Report No. 02

Field Evaluation and Model Calibration for Agricultural Pesticide Transport to Groundwater, Phase II

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SYNOPSIS

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Title: Field Evaluation and Model Calibration for Agricultural
          Pesticide Transport to Groundwater, Phase II

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           hydraulic properties, organic matter

SUMMARY OF RESEARCH PROJECT:

Problem and research objectives:

Groundwater quality surveys, which have detected
agricultural chemicals (pesticides, herbicides, etc.) in
several aquifers in the Midwest, have resulted in
considerable public concern and apprehension about how these
chemicals are used and their potential for environmental
contamination. Leaching of agricultural chemicals through
soil is one potential mechanism through which groundwater
can be contaminated. Transport of chemicals encompasses
exchange,   exclusion,   dissolution,   precipitation,
volatilization, chemical and biological transformations, and
other processes in the soil profile. Obviously, these
processes are affected by environmental conditions.
Therefore, the study of environmental conditions and other
factors which influence the transport of solutes is needed
for prediction of potential leaching. Several soil factors
which influence the transport of organic and inorganic
solutes are the organic matter content, saturated hydraulic
conductivity, and water retention relation of the soil. The
objective of this second phase of the study was to evaluate
the variability of the organic matter content, soil water
characteristics,   bulk   density,   saturated   hydraulic
conductivity, and texture of the soils at a site which had
been used to study atrazine and bromide leaching. In

2

addition, soil samples were removed to evaluate the long term persistance of atrazine and characterize the leaching of bromide after one year.

Methodology:

The field site had been used to study atrazine and bromide leaching in 1987 and was located near Hartsburg, Missouri. The soils were Sarpy (loamy, mixed, mesic Typic Udipsamments) with the surface texture varying from silt loam to loamy sand. At the site during 1988, 455 undisturbed soil samples were removed from the field. These samples were used to measure selected hydraulic properties. They were removed at 91 points on seven transects in the field. There were 13 sampling locations along each transect. The transects were 4 meters apart, and sampling points in each transect were 2.2 meters apart. At each location, samples were taken at five different depth increments. These depths were: 3.0-10.6, 20.0-27.6, 37.4-45.0, 52.4-60.0, and 72.4-80.0 cm. These samples were 7.62 cm in diameter and 7.62 cm in height. First, the samples were placed on pressure plates and water characteristics were measured at the following soil water potentials: 0.0, -1.0, -2.5, -5.0, -7.5, -10.0, -15.0, -20.0, -25.0, -30.0, and -40.0 kPa. Then the samples were resaturated, and saturated hydraulic conductivity was measured using the constant head method. The samples were oven-dried at $105^{\circ}C$, and the mass of the soil solids were determined and used to calculate the bulk density. Finally, 60 grams of each sample was used for particle size analysis to determine the texture. Organic matter content of the soils was determined, using the bromide samples removed in September 1987. A Leco CR-12 carbon analyzer was used to measure the organic carbon content of the samples. In this measurement, 0.3 g of the soil was heated to $1093^{\circ}C$ while oxygen was used as an oxidizer. Organic carbon content values were then multiplied by the factor 1.79 to convert to organic matter content.

Principal findings and significance:

Results from the hydraulic property evaluation indicate that the water content of the soils decreased drastically from saturation to -10 kPa soil water potential. This is due mainly to the coarse texture of the soils at the site. Another interesting result is the decrease in bulk density as a function of soil depth which is attributed to the increase in size and roughness of soil particles with increasing soil depth. However, the decrease in bulk density was from 1.51 to 1.41 g/cm^3 which was not large. Saturated hydraulic conductivity increased from 5 to 35 cm/hr as a function of soil depth from the 5 to 70 cm depths,

3

respectively. This result also suggests that the soil particles are coarser with increasing depth. Organic matter content was about 1.6% at the surface and decreased to 0.4% at the 30 cm depth. At about the 90 cm depth, the organic matter content increased to 1.2% which is due to plant residues deposited and buried in the alluvial area.

Publications and professional presentation:

Kazemi, H.V., and S.H. Anderson. Field variability of atrazine leaching under no-till management. ASAE Paper No. 88-2641, presented at the 1988 Winter ASAE Meeting, Chicago, Illinois.

M.S. theses:

Kazemi, H.V. 1989. Field variability of atrazine and bromide leaching under no-till management.

Ph.D. dissertations: None.

Field Evaluation and Model Calibration for Agricultural
Pesticide Transport to Groundwater, Phase II 1/

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Additional Index Words: Spatial variability, pH, organic matter content, bulk density, saturated hydraulic conductivity, water retention curves, texture.

ABSTRACT

Certain soil physical and chemical property data are needed to predict transport of agricultural chemicals (pesticides, herbicides, etc.) to groundwater. The objective of this investigation was to evaluate the soil variability of selected soil physical and chemical properties in a field used to study atrazine and bromide leaching. The site was divided into three areas due to differences in surface texture. Area I had a surface texture of sand, Area II sandy loam, and Area III loam. Soil physical properties were measured on 455 undisturbed soil samples taken systematically at 91 locations at five selected depths (15 to 20 cm depth increments to a depth of 85 cm) throughout the field. Additional samples were taken for measurement of organic matter content and pH. Organic matter content values of the three soil areas were similar throughout the soil profile. However, there was an additional peak (besides that at the soil surface) of organic matter content at the 100 cm depth in all areas. This was probably due to buried plant materials. Salt pH of Area I was higher down to the 65 cm depth compared to Areas II and III. Soil bulk density values throughout the soil profile were similar for the three soil areas. Interestingly, bulk density decreased with increasing soil depth which was attributed to the coarser texture of soil particles with increasing depth. Below the third depth, over 80% of the samples had 90% or more sand of which at least 85% was very coarse (1.0 to 2.0 mm). Saturated hydraulic conductivity values

7

of the three areas were similar for the shallow depths. At the 55 cm depth however, Area I had higher saturated hydraulic conductivity values than Areas II and III. The soil water characteristics of the three areas were similar for the five measured depths.

INTRODUCTION

Recent field surveys have focused on measurement of pesticide concentrations (for selected chemicals) in groundwater. The United States EPA and the Environmental Assessment Council have sponsored a series of groundwater monitoring programs (Pye and Kelly, 1984). These studies have revealed considerable contamination of groundwater supplies caused by agricultural and industrial organic chemicals.

Movement of agricultural chemicals through the soil profile is affected by soil and crop management as well as climatic conditions and soil properties. Management factors which influence the movement of chemicals include the type of chemical, method, and rate of application, specific crop, tillage, irrigation, etc. Climatic conditions include rainfall, temperature, evapotranspiration, humidity, solar radiation, etc. The extent to which a chemical applied to soil is dispersed depends on variability of water application rates and of travel time within the soil (Jury, 1982). Organic matter type and content, hydraulic conductivity, bulk density, water retention, etc. are some of the important soil properties influencing chemical transport in soils.

Field research on fate and transport of pesticides, through the unsaturated soil zone is limited since these studies are expensive. Jury et al. (1986) studied the movement of napropamide under field conditions. They observed that 20% of the commercially applied napropamide pulse moved to depths

between 0.2 and 1.8 m after two weeks of irrigation totaling 25 cm when the adsorption coefficient measurements suggested that the compound would be found between the surface and the 0.2 m depth.

Laboratory studies are more plentiful since fewer costs are included. Helling, 1971, studied the influence of selected soil properties on mobilities of 12 pesticides on 14 soils using soil thin-layer chromatography. Pesticide mobility tended to be directly related to increased water flux. Mobility of nonionic compounds was found to be inversely related to adsorption of the chemicals which was related to organic matter content, clay content, and cation exchange capacity.

Soil hydraulic properties are also important factors since they provide a quantitative measure of the retention and transport of water which also transports dissolved solutes in the profile (Biggar and Nielsen, 1976). Soil hydraulic properties include soil water retention and hydraulic conductivity which are used to predict consumptive use of water by cultivated crops and other vegetation, groundwater recharge, run-off and erosion potential, land drainage requirements, and similar processes. Of particular interest is the amount of the applied chemical which is transported below the root zone.

Since soils are variable, their chemical and physical properties which influence solute transport are also variable. Several studies quantifying the spatial variability of soil properties (Biggar and Nielsen, 1976; Amoozegar-Fard, 1982; Anderson and Cassel, 1984) have been conducted. Since the soil

hydraulic and chemical properties affect agricultural pesticide transport, it is necessary to have these data available if we desire to accurately predict the probabilities of contamination. The objectives of this study were to evaluate the spatial variability of selected physical and chemical properties of an alluvial soil used to study atrazine and bromide leaching.

MATERIALS AND METHODS

Location of Experiment

The site of the field experiment for the study was near Hartsburg, Missouri. The soil was on the flood plain of the Missouri River and was classified as Sarpy (mixed, mesic Typic Udipsamments). The soil surface texture varied from sand to loam (Fig. 1). The experimental site was 0.1 ha in size. In the first phase of the study (Kazemi et al., 1988) the site was divided into 49 plots having 4m x 4m dimensions.

Chemical Analysis

In May 1988, soil cores were removed using a truck-mounted hydraulic soil probe. Samples were taken at four locations for atrazine and bromide concentration analysis (Fig. 2). Soil cores were extracted to a depth of 2 m and segmented into 7.5 cm increments. In the first year of the experiment, atrazine samples removed five months after chemical application were analyzed. The results indicated atrazine was totally degraded after five months so that little could be detected using a detection limit of 1 μg/kg. Therefore, there was no reason for analyzing the samples removed one year after chemical application.

Additional soil samples were removed for bromide analysis. Samples were mixed with distilled water at 1:1 ratio (Adriano and Doner, 1982). Then the bromide halide electrode, which was hooked up to a pH meter, was used to measure the activity of the bromide in millivolts which indicated the bromide concentration.

12

This measurement was done by direct reading from the soil-water mixture. The bromide concentration (mg/kg) was derived after the standard curves were constructed based on the known sample concentrations.

Measurement of Soil Physical and Chemical Properties

Undisturbed soil samples were removed at 91 systematic sampling locations at five selected depths. At the site, 455 undisturbed soil samples were removed using a double-cylinder, hammer-driven core sampler (Blake and Hartge, 1986). The schematic diagram of the sampling locations are presented in Fig. 3. These samples were removed at 91 points on seven transects in the field. There were 13 sampling locations along each transect. The transects were 4 meters apart and sampling points in each transect were 2.2 meters apart. At each location, samples were taken in the middle of five selected depth increments. These depths were: 0.0-15.0, 15.0-30.0, 30.0-45.0, 45.0-65.0, and 65.0-85.0 cm. The samples were 7.62 cm in diameter and 7.62 cm in height. The samples were sealed in plastic bags and stored at 4° C until analyses were performed. The samples were taken from storage and transferred to pressure chambers for measuring the volumetric water content as a function of pressure head (Klute, 1986). The amount of water retained in the samples were measured at the following soil water potentials: 0.0, -1.0, -2.5, -5.0, -7.5, -10.0, -15.0, -20.0, -25.0, -30.0, and -40.0 kPa.

The samples were then slowly resaturated from the bottom for three days and transferred to a constant head permeameter to

13

determine the saturated hydraulic conductivity (Klute and Dirksen, 1986). The samples were then oven-dried at 105° C for 48 hours. The mass of the soil solids was determined and used to calculate the bulk density (Blake and Hartge, 1986). Finally, 60 grams of each sample was used to determine the texture using hydrometer method (Gee and Bauder, 1986).

Organic matter content of the soils was the soil samples taken in September 1987 (Kazemi et al., 1988) was determined using Leco CR-12 carbon analyzer. In this measurement, 0.3 g of the soil sample was heated to 1093°C while oxygen was used as an oxidizer. Organic carbon values were then multiplied by the factor 1.79 (Brown and Rodiguez, 1983) to convert to organic matter content. Salt pH was measured using a standard pH electrode connected to a pH meter. This measurement was done using a 1:1 mixture of soil with distilled water.

RESULTS AND DISCUSSION

Soil texture results are presented in Table 1. Texture was analyzed at 91 locations throughout the experimental site. The site was divided into three areas due to differences in surface texture. These areas were: Area I, sand; Area II, sandy loam; and Area III, loam (Fig. 1). Texture analysis indicated a high variation between the three soil areas and low variations within each area.

The bromide concentrations of the samples one year after chemical application indicated no bromide present at all four locations to a depth of 2 m. Since bromide is usually not degraded, it probably had been leached deeper than 2 m and was probably in the ground water since ground water levels often rise to the 2 m depth over winter at this site.

The organic matter content of the three soil areas as a function of soil depth is presented in Figure 4a. The organic matter content of the three soil areas is somewhat similar throughout the soil profile. Area I with 1.25% organic matter had the lowest and Area III with 1.71% had the highest organic matter at the surface. The organic matter content of the soil areas decreased below 0.50% at the 40 cm depth and then increased below the 40 cm depth. At the 85 cm depth, another peak of higher organic matter content begins. The average organic matter concentration increases to 0.65% around the 100 cm depth. This peak drops again to lower values at deeper depths. The appearance of the soil suggested that some decaying plant materials were present at about the 100 cm depth in all areas. This is probably

15

due to deposited plant materials by the Missouri River which were buried in this relatively young alluvial soil.

The salt pH was highest in Area I from the soil surface down to the 65 cm depth compared to Areas II and III (Fig. 4b). Below the 65 cm depth, pH is relatively uniform for all areas.

Table 1 illustrates the soil texture as a function of soil depth for the three soil areas. Area I has highest amount of sand and lowest amounts of silt and clay, at the surface compared to Areas II and III. As soil depth increases, the sand contents of Areas II and III increase considerably with all of the areas below the third depth having approximately 90% sand. The distribution of sand sized particles are illustrated in Table 2. Below the second depth, over 70% of the sand particles are larger than 0.50 mm in size.

The bulk density of the soil areas at different soil depths was also measured (Fig. 6). Interestingly, the bulk density of the three areas increases as soil depth increases. However, Area I has higher bulk density throughout most of the profile compared to Areas II and III.

Saturated hydraulic conductivity of the soil areas is similar down to the 25 cm depth (Fig. 7). Below this depth, saturated hydraulic conductivity increases more in Area I than Areas II and III. This is probably due to the coarser particles in Area I compared to Areas II and III. At the 56 cm depth, saturated hydraulic conductivity of Area I is about 37.5 cm/hr while that in Areas II and III is about 16 cm/hr.

The water characteristics (Fig. 8) were measured for the

16

three soil areas. In the first depth (Fig. 8a), Areas II and III are very similar and Area I has lower volumetric water content at all soil water potentials measured. In the second depth (Fig. 8b), all of the areas responded similarly. For the third and fourth depths (Figs. 8c and d), the volumetric water content at different soil water potentials are also similar for the three soil areas. At these depths, Area I has the lowest values of volumetric water content. However, the differences in the water contents are not considerable. In the lowest depth (Fig. 8e), all of the areas responded similarly with Area III having the lowest values of volumetric water content at -5 kPa and lower soil water potential.

CONCLUSION

This study was conducted in a field of alluvial soils with surface textures varying from sand to loam. Organic matter content at the soil surface and the bulk density data confirmed the differences among the soil areas. The water characteristic and texture data indicate that Areas II and III hold more water at high soil water potentials compared to Area I, down to the 45 cm depth. Area I has a very low water holding capacity throughout the soil profile due to its coarse texture. However, below the 45 cm depth all areas have similar characteristics due to the high sand content of the soils. Coarser sand particles in the lower part of the soil profile can also be a reason for decreasing bulk density as the soil depth increases. Preliminary comparisons of the variability of soil physical and chemical properties with bromide and atrazine concentrations at this site (Kazemi et al., 1988) suggest that greater leaching occurs in Area I compared to Areas II and III due to its coarser surface texture. More quantitative analyses are underway to confirm these conclusions.

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List of Tables and Figures

Table 1. Particle size distributions as a function of soil depth for the three soil areas.

Area	Depth (cm)	Sand (%)		Silt (%)		Clay (%)	
		X	SD	X	SD	X	SD
I	0.0-15.0	90.03	4.23	7.75	3.68	2.23	1.46
	15.0-30.0	89.46	5.89	8.33	4.23	2.24	2.34
	30.0-45.0	92.31	2.90	5.87	2.43	1.82	0.96
	45.0-65.0	93.30	2.08	5.65	2.03	1.05	0.45
	65.0-85.0	91.83	3.07	6.41	3.19	1.82	0.99
II	0.0-15.0	70.01	11.62	22.69	9.99	7.30	3.36
	15.0-30.0	75.28	10.53	19.02	8.51	5.69	3.44
	30.0-45.0	81.84	9.16	14.18	6.62	3.99	3.01
	45.0-65.0	91.48	2.78	7.24	2.53	1.28	0.74
	65.0-85.0	91.31	3.72	6.79	3.27	1.93	1.15
III	0.0-15.0	52.27	10.29	37.97	9.35	9.77	3.23
	15.0-30.0	73.53	8.79	20.95	6.97	5.52	3.42
	30.0-45.0	84.06	7.12	13.47	7.17	3.35	2.52
	45.0-65.0	90.47	3.34	7.77	3.00	1.76	1.14
	65.0-85.0	90.69	3.96	7.60	3.50	1.71	1.00

X = mean, SD = Standard deviation

Table 2. Sand fraction percentages as a function of soil
depth for the three soils.

Area	Depth (cm)	Size of sand particles (mm)				
		1.0-2.0 (%)	0.5-1.0 (%)	0.25-0.5 (%)	0.1-0.25 (%)	0.05-0.1 (%)
I	0.0-15.0	73.6	15.1	5.0	3.8	2.4
	15.0-30.0	82.5	6.0	2.1	4.9	4.4
	30.0-45.0	71.2	11.8	4.5	8.8	3.8
	45.0-65.0	91.3	3.0	1.8	3.0	0.9
	65.0-85.0	94.6	1.9	1.3	1.7	0.5
II	0.0-15.0	62.1	7.0	9.6	4.2	17.0
	15.0-30.0	67.4	15.5	4.6	5.4	7.0
	30.0-45.0	56.6	13.3	8.3	7.3	14.5
	45.0-65.0	83.0	10.0	1.7	1.8	3.4
	65.0-85.0	89.1	2.0	2.3	2.3	4.2
III	0.0-15.0	56.5	22.4	9.5	8.0	3.6
	15.0-30.0	65.1	20.6	8.0	4.7	1.5
	30.0-45.0	81.4	5.2	4.8	7.0	1.6
	45.0-65.0	84.7	12.0	1.8	0.6	0.9
	65.0-85.0	86.4	6.9	3.5	2.3	1.0

Fig. 1. Distribution of soil areas designated by differences in surface texture at the experimental site.

Area I
Sand

Area II
Sandy Loam

Area III
Loam

28 m

28 m

N
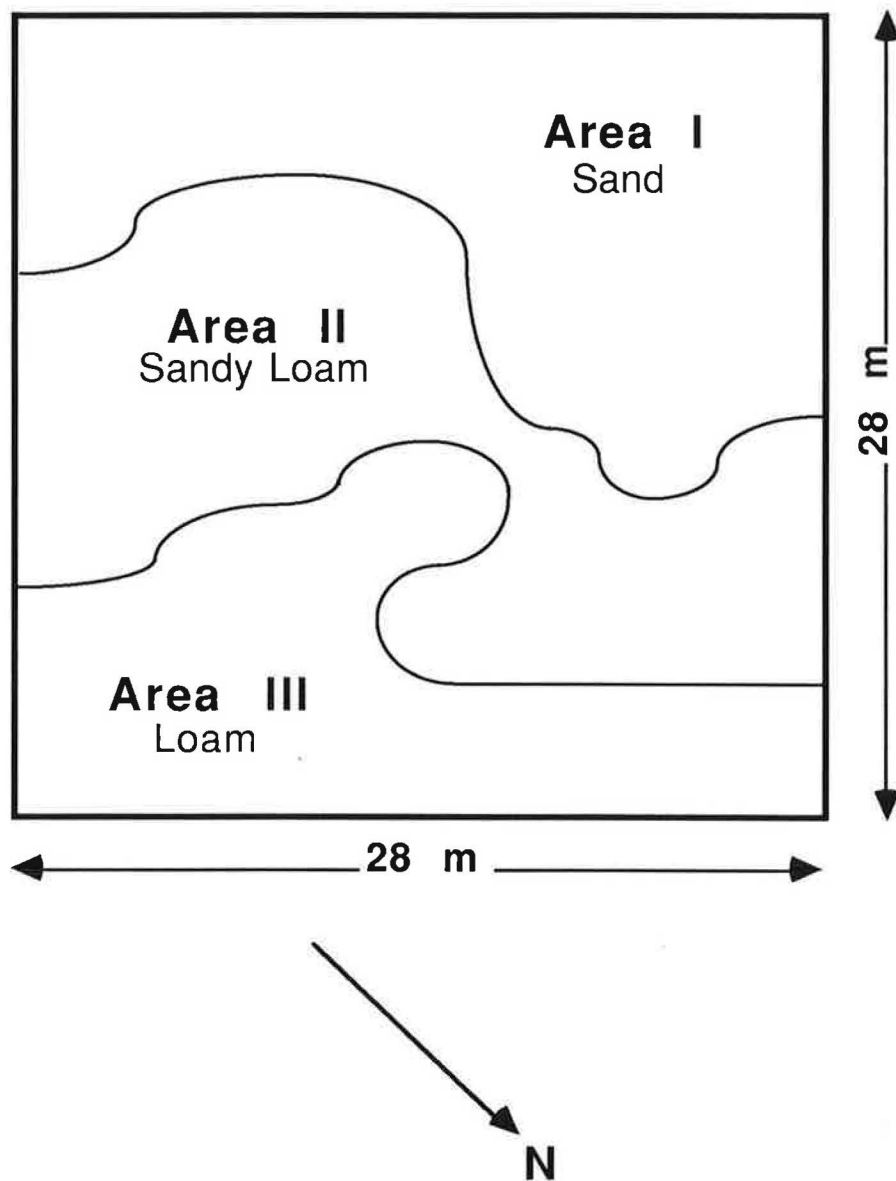
Klute, A. 1986. Water retention : laboratory methods. In A Klute (ed.) Methods of soil analysis, part 1. 2nd edition. Agronomy. 26:635-662.

Pye, V., and J. Kelly. 1984. The extent of groundwater contamination in the United States. In Groundwater contamination. National Academy Press, Washington, DC. pp. 23-44.

Fig. 2. Diagram of the experimental site outlining atrazine and bromide sampling locations one year after application.

× Atrazine Sampling Site
+ Bromide Sampling Site
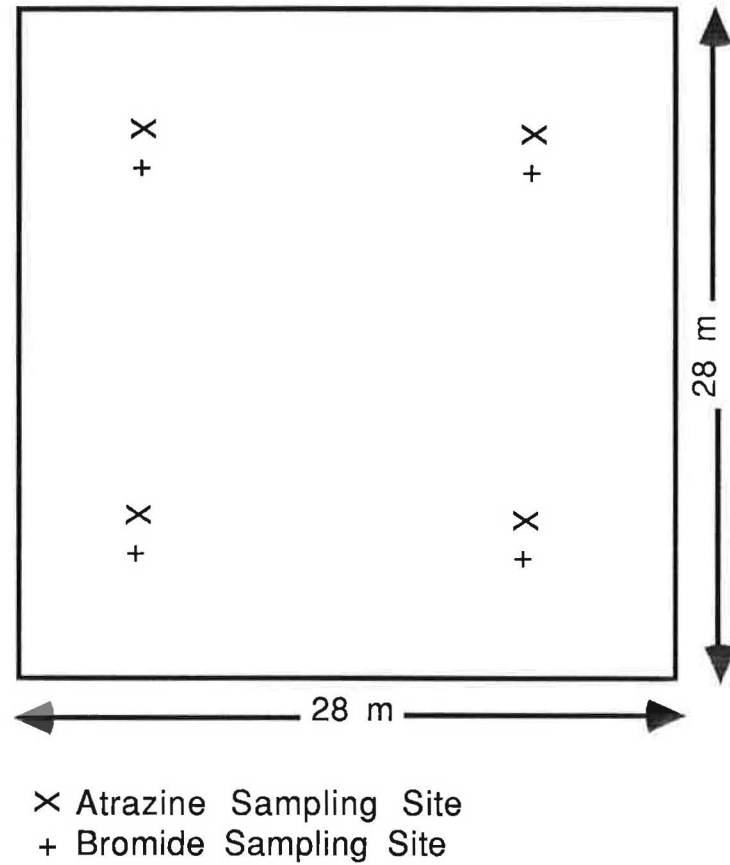
Fig. 3. Schematic diagram of the soil core sampling locations throughout the experimental site.
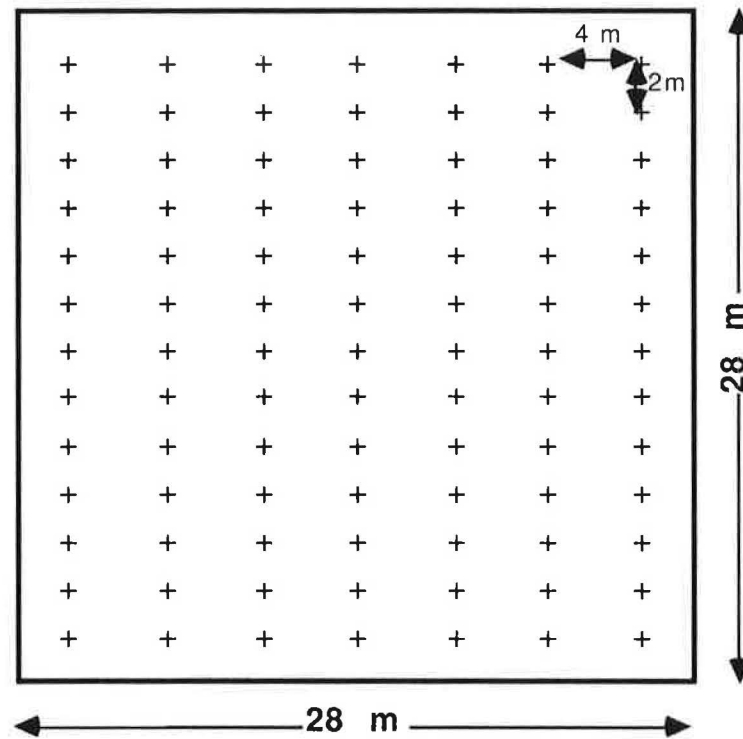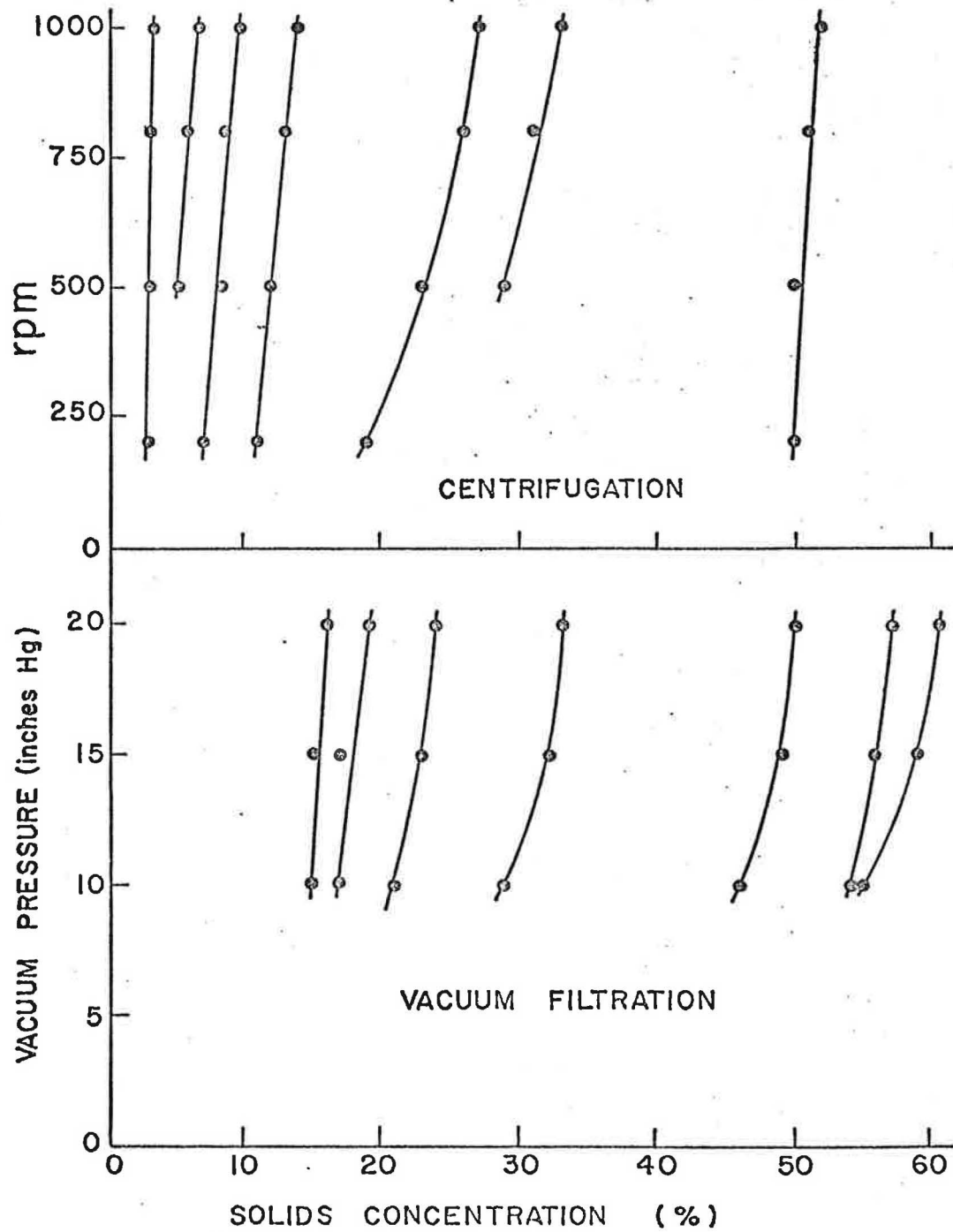
Figure 6. Variation in dewatered solids with applied pressure or centrifuge speed.

The physical properties of several of the sludges from this study were measured at variouw solids concentrations. Shear was determined using a Torvane Apparatus[1] and viscosity was measured with a Fisher-Mac-Michael[2] viscometer. The shear and viscosities were compared to the settled solids as shown in Figure 7 in a manner analogous to the dewatering plot of Figure 5 so that sludge physical properties could be compared to the solids concentration achieved by dewatering. Calkins (1973) has observed that a sludge becomes handleable in the shear range of 0.02 to 0.05 tons per square foot depending upon the specific dewatering method and sludge handling technique used. From the data shown in Figures 5 and 7 it appears that vacuum filtration will provide a handleable sludge while the non-filtering processes do not. Sand bed drying which combines filtering with evaporative drying requires a substantial amount of water loss following draining in order to achieve handleability.

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[1]Soiltest Inc., 2205 Lee Street, Evanston, Ill. 60202
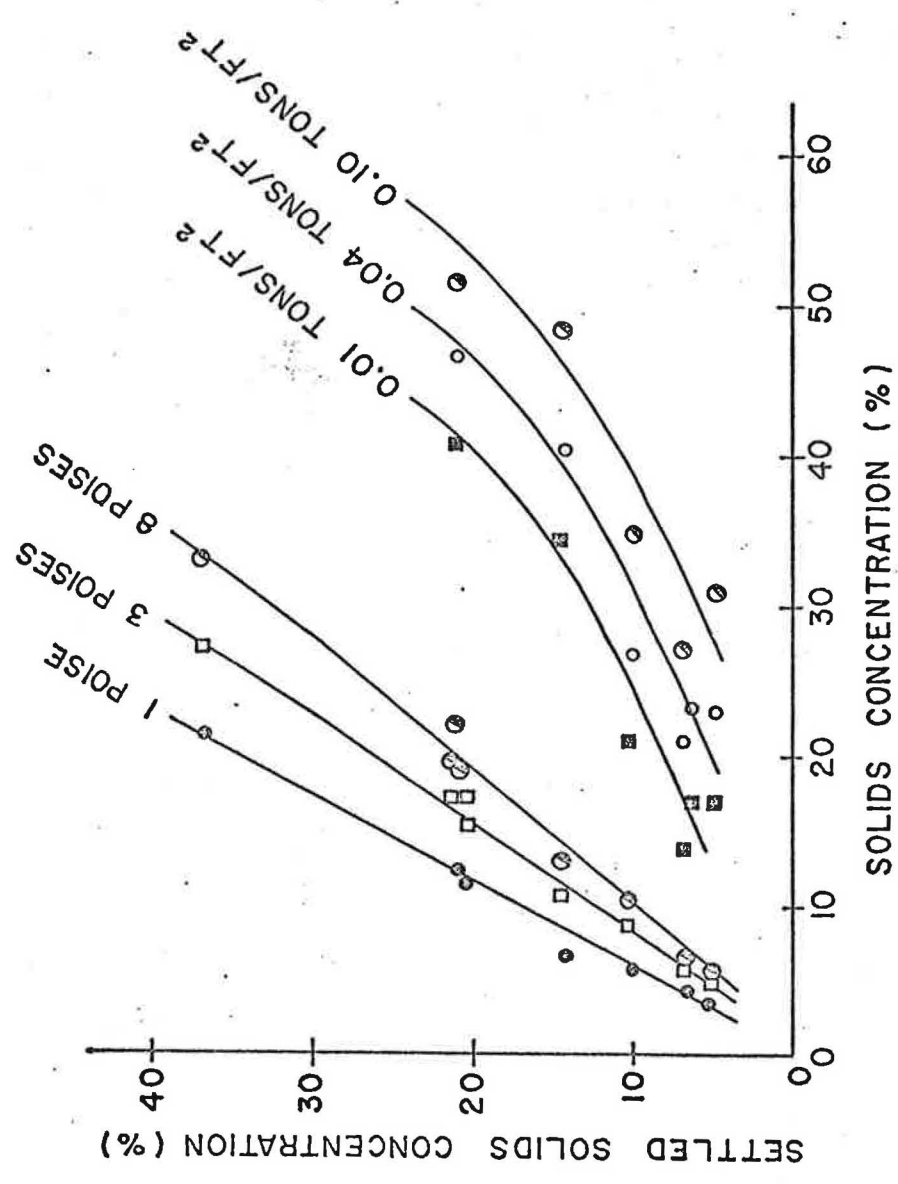[2]Fisher Scientific Company, 711 Forbes Avenue, Pittsburgh, Pa. 15219

Figure 7. Shear and viscosities of dewatered sludges.

Dewatering Rates and Process Yield

Sludge dewatering rates depend upon the rate which free water can be removed from the mass of solids. For filtering processes resistance to the passage of free water is provided by the force of friction of the filter cake, therefore the sludge specific resistance is a reasonable index of filtering rates for filter presses, sand beds and vacuum filters (Weber 1972; Eckenfelder 1970; Calkins 1973).

The process yield for vacuum filtration can be related to the concentration of the filter cake (c_f) and the specific resistance (r) as shown in Figure 8. Although not specifically tested in this study, it is reasonable to assume that a similar relationship would be observed for the filter press.

Sludge applied to sand beds has been found to drain at a rate dependent upon the applied sludge depth, the specific resistance and the solids concentration of the sludge. Data presented by Novak and Montgomery (1973) and plotted in Figure 9 demonstrate this more clearly. The drying rate of drained sludge is somewhat more difficult to quantify, since this depends upon many environmental factors. Preliminary data indicates that drying depends upon the drained solids concentration and the applied sludge depth as indicated in Figure 10. The design or sizing of sludge drying beds may be accomplished by selecting the appropriate draining time from Figure 9 and then estimating a drying time from data similar to that shown in Figure 10 for the geographic area where the beds are located.
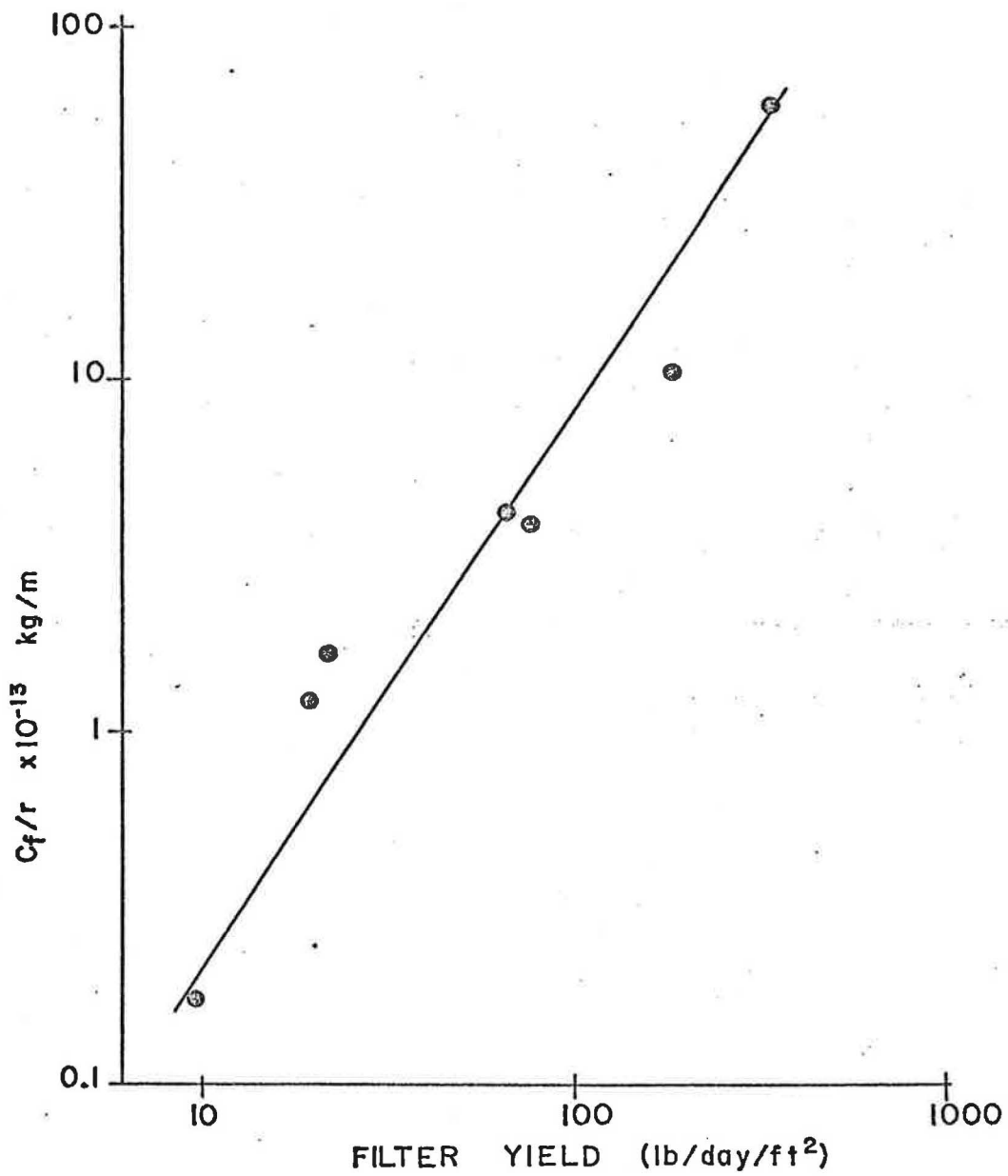
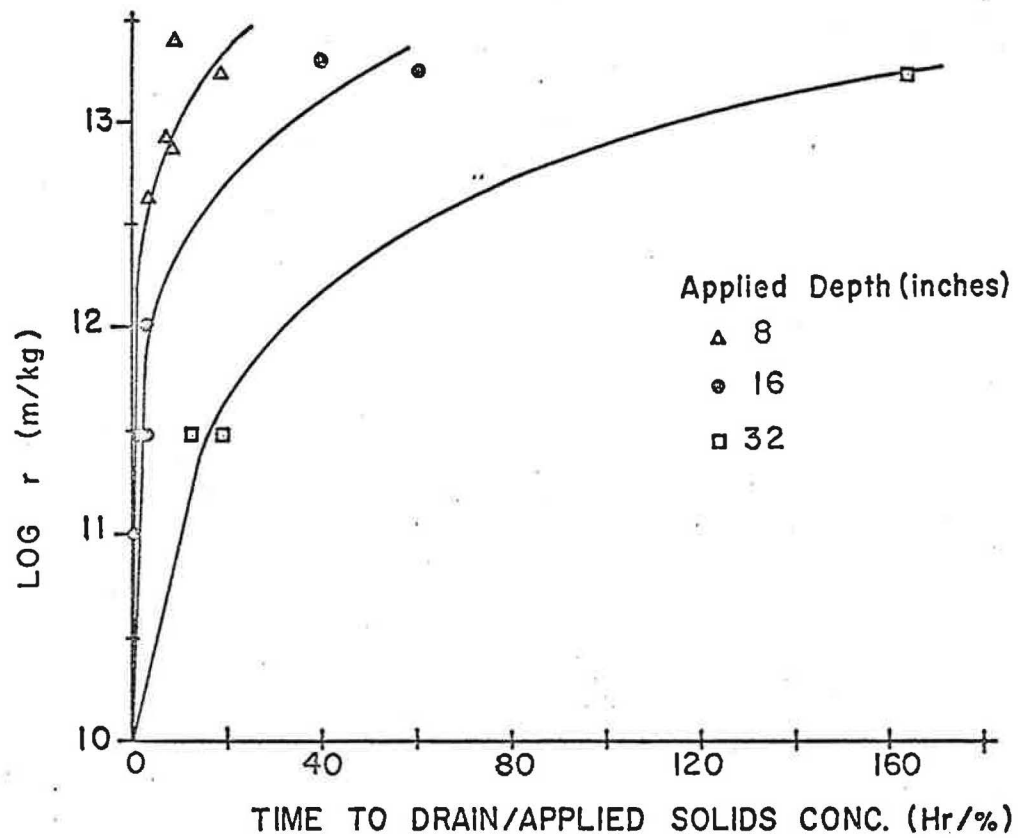Figure 8. Prediction of vacuum filter yield from Buchner funnel test.

Figure 9.   Effect of specific resistance on the time to drain a sludge
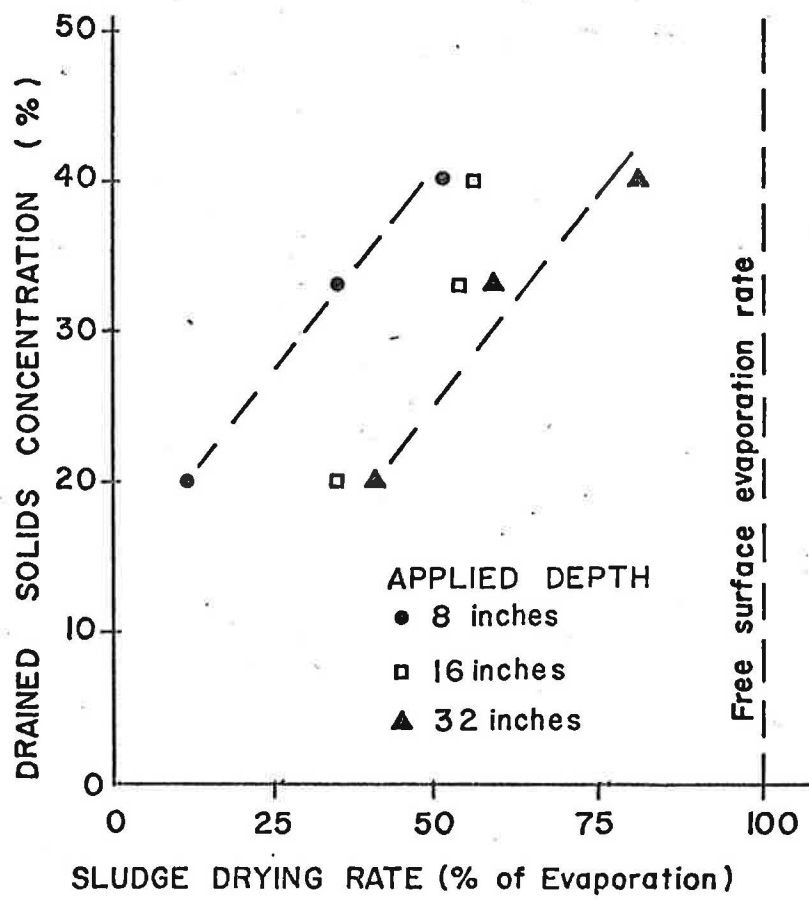applied to a sand bed.

Figure 10. Effect of drained solids concentration and applied depth on the sludge drying rate.

In processes where the sludge solids pass through the water the dewatering rate appears to depend upon the nature of the sludge particles and is unpredictable from conventional sludge characterization parameters but easily measured in the laboratory.

Sludges have been found to settle in a gravity thickener at a velocity dependent upon their solids concentration (Viesland 1968). Centrifuged solids respond in a similar manner as shown in Figure 11. From such data a flux curve can be generated as shown in Figure 12 and the required thickener or centrifuge capacity selected to provide a sludge of the desired underflow concentration. The slope of the ln v vs. c plot has been found to depend upon the solids concentration the sludge will achieve following dewatering as shown in Figure 13. Those sludges which attain a highly concentrated settled solids concentration thicken rapidly at a rate less dependent on the solids concentration than those sludges which attain a lower settled solids level. In Figure 14, the slopes for settling and centrifugation at 200 rpm taken from plots similar to Figure 11 for several sludges are plotted versus the ultimate solids achieved by each of the thickening methods. These data indicate that a simple laboratory analysis to determine a single velocity at a known concentration is sufficient to permit generation of a flux curve and subsequent design of the thickening unit. Selection of the desired sludge thickness will depend upon the maximum solids level attainable with some fraction of the maximum value usually being selected as the desired underflow concentration.

An empiric equation has been found useful for predicting the ultimate solids accumulation for the laboratory centrifuge used in this study. The ultimate solids may be related to the solids level obtainable by gravity settling and to the centrifuge speed in gravities as follows:

$$\text{Percent Solids Obtained by Centrifugation} = \text{Gravity Settled Solids Concentration} + \text{Gravity Settled Solids Concentration} \; (.0295)\sqrt{Z}$$
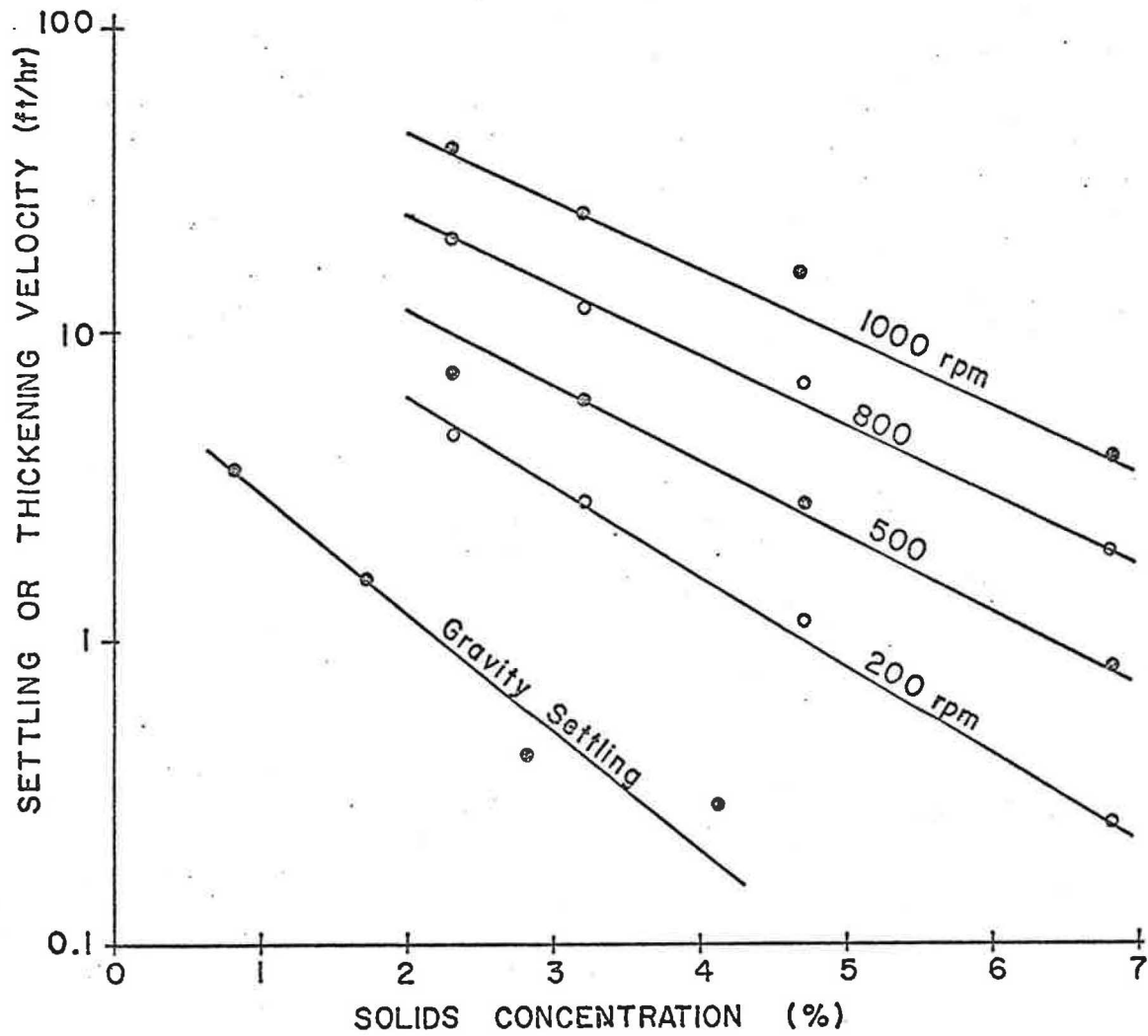
Figure 11. Interfacial settling velocity as a function of solids concentration for the gravity thickening and centrifugation processes.
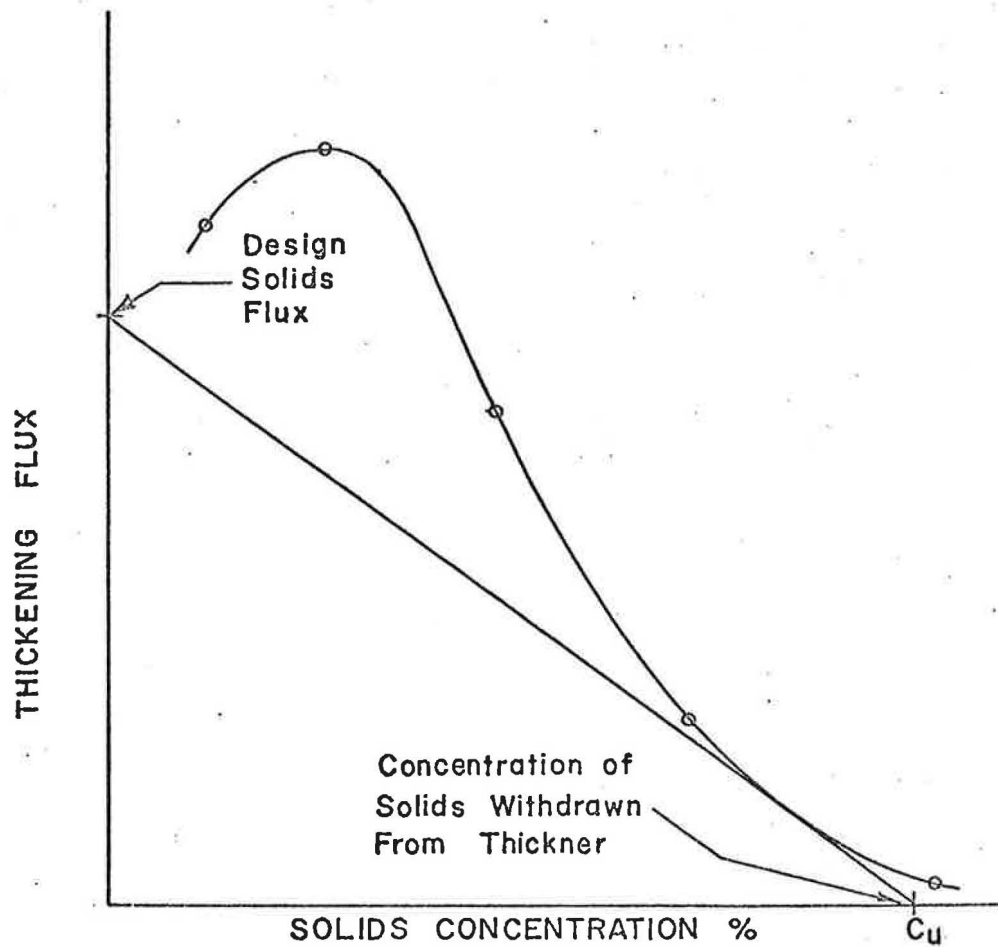
Figure 12. Idealized plot of thickening flux and solids concentration for gravity settling or centrigugation processes.