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ADSORPTION OF BROMIDE TRACERS ONTO SEDIMENT

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ABSTRACT

Information concerning hydraulic parameters on upland areas could be greatly expanded through the use of tracing techniques. If bromide is used as a tracer, adsorption of bromide onto sediment may be of concern. Therefore, a laboratory study was conducted to identify the effects of sediment content and initial bromide concentration on adsorption of bromide for selected soils.

When bromide solutions were used within the appropriate instrument measurement range, neither soil texture, liming, nor sediment content were found to significantly affect adsorption of bromide. In contrast to systems using fluorescent dyes, correction factors for estimating adsorption of bromide are unnecessary. Since it is not readily absorbed onto sediment, bromide appears to be very well-suited for use as a tracer in dilution studies.

INTRODUCTION

Floats, chemical salts, actual contaminants, and radioisotopes have all been used as tracers (Chase and Payne, 1968). Dye-tracing techniques have been employed most extensively in stream and river studies. However, dye dilution procedures may also be used to measure flow components on upland areas (Finkner and Gilley, 1988).

Fluorescent dyes have been widely used for characterizing flow (Replogle et al., 1966; Wilson, 1968). However, significant amounts of fluorescent dye may be adsorbed onto sediment (Finkner and Gilley, 1986). Thus, when making discharge measurements on upland areas using fluorescent dyes, equations for estimating dye adsorption must be developed.

Recently, bromide salts have been identified as excellent tracer materials. The bromide ion may be used in concentrations low enough to not constitute a health or pollution problem (Schmotzer et al., 1973) and bromide background levels in soils are generally quite low (Maw and Kempton, 1982). Many bromide salts are highly soluble and non-degradable and the bromide ion can be measured quantitatively in very low concentrations.

Bromide has been used to monitor water movement in irrigation studies (Tennyson and Settergren, 1980). Owens et al. (1985) utilized bromide to discern groundwater quality changes using surface bromide application to a pasture. Bromide has also been used as an indicator of nitrate movement in soils since both are anions and have similar mobilities (Smith and Davis, 1974). Hargrove and Bausch (1973) used bromide as a standard of comparison for the leaching of three nitrogen fertilizer sources. Nitrate and bromide were found by Onken et al. (1977) to move similarly in soil on large irrigated field plots.

Bromide also appears to be well suited for use in surface water investigations. However, the extent to which bromide is adsorbed by soils and sediments under varying conditions has not been adequately studied. The objective of this investigation was to determine the effects of soil type and sediment concentration on bromide solution concentrations.

PROCEDURE

Barnes, Caribou, Caribou (limed), Cecil, Cecil (limed) and Houston Black soils were used to evaluate bromide adsorption. Each of these series represent important cropland soils found in widely diverse agricultural regions of the United States. These soil series were selected because of their widely-varying chemical and physical properties. Bromide adsorption onto these soils should be indicative of losses expected for many cropland sites.

SOIL CHARACTERISTICS

Cecil and Caribou soils used for agricultural production usually have relatively low pH values. As a result, crops grown on these soils may experience significant nutrient deficiencies. These soils are typically limed to counteract low pH values. Limed treatments of the Caribou and Cecil soils were included in the experimental design to determine the effect, if any, of liming on adsorption of bromide.

Soil texture, percents sand, silt and clay, organic matter content, and pH for these six soils are given in Table 1. Particle size analysis was performed using experimental procedures outlined by Gee and Bauder (1986) while methods identified by Nelson and Sommers (1982) were used to determine organic matter content. Soil pH was measured using the calcium chloride technique described by McLean (1982).

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TABLE 1. Texture, particle size, organic matter content, and pH of the soils

Soil Series	Texture	Particle size, %			Organic matter, %	pH
		Sand	Silt	Clay		
Barnes	loam	39 3	37 7	23 0	4 4	6 5
Caribou	loam	39 3	48 8	11 9	4.4	4 4
Caribou (limed)	loam	39 9	48 8	11 9	4.4	6 6
Cecil	sandy loam	70.3	21.3	8.4	5 4	4 2
Cecil (limed)	sandy loam	70 3	21 3	8 4	5 1	6 5
Houston Black	silty clay	12 3	41.9	45 8	2 4	7 9

The Barnes series (fine-loamy, mixed Udic Haploborolls), consists of deep, well-drained soils formed in glacial till on uplands. The surface layer of this soil, obtained in Pierce County, North Dakota, is black loam approximately 18 cm (7 in.) thick. Most of these soils are used for cropland.

Aroostook County, Maine was the location from which the Caribou soil (coarse-loamy, frigid Typic Haplorthods) was obtained. The Caribou series consists of deep, well-drained upland soils formed in glacial till which was derived mainly from calcareous slate and limestone. Typically, these soils have a dark brown gravelly loam surface approximately 20 cm (8 in.) thick.

Parent material for the Cecil series (clayey, kaolinitic, thermic Typic Hapludult) is residuum from crystalline rock. Native vegetation for this sampling site in Oconee County, Georgia was a hard wood forest. This soil contains erodible kaolinitic clay.

The Houston Black series (montmorillonitic, thermic, Udic Pellusterts), sampled in Bell County, Texas, consists of deep moderately well-drained soils on nearly level to gently sloping areas on uplands. These soils formed in calcareous marine clays and marls. In a representative profile, the surface layer is very dark gray clay about 60 cm (24 in.) thick.

Bromide Measurement

The soils were air dried and sieved through a 2 mm (0.08 in.) screen prior to testing. Soil was added to each bromide solution to obtain soil concentrations of 2.5, 10, 40, 70, and 100 g/L. Total volume of the solution was 400 mL. It was assumed that the bromide background levels for each of the soils was minimal.

Initial bromide concentrations of approximately 0.1, 8, 700, and 77 000 μg/L were used in a factorial combination of the above sediment concentrations. Sodium bromide in crystalline form was diluted to the appropriate solution concentration. A concentration of 0.01 μg/L is near the minimum detectability of the ion chromatograph, the instrument used to determine bromide concentration (Johnson and Stevenson, 1978).

Two replications of each combination of sediment and bromide concentration were run for each of the soils. The samples were stirred and allowed to stand for one hour at room temperature. Sediment was then removed from the solution by filtering. The filtrate was stored for future analysis using the ion chromatograph.

Results

The principal variables in this study included soil type, sediment content, and bromide concentration. The effects of each of these variables on absorption of bromide is described below.

TABLE 2. The F ratios for analysis of variance of final bromide concentration with soil series and sediment content

Source of Variation	F Ratios*			
	Initial Bromide Concentration, μg/L			
	0.1	8	700	77,000
Soil Series	0.95	0.77	1.29	0.46
Sediment Content	0.61	1.01	1.22	1.55
Soil-Sediment Interaction	0.22	0.65	1.25	0.58

*None of the values were statistically significant at the 10% level.

Factors Affecting Dye Adsorption

Analysis of variance was used to determine the effects of soil and sediment content on adsorption of bromide for each of the initial bromide concentrations. The F ratios shown in Table 2 can be used to identify the degree of significance of selected variables. For each of the initial bromide concentrations, neither soil series nor sediment content were found to significantly influence final bromide concentration. In addition, no significant soil-sediment interaction was apparent at any initial bromide concentration. Thus, results of the analysis of variance would indicate that final bromide concentration was not significantly affected by either soil series or sediment content.

Bromide Adsorption for Selected Soils

Bromide concentrations in the filtrate from the various sediment sources (soils) are shown in Table 3. The final bromide concentrations are the means of the values from all five soil concentration solutions for each soil. Within a given column, the smallest reported bromide concentration would indicate the potential for greatest adsorption of bromide. Duncan's multiple range test was used to determine if significant differences in bromide concentration occurred between soil series.

For the least concentrated solution (0.1 μg/L), significant differences in bromide concentration were found between the Barnes and Houston Black soil series. No significant difference in bromide concentration was determined between soil series for the other three solutions (8, 700 and 77 000 μg/L). For all of the solution concentrations, no significant difference in final solution

TABLE 3. Mean filtrate bromide concentration for selected soils following addition of sediment*

Soil Series	Initial Bromide Concentration, μg/L			
	0 1	8	700	77,000
Barnes	0.141 a†	7.70 a	730 a	77,600 a
Caribou	0.134 ab	7.74 a	743 a	76,500 a
Caribou (limed)	0.138 ab	7.69 a	722 a	77,300 a
Cecil	0.132 ab	7.72 a	721 a	75,800 a
Cecil (limed)	0.133 ab	7.64 a	727 a	78,400 a
Houston Black	0.123 b	7.75 a	742 a	77,500 a

*For each soil, sediment was added to a given solution of bromide at rates of 2.5, 10, 40, 70 and 100 g/L Two tests were run at each sediment and bromide concentration for each of the soils.

†Within a given column, differences in bromide concentration are significant at the 5% level (Duncan's multiple range test) if the same letter does not appear.

TABLE 4. Mean filtrate bromide concentration at selected sediment contents following addition of sediment

Sediment Content g/L	Initial Bromide Concentration, μg/L			
	0.1	8	700	77 000
2.5	0.128 a†	7.72 a	720 a	75 900 b
10	0.130 a	7.73 a	739 a	79 700 a
40	0.136 a	7.70 a	725 a	77 500 ab
70	0.138 a	7.74 a	731 a	76 200 b
100	0.135 a	7.64 a	740 a	76 700 ab

*Barnes, Caribou, Caribou (limed), Cecil, Cecil (limed) and Houston Black soils were added up to a given sediment content to a given initial bromide solution. Two tests were run for each sediment and bromide concentration for each soil.

†Within a given column, differences in bromide concentration are significant at the 5% level (Duncan's multiple range test) if the same letter does not appear.

concentration of bromide was found between limed and unlimed soils.

For the most dilute bromide solution (0.1 μg/L), the bromide concentration of the filtrate from the Houston Black soil was smallest. This should indicate greatest bromide adsorption. However, for each for the other solutions, there were no differences in bromide concentration, and associated adsorption, between soils.

The range of bromide concentrations used in this study covered six orders of magnitude. The readings at the 0.1 μg/L concentration were near the minimum detectability of the ion chromatograph. In this lower instrument range, readings were probably not as precise as values in the intermediate concentration range. Thus, for the solutions with 0.1 μg/L initial bromide concentration, differences in filtrate bromide concentration between the Barnes and Houston Black soil series may have been caused by limitations in instrument sensitivity.

Bromide Adsorption at Selected Sediment Contents

Table 4 shows mean final bromide concentrations of all soils at different sediment and initial bromide concentrations. Where statistically significant differences exist within a given column, the potential for greatest adsorption of bromide would be expected for the smallest bromide concentration. Significant differences in bromide concentration at varying sediment contents were identified using Duncan's multiple range test. For the most concentrated initial bromide solution (77 000 μg/L), significant differences in filtrate bromide concentration were found between selected sediment contents. No significant differences in bromide concentration was determined between the various sediment contents for the other three solutions (0.1, 8, and 700 μg/L).

For the 77 000 μg/L bromide solution, the lowest mean filtrate bromide concentration and therefore the greatest implied degree of bromide adsorption was found at a sediment content of 2.5 g/L. It would be expected that bromide adsorption would increase with greater sediment content. However, this trend was not shown in the experimental data.

The ion chromatograph was unable to make direct readings for samples of the most concentrated solution (77 000 μg/L). The samples for this concentration were first diluted to a range which the instrument could detect. Because of possible errors in the dilution procedures, measurements for the 77 000 μg/L concentration were probably not as accurate as values obtained under nondiluted conditions. Therefore, differences in filtrate bromide concentration between selected sediment contents for the solution with a concentration of 77 000 μg/L may have been caused by dilution errors.

Discussion

When using bromide in tracer studies, selection of an appropriate initial bromide concentration is critical. The sensitivity, minimum detectability, and range of the measuring instrument should also be considered. Once the optimum instrument detection range has been determined and an estimate of the amount of dilution has been made, a suitable initial bromide concentration can be selected.

For initial bromide concentrations of 8 and 700 μg/L, neither soil texture, liming, nor sediment content were found to significantly influence filtrate bromide concentration. In effect, adsorption of bromide onto sediment was not affected by these variables under the conditions of this study. Thus, when the above range of initial bromide concentrations are used, bromide appears to be well suited for use as a tracer in dilution studies.

In this investigation, bromide was in contact with the soil for a one-hour period. The effects of additional contact time on adsorption of bromide was not examined. Additional tests to identify whether significant bromide adsorption occurs over longer time periods would be very useful.

This laboratory study was conducted to evaluate the effects of sediment content and initial bromide concentration on adsorption of bromide for selected soils. When bromide is used as a tracer under field conditions, several other factors must be considered (Finkner and Gilley, 1986). Temperature, pH, and background bromide concentration of soil may be of concern. Potential plant and animal toxicity to bromide should also be considered. Cost of tracer materials and laboratory analysis are other important concerns.

For the intermediate concentration range of 8 to 700 μg/L, perhaps a bromide ion electrode would serve as a suitable detection instrument, thereby reducing analytical costs. Some other less sensitive and less expensive instruments may also be adequate. Additional work is needed to identify if significant differences exist in bromide concentration measurements obtained using other analytical procedures.

Summary

Bromide salts have proven to serve as excellent tracer materials since they are highly soluble, non-degradable, relatively inexpensive, and can be measured quantitatively in very low concentrations. Many existing procedures for measuring discharge and velocity are not well suited for use with the relatively small runoff quantities found on overland flow areas. Therefore, dilution techniques may be well suited for measuring hydraulic variables on upland regions.

Adsorption of bromide onto sediment may be of concern on upland areas. A laboratory study was therefore conducted to determine for selected soils the effects of sediment content and initial bromide concentration on adsorption of bromide. Bromide adsorption onto six soils with widely varying chemical and physical properties was examined.

Difficulties with bromide measurement procedures at very dilute and very concentrated solutions were experienced. When measuring bromide concentrations, it is essential that readings be obtained within the optimum instrument detection range. In this study, when bromide measurements were made in appropriate bromide concentration ranges, neither soil texture, liming, nor sediment content were found to significantly affect adsorption of bromide onto sediment.

Since bromide, at concentrations in the range of 8 to 700 μg/L, is not readily adsorbed onto sediment, bromide at these concentrations appears to be well suited for use as a tracer in dilution studies. In contrast to fluorescent dyes, use of correction factors for estimating adsorption are unnecessary. Several factors must be considered when bromide is used as a tracer under field conditions. Certainly one of the most important considerations is proper selection of initial bromide concentration.

Use of bromide as a tracer for upland flow characterization has considerable potential. Information concerning hydraulic parameters on upland areas could be greatly expanded by using tracing techniques. Further testing of bromide as a tracer under field conditions is recommended.

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