ADSORPTION OF BORON BY MICHIGAN SOILS

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ABSTRACT

ADSORPTION OF BORON IN MICHIGAN SOILS

By

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An investigation was conducted to determine the extent to which Michigan soils may adsorb B. With an increasing interest in using soil as a renovator of wastewater, the presence of B in wastewater could be a potential hazard to plant growth.

Undisturbed soil cores of a Lenawee loam (Mollic Haplaquept), Brookston loam (Mollic Ochraqualf), and a Metamora sandy loam (Aquic Hapludalf) were collected from a small watershed on the site of the Water Quality Management Project at Michigan State University. Soil series were split into replications of topsoil and subsoil. An apparatus was constructed to apply a 1.13 mg/liter B solution to the soil cores following a rate and schedule of 1.27 cm/hour for four hours on two days each week. By graphical and soil analysis the amount of B adsorbed was determined.

Less than 1 μg B/g of soil was adsorbed in each soil and at each depth. There were slight adsorption

differences among soils and no differences between depths. The limited adsorption was attributed to an acid soil pH and low extractable Fe and Al. Since soils had little retention capacity for B, an early equilibrium state between soil and the applied wastewater was expected. Under these conditions plants may be subject to B concentrations found in the wastewater which may be toxic to plant growth if at sufficiently high levels.

ADSORPTION OF BORON BY MICHIGAN SOILS

By

Garry William Rowe

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INTRODUCTION

The use of soil in the treatment of wastewater has become increasingly popular. Therefore, every aspect of wastewater application on soil and its environmental impact should be carefully examined. Depending upon the concentrations found in the wastewater and the environmental conditions, B could be a limiting factor for application of wastewater on agricultural land.

Industries that have used B extensively include glass manufacturing, metal production, agricultural chemicals, leather production, cosmetics, photography, soaps and many more. This usage results in a significant amount of B being discharged into the wastewater system. Concentrations of B in wastewater vary over a wide range depending on the effluent source and treatment. Concentrations of 0.5 mg/liter to 1.0 mg/liter are common, but concentrations may reach as high as 4.0 mg/liter (22, 30, 43). For many crop species in the sensitive and semi-tolerant category, 4.0 mg/liter is above permissible limits for B concentrations in irrigation water (39). Eaton (9) has shown that when soil and water are in equilibrium, B concentrations in the soil solution are equal to that of

irrigation water. The effect on plant growth can be predicted from the concentration in the applied water. If the soil has a small capacity to adsorb B, the equilibrium between B in the soil and irrigation water may be quickly established. Plants would then be subject to B levels found in the applied water.

Boron has a narrow range of concentration in soil solution where it is adequate for plant growth and where plant toxicity begins. Eaton (8) found that with sensitive plants injury began at 1 to 5 mg/liter of B in solution. This includes most citrus crop species such as lemon (Citrus limonia osbeck) and peach (Prunus persica (L.) Batsch). Semi-tolerant crops showed toxicity symptoms when B concentrations were 5 to 25 mg/liter, which include corn (Zea mays L.) and alfalfa (Medicago sativa L.) Tolerant crop ranges were 10 to 25 mg/liter and include sweet clover (Melilotus indica (L.) All.) and sugar beet (Beta vulgaris var. crassa Alef.). Tolerance of plants to B have also been shown to depend on the rate at which B is adsorbed by the plants (32).

Transpiration in the plant appears to be the controlling factor in B uptake (23), and toxicity symptoms appeared in the leaf where B would be localized by the transpiration stream. With the plant acting as a sink taking B from the applied wastewater, relatively low concentrations, such as 1 mg/liter, could still produce a

toxic condition in the plant. Neary, Schneider and White (22) found that when irrigated with wastewater low in B (0.51 to 0.91 mg/liter), toxicity symptoms appeared in red pine (Pinus resinosa Ait.). This toxic condition was attributed to site loading of B in the soil, however, this may have been caused by direct absorption of B from the wastewater by the plant. With limited adsorption of B by the soil, this condition could be produced in a relatively short time.

Little is known about the retention capacities of B in Michigan soils. Most of the studies have been on soils in the Western and Southwestern portions of the United States, as well as in Mexico and Hawaii. Much of this work has also been done on soil fractions rather than on undisturbed soils.

This study was conducted to determine the extent to which Michigan soils adsorb B. The principal objective was to determine how much B would be adsorbed by the soils and how quickly equilibrium was established between the soil and applied solution.

LITERATURE REVIEW

Reactions of B in Soil

Once B is introduced into the soil in fertilizer or irrigation water, it may be taken up by plants or microorganisms. It may also precipitate in or react with the soil, or it may be leached from the soil profile. Most B fertilizers are expected to hydrolyze to boric acid (H_3BO_3) and at pH ranges common in soils the predominate form is undissociated H_3BO_3 (18). Likewise, Wilcox (44) has also shown that B in sewage is mostly undissociated H_3BO_3. Because B levels in soil are quite low and most borate compounds are very soluble, precipitation of a borate salt should not occur unless evaporation exceeds rainfall and irrigation.

From the standpoint of potential toxicity problems, the amount of B retained or adsorbed in the soil may be one of the most important factors. For this reason, this study was devoted to adsorption of B. However, effects due to a plant actively growing in the system, along with leaching losses and runoff, cannot be ignored under actual field conditions.

Adsorption of B in Soil

Various investigations have shown that B applied to soil in irrigation water or as fertilizer was adsorbed or fixed (2, 3, 13, 14, 21, 25, 31, 37). Some work has also shown that B is fixed more easily than it is removed by leaching.

Possible mechanisms for B adsorption include ion exchange, molecular adsorption, uniting with diols in organic matter, and entrance of B into clay lattices. Various factors have also been found to influence B adsorption. These included temperature, soil texture, soil drying, time, amount of B added, clay type, organic matter, pH, and the presence of Fe, Al, and Mg hydroxides.

Factors in B Adsorption

Physical

Probably the most significant physical factor for B adsorption in soils was texture. Generally, fine textured soils were reported to adsorb more B than coarse (2, 13, 21, 24).

Hatcher, Bower and Clark (14) found that the surface area of soils was significantly correlated with B adsorption and only surface hydroxides were active in adsorption. Couch and Grim (7) found that with illite clays, the specific surface area of the clay was the strongest factor in B adsorption. Calculating B adsorption on a per unit area basis showed that different

illite clays fixed the same amount of B. Also, by wet and dry treating the clay, breakdown of the mineral occurred and exposed more surface area for adsorption. Parks (27), using a fine sandy loam, also increased B fixation by increasing drying cycles and reduced the amount of hot-water extractable B. Eaton and Wilcox (9) found that soils originally low in their capacity to fix B, had increased capacity upon drying. Other studies have shown similar results with wet and dry treatments, and most researchers have attributed the increased B adsorption to the breakdown of primary and secondary minerals which exposed more surface area for adsorption.

Chemical

Many studies have found that pH of the equilibrated solution had a very significant affect on the amount of B adsorbed. Sims and Bingham (34) found a striking dependency of pH upon B adsorption in clays and hydroxy Fe and Al materials. Maximum retention was obtained at pH values of 8.0 to 9.0. Work on soils from Mexico and Hawaii (3) revealed similar relationships between pH and maximum B adsorption. Another study on Hawaiian soils (25) resulted in similar findings when pH was increased to 8.0 and 9.0. Hingston (15) working with clay also found that B retention depended largely on pH. Hatcher, Bower and Clark (14), working with soils, found that B adsorption was enhanced at higher pH levels.

Some researchers hypothesized that higher pH resulted in increased formation of borate ions ($B(OH)_4^-$). The $B(OH)_4^-$ ion is the favored species for adsorption, and adsorption therefore increases with increasing pH up to a pH of 9.0. Above the pH of 9.0 adsorption rapidly decreases due to competition with hydroxl ions, and hydrous oxides also take on a negative charge resulting in repulsion of the $B(OH)_4^-$ anion.

Some studies have also shown that salt content and salinity may influence B adsorption. Fleet (10) kept the B concentration of a solution applied to illite clay constant, and varied the salt content. A two-fold increase in adsorption was found by increasing the salinity from 1.07 to 34.3 percent. Kemp (17) found that in the presence of a neutral salt, especially with hydrated cations, the dissociation of H_3BO_3 increased. Increasing salinity and greater dissociation of H_3BO_3 would then result in more $B(OH)_4^-$ ions for adsorption.

All the studies showed a wide range of B concentrations being applied to soil or clay. Some investigations have found that increased concentrations of B in the applied solution increased B adsorption. Fleet (10) kept salinity constant and noted an increase in B adsorbed in illite clay as the B concentration increased in the applied solution. Eaton and Wilcox (9) obtained increased B fixation with each increase in B concentration. A

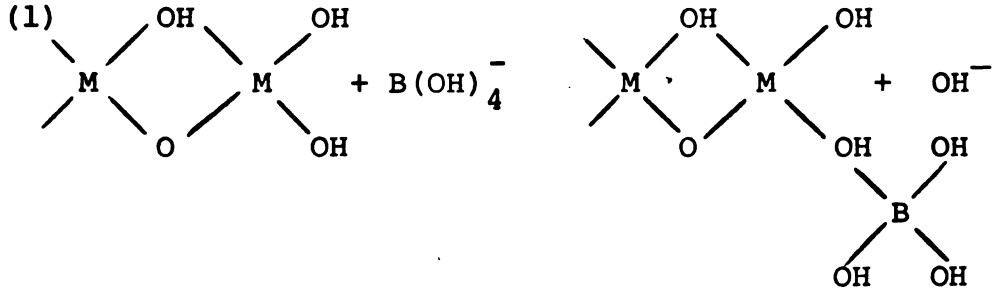
proportional decrease was obtained as the concentration exceeded 10 or 15 mg/liters. Parks (27) found that only at lower concentrations did the percent of B fixed increase as concentration increased.

Certain materials in soil organic matter may have an affinity for B. Parks and White (29) found that humus had an affinity for B, but that it depended on the type of humus material. They suggested that fixation may result from uniting with diols in organic matter. In contrast to this Sims and Bingham (36) reported a negative correlation between B retention and organic matter content. Harada and Tamai (11) found a significant correlation between B adsorption and organic matter of soils, but upon destruction of the organic matter an increase in adsorption occurred. This was attributed to metals released from the organic matter and forming hydroxyl groups available for adsorbing B. While organic matter may have some affinity for B, it may also complex metal compounds that otherwise would fix B. Decomposing organic matter should increase adsorption.

A majority of the research has indicated that the amount of B adsorbed by soil is related to the amount of Fe, Al, and Mg hydroxides. Sims and Bingham (35) found that Fe and Al hydroxy compounds appeared to be responsible for most of the B retained in clay minerals. Hydroxy Al compounds were more effective adsorbers than hydroxy Fe

compounds. They suggested reactions involving the $B(OH)_4^-$ ion exchanging for a hydroxyl ion (Equation 1), or becoming the end member of a hydroxy Fe or Al polymer (Equation 2).

(1)



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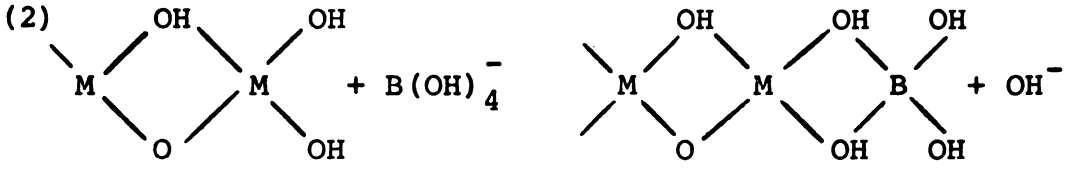
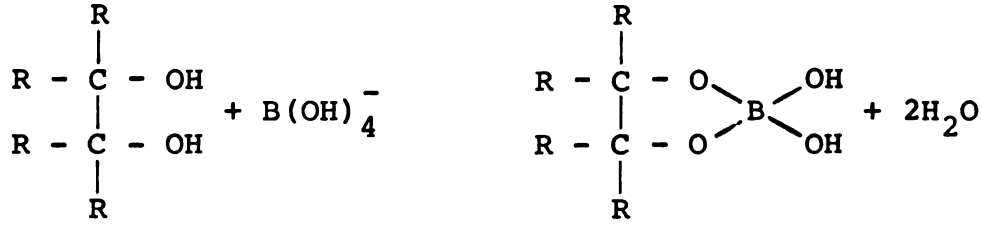


An additional reaction given was analogous to the formation of the borate-diol complex (Equations 3 and 4).

(3)



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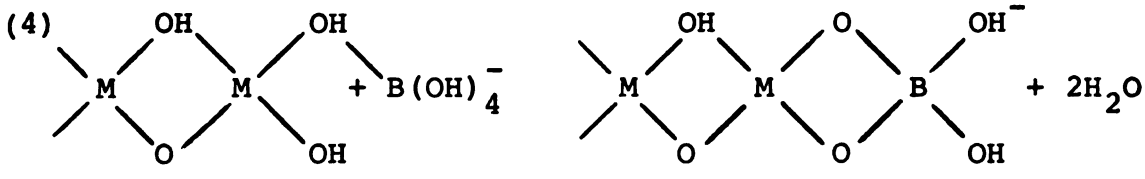


Another study by Sims and Bingham (36) revealed that the hydroxy Fe and Al compounds are dominate over clay minerals in determining B retention of layer silicates. The data also showed that retention characteristics may be conditioned by the clay mineral species present.

Research by Harada and Tamai (11) indicated that Al_2O_3 and Fe_2O_3 contents were highly correlated with B adsorption in soil. However, when Al_2O_3 and Fe_2O_3 were removed from the soil high B adsorption still occurred. This high B adsorption was due to the clay fraction of the soil. Soil clay may have a large affinity for B, but this adsorption ability may be greatly masked by Al_2O_3 and Fe_2O_3 on the clay surface.

Bingham and Page (3), working with amorphous soils from Mexico and Hawaii, found a significant correlation between B adsorption and SiO_2 plus Al_2O_3 content, but a higher correlation was found with Al_2O_3 alone. Hatcher, et al. (14) also showed that for a wide range of soils B adsorption was highly correlated with surface area and citrate-extractable Al.

Rhoades, Ingualson and Hatcher (33) found that with arid soils, silt and sand fractions had appreciable B adsorption capacities. This appeared to be due to clusters or coatings of Mg hydroxide on weathered surfaces of ferromagnesium material. A significant correlation was found between various minerals high in Mg hydroxy coatings

and with B adsorption. These minerals were also low in Fe and Al content indicating the importance of the Mg material.

Most of the studies point to Al, Fe and Mg hydroxides as being key factors in B adsorption in soils. Consideration of these compounds is important in predicting how a soil will react to B applied as a fertilizer or in irrigation water.

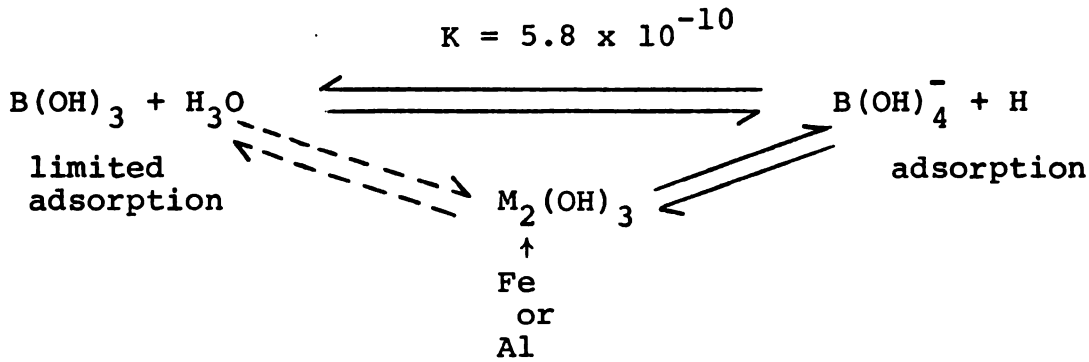
Bingham and Page (4) showed that the adsorption of B appeared to be distinctly different from that of other anions which are more common in soils. Maximum adsorption of SO_4, PO_4, Cl, and NO_3 was found under acid conditions while maximum B adsorption occurred under alkaline soil conditions. Because of a difference in behavior of B with these other anions present, no competition with them was expected.

A Two-Step Mechanism for B Adsorption

Couch and Grim (7) proposed a two step mechanism from their results with illite clays. The first step was an initial rapid adsorption of $B(OH)_4^-$ onto the clay mineral surface. With illite clays this might occur on frayed edges of the illite flake. The next step was diffusion of B into the interior of the clay crystal. Fleet (10) proposed a similar mechanism involving an initial chemical adsorption followed by B installation into the tetrahedral lattice sites. This first step

probably proceeded quite rapidly and the second step was slower. In this second step B might replace Al or Si as it migrates into the clay tetrahedral lattice sites. Data from Parks and Shaw (28) also agreed with the concept of B being fixed by entrance of B into the clay lattice.

Reports appear to support this two step mechanism. First there was an initial rapid adsorption by surface sites such as Al, Fe, or Mg hydroxide compounds followed by a slower process of migration to sites in the clay lattice. Based on the reviewed literature, the major soil factors involved with adsorption of B include pH and the presence of Fe and Al oxyhydroxides. Undissociated H_3BO_3 is the predominate form of B expected in soils, but the borate ion, $B(OH)_4^-$, is the favored species for adsorption. The adsorption process may be represented by the following diagram:



For Michigan soils with pH values of less than 7, most B would be in the form of H_3BO_3. Figure 1 shows species of B in solution at various pH values. Only above pH values of 9.2 does $B(OH)_4^-$ become predominant.

Soils in Michigan are usually low in extractable Al and Fe oxyhydroxides and under acid conditions small levels of $B(OH)_4^-$ ions are available for adsorption. Under these conditions little or no adsorption of B was expected by the soils used in this study. Equilibrium with a solution or wastewater containing 1 mg/liter B should occur in a relatively short period of time.

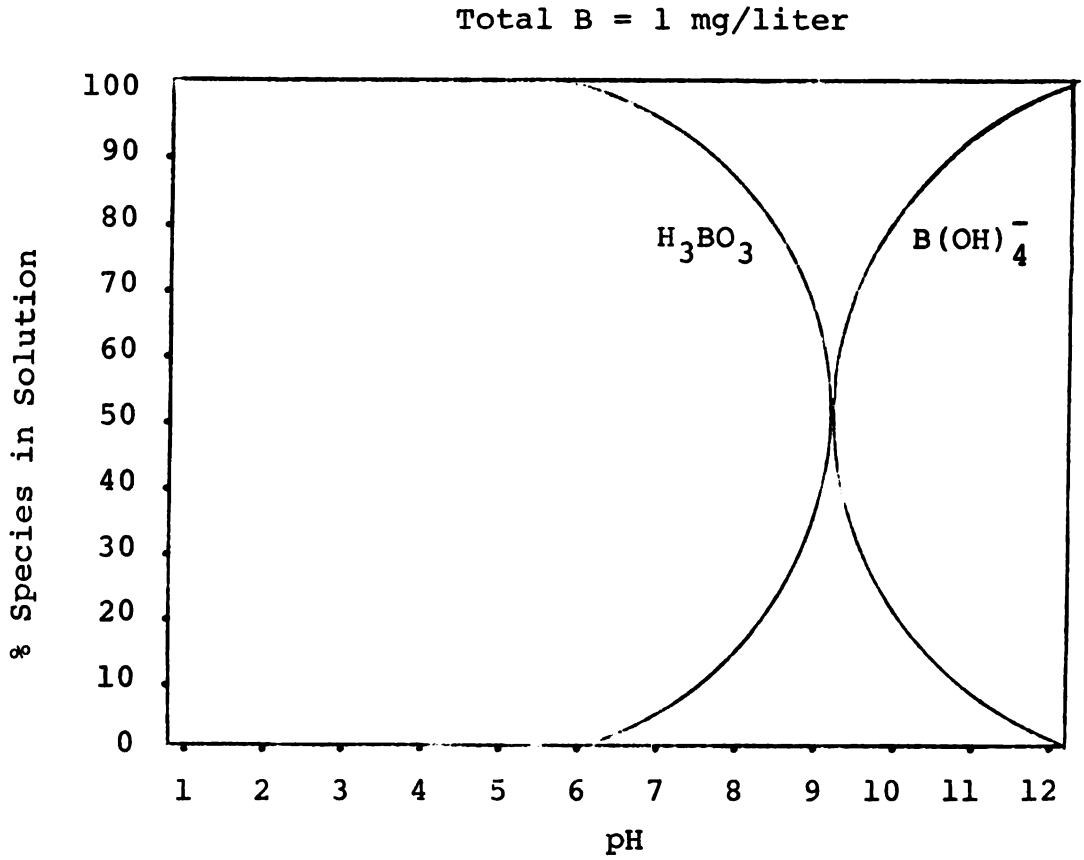


Figure 1.--Species of B in solution at various pH values.

METHODS AND MATERIALS

Leaching Experiment

Undisturbed soil cores were collected from a small watershed on the site of the Water Quality Management Project at Michigan State University during the fall of 1975. The cores were taken using a Giddings hydraulic soil sampler fitted with a 6.35 cm diameter metal tube which housed an acrylic plastic sleeve. Six replicate samples of the topsoil (0-30 cm) and of the subsoil (30-60 cm) were collected for each soil type used. Three different soil series, identified at the sampling site, were used: a Lenawee loam (Mollic Haplaquept), Brookston loam (Mollic Ochraqualf), and a Metamora sandy loam (Aquic Hapludalf). Descriptions of the soils including physical and chemical properties are given in Table 1. Complete data of all the soil replicates are in Appendix I. Undisturbed cores could not be obtained from the Metamora sandy loam subsoil, and it was packed in the column by hand to approximate field bulk density. Soil from each column was removed from the top and bottom of each core to give a final soil column height of 15 cm. The soil removed from each core was used for preliminary analysis of pH, conductivity, and hot-water extractable B content.

Table 1.--Physical and Chemical Properties of the Soil.

Soil Series	Horizon	Number of Observations	pH initial	pH final	Conductivity initial	Conductivity final	Organic Matter	Al_2O_3 †	Al_2O_3 *	Fe_2O_3	Sand	Silt	Clay	Bulk Density
					(μmhos)		--%	%						g/cm^3
Lenawee loam	Topsoil	5	5.8	6.0	110	127	2.03	.064	.003	0.43	44	21	35	1.32
	Subsoil	3	6.3	6.5	46	136	--	.040	.004	0.95	33	24	43	1.61
Brookston loam	Topsoil	5	6.3	6.4	86	129	1.60	.043	.002	0.51	56	20	24	1.43
	Subsoil	3	7.5	7.4	107	151	--	.021	.003	1.11	55	19	26	1.68
Metamora sandy loam	Topsoil	6	5.2	5.3	101	130	1.04	.088	.016	0.56	70	15	15	1.34
	Subsoil	4	5.5	5.8	22	100	--	.043	.010	0.78	74	12	14	1.89

†NH_4F extractable

*NH_4OAc extractable

The leaching experiment was conducted in a constant temperature chamber at 23^{0}C. Leachate was applied to each column at approximately 1.27 cm/hour for four hours on two days each week. This application rate and schedule was typical of the wastewater application rate and schedule used at the Michigan State University Water Quality Management Project site.

A leaching apparatus was constructed as follows. A 45 liter polyethylene carboy containing the leaching solution, which was connected to a distribution system, served as a reservoir. A tube placed through the cap of the carboy was used to maintain a constant liquid head. Teflon medical grade capillary tubing, .381 mm I.D. by 19 cm length, was used to apply the leaching solution and control flow directly onto the soil. Distribution of the leaching solution to the capillary tubes was through a 7.0 mm I.D. Tygon tube and Nalgene plastic T's. The capillary tubes were held stationary by cementing them inside a 5.0 mm I.D. acrylic plastic tubing using Sears filled epoxy resin (catalog no. 980557). A diagram of the system is shown in Figure 2 with a detailed sketch of the column in Figure 3. Preliminary trials showed that the system delivered a constant (within 10 percent) application rate over a four hour period for all columns. To improve accuracy, the effluent volumes from each column were measured after each application.

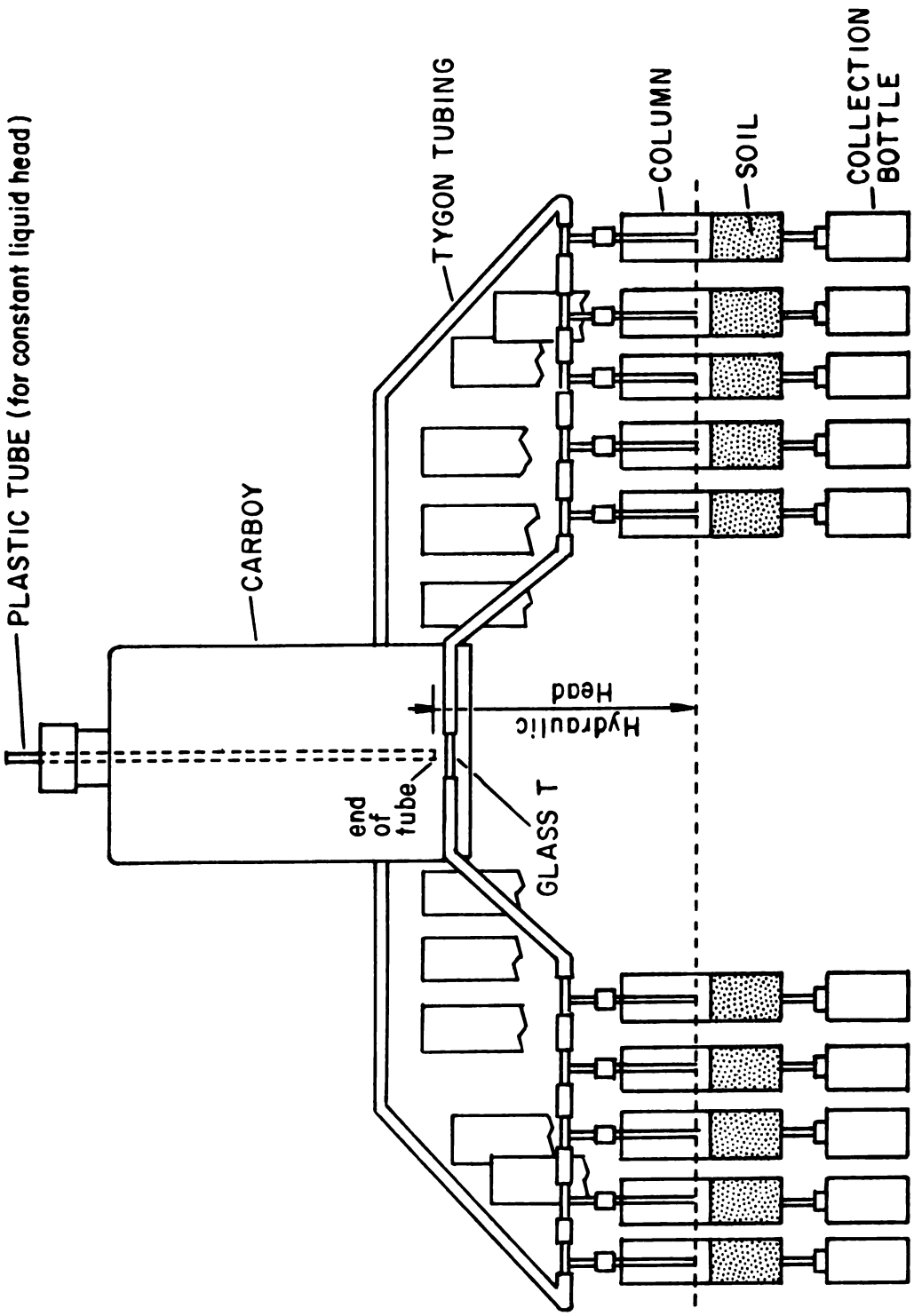


Figure 2.--Schematic diagram of the system used to deliver the leaching solution to the soil columns and collect the effluent.

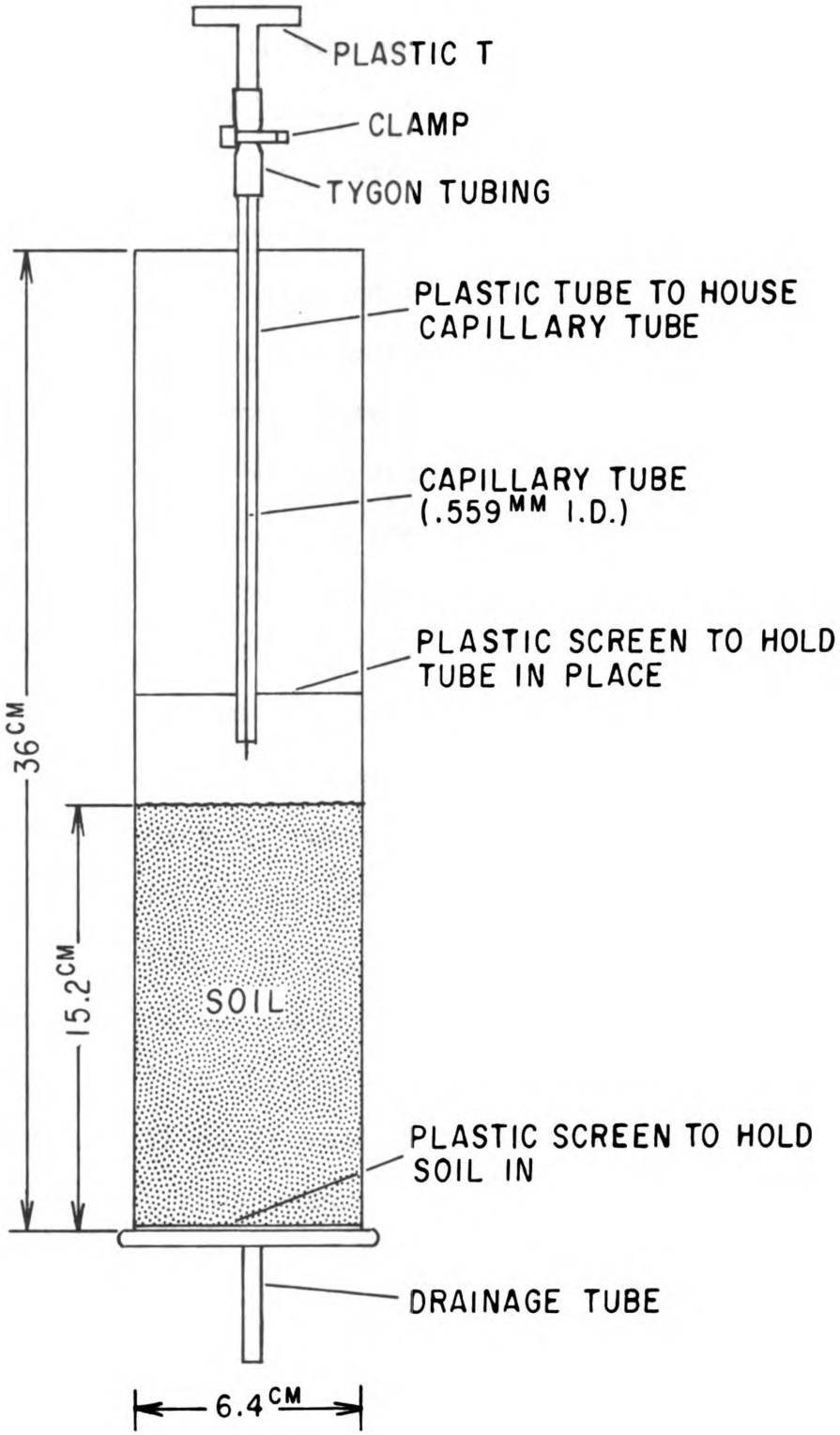


Figure 3.--Diagram of soil column and attachments used to deliver leaching solution to soil.

The leaching solution contained an average concentration of 1.13 mg B/liter. This level was chosen because it represented the approximate average concentration found in most wastewaters (22, 30). Other ions were also added to simulate the wastewater used at the Water Quality Management Project site.

The following compounds were added to 45 liters to give the final ion concentrations desired. Calcium was added as calcium chloride ($CaCl_2$), 4.98 g; magnesium as magnesium hydroxide ($Mg(OH)_2$), 2.99 g; sodium as sodium carbonate (Na_2CO_3), 8.36 g; potassium as potassium chloride (KCL), 712 g; sulfate as sulfuric acid (H_2SO_4) 98 percent w/v, 5.94 g; chloride as hydrochloric acid (HCl) 37 percent w/v and as $CaCl_2$ and KCl. Carbonate (HCO_3) was obtained from Na_2CO_3 and HCl. Boron was added from a 100 mg/liter B stock solution made from boric acid (H_3BO_3).

An initial leaching solution without B was applied to the columns for two weeks to allow flow and drainage conditions to stabilize in each column. Boron was added to the leaching solution after two weeks and the leaching continued for a period of 26 weeks. By the end of this time period, all the columns had equilibrated with B and the concentration of B in the effluent equaled the concentration in the leaching solution.

The leaching solution was expected to displace the initial soil water by miscible displacement. To

separate miscible displacement from actual B adsorption, Br was added as a tracer to the leaching solution. Graphs or curves were made showing the drainage characteristics of both B and Br as they came into equilibrium with the soil. These types of curves have been referred to as breakthrough curves (41). By direct comparison of the observed B breakthrough curve to a breakthrough curve of an ion which does not exhibit adsorption such as Br (16), the amount of B adsorbed could be calculated from the difference of the two curves. The Br concentration of the leaching solution was 7.6 mg Br/liter, or the same molecular concentration as that of B.

Soil Analysis

The soil sampled from each column prior to application of the leachate solution was analyzed for pH (1:1 soil paste) and conductivity (1:2 soil:water paste). Boron was extracted from the soil by a hot-water method (1) and determined colorimetrically by the carmine method (44). At the end of the experiment the soil cores were removed from the plastic sleeve and the upper and lower 5 cm was dried, mixed and analyzed for pH, conductivity and hot-water extractable B as before. The center section was used for bulk density computation.

Aluminum was extracted with 0.5N NH_4F at pH 8.2 by procedures outlined by Tandon (40), and with a 1.0N

NH_4OAc at pH 4.8 by procedures outlined by Mclean (19). The Al was determined colorimetrically by the aluminon method (26). Iron was extracted using a citrate-dithionite method (20) and determined by atomic adsorption spectrophotometry. Total C was determined by dry combustion on a Leco carbon analyzer and inorganic C titrametrically by methods outlined by Bundy and Bremmer (6). Organic matter was estimated as 1.9 times the difference of the total C and inorganic C. Soil particle size analysis was done by the hydrometer method (5).

Graphical and Statistical Analysis

For each soil, ratios of the effluent concentration of B and Br to that in the leaching solution were calculated, and the ratios (C/Co) were plotted against cumulative pore volumes. A third degree polynomial equation derived by least squares analysis (38) was used to fit the curves. For each core the B and Br breakthrough curves were plotted together for comparison. The area between the curves represents the fraction of B adsorbed.

Micible displacement or breakthrough curves may take on three general shapes (41). Where there is no solute-solid interaction and where there is an equal pore velocity distribution, the breakthrough curve is symmetrical about the point of 50 percent displacement at one pore volume of effluent. Under conditions where a wide range of pore velocity distributions is present, such as is

normally found in the soil, the curve shifts to the left. When chemical or physical interaction occurs between solute and solid, such as adsorption, the curve is shifted to the right.

In order to determine if the difference between the B and Br curves were meaningful, an analysis of variance of unweighted cell means (38) was conducted among the soils and between depth on the pore volumes needed to reach equilibrium for both B and Br. A paired t test (38) was also conducted to determine if there was a significant difference between adsorption values calculated from the graphs and from soil analysis. Separate analysis of variance of unweighted means were then conducted on the adsorption values obtained from graphical methods and from soil analysis to determine any differences between soil depth, soil series, and depth by soil interaction.

RESULTS AND DISCUSSION

A typical B and Br adsorption graph (Lenawee loam topsoil) is shown in Figure 4. Complete graphs representing each soil series and horizon are given in Appendix II. The Br curve showed no interaction of Br with the soil. It was shifted slightly to the left of one pore volume at 50 percent breakthrough. The B curve was shifted to the right indicating an interaction of B with the soil. The area between the two curves represents adsorption of B. The calculated values of B adsorption from this area indicated that relatively low amounts of B were adsorbed (Table 2) compared to other adsorption studies (2, 3, 13, 14, 25, 37).

Amounts of B adsorbed was also estimated by soil analysis. The initial soil level minus the final soil level (corrected for the amount in the leachate solution left in the column) equaled the increase in adsorbed soil B (Table 2). The B adsorption values for all the soils by this method were also low, but slightly higher than those indicated by the graphical method. The paired t test showed a significant difference between values given by the two methods. The coefficient of variation was

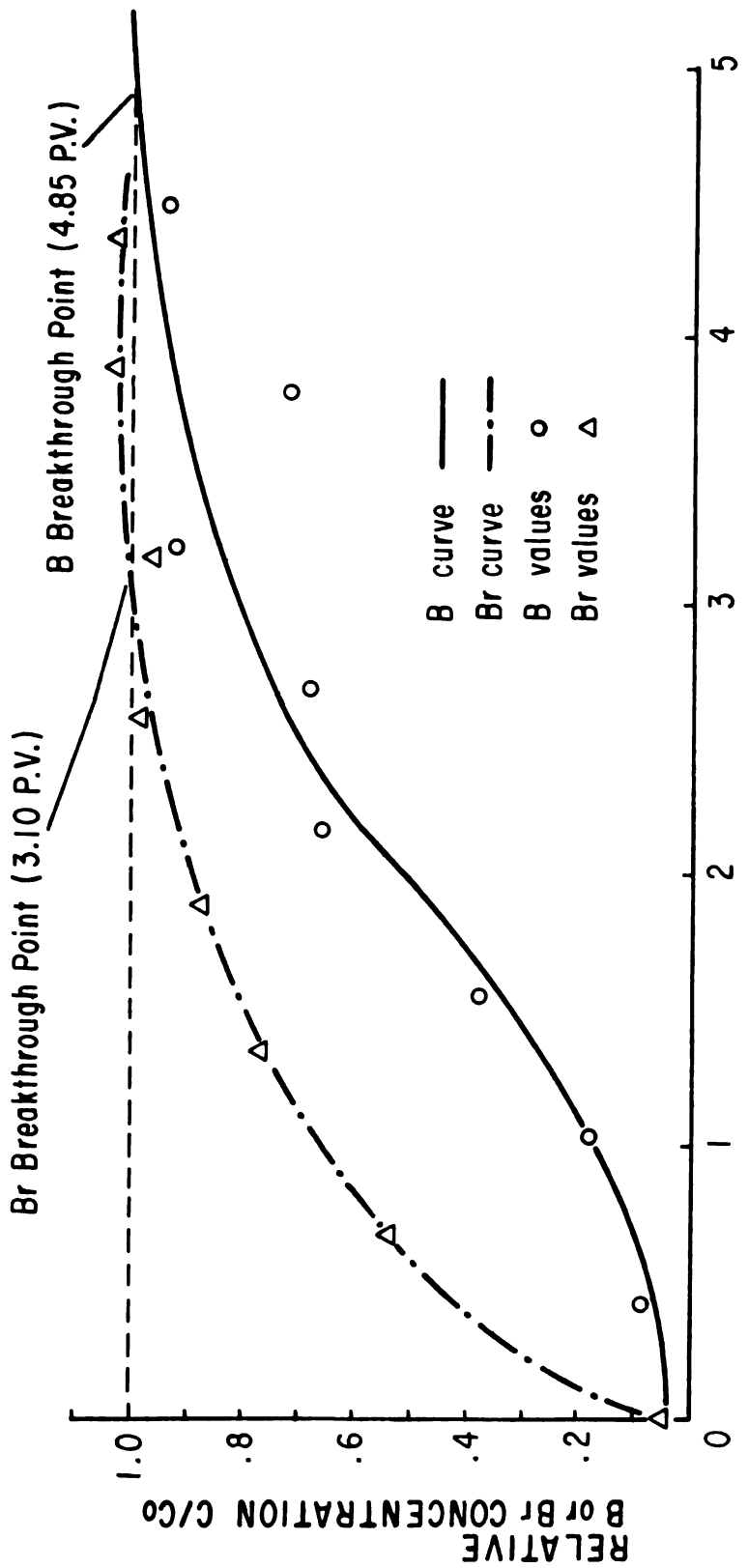


Figure 4.--Boron and bromide breakthrough curves for the Lenawee loam topsoil abbreviated to show the breakthrough points and the area used to calculate boron adsorption.

Table 2.--Calculated Values of B Adsorption from Graphical and Soil Analysis.

Soil Series	Horizon	Number of Observations	B adsorbed	
			Graphical Analysis	Soil Analysis*
			μg B/g soil	
Lenawee loam	Topsoil	5	0.44 (10%)†	0.75 (32%)
	Subsoil	3	0.40 (49%)	0.72 (72%)
Brookston loam	Topsoil	5	0.34 (15%)	0.89 (14%)
	Subsoil	3	0.45 (21%)	0.73 (46%)
Metamora sandy loam	Topsoil	6	0.09 (28%)	0.38 (49%)
	Subsoil	4	0.24 (29%)	0.26 (44%)

†Value in parenthesis is coefficient of variation.

*Corrected for the amount in the leachate solution left in the column.

also generally higher in the soil method than in the graphical method (Table 2) indicating that the graphical method may be a better estimate of the amount of B adsorbed.

Results of the analysis of variance of the B and Br breakthrough points, revealed significant differences between B and Br breakthrough points (Tables 3 and 4). Comparison of means of B and Br breakthrough points (Table 4) revealed that for all the soils and depths except the Metamora sandy loam topsoil, a significant difference was obtained. This supports the graphical interpretation that adsorption was observed in the soils by the difference between the B and Br curves.

Table 3.--Analysis of Variance of the Breakthrough Points of Br and B--Main Effects and Interactions Calculated on the Unweighted Cell Means.

Source	Degrees of Freedom	Sum of Squares	Mean Squares	F Value
Breakthrough (B)	1	53.26	53.26	142.03**
Soil Series (s)	2	3.38	1.69	4.51
B X S	2	4.79	2.40	6.39**
Depths (D)	1	14.61	14.61	38.96**
B X D	1	13.52	13.52	36.05**
S X D	2	1.58	.79	2.11
Estimated error			.38	

**Significant at the 1 percent level.

Table 4.--Mean Values of the Breakthrough Points of B and Br curves.

		Soil Series		
		Lenawee loam	Brookston loam	Metamora sandy loam
		pore volumes		
Topsoil	B	5.21a*	5.63a	3.54
	Br	2.82b	3.32b	2.97
Subsoil	B	8.70a	11.10a	7.57a
	Br	2.14b	3.18b	3.04b

*Different letters indicate significant differences between B and Br breakthrough points within soil series and depth. LSD (.05) = 1.75.

Both graphical and soil analysis supported the hypothesis that little or no adsorption of B was expected. Replications of both graphical and soil analysis were quite comparable. The coefficient of variation was highest in the subsoils, probably due to a more erratic flow pattern of the leachate moving through the heavier soil. Most of the subsoils showed slightly higher B adsorption than did the topsoils based on graphical interpretation, although topsoils exhibited a higher adsorption by the soil analysis.

Based on the graphical data, the Lenawee loam topsoil had an average adsorption of 0.44 µg B/g of soil compared to 0.40 µg B/g for the subsoil. The Brookston loam topsoil had an average adsorption of 0.34 µg B/g,

and the subsoil 0.45 µg B/g. The Metamora sandy loam topsoil showed virtually no adsorption of B giving only 0.09 µg B/g of adsorbed compared to 0.24 µg B/g for the subsoil. Analysis of variance on the graphical data indicated significant differences among soil series but not depths (Table 5). There was also no significant difference between soil series and depth (Table 5).

Table 5.--Analysis of Variance of Graphical Analysis Using Mean Calculated Adsorption Values.

Source	d.f.	S.S.	M.S.	F
Depth	2	.0088	.0044	2.68
Soil	1	.0739	.0739	45.10*
Soil X Depth	2	.0117	.0056	3.41
Error	20		.0016	

*Significant at the 1 percent level.

Table 6.--Analysis of Variance of Soil Analysis Using Mean Calculated Adsorption Values.

Source	d.f.	S.S.	M.S.	
Depth	2	.0179	.0089	00.56
Soil	1	.2614	.2614	16.34*
Soil X Depth	2	.0051	.0025	00.16
Error	20		.0160	

*Significant at the 1 percent level.

Using the soil analysis, smaller differences were seen between topsoil and subsoil. The Lenawee loam showed an average adsorption of 0.75 µg B/g of soil in the topsoil and 0.72 µg B/g in the subsoil, and the Brookston loam 0.89 µg B/g and 0.73 µg B/g respectively. The Metamora sandy loam topsoil showed virtually no adsorption by graphical analysis, but 0.38 µg B/g adsorbed in the topsoil by soil analysis. This value was higher than 0.26 µg B/g seen in the subsoil. This discrepancy may indicate that the hot-water extractable B value may have removed some residual soil B. Analysis of variance on the soil analysis also indicated a significant difference among soil series, but not depths or between soil series and depth (Table 6). Since both statistical analysis showed no significant differences between depths, soil property differences between the topsoil and subsoil such as organic matter, clay, aluminum and iron-oxyhydroxide content, may not be a major factor for any B adsorption found in these soils.

The Lenawee and Brookston loam soil were the most similar in results. Adsorption based on both graphical and soil analysis revealed that both topsoils and subsoils gave comparable results (Table 2). The Lenawee and Brookston loam soils were also the most similar in chemical and physical properties (Table 1) of the three soil series used. The Metamora sandy loam topsoil and

subsoil gave lower B adsorption values in both graphical and soil analysis than the other two soil series. This soil had the lowest pH and lowest percentage of clay. Based on other studies, lower adsorption is expected since soils higher in clay content have a higher affinity for B. It was also noted that the Fe_2O_3 and Al_2O_3 content was higher in the Metamora sandy loam (Table 1), which further indicated the minor role these soil constituents may have in B adsorption by these soils at existing pH values.

Soil pH and clay content were considered the main reasons for the differences seen between the soil series and apparently were the predominant factors involved with any B adsorption. The acid pH and low extractable Fe and Al content were considered the primary reasons for the limited B adsorption observed.

A representative graph of extended leaching of the soil is shown in Figure 5. Boron adsorption curves of all the topsoils gave a noticeable area above the equilibrium point. This area of apparent B desorption was close to the value of adsorption in both Lenawee and Brookston loam soil series. However, soil analysis showed a net gain in soil B which contradicts this. An even larger mystery is the fact that a much greater area of desorption was noted in the Metamora sandy loam topsoil,

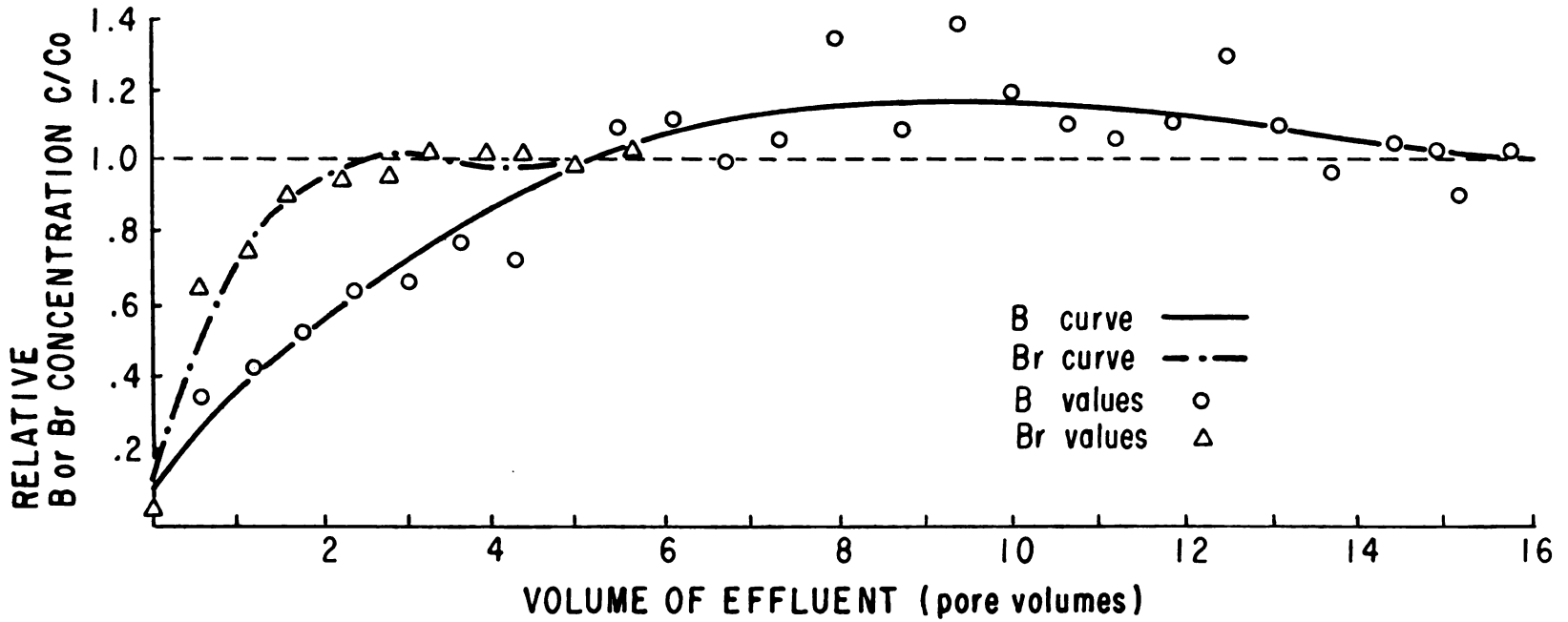


Figure 5.--Boron and bromide breakthrough curves for the Lenawee loam topsoil.

where little or no adsorption was seen. This phenomenon was not observed in any of the subsoils.

No data from the study offers any conclusive explanation for this observed effect. It may have been due to experimental error, pH changes, anion competition or compound formation of B with some other substance and a subsequent leaching out of the compound. Random experimental error did not appear to be the answer since reproducibility of the graphs were very good and the effect was unique for the topsoils. A pH change may have occurred where a short term alkaline state developed in the soil causing increased adsorption, followed by a quick drop to normal pH causing B desorption. The buffering capacity of the soil is usually high and this effect was not expected. Adsorption of other anions common in the soil such as Cl, PO_4, SO_4, and NO_3, have been found to be significantly different from B adsorption and competition or affects by these other anions was not expected (4). There are also no data offered from this study to indicate that B may have formed a new compound in the soil and was then leached out. Upon further leaching the curves did return to equilibrium.

SUMMARY

With little work available on B adsorption by soils in the Northeastern United States and Michigan, an experiment was designed to determine the extent to which some Michigan soils would adsorb B. Because of an increasing interest in using soil as a renovator of wastewater, the presence of B in wastewater makes it an important consideration for management of such a system.

An apparatus was constructed to apply a 1 mg/liter B solution to undisturbed soil columns. By graphical and soil analysis the amount of B adsorbed was determined. A Lenawee loam, Brookston loam, and Metamora sandy loam soil were used. The soils were acid in pH and contained little extractable Fe and Al.

Results revealed that under extended leaching, little or no adsorption of B was found among the soils, and small differences were noted between topsoil and subsoil. Some area of desorption was seen on topsoil graphs, but no evidence was obtained by the study as to its cause. Analysis of variance and L.S.D. tests supported the graphical interpretation that differences were seen between B and Br adsorption curves except for the Metamora

sandy loam. Other statistical analysis showed a significant difference between soil series for the amount of B adsorbed.

The data supports the hypothesis that little or no adsorption was expected by these soils under application of a 1 mg/liter B solution. This was attributed to an acid soil pH and low extractable Fe and Al. Since these soils had little retention for B, an early equilibrium state between the soil and irrigation water containing B is expected. Levels of B in the soil solution should be equal or close to those in the irrigation water. Under management of a wastewater disposal system, the use of semi-tolerant to tolerant crop species is recommended since adsorption of B was quickly established and levels of B in wastewater can be potentially toxic to plant growth. Considerations of climate, topography, soil type and crop species should be made in reference to B as a potential limitation to the use of soil in a disposal system.

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APPENDIX

Table I.--Complete Data of Physical and Chemical Properties of the Soils.

	rep.	pH initial	pH final	Conductivity initial	Conductivity final	Organic C	Organic Matter	Sand	Silt	Clay	Fe	Al†	Al*	B.D.
				(μmhos)		%					μg/g			g/cm³
Lenawee Loam														
Topsoil	1	5.7	6.1	90.0	128.0	0.82	1.56	41	23	36	2366	329	16.67	1.32
	2	5.8	6.0	101.0	110.0	1.00	1.90	45	23	32	3200	345	20.00	1.36
	3	5.8	6.0	137.0	130.0	1.04	1.98	44	23	33	3234	325	13.76	1.31
	4	5.9	5.9	76.0	130.0	1.14	2.17	44	23	33	3234	370	22.51	1.34
	5	5.6	6.0	148.0	138.0	1.34	2.55	46	13	41	2866	312	16.26	1.21
Average		5.8	6.0	110.4	127.0	1.09	2.03	44	21	35	2980	336	17.84	1.32
Subsoil	1	6.3	6.3	-	142.0	-	-	31	24	45	6750	229	18.34	1.57
	2	6.4	6.4	-	124.0	-	-	34	24	42	4750	204	24.18	1.55
	3	6.2	6.8	46.0	142.0	-	-	34	23	23	8415	195	24.18	1.70
Average		6.3	6.5	46.0	136.0	-	-	33	24	43	6638	209	22.23	1.61
Brookston Loam														
Topsoil	1	6.7	6.4	-	130.0	0.89	1.69	55	21	24	3165	216	10.00	1.53
	2	6.0	6.5	-	132.0	0.84	1.60	56	20	24	3585	216	9.17	1.45
	3	6.1	6.4	108.0	130.0	0.86	1.63	56	19	25	3630	327	11.67	1.38
	4	6.6	6.3	57.0	120.0	0.82	1.56	56	21	23	3585	216	10.42	1.46
	5	6.2	6.5	92.0	134.0	0.80	1.52	55	21	24	3790	229	9.17	1.33
Average		6.3	6.4	86.0	129.0	0.84	1.60	56	20	24	3551	241	10.09	1.43
Subsoil	1	7.3	7.3	70.0	136.0	-	-	53	18	29	5915	116	20.84	1.70
	2	7.1	7.2	-	130.0	-	-	58	18	24	8585	150	13.76	1.60
	3	8.0	7.8	144.0	198.0	-	-	54	20	26	8585	70	15.00	1.73
Average		7.5	7.4	107.0	151.3	-	-	55	19	26	7695	112	16.53	1.68
Metamora sandy loam Topsoil	1	5.1	5.3	136.0	134.0	0.49	0.93	69	16	15	4085	450	79.32	1.33
	2	5.4	5.2	90.0	140.0	0.55	1.05	69	16	15	3915	466	95.02	1.30
	3	5.3	5.4	80.0	136.0	0.58	1.10	70	15	15	3800	483	81.68	1.42
	4	5.2	5.3	180.0	121.0	0.85	1.62	70	15	15	3800	437	90.02	1.30
	5	5.3	5.5	95.0	118.0	0.48	0.91	71	15	14	3800	483	81.68	1.36
	6	5.0	5.3	26.5	136.0	0.33	0.63	71	15	14	3830	483	90.02	1.30
Average		5.2	5.3	101.3	130.8	0.55	1.04	70	15	15	3872	467	86.12	1.34
Subsoil	1	5.5	5.8	21.5	102.0	-	-	74	12	14	5500	216	50.02	1.70
	2	5.5	5.9	21.5	102.0	-	-	75	10	15	5330	229	51.70	1.82
	3	5.5	5.9	21.5	95.0	-	-	74	12	14	5330	216	51.70	2.07
	4	5.5	5.6	21.5	100.0	-	-	74	12	14	5330	237	56.70	1.86
Average		5.5	5.8	21.5	99.8	-	-	74	12	14	5373	225	52.53	1.89

†NH_4F extractable.

*NH_4OAc extractable.

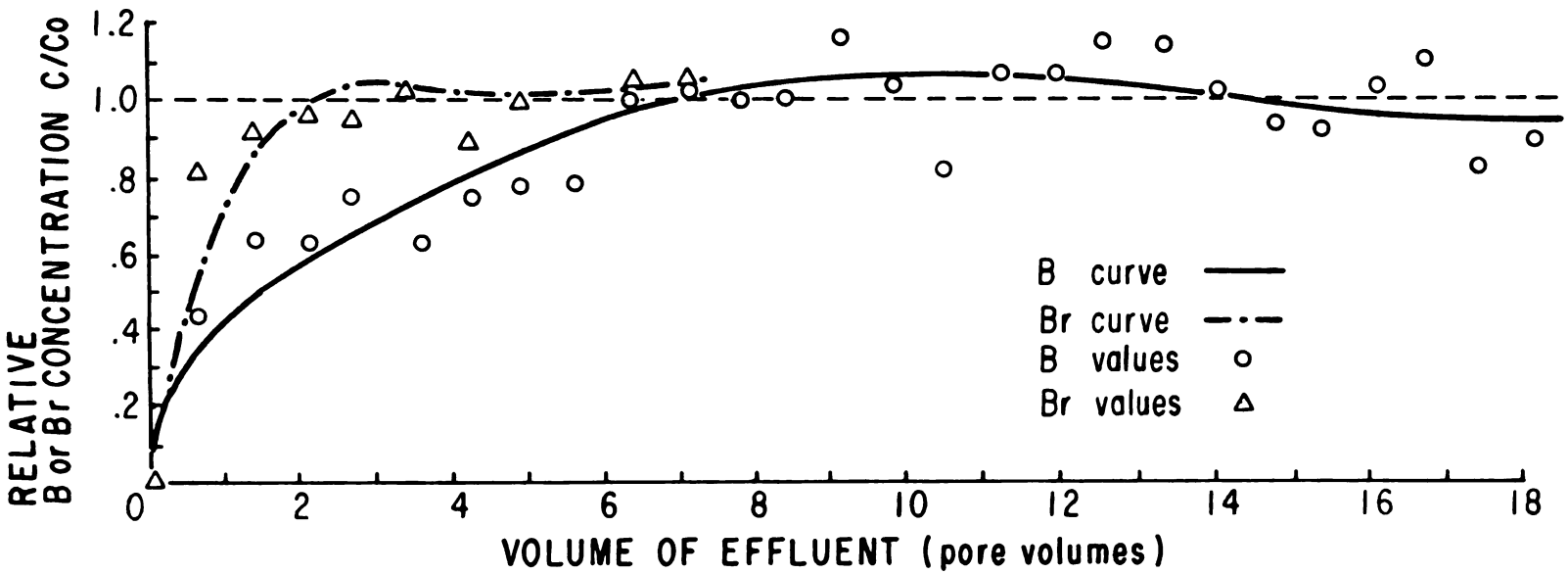

Figure II-1.--Boron and bromide breakthrough curves for the Lenawee loam subsoil.

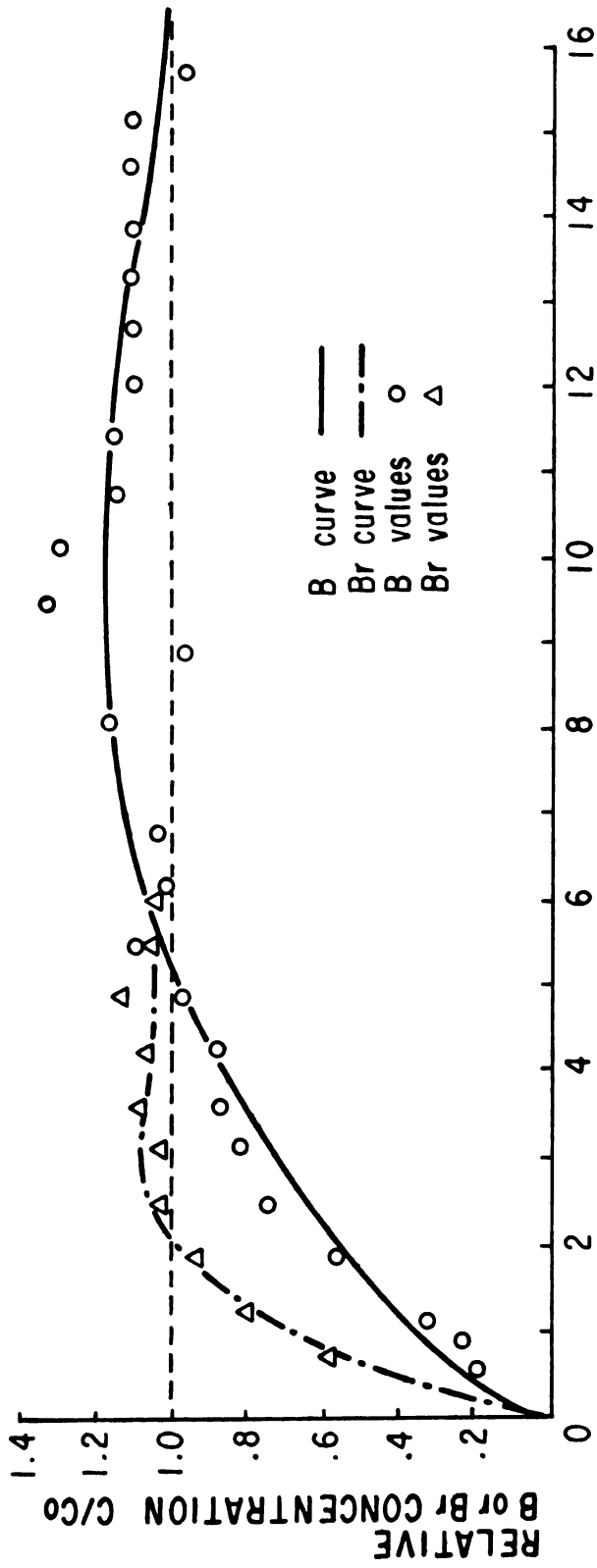

Figure II-2.--Boron and bromide breakthrough curves for the Brookston loam topsoil.

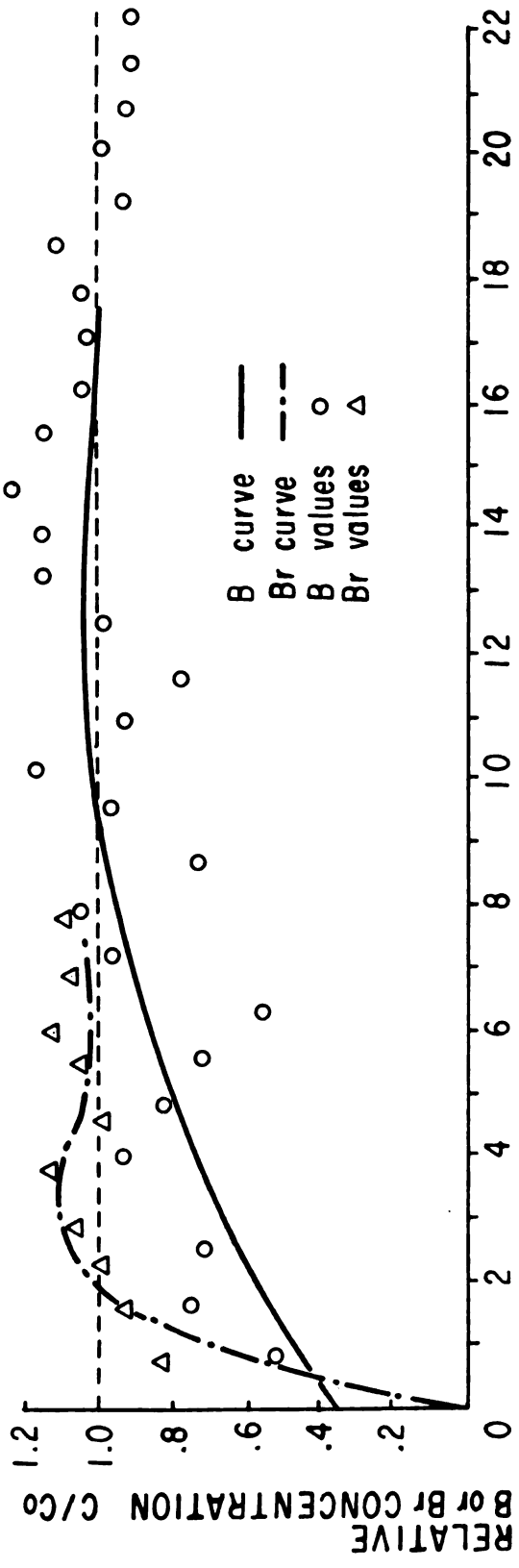

Figure II-3.--Boron and bromide breakthrough curves for the Brookston loam subsoil.

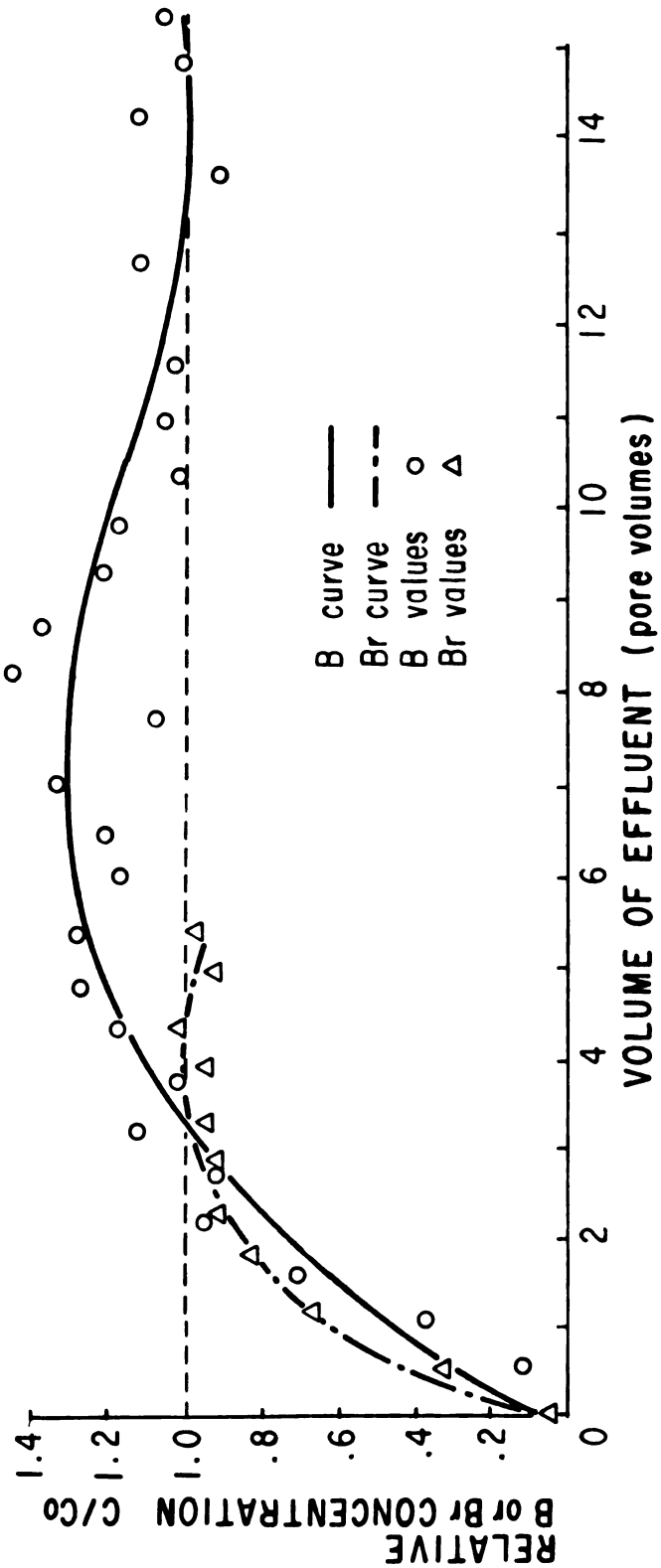

Figure II-4.--Boron and bromide breakthrough curves for the Metamora sandy loam topsoil.

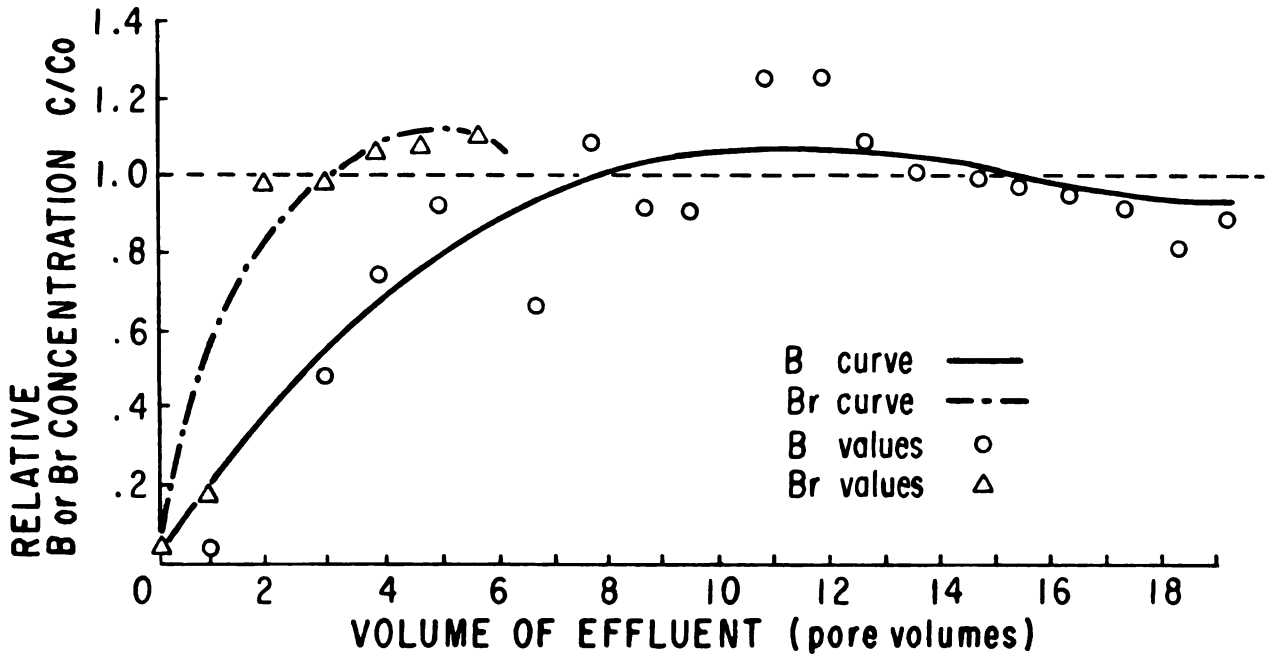

Figure II-5.--Boron and bromide breakthrough curves for the Metamora sandy loam subsoil.