Report for 2001WA1041B: Dye Tracers for Vadose Zone Hydrology

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Report Follows:

PROBLEM AND RESEARCH OBJECTIVES

The solutions to many of the critical regional or state water problems rely on experimental data collection. Point and non-point source groundwater pollution, chemical transport in surface and subsurface waters, irrigation-related water quality and distribution problems, to name a few, can be addressed to some degree by the experimental investigation of water flow pathways and travel times. In hydrological research and hydrology, tracers have played a significant role in elucidating our current understanding of the hydrological cycle and subsurface flow and transport processes. Tracers are used to investigate flow pathways, to estimate travel and residence times, or to assess risks associated with pollution. While a wide variety of different tracers are frequently used, dyes have been, and are still, among the most prominent subsurface water tracers. The main reasons for the use of dyes in hydrological research are the ease of detection at low concentrations in aqueous solution, the possibility to visualize the flow pattern in rivers, and soils and the ease of quantification by chemical analysis. Hundreds of dyes are commercially available, and many may be potentially useful as hydrological tracers. Only few of the currently available dyes have been used and tested as hydrological tracers.

The objective of this study was to evaluate four selected dyes in respect to their suitability as hydrological tracers. Specifically, we address the following objectives:

1. Measure sorption and transport behavior of selected organic dyes using laboratory batch and column studies.
2. Compare adsorption isotherms measured by batch and column experiments.

METHODOLOGY

Four dyes with the same molecular backbone but different substituent groups, i.e., type, number and position were used in this study. These dyes were commercially available in solid forms and obtained directly from manufacturers. All the four dyes are from the same chemical class of Triphenylmethane.

Column experiments were performed under water saturated conditions. An Omnifit glass chromatography column with an inner diameter of 1.5 cm and the length between the top and the bottom plates of 12.2 cm was used in the experiment. The end plates of the column consisted of porous polypropylene disks to assure uniform flow within the column. The inlet end of the column was connected to a pump that allows flow rate adjustments and the outlet end was connected to a fraction collector (LKB Bromma, 7000 Ultrorac, Sweden). Teflon tubings with an inner diameter of 1.5 mm and 0.75 mm were used to connect the inlet to the pump and the outlet to the fraction collector, respectively.

A pulse-input was used to introduce chemicals into the column. Calcium nitrate [$Ca(NO_3)_2$] and dyes used in the experiments were dissolved in the background solution (0.01 M $CaCl_2$). The concentrations of nitrate and dye solution were 0.01 mmol L^{-1} and 2.5-2.9 mmol L^{-1} (2 g L^{-1}), respectively. The effluent of the column was collected in glass culture tubes with the fraction collector. Because some degree of impurity was observed in the Acid Blue 7 dye sample, the dye solution was sequentially filtered using 11 μm filter paper (Whatman Ltd., UK) and with a 0.4

μm membrane filter (Nuclepore Corporation., CA) before introduction to the column Relative concentration (outflow concentration/ input concentration) and numbers of pore volume were plotted to obtain nitrate breakthrough curves, but the actual dye concentrations of column outflow were plotted against the numbers of pore volume to obtain dye breakthrough curves.

Batch experiments were performed using nine different dye concentrations ranging from 0.0001to 2.9 mmol L^{-1} (0.1, 1, 10, 50, 100, 200, 500, 1000, 2000 mg L^{-1}) and two solid-solution ratios (1:6, 1:1). The solid-solution ratio of 1:6, where 10 g of soil was shaken with 60 mL of dye solution, was used at the concentration range from ~0.0001 to 0.0015 mmol L^{-1} (0.1 to 10 mg L^{-1}). However, 20 g of soil was shaken with 20 mL of dye solution (1:1 ratio) at the concentration above 0.015 mmol L^{-1}. The requirement of a different solid-solution ratio at high concentrations is because of adsorbed dye concentration in the samples with 1:6 ratio was very small compared to the input concentration and found to be in the range of the measurement error.

PRINCIPAL FINDINGS AND SIGNIFICANCE

The hydrodynamics of the column was indicated by the Peclet number calculated from the nitrate breakthrough curves. The Peclet number for the first and the second column were 150.7 ± 0.77 and 146.6 ± 0.71, respectively. The breakthrough data fit the model parameter well. The Peclet numbers of both columns were relatively high, so that it is reasonable to ignore the dispersion term in the convection-dispersion equation used for calculation of adsorption isotherms.

A comparison of dye breakthrough curves showed that the dye fronts of the Food Blue 2 and Food Green 3 closely follow one after another and the breakthrough occurs at about 2.5 to 3 pore volumes. The breakthroughs of the Acid Blue 7 and Acid Green 9, however, occur at about 5 to 6 pore volumes. Unlike in the case of other three dyes, the maximum concentration in the outflow of the Acid Green 9 was measured only about one half of the input concentration. As of the adsorption isotherms, for the input concentration used in the experiments, the maximum sorbed concentration for the Food Blue 2 and Food Green 3 was ~0.5 mmol kg^{-1} and for the Acid Green 9 and Acid Blue 7 were ~1.6 and ~3 mmol kg^{-1}, respectively. Food Green 3 seems to be less absorbed compared to Food Blue 2. The sorbed concentration of the Acid Green 9 was lower than that of Acid Blue 7. However, column breakthroughs of these two dyes suggest a contrasting result that the breakthrough of the Acid Blue 7 occurred earlier than that of the Acid Green 9. The evidence suggested that sorbed concentration of Acid Green 9 showed by column data might be under estimated and more associated with experimental errors.

Adsorption isotherms calculated from column data do not agree very well with those obtained from batch studies. With an exception to the Acid Green 9, the sorbed concentrations calculated from column data were higher than that of batch studies. On a linear scale, column and batch techniques more likely agree at lower concentration part of the isotherms, but column data tend to over estimate the sorbed concentrations at the high concentration portion of the curves. On a double logarithmic scale, however, isotherms measured with the two methods tend to have a good agreement at the high concentration zone of the isotherms. Column data again seem to over estimate the sorbed concentrations in the lower concentration portion of the curves.

Based on the results obtained from both column and batch studies, Food Blue 2 and Food Green 3 were less adsorbed than Acid Blue 7 and Acid Green 9 on the Vantage sand medium. The main difference among these four dyes is the number of sulfonic acid groups in their structures. As previously mentioned, Food Blue 2 and Food Green 3 consists of three sulfonic acid groups but Acid Blue 7 and Acid Green 9 contains only two. Adsorptions of these dyes on a soil medium agreed with previous findings that dyes consisted of more sulfonic acid groups tend to be less sorbed and have a better mobility in soil. However, further studies is needed to be able to explain why the adsorption of dyes with the same number of sulfonic acid groups, e.g., Acid Blue 7 and Acid Green 9, differs from one another. The difference in position of sulfonic acid groups in the molecular structure might also influence the sorption of these tested dyes in soil. Not only the number and position of sulfonic acid groups, but containing different substituent groups might also effect the sorption of the dyes. For instance, Food Green 3 tends to be less adsorbed compared to the Food Blue 2 although they contain the same numbers of sulfonic acid group at exactly the same positions on the molecular backbones. The only structural difference between these two dyes is that Food Green 3 consists of one hydroxyl group, but Food Blue 2 does not.