research Paper FPL 195, Madison, Wisconsin

Wood W (1978) Use of laboratory data to predict sulfate sorption during artificial ground-water recharge. Ground Water 16: 22-31

Received August 1, 1983; Accepted September 13, 1983