

# Use of Hollow-fiber Membranes for Measurement of Diffusive Flux of Compounds in Sediments

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## ABSTRACT

A new technique for measuring diffusive flux of compounds in saturated sediments that utilizes hollow-fiber microfiltration membranes was tested on six sediments of varying clay and organic matter content. Diffusive flux of bensulfuron methyl (BSM) in the sediments was a function of interstitial water concentration of BSM, which was determined by the partitioning coefficient. The diffusion coefficient of BSM in the sediments, calculated from Fick's Law, was not a function of bulk density or tortuosity in the test sediments. Lack of an effect of physical sediment characteristics on the diffusion coefficient was attributed to short run times, and high BSM concentrations, which did not permit development of sediment depletion zones around the fibers. The technique described has the potential for providing a convenient method of measuring diffusive flux of toxic compounds and plant nutrients in soils.

*Key words:* bensulfuron methyl, diffusion, herbicide mobility, bulk density, tortuosity.

## INTRODUCTION

The sediment has long been recognized as an important influence upon aquatic plant growth and distribution (Misra 1938, Pearsall 1920). Barko and Smart (1986) reported that growth of *Hydrilla verticillata* (L.f.) Royle on low-density, highly organic sediments was limited by the rate of diffusive flux of plant nutrients in the sediment. Diffusive processes in sediments are also important in terms of off-site movement and availability of sediment-applied herbicides. Diffusion of nutrients to plant roots has received much attention in terrestrial plant nutrition (Brewster and Tinker 1972, Nye 1977, Nye and Tinker 1977, Barber 1984). In aquatic systems, research on diffusive movement of sediment constituents has focused on nutrient flux from sediments to the hypoxic hypolimnion of stratified lakes, which can influence lake trophic status (Wetzel 1983, Carignan and Lean 1991).

Application of bensulfuron methyl (Mariner™) to sediments exposed by drawdown has proven effective in reducing growth of aquatic macrophytes in irrigation and drainage ditches in California (Anderson 1988). Accumulation of toxic concentrations of soil-applied herbicides in plants is a function of the rate that the soil can supply the compound and the rate of plant uptake (Casely and

Walker 1990). Economic, environmentally sound, and effective sediment application of herbicides requires a consideration of both sediment supply and root uptake rates.

Standard laboratory techniques for assessing herbicide mobility in soils involve elution of the compound from soil columns, or measuring migration with soil thin-layer chromatography (Beyer et al. 1988, Blair and Martin 1988). Potential mobility is estimated indirectly by the octanol partitioning coefficient (Bohn et al. 1985). These techniques often require severe alteration of sediment physical and chemical properties that may influence mobility of the compound under study, particularly in hydrosoils.

The objective of this study was to test the utility of hollow-fiber microfiltration membranes for measurement of diffusive flux of herbicides in sediments. The technique is based upon methodology developed to sample sediment interstitial water for nutrient analysis. A variety of samplers that utilize membrane filters or dialysis membranes have been used to study water column and sediment-water chemistry (Bottomley and Bayley 1984, Dombek et al. 1984, Hesslein 1976, Mayer 1976, Vincenzini et al. 1986). The typical application in sediment-water sampling allows a dialyzate solution (usually distilled water) to equilibrate with the sediment interstitial water via a membrane or filter. The filter or membrane is thus used in a static mode. Diffusion cells, for measurement of diffusion of nutrients in soils, have also incorporated membranes of various types to separate labeled and unlabeled soils (Tinker 1969, Olsen et al. 1965, Elgawhary et al. 1970a). The technique described here is a dynamic system that uses a hollow-fiber microfiltration membrane as a root analog. Hollow-fiber membrane filters consist of a porous tube lined with a microfiltration membrane. Ceramic tubes have been used in a similar manner in studies of nutrient flux in terrestrial soils (Elgawhary et al. 1970b).

## MATERIALS AND METHODS

Cuvettes for measuring diffusion of BSM in sediments with hollow-fiber membranes were constructed of extruded, plexiglass tubing with a 5.5-cm, square cross section (Figure 1). One side of the square tubing was removed and end plates of 5.5 x 5.5 x 0.3 cm were attached to each section to form a 242 ml cuvette. Holes were drilled in the end plates of the cuvettes and nylon tubing connectors were attached with epoxy glue to receive the inlet and outlet tubing and to hold the fibers in place within the cuvette. Hollow-fiber, polysulfone microfiltration membranes (A/G Technology Corp., Needham, Ma., USA) 3 cm long (3 mm i.d., 0.1 µm pore diameter) were attached to the nylon tubing connectors with epoxy glue and silicone sealant.

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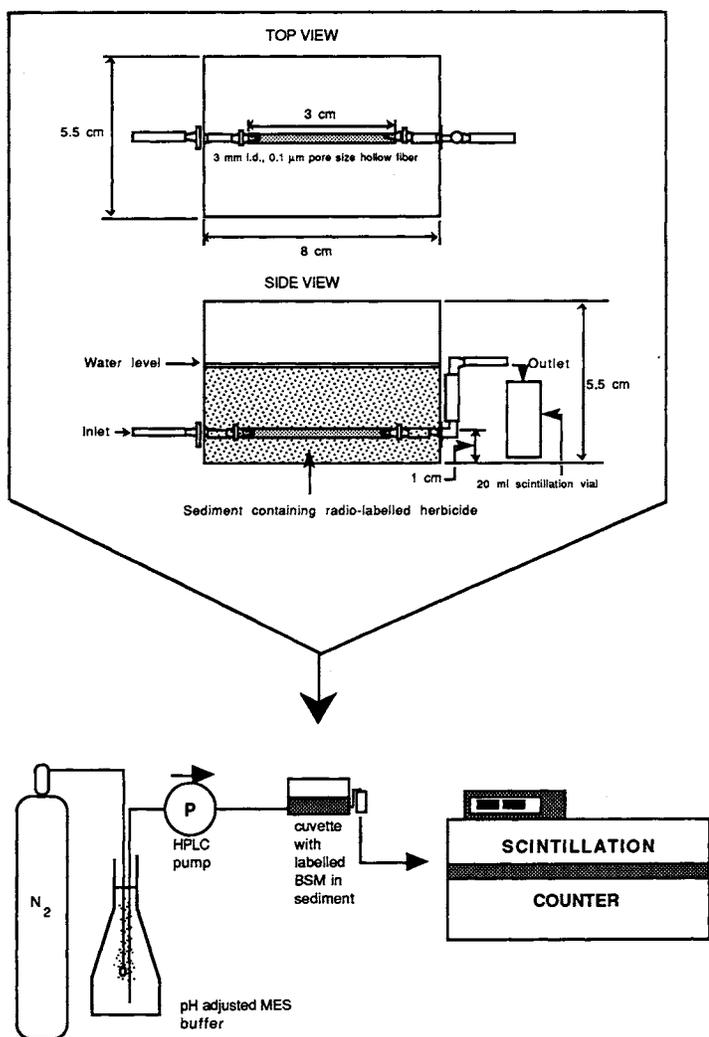


Figure 1. Diagram of system and cuvette used to measure diffusive flux of BSM in sediment using hollow-fiber microfiltration membranes.

Cuvettes were pressure tested to check for leaks in the connections. Preliminary studies with  $^{14}\text{C}$ -labeled BSM in 3mM  $\text{NaHCO}_3$  buffer (pH 7) in the cuvette, were used to establish dialyzate flow rates and system configuration. At flow rates greater than  $0.6 \text{ ml min}^{-1}$  positive hydrostatic pressure developed within the hollow fiber, which caused exfiltration of the dialyzate and reduced measured flux rates.

A series of sediments was prepared to assess the effect of organic matter and clay content on diffusion of BSM. Montmorillonite clay and dried, ground parrotfeather (*Myriophyllum aquaticum* (Vell.) Verdc.) biomass were added to Yolo sandy loam soil to give clay:organic matter ratios (% dry weight basis) of 7:2.5 (unamended), 7:15, 7:30, 15:2.5, 15:15, and 15:30. (Note: in order to maintain the appropriate clay:organic matter ratio it was necessary to add some clay to the 7:15 and 7:30 sediments). Sediments were saturated and stored in a greenhouse for three months to develop stable microbial, physical, and chemical characteristics prior to use in diffusive flux studies. Some organic matter was undoubtedly metabolized during the

equilibration period, although sediments were anoxic and decomposition rates were probably low. Three sediment samples were prepared for each clay:organic matter combination. Particle size was determined by the hydrometer method of Patrick (1958). Cation exchange capacity (CEC) was measured by saturation with neutral ammonium acetate and extraction with acidified sodium chloride (Chapman and Pratt 1961). Ammonium in the final extract was determined after alkalization by the conductimetric method of Carlson (1978). Sediment pH was determined by insertion of a Ross Sure-Flow combination electrode (Orion) into the saturated sediment. Sediment bulk density was estimated by drying and weighing a known volume of sediment obtained with a table-top piston corer that permitted sampling of the sediment without compaction (M.D. Sytsma, unpublished). Berner (1980), Sweerts et al. (1991), Nye and Tinker (1977), and Olsen et al. (1965) discussed the concept and role of tortuosity in diffusion of materials in soils and sediments. Briefly, tortuosity refers to the length of the diffusion pathway. High-density sediments have high tortuosity and low-density sediments low tortuosity because the high porosity of low-density sediments permits a more direct diffusion path. Porosity was estimated as the volumetric water content (% of total sediment volume). Tortuosity of the test sediments was calculated as porosity<sup>-0.1</sup>, according to relationships developed by Sweerts et al. (1991).

BSM diffusive flux in the test sediments was measured in a growth chamber at 25 C. Two milliliters of 3mM  $\text{NaHCO}_3$  buffer at pH 7 containing 0.2 mg of  $^{14}\text{C}$ -labeled BSM with a specific activity of  $1.96 \times 10^6 \text{ Bq/mg}$  was added to 100 ml of saturated sediment. Sediment concentrations used were based upon a field application rate of 200 g/ha and the assumption that BSM in field applications is distributed in the top 1 cm of sediment. The labeled compound was homogeneously distributed in the sediment by hand-mixing for five minutes prior to transfer to the cuvette. The labeled sediment was allowed to equilibrate in the cuvette at 25 C for 24 to 30 hr prior to measurement of diffusive flux.

Diffusive flux of radio-labeled BSM was measured by pumping  $\text{N}_2$ -sparged, 3 mM MES buffer, adjusted to sediment pH, through the hollow fiber at  $0.6 \text{ ml/min}$ . After an initial flush of 10 minutes, five 1-ml fractions were collected in 20 ml scintillation vials (100-sec intervals). Counts of  $^{14}\text{C}$ -BSM in the fractions were made on a Beckman LS 100 C liquid scintillation counter. Counting efficiency was determined using the external standard ratio method. Flux rate ( $\mu\text{g BSM min}^{-1}$ ) was estimated by the slope of a linear regression of cumulative BSM flux into the fiber on time (see Figure 2). Analysis of covariance was used to test for significant differences in BSM flux rates. Multiple comparisons among slopes were done by the minimum significant difference method using the T'-method (Sokal and Rohlf 1981). Statistical significance was determined at  $p = 0.05$ .

BSM concentration in sediment interstitial water was estimated by sampling ( $250 \mu\text{l}$ ) the water overlying the sediment after the equilibration period and counting as above. The partitioning coefficient ( $K_D$ ) for BSM in the test sediments was calculated as:

## RESULTS AND DISCUSSION

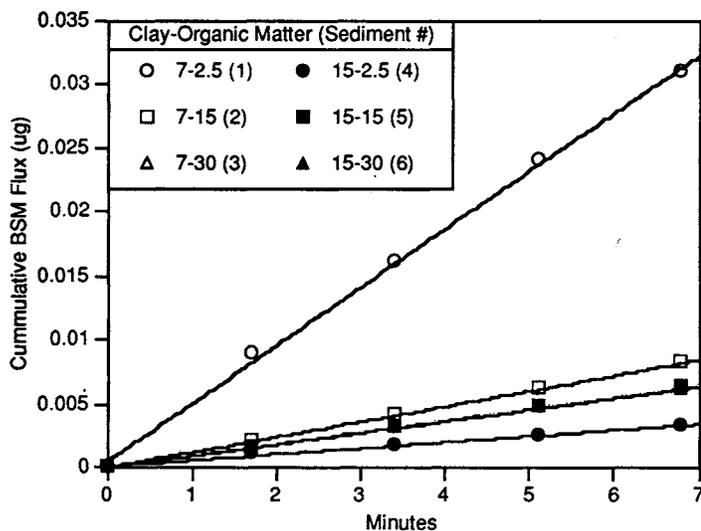


Figure 2. Cumulative diffusive flux of BSM into hollow fiber in six sediments. Plotted points are the means of three replicate measurements. Note: regression lines for sediments 7-30 (3) and 15-30 (5) are hidden by 15-15 (6). (Slope of  $1 > 2 > 3 = 5 > 6 > 4$ ).

$$K_D = \frac{\text{BSM in Sediment Solids}}{\text{BSM in Interstitial Water}}$$

The diffusion coefficient for BSM in the test sediments was calculated from Fick's First Law:  $F = D (\Delta C / \Delta \chi)$ . Where:

$F$  = Flux into the fiber ( $\mu\text{g BSM cm}^{-2} \text{sec}^{-1}$ )  
 $D$  = Diffusion coefficient ( $\text{cm}^2 \text{sec}^{-1}$ )  
 $\Delta C / \Delta \chi$  = the concentration gradient with  $\chi$  taken as the radius of the fiber ( $\mu\text{g cm}^{-3} / \text{cm}$ ).

The concentration of BSM within the fiber increased as the dialysate traveled down the fiber. the  $\Delta C$  used in the calculation of  $D$  was:

$$\Delta C = C_C - (0.5C_O)$$

Where:

$C_O$  = concentration of BSM in the outflow  
 $C_C$  = concentration of BSM in the sediment interstitial water

Sediments used in the BSM diffusion experiments covered a broad range of bulk densities and porosities (water content) (Table 1).

BSM flux measured with the diffusion cuvettes differed among the sediments tested (Figure 2). Flux rate was greatest ( $0.0045 \mu\text{g BSM min}^{-1}$ ) in the unamended sediment and lowest ( $0.00048 \mu\text{g BSM min}^{-1}$ ) in the high clay (15%), low organic matter (2.5%) sediment. The coefficient of variation in the measured flux averaged 15.1% and ranged from 5.5% (sediment 6) to 33.4% (sediment 4).

The data suggest that BSM flux was a nonlinear function of the partitioning coefficient (Figure 3). Concentration gradients are the driving force for diffusive flux of materials in sediments. The partitioning coefficient influenced flux primarily through its determination of BSM concentration in sediment interstitial water (Figure 4).

Diffusion of sediment constituent is a function of the tortuosity of the diffusion pathway (Berner 1980, Nye and Tinker 1977). The experimental sediments differed in water content, bulk density, and particle size distribution, important determinants of the porosity and tortuosity; however, regression analysis indicated that neither bulk density or tortuosity significantly influenced the diffusion coefficient. The averaged BSM diffusion coefficient was  $2.8 \times 10^{-6} \pm 0.12 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$  ( $\pm 1 \text{ SE}$ ,  $n=6$ ). Lack of a significant effect of tortuosity on the diffusion coefficient of BSM in the test sediments may have been a result of short experimental run times and high interstitial water BSM concentrations. Under the test conditions it was unlikely that a depletion zone developed around the hollow fiber during the experimental run. As a consequence, the flux of BSM to the fiber, and the diffusion coefficients calculated, were primarily a function of the BSM concentration in the interstitial water immediately adjacent to the fiber surface. Longer run times and lower BSM concentrations should result in development of a depletion zone around the fiber, which is necessary for measurement of diffusion mediated flux in sediments.

The results indicate that the hollow-fiber system provides a relatively simple and efficient method of assessing rates of diffusive flux of compounds in sediments, although the technique requires further testing and development. Counter diffusion of compounds from the dialyzing solution may alter sediment chemistry and diffusive flux. The organic buffer used in these experiments does not bind cations and maintains pH with  $\text{N}_2$  sparging, two crit-

TABLE 1. CHARACTERISTICS OF SEDIMENTS USED IN BSM EXPERIMENT TO MEASURE DIFFUSIVE FLUX WITH THE HOLLOW-FIBER SYSTEM ( $\pm 1 \text{ SE}$ ,  $n=3$ ).

Sediment	% Clay	% Organic matter	pH	CEC (meq/100g)	Bulk density (g DW/ml)	% Water	Tortuosity
1	7	2.5	$7.8 \pm 0.3$	$18.2 \pm 0.3$	$1.92 \pm 0.08$	$24 \pm 1$	1.051
2	7	15	$7.8 \pm 0.3$	$38.5 \pm 0.5$	$0.81 \pm 0.04$	$46 \pm 2$	1.038
3	7	30	$6.6 \pm 0.0$	$26.8 \pm 0.3$	$0.43 \pm 0.01$	$63 \pm 1$	1.032
4	15	2.5	$6.3 \pm 0.06$	$33.5 \pm 4.1$	$1.35 \pm 0.05$	$24 \pm 1$	1.089
5	15	15	$6.6 \pm 0.06$	$27.3 \pm 2.2$	$0.88 \pm 0.03$	$44 \pm 2$	1.038
6	15	30	$6.4 \pm 0.0$	$21.2 \pm 0.3$	$0.47 \pm 0.08$	$63 \pm 4$	1.023

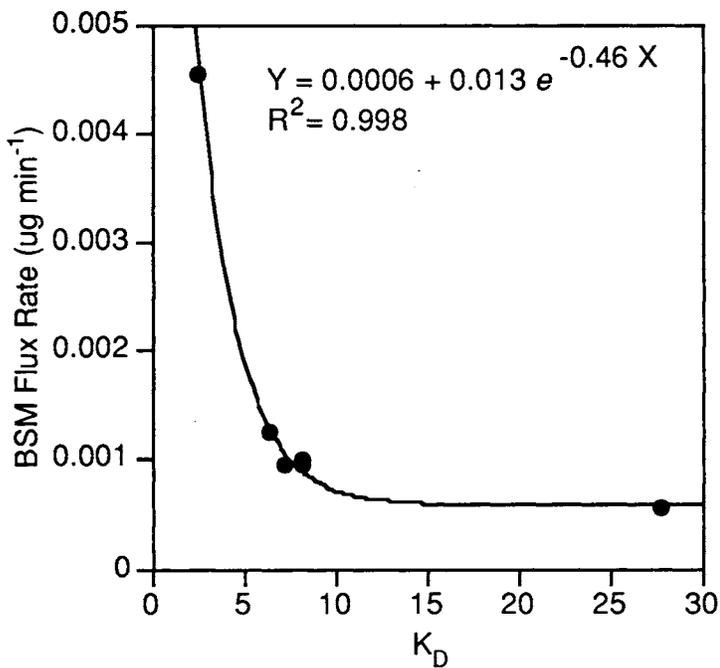


Figure 3. Effect of the BSM partitioning coefficient ( $K_D$ ) on BSM flux in six test sediments. Some points overlap.

ical features of any dialyzing solution used in this system. The performance of other dialyzing solutions should be investigated. Osmotic adjustment of the dialyzing solution would permit application of the technique to terrestrial soils.

The hollow-fiber system allows sampling of interstitial water on a scale not possible with coring techniques. The system may be modified to investigate changes in sediment chemistry in specific zones in the sediment. For example, zonal differences in sediment-applied herbicide decomposition may be investigated by assaying fiber outflow for decomposition products. In addition, the system provides a technique for testing current theories on how sediment

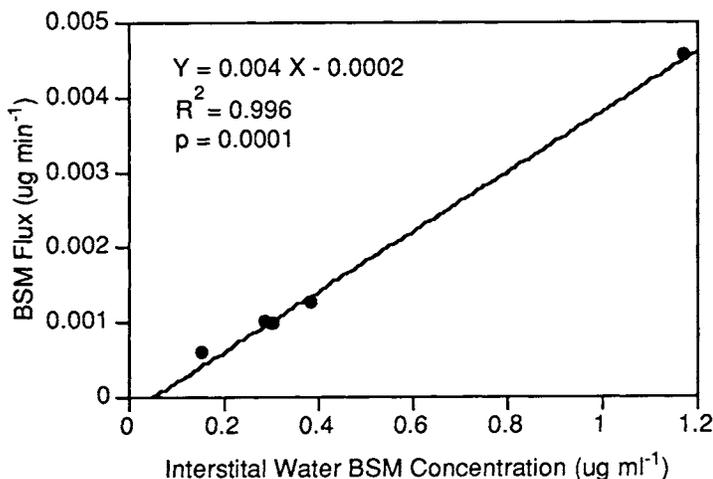


Figure 4. Relationship between interstitial water BSM concentration in six sediments and flux rate measured with the hollow-fiber system. Some points overlap.

characteristics influence productivity and community structure of rooted aquatic plants (Barko and Smart 1986).

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#### LITERATURE CITED

- Anderson, L. W. J. 1988. Growth regulator activity of bensulfuron methyl in aquatic plants. In: Chemical Vegetation Management, J. E. Kaufman and H. E. Westerdahl (Eds.), Plant Growth Regulator Society of America. pp. 127-145.
- Barber, S. A. 1984. Soil Nutrient Bioavailability. A Mechanistic Approach. John Wiley and Sons. New York. 398 pp.
- Barko, J. W. and R. M. Smart. 1986. Sediment-related mechanisms of growth limitation in submersed macrophytes. Ecology 67:1328-1340.
- Berner, R. A. 1980. Early diagenesis: A theoretical approach. Princeton University Press, Princeton, NJ. 241 pp.
- Beyer, E. M., M. J. Duffy, J. V. Hay and D. D. Schlueter. 1988. Sulfonylurea herbicides. In: Herbicides: Chemistry, Degradation, and Mode of Action, Volume 3, P. C. Kearner and D. D. Kaufman (Eds.), Marcel Dekker, Inc., NY. pp 117-189.
- Blair, A. M. and T. D. Martin. 1988. A review of the activity, fate and mode of action of sulfonylurea herbicides. Pesticide Science 22:195-219.
- Bohn, H., B. McNeal and G. O'Connor. 1985. Soil Chemistry. Wiley and Sons, New York. 341 pp.
- Bottomley, E. Z. and I. L. Bayley. 1984. A sediment porewater sampler used in root zone studies of the submerged macrophyte, *Myriophyllum spicatum*. Limnology and Oceanography 29:667-670.
- Brewster, J. L. and P. B. H. Tinker. 1972. Nutrient flow rates into roots. Soils and Fertilizers 35:355-259.
- Carignan, R. and D. R. S. Lean. 1991. Regeneration of dissolved substances in a seasonally anoxic lake: The relative importance of processes occurring in the water column and in the sediments. Limnology and Oceanography 36:683-707.
- Carlson, R. M. 1978. Automated separation and conductimetric determination of ammonia and dissolved carbon dioxide. Analytical Chemistry 50: 1528-1531.
- Caseley, J. C. and A. Walker. 1990. Entry and transport of herbicides in plants. In: Weed Control Handbook, R. J. Hance and K. Holly (Eds.), Blackwell Scientific, Oxford. pp. 183-200.
- Chapman, H. D. and P. F. Pratt. 1961. Methods of Analysis for Soils, Plants, and Waters. Pub. No. 4034, Division of Agricultural Sciences, University of California, Berkeley, CA. 309 pp.
- Dombeck, M. P., R. W. Bachmann and B. W. Menzel. 1984. A method for measuring oxygen in aquatic microzones. Journal of Freshwater Ecology 2:535-540.
- Elgawhary, S. M., W. L. Lindsay and W. D. Kemper. 1970a. Effect of EDTA on the self-diffusion of zinc in aqueous solution and in soil. Soil Science Society of America Proceedings 34:66-70.
- Elgawhary, S. M., W. L. Lindsay and W. D. Kemper. 1970b. Effect of complexing agents and acids on the diffusion of zinc to a simulated root. Soil Science Society of America Proceedings 34:211-214.
- Hesslein, R. H. 1976. An in situ sampler for close interval pore water studies. Limnology and Oceanography 21:912-914.
- Mayer, L. M. 1976. Chemical water sampling in lakes and sediments with dialysis bags. Limnology and Oceanography 21:909-912.
- Misra, R. D. 1938. Edaphic factors in the distribution of aquatic plants in the English Lakes. Journal of Ecology 26:411-451.
- Nye, P. H. 1977. The rate-limiting step in plant nutrient absorption from soil. Soil Science 123:292-297.
- Nye, P. H. and P. B. Tinker. 1977. Solute Movement in the Soil-Root System. University of California Press, Berkeley, CA. 342 pp.
- Olsen, S. R., W. D. Kemper and J. C. van Schaik. 1965. Self-diffusion

- coefficients of phosphorus in soil measured by transient and steady-state methods. Soil Science Society of America Proceedings 29:154-158.
- Patrick, W. H. 1958. Modification of method of particle size analysis. Soil Science Society of America Proceedings 22:366-367.
- Pearsall, W. H. 1920. The aquatic vegetation of the English Lakes. Journal of Ecology 8:163-199.
- Sokal, R. R. and F. J. Rohlf. 1981. Biometry. W. H. Freeman and Company, New York. 859 pp.
- Sweerts, J.-P. R. A., C. A. Kelly, J. W. Rudd, R. Hesslein and T. E. Cappenberg. 1991. Similarity of whole-sediment molecular diffusion coefficients in freshwater sediments of low and high porosity. Limnology and Oceanography 36:335-342.
- Tinker, P. B. 1969. A steady-state method for determining diffusion coefficients in soil. Journal of Soil Science 20:336-345.
- Vincenzini, M. R., A. E. De Philippis and G. Florenzano. 1986. Ammonia photoproduction by *Cyanospira ripphae* cells 'entrapped' in dialysis tubes. Experienta 42:1040-1043.
- Wetzel, R. G.. 1983. Limnology. Saunders College Publishing, Philadelphia, PA. 767 pp.