

**CONTAMINANT TRANSPORT AND
MASS TRANSFER TO RUNOFF
INCLUDING INFILTRATION**

by

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DEDICATION

Till pappa Friedhelm och mamma Aimée för deras stöd och förtroende i alla mina företaganden. Tack!!

Tre högst besynnerliga ord

Medan jag säger ordet Framtid
blir första stavelsen förfluten.

Medan jag säger ordet Tystnad
bryter jag den.

Medan jag säger ordet Ingenting
skapar jag nånting som inte ryms i något intet.

Wisława Szymborska

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ABSTRACT

Experiments were conducted in a flume (3.0 meter long, 0.3 meter wide by 0.3 meter deep) to examine chemical loss to surface runoff. The bottom of the flume was made of a perforated steel plate, which allowed infiltration to occur during the runoff event. Three experiments were conducted. The objective of the first experiment was to introduce a calcium chloride solution as surface flow into the flume which was pre-saturated with calcium bromide. This experiment allowed the transfer of chemicals from soil to runoff to be examined. The second experiment was the reverse of the first experiment, i.e. the soil was saturated with calcium chloride and the surface flow contained calcium bromide. This experiment was done to examine chemical transport from runoff to the soil. In the last experiment, the soil was saturated with a mixture of calcium bromide, sodium benzoate, and pentafluorobenzoic acid (PFBA), and the surface flow contained calcium chloride. The sodium benzoate was chosen to examine biodegradation. The PFBA and bromide, both non-reactive tracers, have different aqueous diffusion coefficients. The results obtained for these two were compared to help determine if the mass transfer in the soil mainly is due to flow, or if diffusion contributes. With this research it has been shown that there are several factors influencing chemical loss to runoff; infiltration, biodegradation, and there are also suggestions that there is transfer due to diffusion processes.

CHAPTER 1

INTRODUCTION

Surface-applied or soil-incorporated pesticides and nutrients are often transferred from soil to surface runoff during periods of heavy rainfall or surface irrigation. This transfer into runoff water decreases the efficiency of the applied chemicals, poses a threat for the environment, and results in an economic loss. Once released to runoff, chemicals may reach surface waters, and dissolved chemicals in ponds and lakes may reach the groundwater. As the use of pesticides, a major non-point source pollutant, increases, so does the potential for serious pollution events. To effectively control non-point chemical pollution sources, for example pesticides, the transport process must be better understood. In the United States, it has been stipulated by Federal Water Pollution control Act Amendments of 1972 (PL 92-500), that the Administrator of the U.S. Environmental Protection Agency (EPA) shall, in cooperation with State and other Federal agencies provide guidelines for control of non-point sources of pollution.

The rate of chemical loss to surface runoff depends on the concentration and type of chemicals applied to the soil phase, the amount and intensity of rainfall, soil properties such as soil type and degree of heterogeneity, infiltration into the soil, and human impacts on the soil. So, to understand the complexity of soil-runoff and chemical transport, several mechanisms and their interactions have to be understood. Reliable mathematical models must be available to predict the rate and amount of chemical transport to runoff.

So far, assessment of the runoff of chemicals used in irrigated fields is based on a limited number of studies, which do not always involve the whole complex system (Snyder et al. (1985), Parr et al. (1987), Schiegg et al. (1990)). This assessment is not an easy process. Soil is composed of solid, liquid, and gas phases and each phase contains organic and inorganic compounds of different amounts. Because soil is of inhomogeneous nature it is difficult to predict chemical transport. In addition, most studies do not account for the impact of infiltration on chemical transport.

There are several basic differences in the characteristics of runoff related to rainfall events versus irrigation events, and in the nature of the interaction with the soil zone underneath the moving water, as discussed by Bailey et al. (1974) and Wauchope et al. (1990).

1. During a rainfall event, runoff will not start before the applied rate exceeds the infiltration rate, i.e. a certain amount of water will infiltrate prior to the onset of runoff. In the case of surface irrigation, water is applied upstream of the field at a discharge rate such that the maximum infiltration rate is exceeded from time zero onward.
2. The mixing and desorption of chemicals in the soil water near the soil surface are accelerated by the kinetic energy of rainfall. During an irrigation process there is only a small amount of kinetic energy due to near-laminar flow.
3. Rainfall is applied simultaneously over the whole area, but surface irrigation progresses as a shock wave downstream on the soil surface. The first transfer process may be different (higher) than the steady state.

4. Surface irrigation can be controlled, but rainfall is distributed randomly over time.
5. In surface irrigation the slopes are small to moderate and relatively uniform. In a natural area, the soil surface is non-uniform, with concave and convex surfaces which causes significant areal and temporal variability in infiltration rates.

Specifically the study is to determine the effect that infiltration has on the transfer of chemicals across the soil-surface flow interface.

CHAPTER 2

LITERATURE REVIEW

One of the first conceptual models predicting pesticide runoff from agricultural land was developed by Bailey et al. (1974). The conceptual model includes (i) source term effects, i.e. pesticide formulations applied to soils can be of five different physical types: solutions, wettable powders, emulsions, dusts, and pellets; (ii) loss of pesticides from the surface zone between rainfall events, i.e. microbial activity, volatilization, organism uptake, chemical and photochemical degradation; (iii) loss of pesticide from soil surface during runoff, because of mass transfer from soil surface into moving runoff. In a state-of-the-art approach, they added their basic model to already existing hydrology and erosion models. The complex system of chemical loss to runoff was not completely appreciated by that time, and the mathematical model is not very advanced, but it is the first runoff model which does not lump all factors, influencing runoff, to one global factor. Following Bailey et al. (1974), more models have been produced to predict chemical transport to runoff.

The transport of chemicals over land is usually simplified by an idealized mass exchange process between the soil solution phase and the runoff (Figure 1), equation 1. It is often assumed that there is a fixed, thin mixing zone at the soil surface where rainwater mixes completely with the soil solution, and that the mixing is instantaneous.

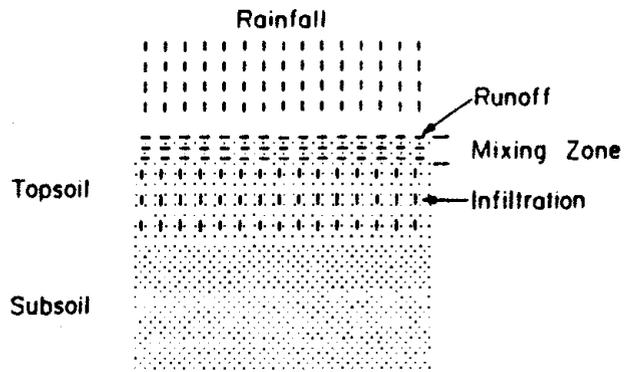


FIGURE 1: A schematic diagram illustrating the concept of a thin zone of complete mixing between rainwater and soil solution, Ahuja et al. (1983).

$$C = C_0 \exp\left[\frac{-R}{(EDI \cdot \theta)} t\right] \quad (1)$$

where

C_0 = the initial concentration

C = concentration of the chemical in the soil water

EDI = effective depth of interaction

R = rate of rainfall

t = time

θ = water content

Ahuja et al. (1983) conducted experiments for a better understanding of the extent and nature of the rainfall-soil interaction in the release of chemicals to runoff in the absence or presence of infiltration. The experiments were conducted in plexiglas boxes (100 cm long, 15 cm wide, and 10 cm deep, with a slope of 4%) with three different soil textures. The bottom of the boxes were either a solid plate, or a perforated plate which allowed free infiltration, or an intermediate infiltration rate which was achieved by covering the perforated plate with a slurry. The investigators suggested that under infiltration conditions chemical is transferred from the surface to an appreciable depth below the surface, which would reduce the concentration in the surface runoff. They found that the bromide concentration in runoff was highest when no infiltration occurred, and the concentration in runoff decreased rapidly as the infiltration rate increased (Figure 2).

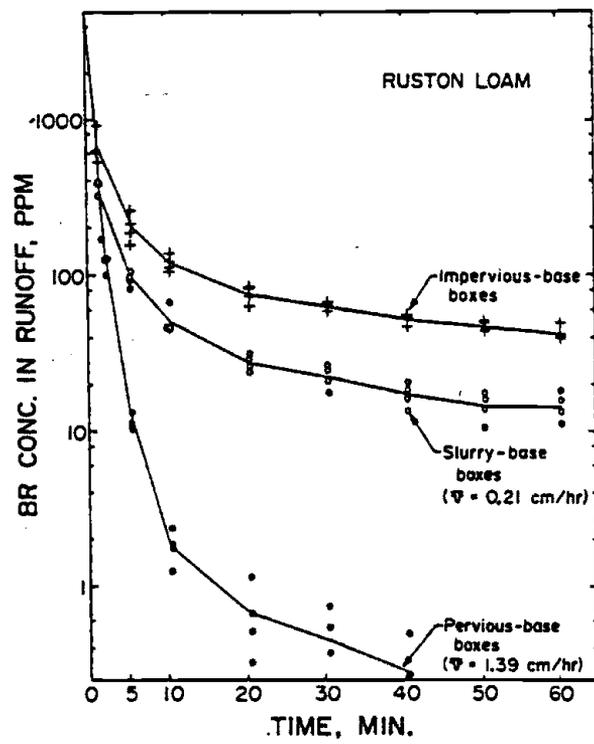


FIGURE 2: Bromide concentration in runoff at different times during rainfall in Ruston loam boxes with an impermeable base, a slurry base, or a pervious bas, Ahuja et al. (1983).

The study showed that chemical can be released to runoff from depths as great as 2 cm. They think that chemical from below the soil surface is brought to the surface by a pumping action associated with raindrop impact, or mixing caused by turbulence generated in soil water by raindrops. Ahuja and coworkers (1983) used a maximum depth of soil interaction with rainfall to be 2 cm. The adsorption-desorption process was represented by a proportional relationship:

$$C_s = \alpha * C \quad (2)$$

where

C_s = concentration of chemical in the adsorbed phase on soil particles (g g^{-1})

C = concentration in soil solution (g mL^{-1})

α = constant

The 2 cm depth of mixing was divided into 20 increments, each increment with a depth of 1 mm. The initial soil water content, bulk density, initial concentration of chemical in solution and adsorbed phases, and a value of α are assumed known for each 1 mm depth interval. Also assumed known are the rainfall rate, runoff initiation time, and runoff rates. The first increment is assumed to raise the water content of the first depth interval to saturate the soil. The second increment mixes with the solution and soil in the first depth interval, and then an equivalent amount moves downward to saturate and mix with the second depth interval, and so on. It was also assumed that the mixing between rainfall and soil solution decreases

exponentially with soil depth. This model provides a calculation of the concentration of chemical in the runoff, and it assumes that the rest of the chemical is infiltrated into the soil. The assumption that the mixing between rainfall and soil solution decreases exponentially may not always be true. But using another function may require additional unknown parameters which might give a more inaccurate result. The model does not take into account that the effective depth interaction, EDI, (the degree of mixing is uniform and equal to the degree of mixing at the soil surface) increases with time during a rainstorm.

In a study by Snyder et al. (1985), experiments were conducted in a tilted plexiglas flume (200 cm long, 10 cm wide, and 30 cm deep) to study the transfer of dye from a saturated sand to runoff with and without infiltration. The investigators used simulated rainfall to generate surface runoff, as Ahuja et al. (1983) did. Ottawa sand was used, due to its light color (easy to see the dye movement), and its extremely high hydraulic conductivity, which seemed to increase the degree of interaction (mixing) with depth. Without infiltration the dye concentration profiles were convexed upward (Figure 3), which is similar to observations reported by Ahuja et al. (1983) for bromide concentration in runoff with no infiltration (Figure 4).

The mixing effect of raindrops and the effects of convective dispersion induced by infiltration causes a dye profile with a "S" shape when infiltration over the full soil length is included. This profile suggests a convective dispersion model with an increasing dispersion

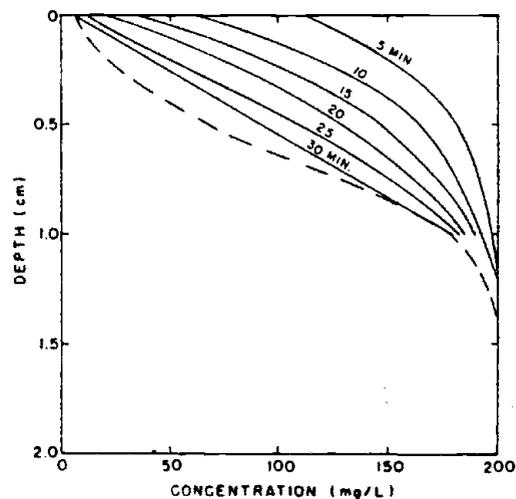


FIGURE 3: Average concentration profiles (slope=0, infiltration rate=0), Snyder et al. (1985).

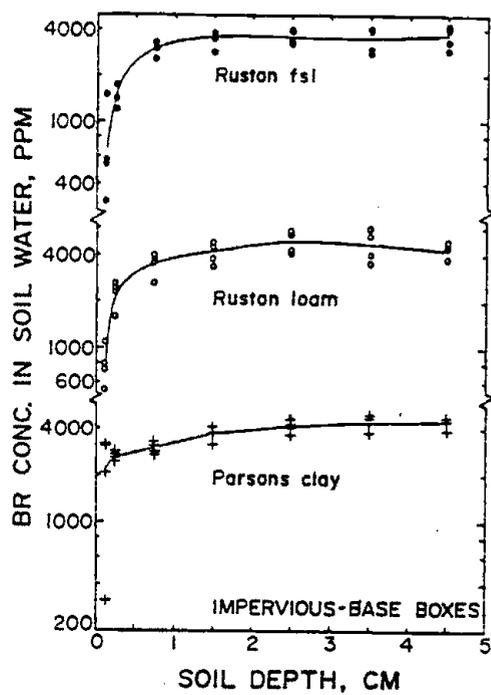


FIGURE 4: Bromide concentration in soil water with depth in soil boxes of the three soils with impervious bases at the end of 1 hour rainfall, Ahuja et al. (1983).

coefficient near the surface. Such a model could be used to describe the detailed movement of chemicals within the mixing zone, as was also suggested by Ahuja et al. (1983).

Ahuja (1986) reviewed the existing models to determine chemical transport to runoff, and the effects of infiltration on chemical movement into surface runoff. He came to the conclusion that the models developed in the past were not quite satisfactory. This is primarily due to the inability to accurately define the depth and degree of rainfall-soil interaction, adsorption-desorption relationships for chemicals, and subsurface pathways of water flow. A nonuniform mixing model, which includes a variable degree of mixing with depth, infiltration rate effects, and a proportional relationship for desorption, was suggested. It is assumed that the degree of mixing between rainfall and soil solution, β , decreases exponentially with soil depth, as Ahuja et al. (1983):

$$\beta = \exp(-Bz) \quad (3)$$

where

B = constant

z = soil depth

Only at the soil surface, where $z = 0$, and β is equal to 1.0, do we get complete mixing between rainwater and soil water. The value of B is determined by calibration, and an average β value is calculated for each increment (2 cm depth of mixing, each increment with a depth of 1 mm, Ahuja et al. (1983)). The change in concentration of the chemical in any depth interval, i , is calculated by the mass balance equation for a unit area:

$$C_i^1 * (\theta_i + \epsilon S_i) = C_i^2 * (\theta_i + \epsilon S_i + \beta_i R \Delta t) \quad (4)$$

where

C_i^1 = the concentration of chemical in solution in depth interval i before mixing with an $R\Delta t$ increment of rainfall (R is rainfall rate and Δt is a small time step).

C_i^2 = the concentration after mixing

θ_i = amount of water in the depth interval

S_i = the mass of soil in the depth interval

β_i = degree of mixing

ϵ = constant

After mixing with all the depth intervals, the concentration of chemical in $R\Delta t$ amount of rainwater, C_r^2 :

$$C_r^2 = \sum_{i=1}^{20} (\beta_i C_i^2) \quad (5)$$

A known value of water with concentration C_r^2 becomes runoff at this time, while the rest infiltrates into the soil.

In 1987 Parr et al. (1987) conducted experiments in a flume (8 ft long, 6 inch wide, and 4 inch deep) to look at pore water chemical uptake by runoff. Water was supplied to the flume in a once-through mode from a constant-head tank to a saturated soil bed. Runoff water was sampled at the downstream end of the flume, and at sand depths of 0.5, 1.0, and 2.0

inches, for bromide concentration. The transfer of pore water chemical to the surface runoff was described as a Fickian diffusion process. The Fickian diffusion approach concentrates on the interaction of the flowing runoff water with the soil surface, like irrigation water, but it does not include rainfall impact, or rainfall induced runoff. The experiments did not include infiltration.

Wallach et al. (1988a) were the first to look at the two ways to induce runoff over a field: rainfall and lateral irrigation. Their paper compared these two mechanisms, using mathematical modeling. They did not use any experimental data in their study and infiltration was neglected.

In a second paper by Wallach et al. (1988b), a physically based diffusion and transport model was developed, which described the movement from the soil to the runoff water as a liquid diffusion process, coupled to the runoff zone through a laminar boundary layer at the runoff interface with the soil surface. In order to model chemical transport, the runoff water zone and the soil water zone are treated as well-stirred reactors, through which water is flowing at a steady rate. The mass transfer coefficient depends on rainfall intensity, soil surface slope, length and roughness, runoff flow, and chemical characteristics, and can be calculated without calibration. The model was used to simulate the reported data by Ahuja et al. (1983), although only the data for suppressed infiltration was used. The major limitation of the model of Wallach et al. (1988b) was its neglect of convective transport with infiltrating water. In a later paper by Wallach et al. (1990) a more comprehensive model considers the effects of infiltration. As can be seen in Figure 5, there is a relatively low or zero

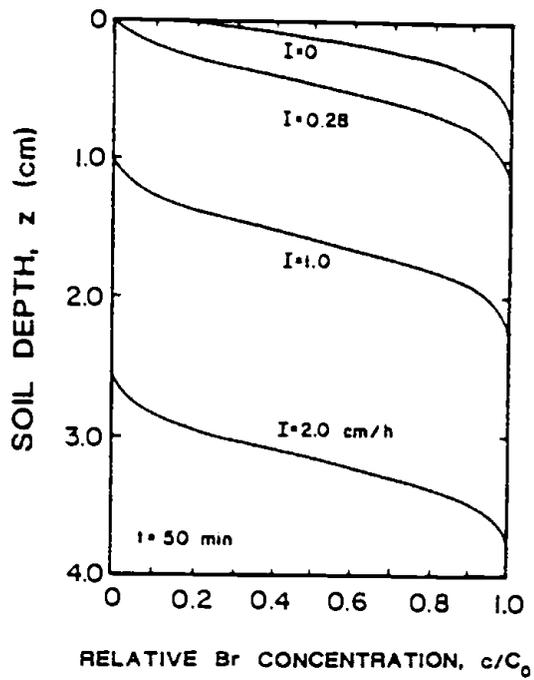


FIGURE 5: Calculated bromide concentrations in soil versus depth after 50 minutes of rainfall and for different infiltration rates, I , Wallach et al. (1990).

concentration near the soil surface, this suggests little or no transfer of chemicals from soil to runoff water for infiltration rates greater than about 0.3 cm/h. This observation is in marked contrast to the measured results of Ahuja et al. (1983). The analytical model discussed in Ahuja's paper assumes that the infiltration rate and the soil water content remain constant during the infiltration-runoff event. This assumption is not appropriate for most field situations, where the water content and the soil water flux is variable throughout the field.

To obtain a more physically based model and extend the theory of their previous (1988b) model, four physical processes were isolated by Wallach et al. (1989): chemical kinetics within the mass transfer from the soil surface to runoff; dissolved chemical transport to the soil surface; mass transfer from the soil surface to runoff; and the dynamics of runoff flow over the surface. Wallach et al. (1989) suggested that the soil chemical loss to surface runoff can be expressed as:

$$\text{output} = f(\text{input}, \text{chemical kinetics}, \text{mass transport}, \text{mass transfer}, \text{flow pattern})$$

where output represents the chemical concentration distribution with time at the field outlet and input stands for chemicals that are added to the system through applied water. Calculations were made by using equilibrium and rate-limited models, and it was found that the main difference between the two models occurred during early runoff, when the equilibrium model predicted greater loss of chemical to runoff. The local flux of chemical (N) to the surface runoff water moving above a fixed region of soil will depend on the diffusivity (D), the concentration difference (ΔC) between the soil solution and the runoff, the kinetic

energy (E) of the rainfall, as well as the hydraulic radius (R), the mean velocity (u_m), the density (ρ), and viscosity (μ) of the fluid. Symbolically:

$$N=f(\Delta C,D,E,R,u_m,\rho,\mu) \quad (6)$$

The suggested model ignores convective transport with infiltration, which affects chemical runoff.

Ahuja (1990) modeled soluble chemical transfer to runoff with rainfall impact as a diffusion process. Both ordinary and accelerated diffusion equations were used on the experimental data from Ahuja et al. (1983) for bromide transfer to runoff, both without and with infiltration. A general diffusion-type equation, involving either ordinary or accelerated diffusion during transfer of a nonadsorbed soluble chemical from a saturated soil to the surface under steady rainfall and water flow conditions was developed. It was assumed that the accelerated diffusion factor was uniform at all depths, and that its value was a certain constant factor times the ordinary diffusion factor. The ordinary diffusion factor was assumed to depend only on molecular diffusion. He concluded that when the concentration gradients are high, molecular diffusion can have a significant impact. The results showed that the chemical concentration in runoff increases with an increase in accelerated diffusion. It was also found that the chemical transfer to runoff increases with an increase in rainfall kinetic energy, as was also shown by Ingram et al. (1980).

Two mass balance equations were combined by Wallach (1991) to model the transfer of dissolved chemicals from soil solution to runoff. One mass balance equation was for the chemicals dissolved in the overland water, and the other for chemicals within the soil profile.

These two equations involve two time scales: the slow time scale, which represents diffusion-based mass transfer and the fast time scale, which represents convective transport. It was suggested that the amount of chemical concentration in the outflow over the field is mainly driven by the chemical transfer through the soil surface. By ignoring rate-limited transfer by assuming instantaneous equilibrium between chemical concentration in the soil solution and the surface runoff, the dual time-scale approach can explain theoretically why errors occur when using an equilibrium assumption to determine surface runoff flow concentration. Wallach (1991) did not attempt to use his model on experimental data. Wallach et al. (1992) modeled surface contamination under transient flow, they did not use their model on experimental data.

Shahnaz (1996) conducted experiments in a flume (10 ft long, 1 ft wide, and 1 ft deep) with silica sand to verify the process of chemical loss in surface runoff during surface irrigation. The purpose of Shahnaz's (1996) experiments was to generate a database of measured data for the modeling of chemical loss to runoff. The experiments did not include infiltration.

Justification and Purpose

It can be concluded from the reviewed literature that the complex system of chemical loss to surface runoff is still not completely understood. The most important problem seems to be to develop a model that can describe measured data. So far several experiments have been conducted (Ahuja et al.(1983), Snyder et al.(1985), Parr et al.(1987), Schiegg (1990)), but only the data reported by Ahuja et al. (1983) has been extensively used in modeling. Only in

the experimental setup by Ahuja et al. (1983) was runoff concentration measured within the flume. They also studied the effect of infiltration on this concentration.

There is a deficiency of experimental data for chemical loss to surface runoff with infiltration, although infiltration is frequently incorporated in conceptual models. Therefore, the goal with this research is to produce a data set that can be used for model development and verification. Solute concentrations will be measured at the flume end, in the surface water, along the longitudinal axis of the flume and at three points vertically for each horizontal location, and for the water leaching from the soil.

CHAPTER 3

MATERIALS AND METHODS

Flume Design

The sand was packed in the flume, 10 ft long, 1 ft wide, and 1 ft deep (3.0*0.3*0.3 meter). The flume is constructed of two plexiglas walls (3.0*0.3 meter). Four iron steel sections (5.1*5.1 centimeter) and 3.0 meter of length support the base plate of the flume. The bottom part of the flume is made of a plexiglas plate (3.0*0.3 meter). One centimeter up from the plexiglas bottom is a perforated steel plate inserted in the plexiglas walls. Between the plexiglas bottom and the perforated steel plate are seven (0.3* 0.3 meter) vacuum chambers. These chambers prevent the drainage from mixing along the 2.1 meter long soil bed. See Figure 6 and Figure 7 for drawings of the flume, and Figure 8 for a photo of the flume. Each chamber has a port, which makes it easy to collect the drainage. A nylon cloth was placed over the perforated steel plate to prevent sand from falling through and mixing with the drainage, Shahnaz (1996) and Wierenga et al. (1989).

On each end of the flume is a reservoir. A water tank (900 liter) was connected to the bottom of the upstream reservoir and a pump pushes water through a valve that was calibrated to control the flow rate before the water reached the sand. As the reservoir overflows, a surface flow is achieved and the infiltration and the runoff flow will start. The reservoir down stream collects the runoff water, which gets sampled and than discharged. The reservoirs are supported with wooden frames (Figure 9).

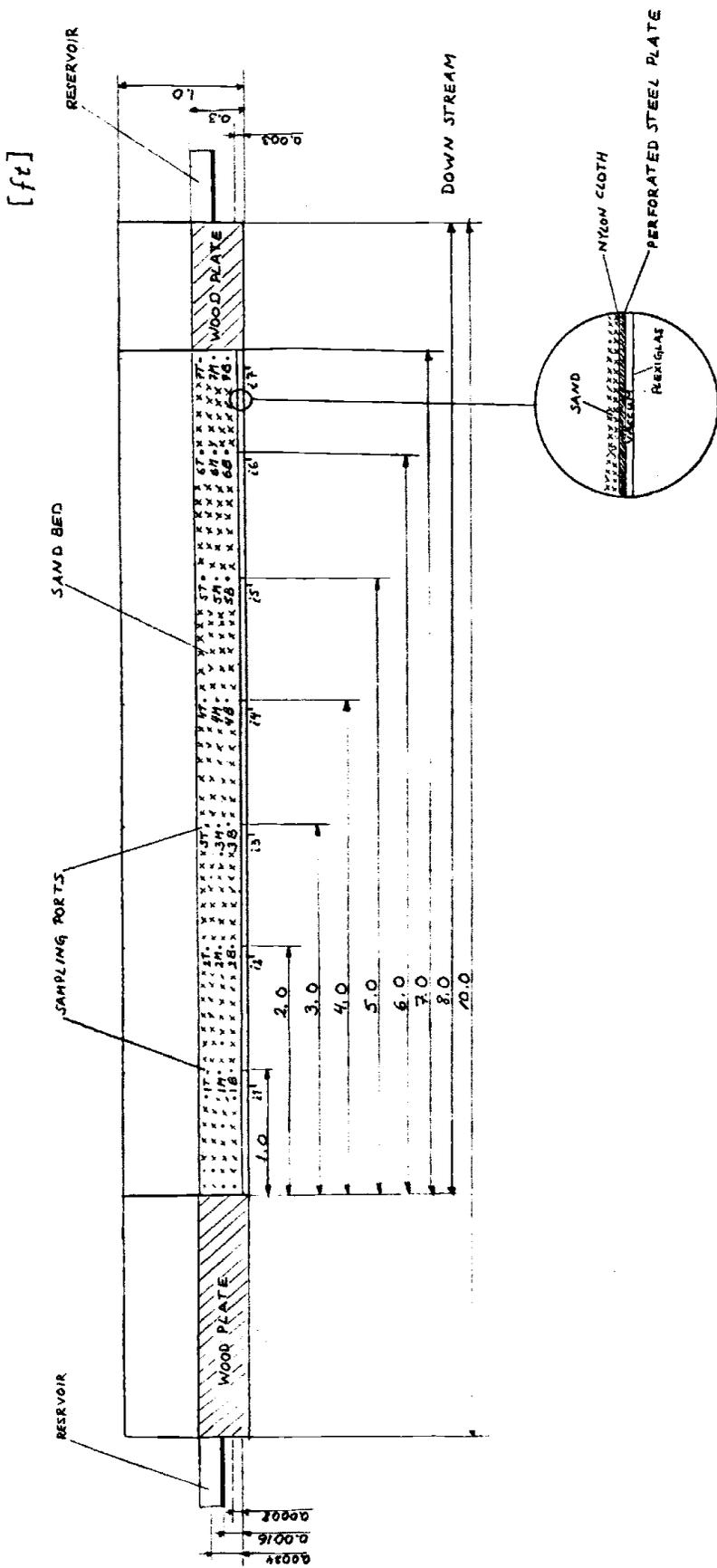


FIGURE 6: Side view of flume showing location and numbering of sampling points. (Flume is supported by an iron steel frame, not shown on this drawing). Dimensions in feet.

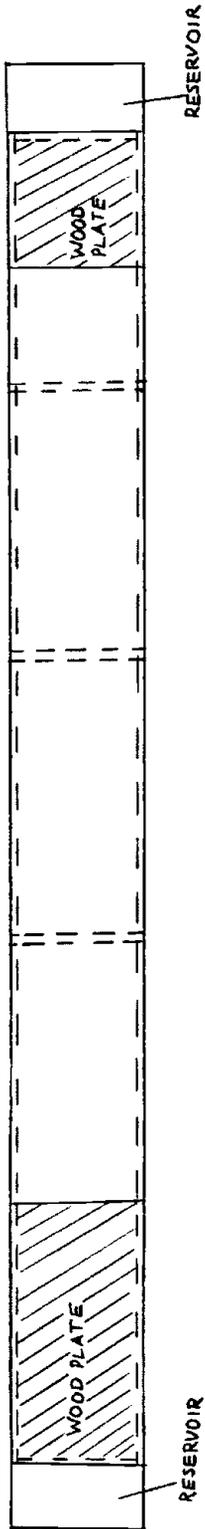


FIGURE 7: Top view of flume, including iron steel frame.

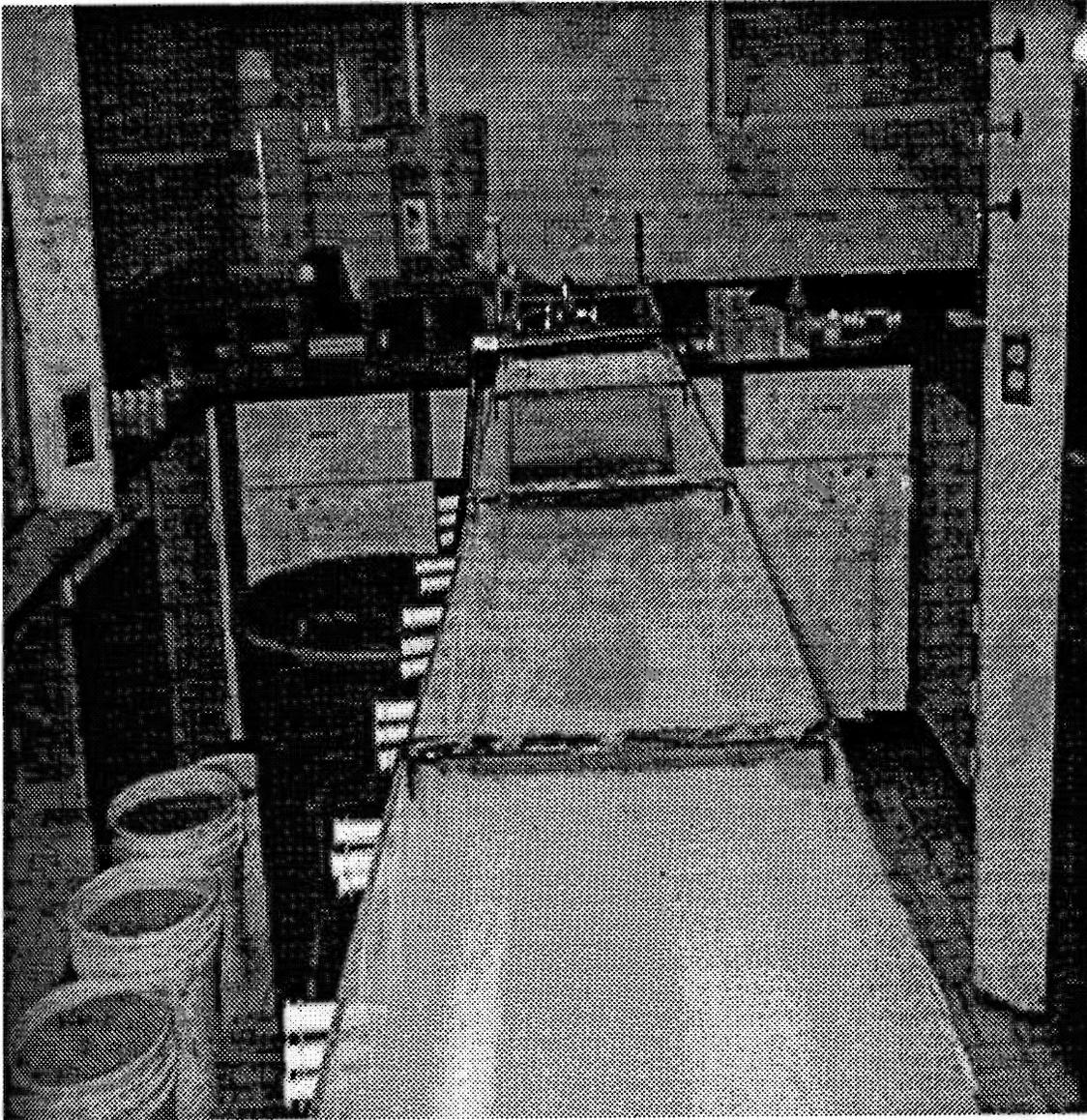


FIGURE 8: Flume photo, top view.

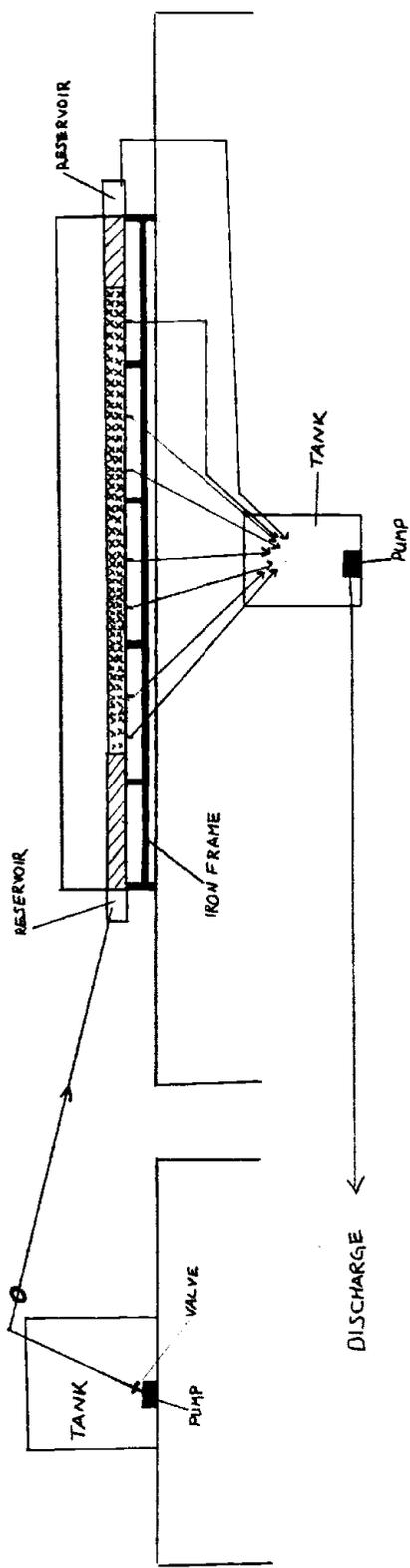


FIGURE 9: Schematic of the experimental setup.

To avoid erosion of the soil bed and to stabilize the surface flow two wooden plates with a thin impermeable layer of silica sand are placed at each end of the flume. The upstream board is longer (0.6*0.3 meter) than the down stream board (0.3 *0.3 meter).

Porous Media Properties

The porous medium used was an unconsolidated silica sand. Silica sand is used to prevent sorption interaction with the tracer. The sand used in the experiments 2 and 3 had a neutral pH and barely measurable organic carbon content. Vinton sand was used for experiment 4; soil properties for both soils used are listed in Appendix 1.

The sand was well mixed and air dried before use. The sand was manually placed in the box with negligible free fall. The soil within the box was packed in increments of 3 cm thickness. After each increment the soil was slowly saturated with water to prevent preferential flow, air pockets and to get better compaction.

Tracers

Bromide

Bromide, introduced as a solution, is not a reactive ion with soil, in the concentrations used. It is used in this investigation as a non-reactive tracer, which means that it is not retarded in the soil system.

Sodium Benzoate ($C_7H_5NaO_2$)

Sodium benzoate was introduced as a solution which is biodegradable. While the reaction involved in the biodegradation is usually aerobic if dissolved oxygen is present which means that the microorganisms need oxygen to degrade, the reaction can also be anaerobic which means that oxygen does not have to be present for degradation. Sodium benzoate is used as a preservative in pharmaceuticals and in food products. It is used in this investigation as a biodegradable tracer, which many of the surface runoff chemicals are.

Pentafluorobenzoic Acid, PFBA ($C_7F_5O_2H$)

PFBA is a larger molecule than Br^- , with a molecular weight of 212 g/mol and a smaller diffusion coefficient. The results obtained with this tracer are compared to the results with $CaBr_2$. If the concentration vs. time curves look similar, this indicates that transport in the soil is mainly due to flow. Conversely, if they exhibit differences, this indicates that diffusion influenced transport, Jury et al. (1991), Brusseau (1993), Hu et al. (1993).

Sampling

Along the 2.1 meter soil bed samples were taken in the vertical and longitudinal (X-Y) direction, from a set of 14 centimeter stainless steel tubes, 12 gauge, in a 7*3 array on the plexiglas walls of the flume. The X-direction (longitudinal) spacings between the tubes are 0.3 meters, and the Y-direction (vertical) spacing is 2.0 centimeters. On the bottom of the box there are seven ports for collecting leachate. One for each 30.0 centimeter vacuum chamber, which corresponds to the sampling points on the side wall of the flume (Figure 6).

The samples from the side wall are taken with syringes attached to 15 gauge needles. The sampling was done manually, and does not disturb the porous soil bed. The 15 gauge needles are inserted in the 12 gauge fixed stainless steel tubes and the pore water sample is drawn.

Samples are also taken from the runoff water (discharge) and from the surface water. At each sampling time 38 samples were taken for experiment 2 and 3, and 24 samples for experiment 4.

A few milliliters of sample were collected to avoid disruption of the flow in the porous bed. The samples were stored in 20 ml plastic vials and analyzed for the bromide concentration with a bromide-electrode and a HPLC was used for analyzing of sodium benzoate and pentafluorobenzoic acid concentrations.

Sample Analysis

Bromide Analysis

A Cole-Parmer[®] Bromide Electrode was used to analyze the samples for bromide concentration. The electrode consisted of a sensing membrane bonded into a glass body. The membrane is composed of silver bromide/silver sulfide. When an electrode potential develops across the membrane, the electrode is in contact with samples containing bromide ions and is capable of measuring free bromide ions. This electrode potential is measured against a constant reference potential, using a standard pH/mV meter.

To adjust the background ionic strength to a high and constant value, NaNO_3 was added to the samples and standards, this makes the readings more sensitive.

A 0.1 M (1000 mg/l) bromide standard solution was prepared from KBr. This solution was serially diluted and plotted with the mV reading (linear axis) against the concentration (log axis). The calibration curve was redone every hour and each calibration curve had a r^2 greater than 0.988, which indicates that the range of standard samples had a good regression line. The upper limit of detection in pure sodium bromide solution is 1 M, and the lower limit of detection is 10^{-4} M Br⁻.

Sodium benzoate and Pentafluorobenzoic Acid Analysis

A high pressure liquid chromatograph was used to analyze sodium benzoate and PFBA. The column used was an adsorbosphere US C18 5U, 150 mm by 4.6 mm, with a wavelength of 253 nm. Solvent A was acetonitrile and solvent B a phosphate buffer with pH 3.6. 40% of solvent A and 60% of solvent B was injected with a flow rate of 1 ml/min. The retention time for PFBA was about 1.76 minutes and for sodium benzoate 3.60 minutes. As tap water was used for flushing the box and to saturate the box, the tap water peaked at a retention time of 1.23 minutes. The samples were divided into high, medium and low concentrations. The injection volumes for the high concentrations were $20\mu\text{L}$, for the medium $35\mu\text{L}$, and for the low $50\mu\text{L}$.

Standards were run between each 20 set of samples, and calibration curves were constructed between the peak area and the concentration, r^2 was greater than 0.998 for all calibration curves.

Methods Overview

The following table lists the experiments performed in the current investigation:

TABLE 1: Table of Experiments Performed.

Experiment Number	Description of the Experiment
1.	The soil bed was saturated with tap water and tap water was introduced as a surface flow.
2.	The soil bed was saturated with 200 mg/l CaBr ₂ solution and 200 mg/l CaCl ₂ solution was introduced as surface flow.
3.	The soil bed was saturated with 200 mg/l CaCl ₂ solution and 200 mg/l CaBr ₂ solution was introduced as surface flow.
4.	The soil bed was saturated with a mixture of 400 mg/l sodium benzoate, 100 mg/l pentafluorobenzoic acid and 200 mg/l CaBr ₂ solution, and 300 mg/l of CaCl ₂ solution was introduced as surface flow.

Experiment 1

The objective of the first experiment was to introduce tap water as a surface flow to the pre-saturated soil bed also containing tap water. This first preliminary experiment was done to demonstrate the viability of the flume system. An inlet flow of 3.0 liter/min (19.4 cm/h) was needed to achieve runoff of 1.30 liter/min (8.38 cm/h) and a leach of 0.455 liter/min (2.93 cm/h). The measured flow rate was converted to velocity by dividing the flow rate by the total surface area of the flume.

Experiment 2

The soil bed was saturated by slowly applying a 200 mg/l solution of CaBr_2 (Figure 10) . A drip application tube was extended over the soil bed's width (0.3 m). The wetting was started upstream of the flume, and as the wetting front advanced downstream about 30 cm (which was measured visually through the plexiglas walls) the trickling application was moved 15 cm downstream, and so on until the entire soil bed was saturated. Some solution drained out, due to the free infiltration. The saturated soil (except for entrapped air) was allowed to equilibrate for one day to ensure uniformity in the distribution of chemical into the soil water. Ahuja et al. (1983) indicated that the above method of wetting the flume gave a uniform distribution of water and bromide content of soil with depth. The 200 mg/l concentration of bromide was chosen to achieve a good signal with the bromide electrode.

After equilibrium was reached, 200 mg/l CaCl_2 solution (as Cl^-) was introduced as a surface flow. The box was leveled, i.e. there was no slope to the sand surface. The CaCl_2 solution was used to minimize the density effects which occur by use of bromide as a non-reactive tracer. The runoff flow was 1.30 liter/min (8.38 cm/h) with a inlet flow of 3.0 liter/min (19.4 cm/h), and the infiltration rate was 0.455 liter/min (2.93 cm/h).

Samples were collected at 5, 10, 20, 40, 60 and 90 minutes after the surface flow started. This time sequence was chosen to see a clear difference of bromide concentration with time, and still have a good signal with the bromide electrode, i.e. not too low bromide concentration. After 90 minutes soil was taken from the top of the box at 5 different locations evenly distributed, these samples were analyzed for moisture content. The average oven dried

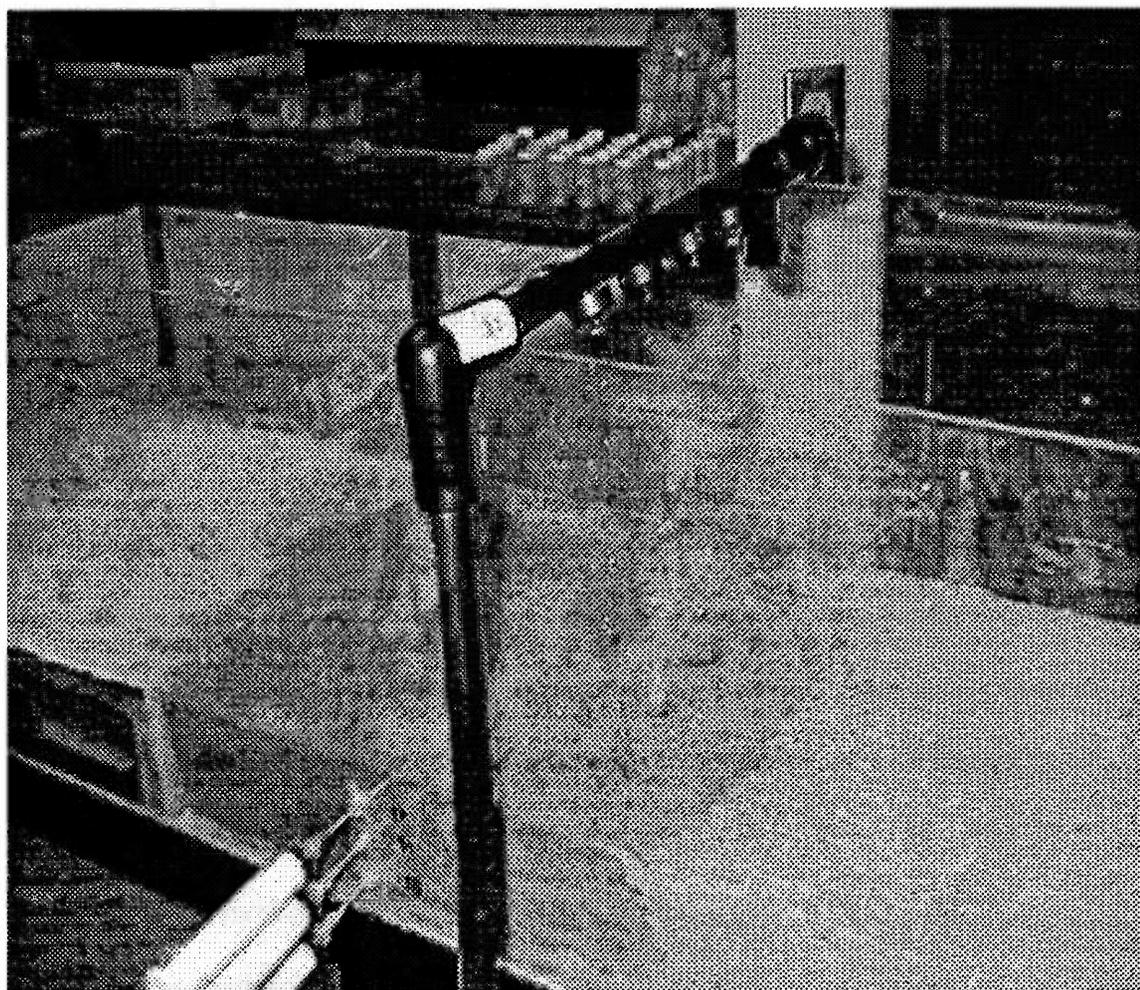


FIGURE 10: Drip application.

sample size and standard deviation were 5.97 ± 1.3 g and the average moisture content and standard deviation were $5.29 \pm 0.27\%$.

Experiment 3

The third experiment was similar to the second experiment. However, instead of saturating the porous medium with CaBr_2 , the drip application tube applied a 200 mg/l CaCl_2 solution. The wetting was achieved the same way as in experiment 2, and the soil was allowed to reach equilibrium for one day. 200 mg/l CaBr_2 solution was then introduced as a surface flow, with a inlet flow of 3.0 liter/min (19.4 cm/h), runoff flow of 1.30 liter/min (8.38 cm/h), and a infiltration rate of 0.455 liter/min (2.93 cm/h).

The samples were collected and analyzed the same way and at the same times as in experiment 2. The average oven dried sample size and standard deviation were 5.57 ± 0.84 g and the average moisture content and standard deviation were $6.00 \pm 1.13\%$.

This experiment is done because most of the previous experiments have emphasized only transfer of chemicals from soil to runoff, but not the opposite process, i.e., chemical transport from runoff to the soil.

Experiment 4

The porous medium (Vinton soil) was saturated with a mixture containing 400 mg/l sodium benzoate, 100 mg/l pentafluorobenzoic acid (PFBA), and 200 mg/l calcium bromide. The wetting was achieved the same way as in experiment 2 and 3, and the soil was allowed to equilibrate with the above chemicals for four days. This time period was chosen because most

fields are not irrigated until three to five days after the pesticides are applied, Hamdi et al. (1994) and Aggasi et al. (1995). A 300 mg/l CaCl_2 solution was introduced as a surface flow to minimize density effects. As the benzoate was in the form of sodium benzoate it did not have to be adjusted for density effects. The CaCl_2 solution was introduced at an inlet flow of 3.0 liter/min (19.4 cm/h), the runoff flow was 1.30 liter/min (8.38 cm/h), and the infiltration rate was 0.418 liter/min (2.70 cm/h).

Samples were collected at 5, 10, 20, 40, 60 and 90 minutes after the surface flow was introduced. Samples were taken from the discharge (runoff), surface flow, leachate and at three different locations evenly distributed along the 2.1 meter long soil bed in vertical and longitudinal directions. The samples were refrigerated after collection to avoid further degradation and PFBA and sodium benzoate were analyzed with a HPLC, and for the CaBr_2 an electrode meter was used. There were problems collecting the samples, because the coarser Vinton soil clogged the syringes in the start of the experiment.

Soil samples were collected for measuring of moisture content, the average oven dried sample size and standard deviation were 8.48 ± 1.11 g and the average moisture content and standard deviation were $23.27 \pm 1.99\%$.

CHAPTER 4

RESULT AND DISCUSSION

Concentration data obtained from the experiments are listed in Tables 2 to 6, (see list of tables). In Table 2, experiment 2, the bromide concentration in mg/l is listed for three depths at seven sampling ports along the soil, runoff, surface flow, and leached, for six times, (see Figure 6 for location of sample points). The data for experiment 3 is listed in Table 3. The concentrations for bromide, sodium benzoate, resp. PFBA are listed for experiment 4 in Table 4 to Table 6. For this experiment, samples were only taken in sampling ports 1, 4, and 7 for three depths, surface flow, runoff, and leached for seven times. In all experiments the soil was in nonsteady infiltration before the runoff was introduced.

The measured data in this investigation will not be compared with Shahnaz (1996), even though the same size of flume and soil was used. This is because the average surface flux in Shahnaz (1996) was much greater, 109 cm/h, than the one in this investigation, 19.4 cm/h.

Bromide concentrations in runoff at different times during the surface flow on the silica sand are presented as semilogarithmic plots in Figure 11 for experiment 2 and in Figure 12 for experiment 3, for an infiltration rate of 2.93 cm/h, and in Figure 13 for bromide in experiment 4, infiltration rate 2.70 cm/h. A solid curve has been drawn through the means of the replicate data points. The semilog plots of the concentration-time curves are nonlinear, which was also observed by Ahuja et al. (1983). This nonlinearity of the plots shows that the concept of complete mixing is not a good assumption. The complete mixing model predicts

TABLE 2: Raw data bromide concentration, mg/l, for three depths at seven ports along the flume, surface flow, runoff, and leachate for six times, experiment 2.
Co= 176 ppm

time	5min	10 min	20 min	40 min	60 min	90 min
1T	5.87	4.62	4.58	4.17	4.08	4.02
1M	7.10	6.75	6.10	5.87	4.60	4.42
1B	10.07	9.10	6.66	6.31	5.92	5.58
2T	5.58	5.28	5.13	4.46	3.72	3.61
2M	8.37	6.15	4.52	4.33	4.03	3.88
2B	10.73	6.25	4.71	4.71	4.41	4.14
	3.02	2.71	2.88	2.87	2.69	2.69
3T	4.54	3.77	3.75	3.51	3.31	3.21
3M	4.88	3.95	3.80	3.68	3.64	3.34
3B	5.49	4.65	3.98	3.95	3.83	3.69
4T	3.55	3.42	3.34	3.11	3.11	3.05
4M	4.39	3.79	3.64	3.39	3.17	3.12
4B	7.16	4.77	3.83	3.66	3.51	3.42
5T	3.74	3.72	3.69	3.49	3.45	3.31
5M	7.59	4.94	4.03	3.66	3.20	3.05
5B	9.61	6.95	4.19	3.93	3.28	3.27
6T	5.94	5.63	4.17	3.85	3.74	3.52
6M	7.59	7.01	5.44	4.33	3.85	3.03
6B	9.74	5.87	4.94	3.42	3.35	2.84
7T	4.46	4.19	3.64	3.20	3.00	2.99
7M	5.51	3.34	3.13	2.98	2.87	1.88
7B	6.63	3.45	3.07	2.96	2.87	2.81
i1	10.24	8.51	5.28	3.05	2.48	2.12
i2	17.72	6.36	4.21	2.50	2.35	2.13
i3	27.59	7.79	3.98	2.68	2.23	2.13
i4	40.50	13.88	5.94	2.41	2.17	1.83
i5	40.33	25.79	4.30	2.76	2.12	1.92
i6	48.55	45.96	7.56	3.55	2.09	2.06
i7	58.95	35.69	11.53	6.63	4.71	2.19
T1	4.69	3.25	2.90	2.77	2.74	2.71
T2	8.26	2.91	2.79	2.70	2.68	2.56
T3	5.02	2.71	2.88	2.87	2.69	2.69
T4	4.98	3.05	2.78	2.71	2.62	2.51
T5	4.00	3.05	2.70	2.68	2.62	2.50
R1	1.80	1.61	1.57	1.37	1.35	1.17
R2	1.24	1.12	1.21	1.18	1.18	1.13
R3	1.38	1.36	1.34	1.34	1.25	1.22
R4	1.64	1.53	1.49	1.47	1.43	1.35
R5	1.87	1.76	1.73	1.68	1.68	1.67

TABLE 3: Raw data bromide concentration, mg/l, for three depths at seven ports along the flume, surface flow, runoff, and leachate for six times, experiment 3.
Co= 196 ppm

time	5 min	10 min	20 min	40 min	60 min	90 min
1T	122.58	153.00	162.35	173.52	174.22	193.00
1M	121.05	156.88	162.30	172.82	172.12	192.82
1B	119.04	145.51	162.14	168.69	172.82	192.64
2T	123.09	143.69	158.48		175.63	193.46
2M	128.35	130.51	157.76	166.66	168.01	193.29
2B	130.51	125.69	156.25	159.43	165.99	193.00
	127.68	143.09	175.64	191.77	192.04	195.50
3T	126.75	134.95	156.88	160.07	164.66	192.57
3M	125.17	120.04	155.62	155.86	159.43	188.58
3B	117.06	116.09	152.74	154.37	156.25	183.91
4T	113.21	116.09	153.13	155.23	158.79	185.46
4M	113.21	113.69		153.98	153.13	172.01
4B	109.94		152.12	154.37		
5T	112.74	118.05	151.90	155.23	164.66	180.10
5M	110.41		151.29	153.36		
5B	107.67	115.12	150.68	160.99	162.68	167.04
6T	107.67	116.58	151.51	154.37	156.88	174.91
6M	107.22	119.54	153.75	153.98	158.15	169.15
6B	106.77	117.55	150.07	151.90	166.96	
7T	103.26	116.58	153.13	156.88	171.29	172.45
7M	103.26	117.55	152.51	156.49	156.25	170.57
7B			135.83	150.07		
i1	109.17	113.90	117.34	120.36	137.87	157.26
i2	107.79	108.25	115.36	116.84	132.71	156.59
i3	105.08	107.22	113.42	114.39	128.82	137.29
i4	88.29	99.44	112.94	113.57	123.47	135.55
i5	46.32	89.59	111.51	111.98	117.34	129.92
i6	23.29	74.51	102.32	106.42	114.39	128.82
i7	14.85	40.78	96.52	105.97	113.22	122.94
T1	130.40		188.65	196.64	196.12	196.33
T2	129.31	146.73	183.91	190.17	192.30	195.44
T3	127.68	143.09	175.64	191.77	192.04	195.50
T4	122.93	144.90	172.73	189.48	191.67	195.15
T5	119.36	138.91	172.01	174.18	189.86	194.12
R1	147.96	157.54	169.86	183.60	183.91	183.60
R2	146.12	156.23	166.35	174.18	179.93	183.60
R3	145.51	155.58	164.27	173.45	179.93	182.86
R4	144.29	154.28	158.87	162.22	179.21	179.93
R5	143.09	153.21	160.87	166.35	176.34	179.93

TABLE 4: Raw data bromide concentration, mg/l, for three depths at three ports along the flume, surface flow, runoff, and leachate for seven times, experiment 4.
Co= 194 ppm

time	0 min	5 min	10 min	20 min	40 min	60 min	90 min
1T		3.40	3.38	3.27	3.00		2.23
1M			3.31	3.23	3.09	2.97	2.80
1B	57.50	3.51	3.25	3.06	3.21	3.06	3.05
2T							
2M							
2B							
3T							
3M							
3B							
4T		3.04	2.90	2.86	2.76	2.67	2.55
4M		3.10	2.93	2.87	2.84	2.70	2.58
4B	81.00	3.18	2.99	2.87	2.84	2.72	2.58
5T							
5M							
5B							
6T							
6M							
6B							
7T	149.30	2.91	2.72	2.68	2.65	2.64	2.55
7M		3.06	2.79	2.68	2.66	2.65	2.61
7B			2.87	2.73	2.66	2.65	2.62
i1	52.50	8.33	3.78	2.75	2.74	2.62	2.58
i2	52.40	14.61	5.02	3.38	2.93	2.90	2.70
i3	52.80	19.06	5.02	3.54	3.10	3.05	2.80
i4	53.30	21.68	5.17	3.58	3.21	3.17	2.86
i5	53.50	31.22	8.73	3.68	3.45	3.40	3.01
i6	55.70	31.62	9.80	3.76	3.76	3.45	3.14
i7	60.00	113.11	57.42	5.47	3.98	3.47	4.00
T1	150.00	2.66	2.55	2.25	2.57	2.31	2.22
T2	155.50	2.51	2.47	2.35	2.51	2.26	2.23
T3	154.20	2.55		2.30	2.84	2.34	2.23
T4	155.30	2.37	2.27	2.33	2.48	2.36	2.22
T5	153.70	2.46	2.43	2.41	2.56	2.37	2.35
R1		5.02	3.18	2.55	2.73	2.62	2.57
R2		4.10	3.02	3.08	2.80	2.57	2.55
R3		3.13	2.93	2.79	2.78	2.60	2.24

TABLE 5: Raw data sodium benzoate concentration, mg/l, for three depths at three ports along the flume, surface flow, runoff, and leachate for seven times, experiment 4.

Co= 417 ppm

time	0 min	5 min	10 min	20 min	40 min	60 min	90 min
1T		0.00	0.00	0.00	0.00		0.00
1M			0.13	0.00	59.51	0.00	0.00
1B	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2T							
2M							
2B							
3T							
3M							
3B							
4T	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4M	0.00	0.00	0.00	0.00	0.00	0.11	0.00
4B	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5T							
5M							
5B							
6T							
6M							
6B							
7T	0.00	0.00	0.00	0.00	0.00	0.00	0.00
7M		0.00	0.00	0.00	0.00	0.00	0.00
7B			0.00	0.00	0.00	0.00	0.00
i1	22.13	0.00	0.00	0.50	0.23	0.15	0.21
i2	99.50	0.00	0.00	0.00	0.00	0.00	0.00
i3	9.92	0.00	0.00	0.00	0.00	0.00	0.00
i4	5.42	0.00	0.00	0.00	0.00	0.09	0.00
i5	151.39	0.00	0.00	0.00	0.00	0.00	0.00
i6	4.54	0.00	0.00	0.00	0.00	0.00	0.00
i7	1.96	0.44	0.00	0.00	0.00	0.00	0.00
T1	0.17	0.00	0.00	0.00	0.00	0.00	0.21
T2	0.00	0.00	0.00	0.00	0.00	0.00	0.05
T3	0.00	0.00	0.00	0.00	0.05	0.04	0.00
T4	0.25	0.00	0.00	0.00	0.00	0.00	0.00
T5	0.17	0.00	0.33	0.08	0.00	0.00	0.04
R1		2.28	0.39	0.00	0.00	0.00	0.00
R2		12.28	2.91	0.00	0.00	0.00	0.00
R3		0.00	0.00	0.09	0.00	0.00	0.00

TABLE 6: Raw data PFBA concentration, mg/l, for three depths at three ports along the flume, surface flow, runoff, and leachate for seven times, experiment 4. Co= 102 ppm

time	0 min	5min	10 min	20 min	40 min	60 min	90 min
1T		0.00	0.00	0.00	0.00		0.00
1M			0.00	0.00	14.64	0.00	0.00
1B	1.68	0.00	0.00	0.00	0.00	0.00	0.00
2T							
2M							
2B							
3T							
3M							
3B							
4T		0.00	0.00	0.00	0.00	0.00	0.00
4M		0.00	0.00	0.00	0.00	33.58	0.00
4B	36.74	0.00	0.00	0.00	0.00	0.00	0.00
5T							
5M							
5B							
6T							
6M							
6B							
7T	1.77	0.00	0.00	0.00	0.00	0.00	0.00
7M		0.00	0.00	0.00	0.00	0.00	0.00
7B		0.00	0.00	0.00	0.00	0.00	0.00
i1	65.82	10.02	1.49	0.44	0.00	0.12	0.12
i2	93.37	9.05	0.59	0.00	0.00	0.13	0.11
i3	89.13	13.35	0.71	0.00	0.00	0.12	0.11
i4	91.84	18.15	3.37	0.23	0.00	0.13	0.12
i5	100.69	22.11	5.00	0.23	0.00	0.13	0.10
i6	96.62	5.37	0.48	0.00	0.00	0.11	0.11
i7	105.32	69.81	30.86	1.58	0.50	0.00	0.00
T1	0.51	0.50	0.00	0.00	0.00	0.14	0.13
T2	0.13	0.00	0.00	0.00	0.00	0.00	0.00
T3	0.19	0.00	0.00	0.00	0.00	0.00	0.00
T4	0.28	0.18	0.00	0.00	0.00	0.00	0.00
T5	0.21	0.00	0.00	0.00	0.00	0.00	0.00
R1		1.54	0.26	0.00	0.00	0.00	0.00
R2		1.17	0.26	0.00	0.00	0.00	0.00
R3		0.00	0.00	0.10	0.00	0.00	0.00

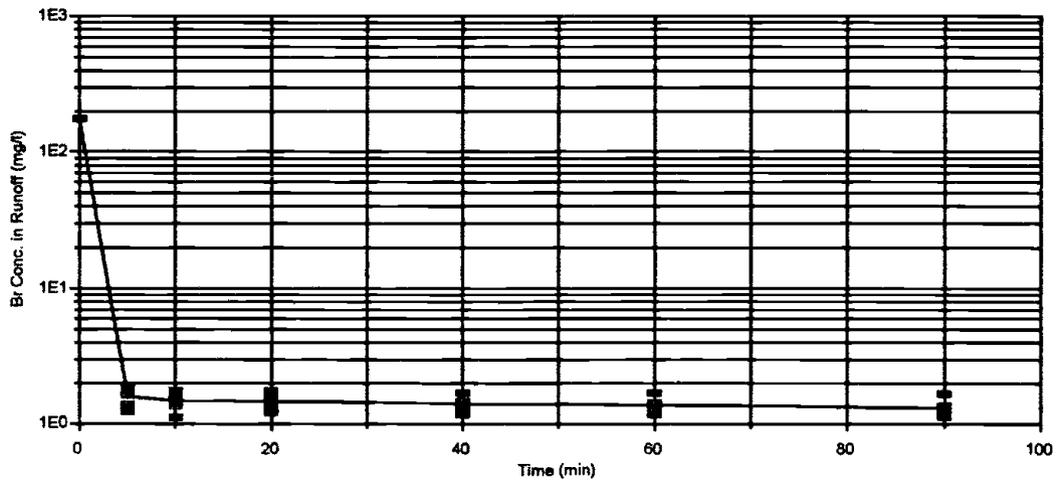


FIGURE 11: Bromide concentration in runoff at different times during the surface flow, experiment 2. Infiltration rate 2.93 cm/h.

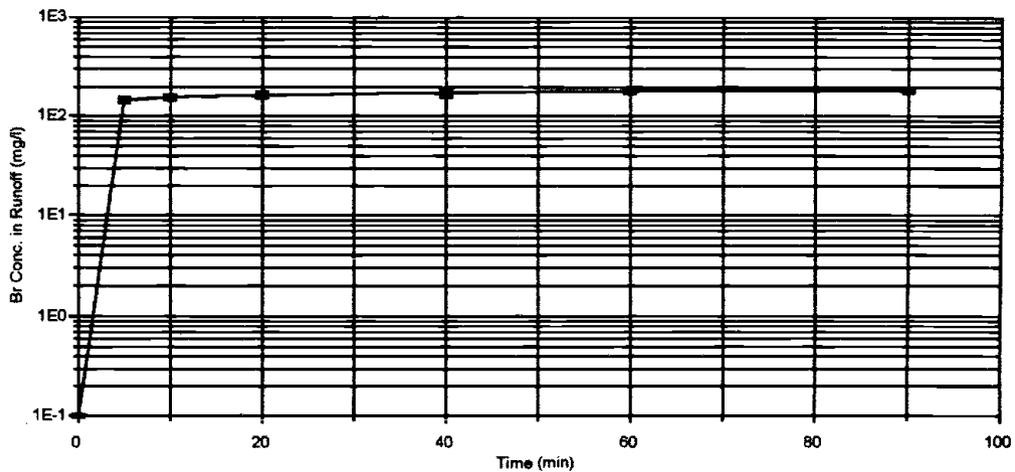


FIGURE 12: Bromide concentration in runoff at different times during the surface flow, experiment 3. Infiltration rate 2.93 cm/h.

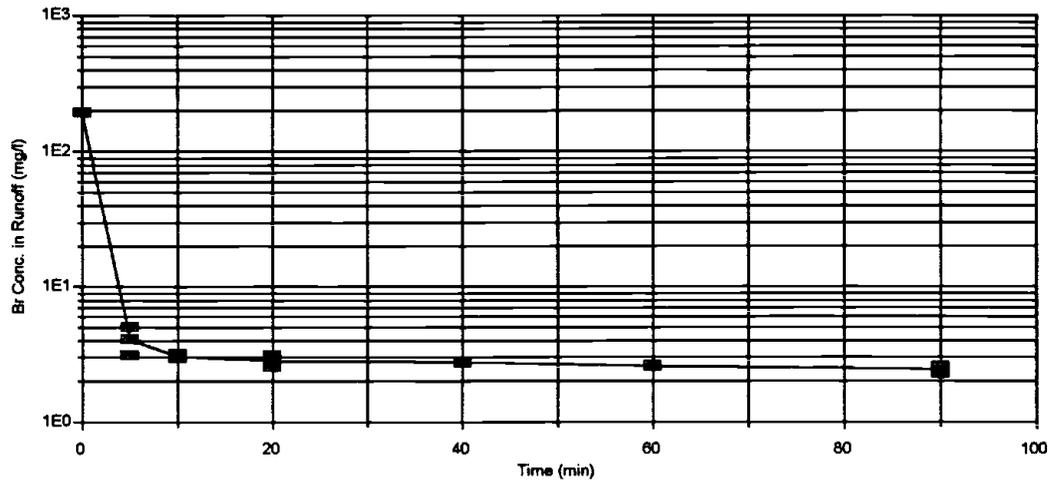


FIGURE 13: Bromide concentration in runoff at different times during the surface flow, experiment 4. Infiltration rate 2.70 cm/h.

that the bromide concentration in runoff for a fixed time would be the same, irrespective of the infiltration rate (assuming EDI unaffected by infiltration conditions), this means that the semilogarithmic plots should be linear. Thus it can be concluded that there is an incomplete mixing between surface water and soil solution. The bromide concentration curves may be approximated as linear if the first 5 minutes are ignored. For the first 5 minutes there is an exponential fit. Thus the concept of complete mixing is valid when free infiltration occurs. This is in line with what Ahuja (1982) found. With free infiltration conditions, it can be seen in Figure 11, Figure 12, and Figure 13 most of the bromide in the mixing zone was lost by infiltration and runoff during the first 5 minutes.

Bromide concentrations in the soil water at different times during the runoff are presented in Figure 14 for experiment 2 and in Figure 15 for experiment 3 as a function of depth below the surface. Both figures represent the concentration variations with time 1.2 meters from where the surface water is introduced (sample port 3, 45% into the flume). The infiltration rate was 2.93 cm/h, this downward movement of water displaced the chemical from the surface zone, and thus reduced the amount released to runoff. The results in Figure 14 can be compared with the study from Hamdi et al. (1994), Figure 16 for the low soil depths. They did a field study at the Colorado State University Agronomy Research Farm in the summer 1989. Eight plots, each 3.5 meter by 3.5 meter, were established in the study area and protected with soil berms. Four plots were sprinkler irrigated and four were irrigated with a ponded system. They found that the travel-depth bromide concentration curves under the ponded irrigation had a high variability and that the bromide mass was transported deeper

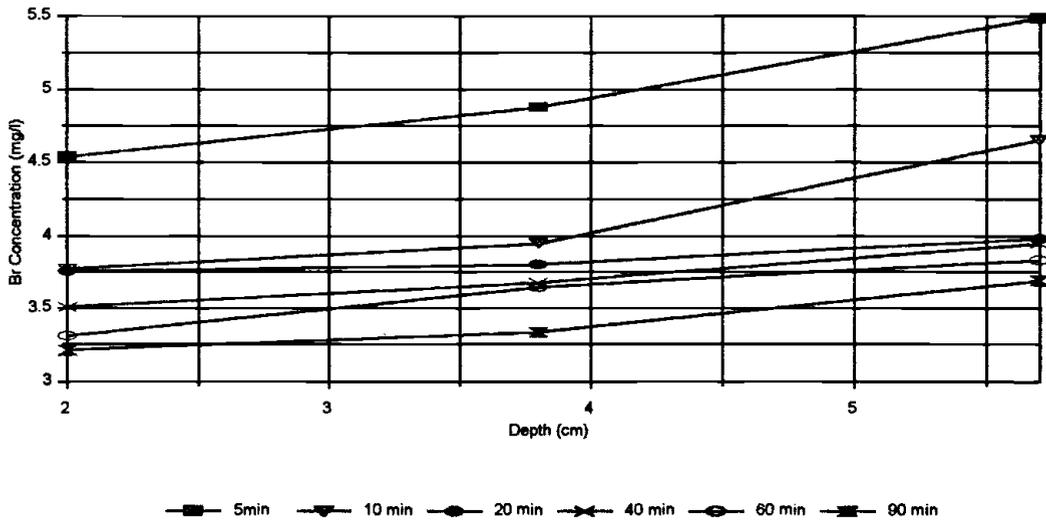


FIGURE 14: Vertical bromide concentration, experiment 2. Infiltration rate 2.93 cm/h, for sample port 3.

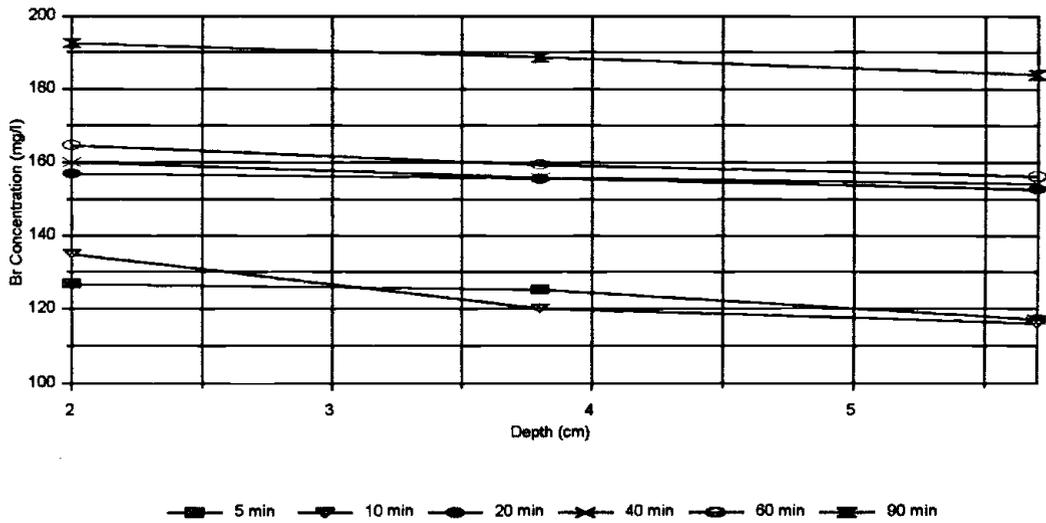


FIGURE 15: Vertical bromide concentration, experiment 3. Infiltration rate 2.93 cm/h, for sample port 3.

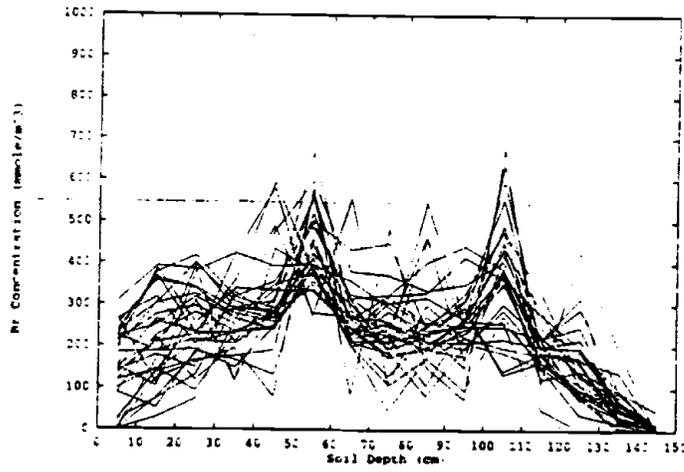


FIGURE 16: Travel depth bromide concentration curves under ponded irrigation, Hamdi et al. (1994).

in the soil profile compared with sprinkler irrigation. The difference can be attributed to the presence of macropore flow in the ponded case. From Hamdi et al. (1994) results it can be concluded that there is a higher risk for groundwater contamination by a conservative tracer under ponded irrigation than under a rainfall or sprinkler irrigation. The results in Figure 14 follows Hamdi et al. (1994) for the low soil depths. As deeper samples could not be taken, the data in this investigation can not be compared with the deeper depths from Hamdi et al. (1994).

In Figure 17 for experiment 2 and Figure 18 for experiment 3 it can be seen that the concentration profile exhibits an approximate "S" shape at all times (sample port 3, 45% into the flume). This reflects the combined effects of convective dispersion induced by infiltration and the mixing and removal induced by the surface flow. By comparing this data set with Snyder et al. (1985) it can be concluded that with a higher infiltration rate the concentration in the surface runoff decreased faster than with a lower infiltration rate, this was also observed by Ahuja et al. (1983). Again, this shows the common complete mixing model, in which the solute concentration in a mixing zone of an assumed depth is equal to the concentration in overland flow, apparently is not a bad approximation to the inferred solute concentration profiles for high infiltration rates.

Figure 19 to 26 shows the bromide concentration in soil water at different time intervals as a function of horizontal distance at three different depths of 1.9 cm (top layer), 3.8 cm (middle layer), and 5.7 cm (bottom layer) of the flume and of the surface flow. Figures 19 to 21 are plotted using data from experiment 2, and Figures 22 to 24 are plotted

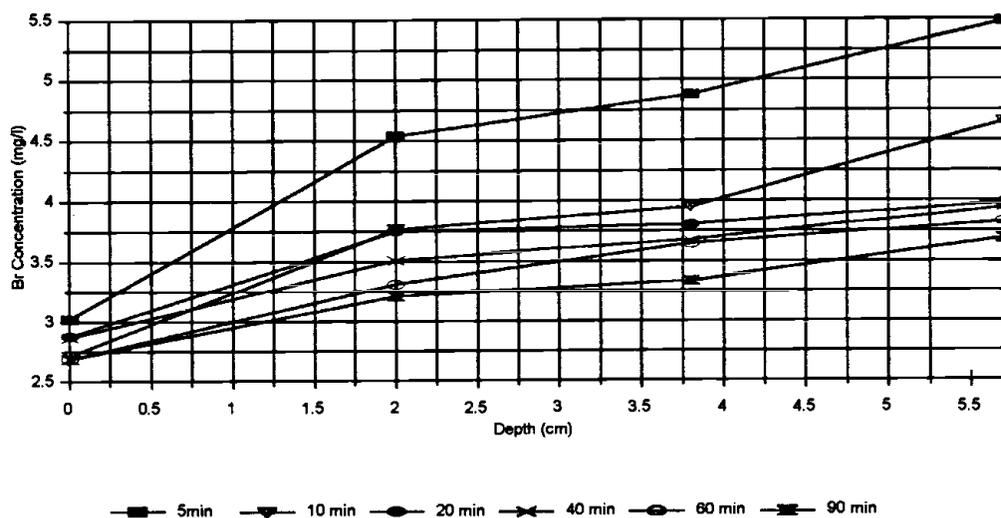


FIGURE 17: Bromide concentration vs. depth, experiment 2. Infiltration rate 2.93 cm/h at 1.2 m from inlet (sample port 3).

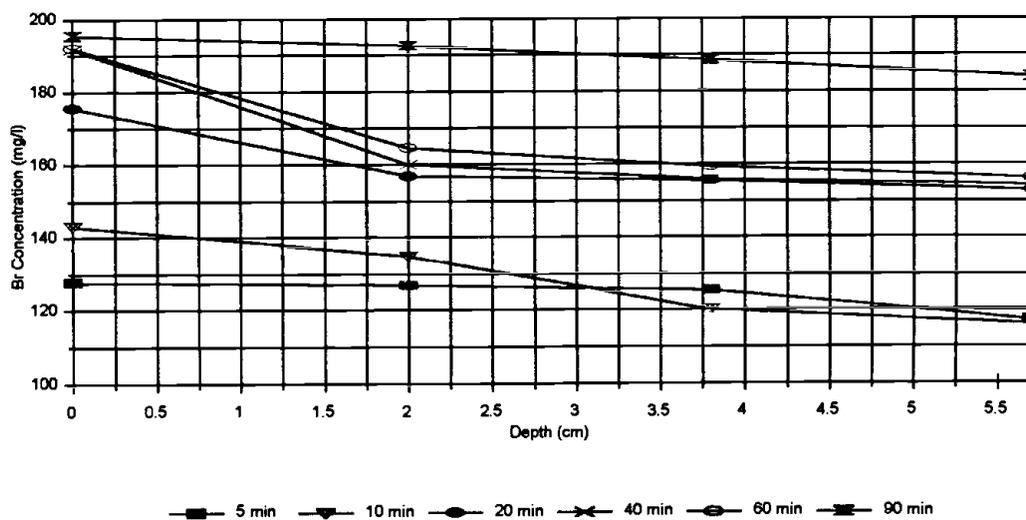


FIGURE 18: Bromide concentration vs. depth, experiment 3. Infiltration rate 2.93 cm/h at 1.2 m from inlet (sample port 3).

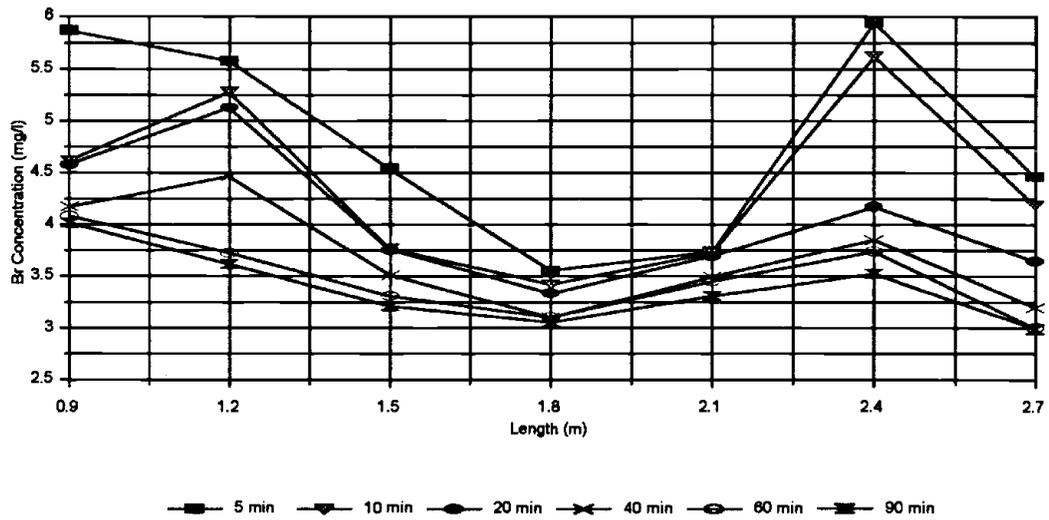


FIGURE 19: Bromide concentration vs. length at 1.9 cm from the surface, (top layer). Infiltration rate 2.93 cm/h, experiment 2.

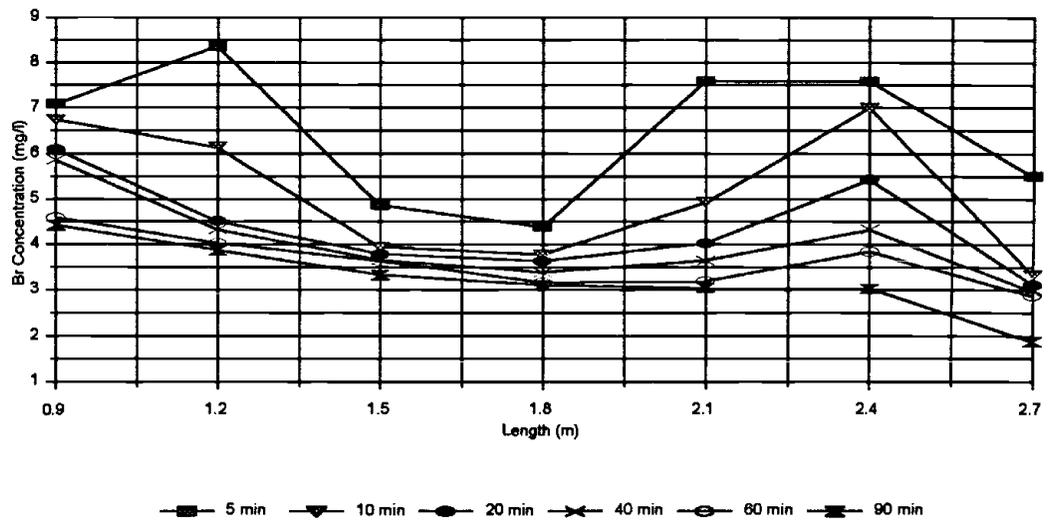


FIGURE 20: Bromide concentration vs. length at 3.8 cm from the surface, (mid layer). Infiltration rate 2.93 cm/h, experiment 2.

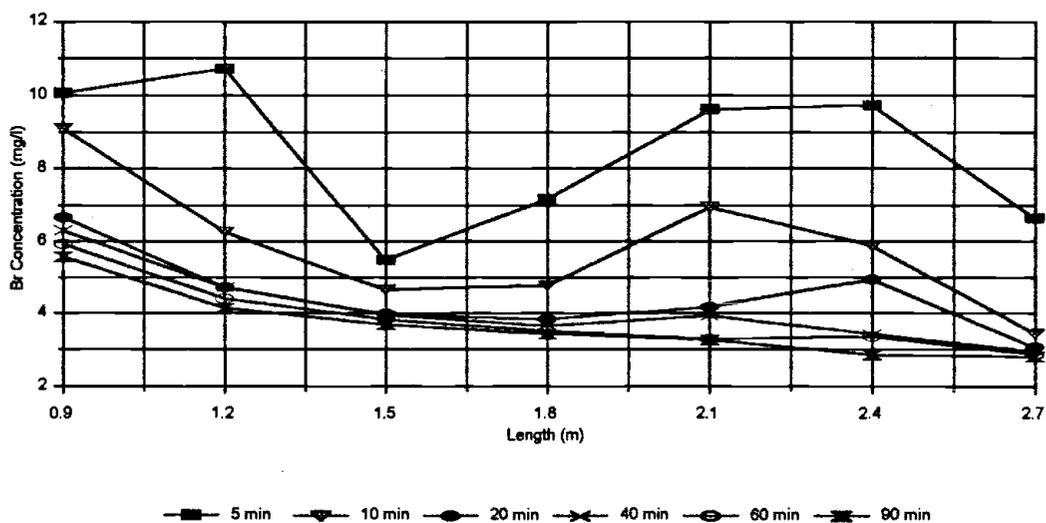


FIGURE 21: Bromide concentration vs. length at 5.7 cm from the surface, (bottom layer). Infiltration rate 2.93 cm/h, experiment 2.

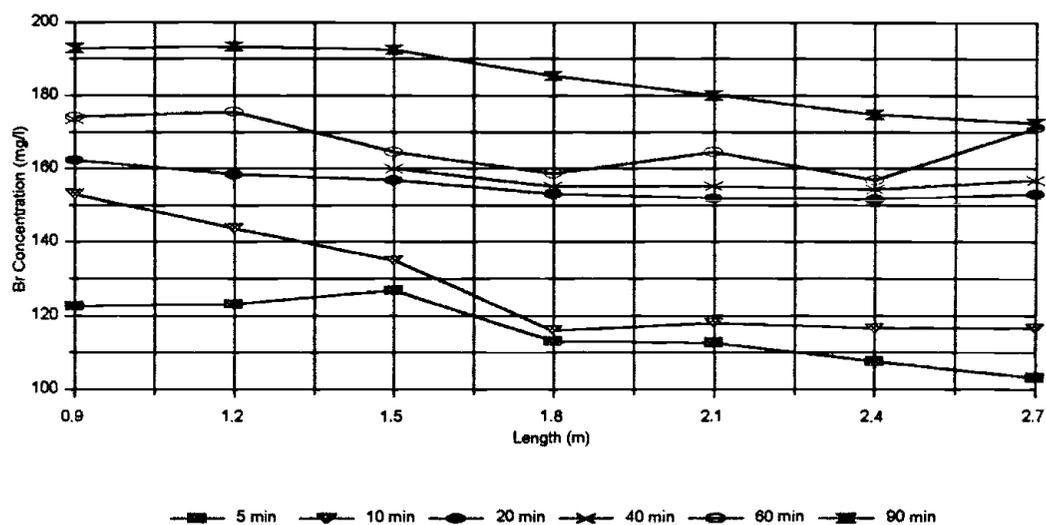


FIGURE 22: Bromide concentration vs. length at 1.9 cm from the surface, (top layer). Infiltration rate 2.93 cm/h, experiment 3.

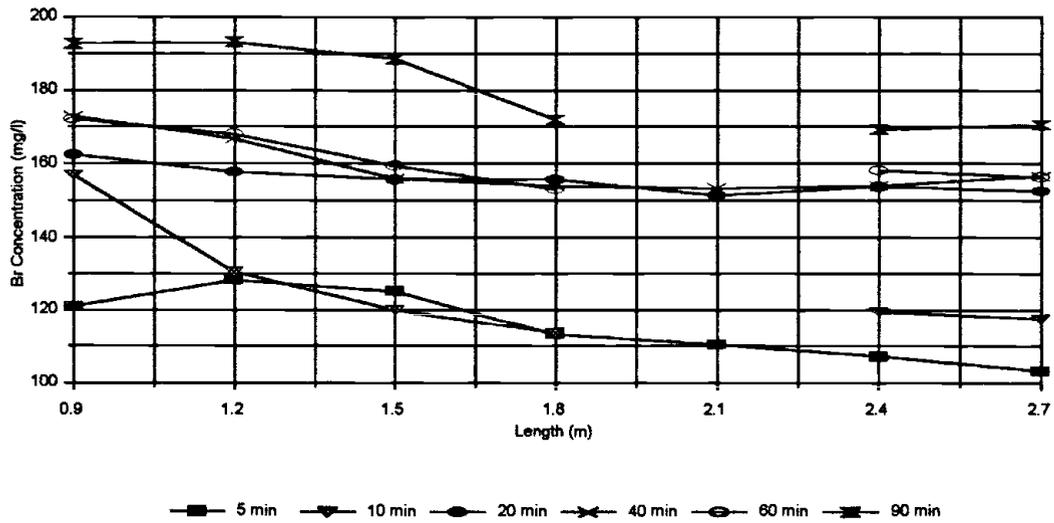


FIGURE 23: Bromide concentration vs. length at 3.8 cm from the surface, (mid layer). Infiltration rate 2.93 cm/h, experiment 3.

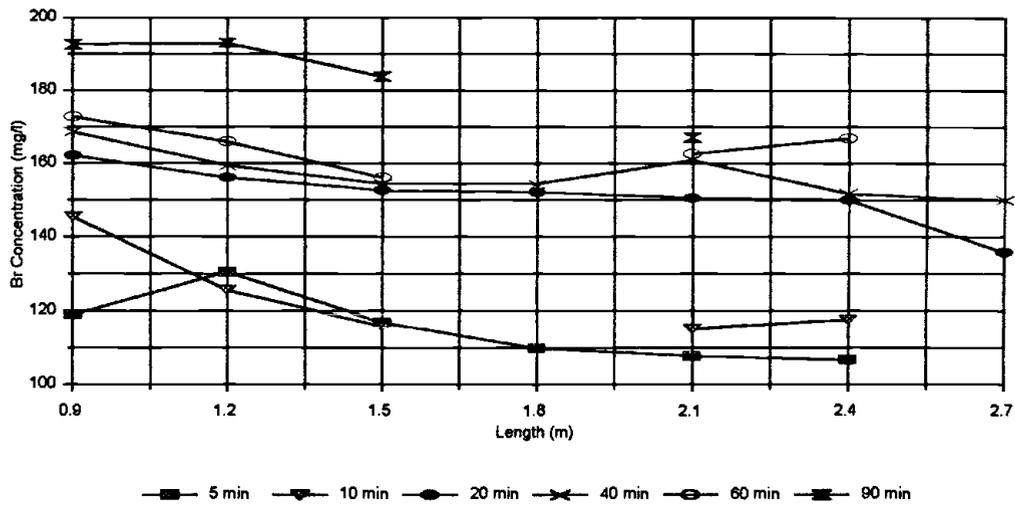


FIGURE 24: Bromide concentration vs. length at 5.7 cm from the surface, (bottom layer). Infiltration rate 2.93 cm/h, experiment 3.

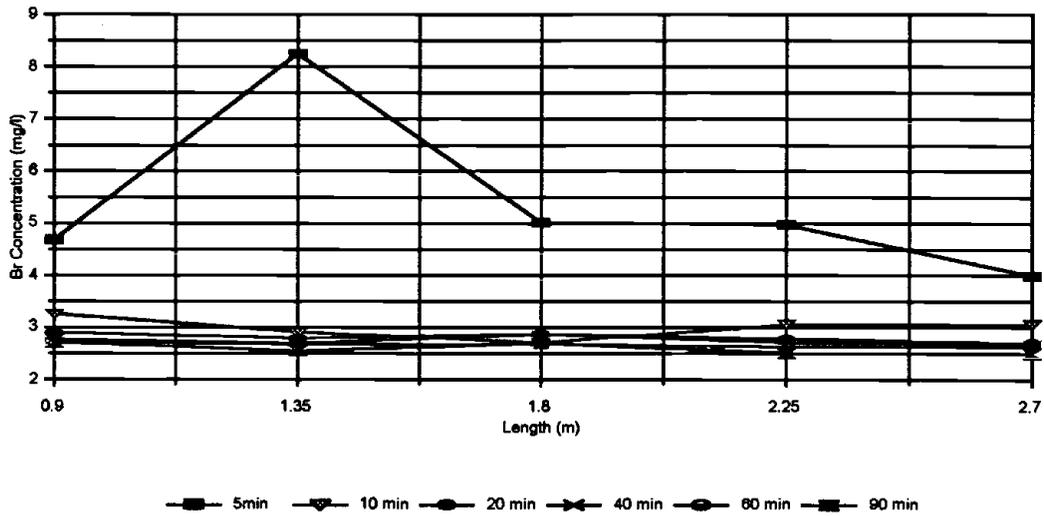


FIGURE 25: Bromide concentration vs. length in surface flow. Infiltration rate 2.93 cm/h, experiment 2.

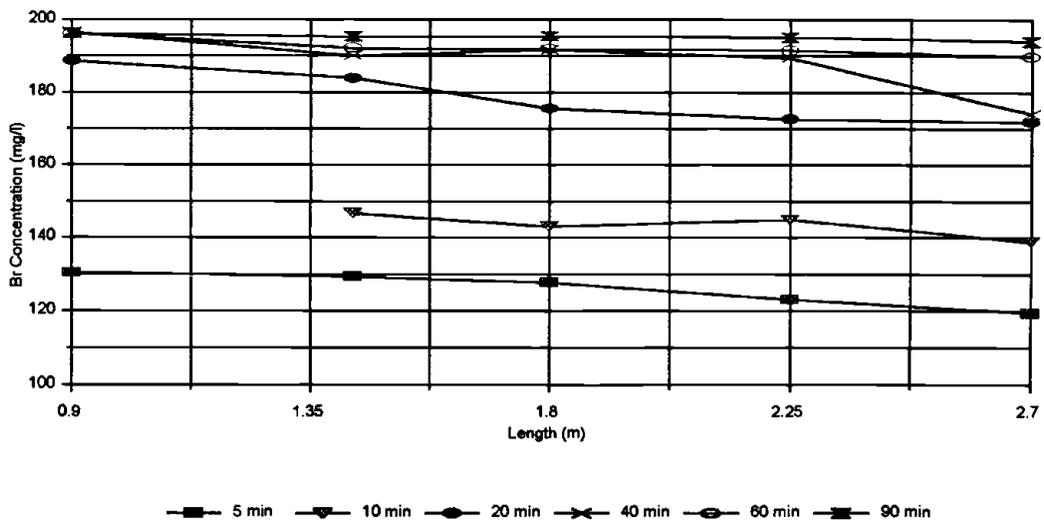


FIGURE 26: Bromide concentration vs. length in surface flow. Infiltration rate 2.93 cm/h, experiment 3.

using data from experiment 3. As discussed in the literature survey (Ahuja et al. (1983), Snyder et al. (1985), Parr et al. (1987)), most of the previous experiments observed vertical movement and did not examine horizontal distribution. As can be seen on the graphs for experiment 2 the bromide concentration starts high, drops at the middle of the box, increases again and drops at the end of the flume at all times. This drop could be due to heterogeneity or that the box was not uniformly saturated with the bromide. For experiment 3 the bromide concentration decreases with the length of the box, which is logical because the water containing bromide enters upstream, so as it migrates downstream the concentration decreases. The graphs showing the bromide concentration in the 1 cm top flow are presented in Figure 25 and 26. As can be seen for experiment 2, with bromide initially in the box, the concentration of bromide in the surface flow decreases with time and length of flume. For Figure 26, experiment 3, with bromide as surface flow, the bromide concentration increases with time. This occurs because the surface flow contains chloride from the initial saturation and bromide replaces the chloride with time.

Figures 27 to 29 are the plots of experiment 2 where the soil profile was saturated with CaBr_2 (200 mg/l) solution and CaCl_2 was used to flush the soil profile. The figures show that the lowest concentration is in the surface flow, but the surface flow does have a small concentration of bromide the first 20 minutes. This suggests that there is mass transfer between the saturated soil and the surface flow. The lowest concentration is in the most upper layer, 1.9 cm, and the highest is in the lowest layer, 5.7 cm. This suggests that the most upper layer of the soil profile has the highest potential for transporting soil chemicals in

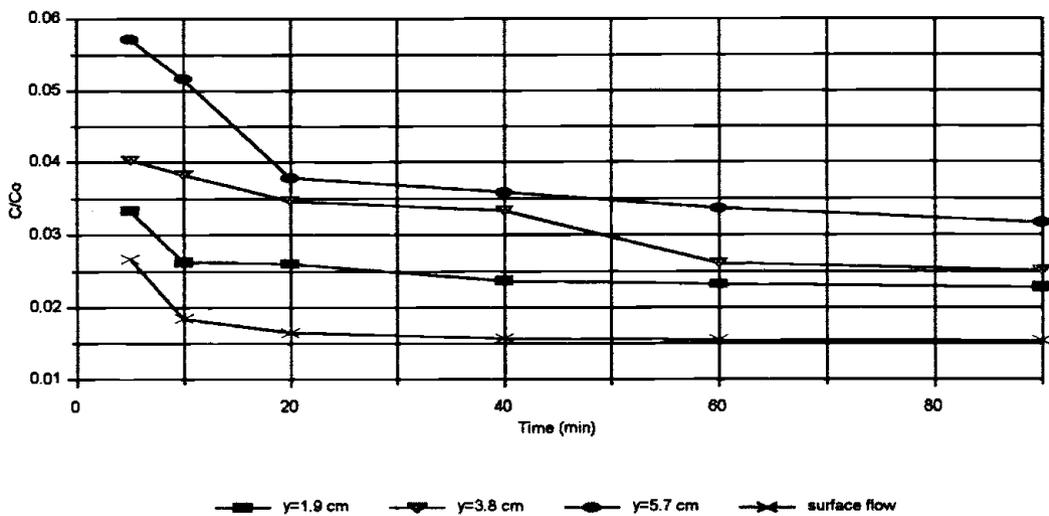


FIGURE 27: Relative bromide concentration vs. time of experiment 2 at horizontal distance of 0.6 m from inlet (sample port 1). Infiltration rate 2.93 cm/h.

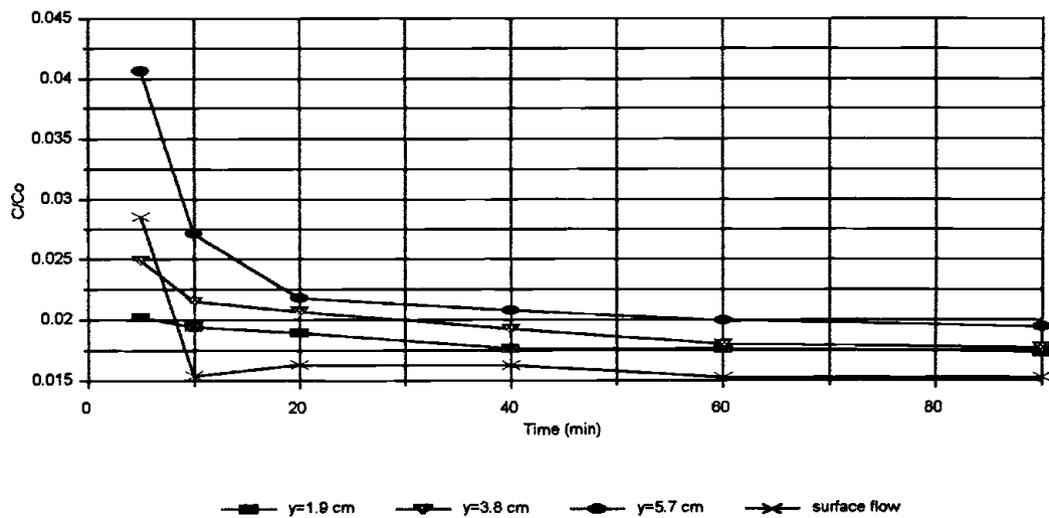


FIGURE 28: Relative bromide concentration vs. time of experiment 2 at horizontal distance of 1.5 m from inlet (sample port 4). Infiltration rate 2.93 cm/h.

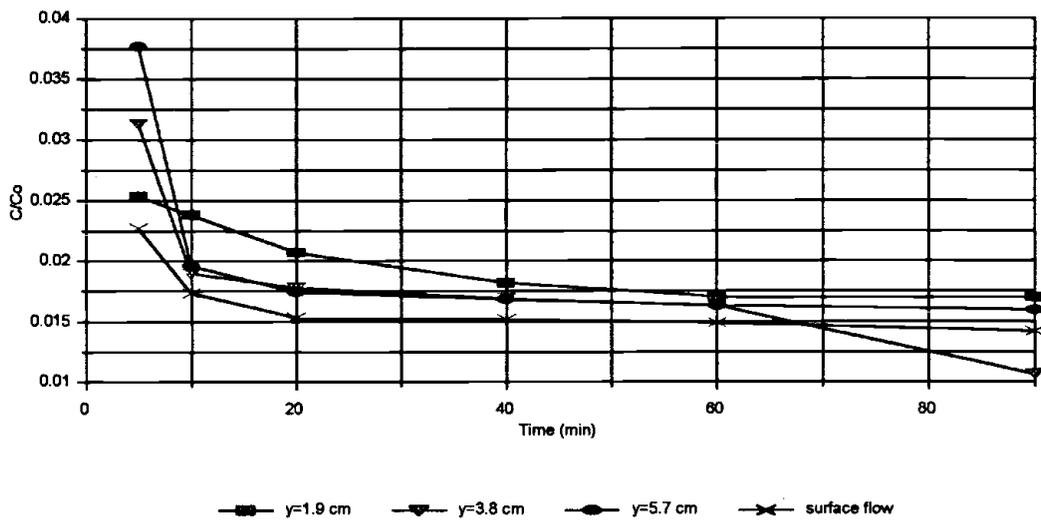


FIGURE 29: Relative bromide concentration vs. time of experiment 2 at horizontal distance of 2.4 m from inlet (sample port 7). Infiltration rate 2.93 cm/h.

solution to runoff. For experiment 3, Figure 30 to 32, with CaBr_2 in the surface flow, showed the highest concentration in the most upper layer, 1.9 cm, and the lowest concentration in the 5.7 cm layer. This agrees with the statement that the upper most layer of the soil has the highest potential for transport of chemicals to the runoff. The surface flow reaches a relative concentration of 0.9 to 1.0 after about 40 minutes, so there is mass transfer between the saturated soil and the surface flow. It has to be noted that most of the bromide leaves the box after about 5 minutes in experiment 2, and the chloride is replaced by the bromide after about 5 minutes in experiment 3.

By comparing the bromide concentration profile in experiment 2 (containing silica sand) with experiment 4 (containing Vinton soil) for three different depths in the soil profile, it can be seen in Figure 33 to 35 that the concentration is higher in the silica sand at all times and depths. This is due to the fact that Vinton soil has a lower infiltration rate than the silica sand. In Figure 36 the bromide concentrations in the runoff at different times are plotted, to compare the silica sand and the Vinton soil. The silica sand has lower runoff concentrations than the Vinton soil, this suggests that the transport of bromide in the Vinton soil to the runoff is greater than for the silica sand. The infiltration rate in the Vinton soil is lower than in the silica sand, this means that there will be a higher transfer of the bromide to the runoff. This was also shown by Ahuja et al. (1983).

The concentrations of sodium benzoate and PFBA are shown in Table 4 and Table 5 respectively. Note that samples were only taken in ports 1, 4 and 7. As can be seen there is no measurable concentrations for the samples taken after 5 minutes in the soil profile along

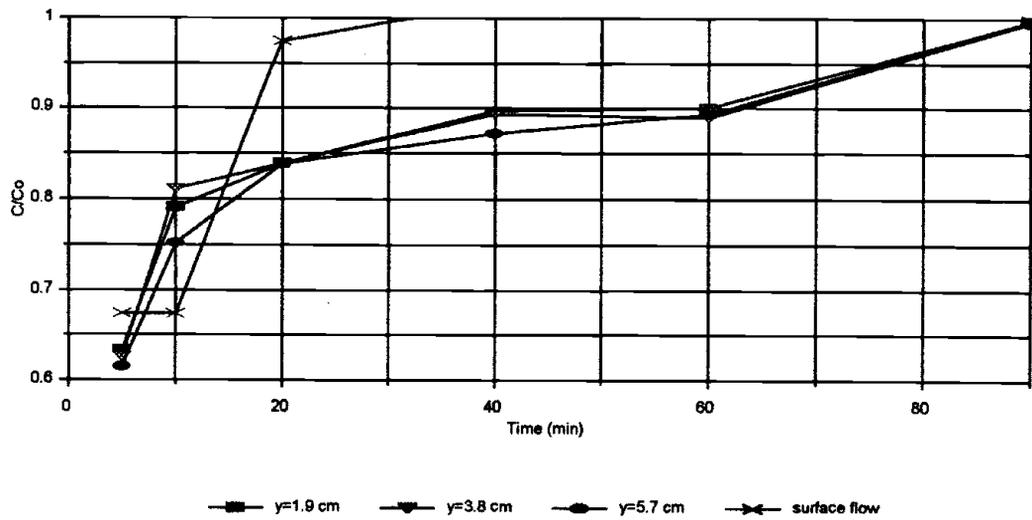


FIGURE 30: Relative bromide concentration vs. time of experiment 3 at horizontal distance of 0.6 m from inlet (sample port 1). Infiltration rate 2.93 cm/h.

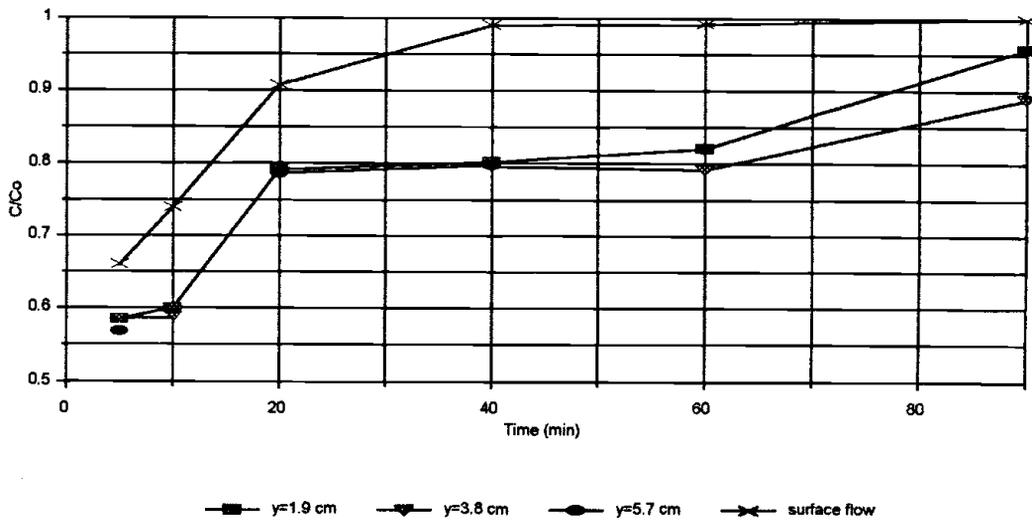


FIGURE 31: Relative bromide concentration vs. time of experiment 3 at horizontal distance of 1.5 m from inlet (sample port 4). Infiltration rate 2.93 cm/h.

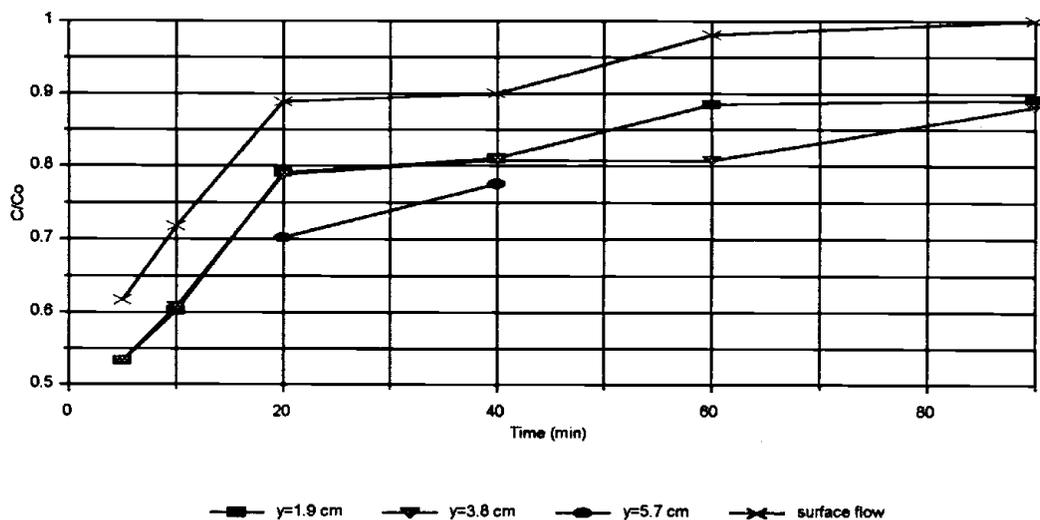


FIGURE 32: Relative bromide concentration vs. time of experiment 3 at horizontal distance of 2.4 m from inlet (sample port 7). Infiltration rate 2.93 cm/h.

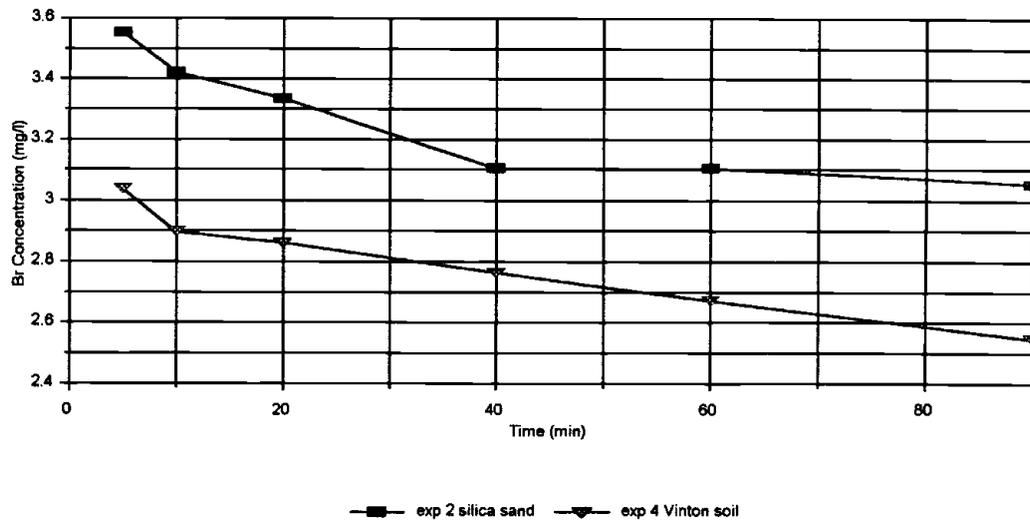


FIGURE 33: Bromide concentration in soil solution at 1.9 cm, 1.5 m from inlet (sample port 4), comparing silica sand (experiment 2) with Vinton soil (experiment 4). Infiltration rate 2.93 cm/h resp. 2.70 cm/h.

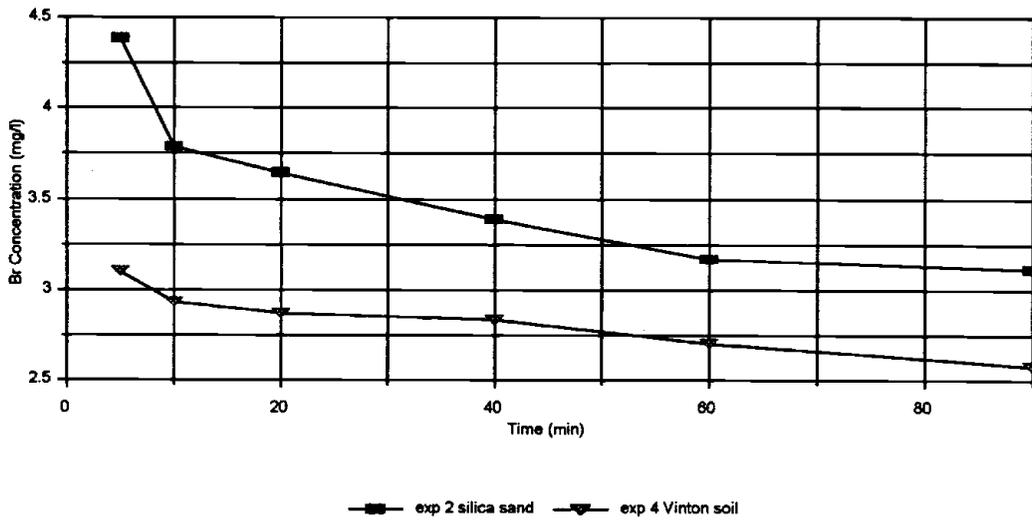


FIGURE 34: Bromide concentration in soil solution at 3.8 cm, 1.5 m from inlet (sample port 4), comparing silica sand (experiment 2) with Vinton soil (experiment 4). Infiltration rate 2.93 cm/h resp/ 2.70 cm/h.

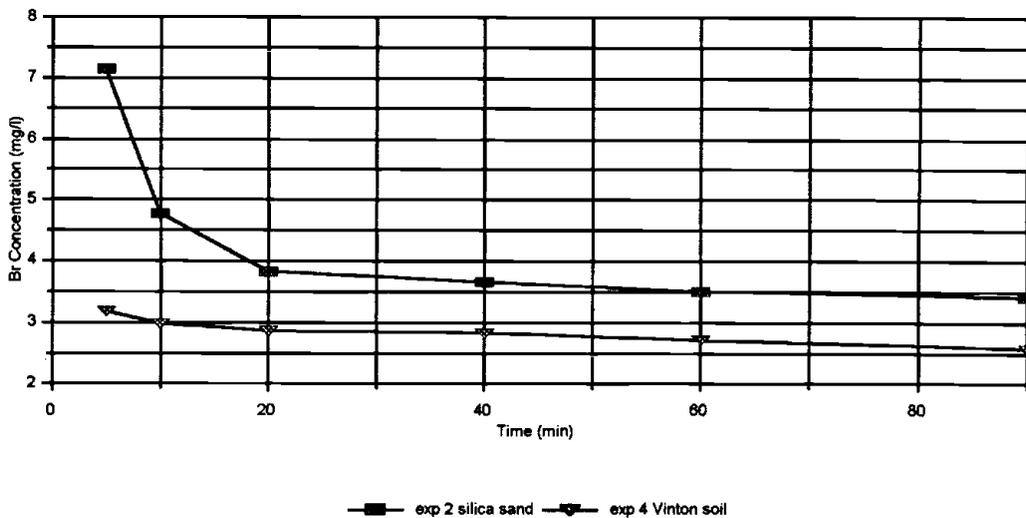


FIGURE 35: Bromide concentration in soil solution at 5.7 cm, 1.5 meters from inlet (sample port 4), comparing silica sand (experiment 2) with Vinton (experiment 4). Infiltration rate 2.93 cm/h resp. 2.70 cm/h.

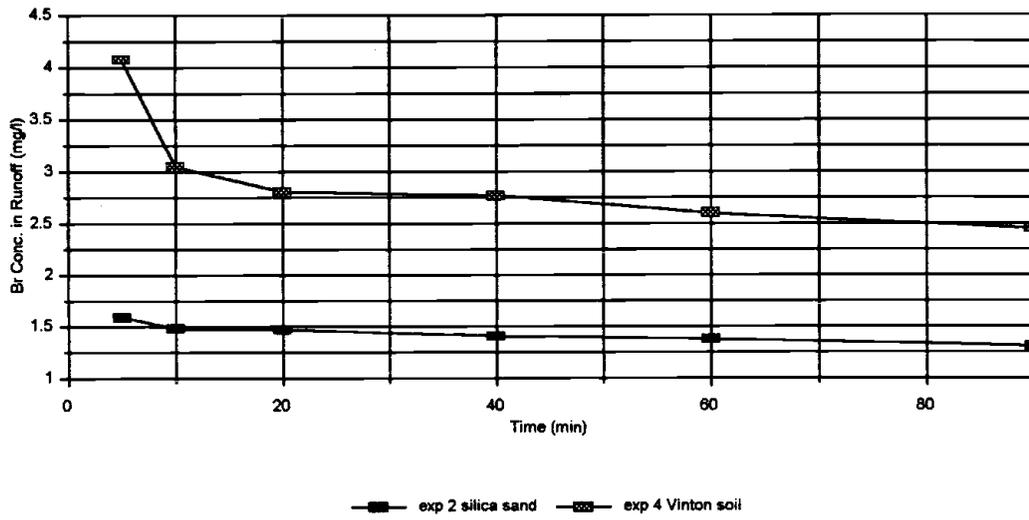


FIGURE 36: Bromide concentration in runoff at different times for experiment 2, silica sand, and experiment 4, Vinton soil. Infiltration rate 2.93 cm/h resp. 2.70 cm/h.

the length of the box. This indicates that most of the chemicals were lost after 5 minutes. However, bromide was measured in experiment 4, (Table 3). The bromide concentrations were detected with a bromide electrode, and the values measured can be influenced by other ions, for example chloride. Thus, it is unclear if the PFBA is delayed in comparison to the bromide. A delay of the PFBA would indicate that the chemical loss to runoff was not only influenced by advection (flow), but also by diffusion processes. If this is true, then the rate of transfer and the contributing soil depth will increase with increase in hydraulic conductivity of the soil surface layer (upper 2-5 cm) relative to that layer below, but decrease with increase in canopy and ground cover. Thus, a cultural practice that increased relative hydraulic conductivity of the soil surface might increase the amount of chemicals in the runoff.

In Figure 37 to 39 the leachate concentration is compared for PFBA and bromide in the Vinton soil, for ports 1, 4, and 7. In comparison to the bromide, the PFBA is somewhat delayed the first 10 minutes of the experiment, for all of the three ports.

Mass Recovery

The mass recovery are shown in Table 7 for bromide in experiment 2, Table 8 for bromide in experiment 4, Table 9 for sodium benzoate in experiment 4, and Table 10 for PFBA in experiment 4. The mass recovery is calculated from equation 7 for the runoff concentration, and from equation 8 for the leached mass. Each leached sample can be seen as a column experiment, and the width of the flume and the overland flow depth do not have to be included.

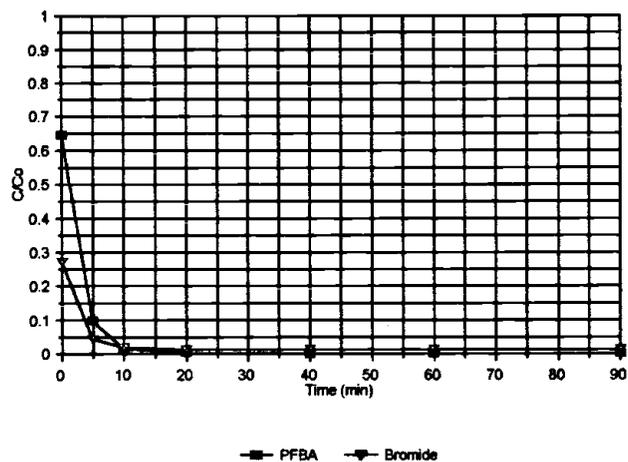


FIGURE 37: Comparison between PFBA and bromide for experiment 4. Leach port 1.

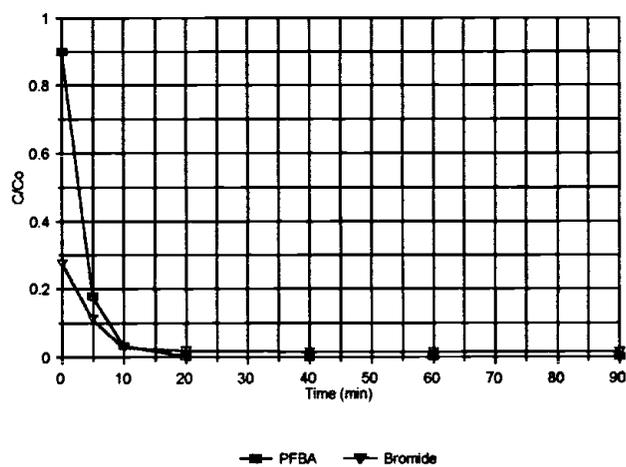


FIGURE 38: Comparison between PFBA and bromide for experiment 4. Leach port 4.

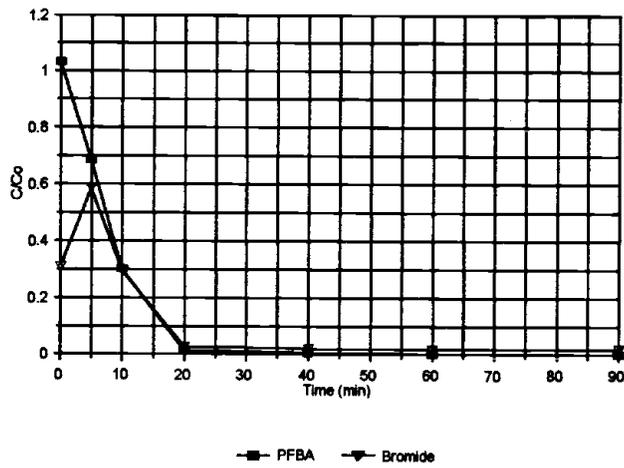


FIGURE 39: Comparison between PFBA and bromide for experiment 4. Leach port 7.

TABLE 7: Mass lost bromide, mg, experiment 2.

time	5min	10 min	20 min	40 min	60 min	90 min		
i1	23.30	19.35	24.03	27.78	22.60	29.00	146.07	
i2	40.31	14.47	19.14	22.79	21.39	29.12	147.22	
i3	62.77	17.71	18.12	24.38	20.34	29.12	172.44	
i4	92.14	31.57	27.05	21.94	19.74	24.91	217.35	
i5	91.75	58.68	19.55	25.11	19.25	26.21	240.54	
i6	110.45	104.56	34.40	32.34	19.01	28.15	328.91	
i7	134.10	81.19	52.44	60.36	42.90	29.87	400.86	1,653.38
R1	0.04	0.03	0.07	0.11	0.11	0.15	0.51	
R2	0.03	0.02	0.05	0.10	0.10	0.14	0.44	
R3	0.03	0.03	0.06	0.11	0.10	0.15	0.48	
R4	0.03	0.03	0.06	0.12	0.12	0.17	0.54	
R5	0.04	0.04	0.07	0.14	0.14	0.21	0.64	2.62

TABLE 8: Mass loss bromide, mg, experiment 4.

time	0 min	5 min	10 min	20 min	40 min	60 min	90 min		
i1	109.73	17.40	7.90	11.50	22.91	21.94	32.36	223.74	
i2	109.52	30.53	10.49	14.13	24.53	24.22	33.92	247.34	
i3	110.35	39.83	10.49	14.82	25.94	25.52	35.11	262.06	
i4	111.40	45.31	10.81	14.94	26.85	26.46	35.87	271.63	
i5	111.82	65.25	18.24	15.40	28.88	28.39	37.76	305.73	
i6	116.41	66.09	20.48	15.73	31.47	28.88	39.42	318.49	
i7	125.40	236.39	120.00	22.85	33.27	29.00	50.12	617.05	2,246.03
R1		0.11	0.07	0.11	0.23	0.22	0.33	1.07	
R2		0.09	0.06	0.13	0.24	0.22	0.33	1.07	
R3		0.07	0.06	0.12	0.24	0.22	0.29	0.99	3.12

$$M_i = \int_0^t C_r V_r y W dt \quad (7)$$

$$M_i = \int_t^0 C_l V_l dt \quad (8)$$

where

M_i = total mass lost

C_r = runoff concentration

V_r = runoff velocity

y = overland flow depth

W = flume width

C_l = leach concentration

V_l = leach velocity

Equation 7 and 8 can be easily evaluated by using numerical integration. Therefore, after obtaining the mass recovery value in each infiltration and runoff point between the known time interval, the total amount of chemical released to the surface runoff and to the infiltrating water can be calculated by taking the sum of the amount of chemical in each individual point. The corresponding columns of raw data in Table 1 present the bromide concentration of the same sample point and time, within 5, 5, 10, 20, 20, 30 minute time intervals. It can be seen from Table 7 that 99% in experiment 2 is lost from leaching, and only

1% is transferred to the runoff. For experiment 4 with Vinton soil 99% of the bromide, the sodium benzoate and the PFBA are lost to infiltration. 28% more solution was applied to the Vinton soil in comparison to the silica sand, i.e. Vinton soil needed more solution to obtain complete saturation before the surface flow was applied. A complete mass of 6400 mg of sodium benzoate was applied to the flume during experiment 4, and a mass of 623.68 mg was lost during the 90 minutes of experiment. This indicates that the sodium benzoate might have been degraded during the four days the soil attained equilibrium. As the flume was open to the atmosphere, oxygen was not limited to the soil, and as sodium benzoate is aerobically degradable, this seems to be the most reasonable explanation why mass in, m_{in} , does not equal mass out, m_{out} . The mass lost is 10%. For both the bromide and the PFBA, the complete applied mass left the flume during the 90 minutes of experiment, i.e. $m_{in}=m_{out}$. For experiment 2, the mass of bromide which left the box was equal to the applied mass.

There are 21 monitoring points along the soil bed, the mass in these points are not calculated. Due to that the leaching velocity at the bottom of the box is different from the surface/runoff velocity, the velocity in each monitoring point will be different. The monitoring point closest to the soil surface will mostly be influenced of the surface flow, and the monitoring point closest to the soil bottom will mainly depend on the infiltration rate. As the flow lines are not known, these velocities can not be calculated. Nonetheless, a mass lost M less than the actual M_i may be determined using the monitoring points. The procedure involves numerical integration between each sampling period based upon the trapezoidal rule using equation 9.

$$M_t = \sum_N^{i=1} \Delta M \quad (9)$$

where

ΔM = an incremental mass loss within a sampling interval

N = the numbers of sampling intervals

This equation can however only be used if the actual mass is known. In this investigation the actual mass in each monitoring point with time is not known.

CHAPTER 5

CONCLUSION

The results of the study enhances our understanding of the extent and nature of the release, uptake and mass transfer of soluble chemicals to or from runoff when downward movement (infiltration) occurs. The investigation shows that with an increased infiltration the chemical loss to the runoff decreases, and that most of the applied chemicals to the soil leaves the flume through infiltration. It has been demonstrated that there are several factors influencing chemical lost to runoff; soil type, infiltration, biodegradation, and there are also suggestions that there is transfer due to diffusion processes. Other factors which this investigation did not include are: rainfall intensity, slope, heterogeneity, unsaturated soil, and chemical application. In order to create an accurate model, knowledge concerning the interaction of above listed factors are required. The models so far have had difficulties defining the depth and degree of water-soil interaction, adsorption-desorption relationships for chemicals, and pathways of water flow. Shallow subsurface flow or interflow can be important pathways for transfer of soluble chemicals in runoff in permeable soils. A layer of high permeability above an impeding layer greatly increases the flow rates and the runoff concentration.

From the research of this investigation, some possible ways to reduce chemical loss to runoff are to i) incorporate chemicals into the soil or apply them below the surface rather than on the surface; ii) minimize the area of application by specific placement of chemicals; iii) maintain and enhance infiltration rate of the soil; iv) increase permeability of the soil by subsoiling and growing deep-rooted crops; v) add surface cover.

More research, on a field scale basis, using other tracers than bromide (which has primarily been used so far) is required. One example of tracers which can be used are sorbing compounds and tracers which are larger than bromide so the hypothesis about diffusion transfer can be evaluated.

APPENDIX 1: Soil Properties**Properties of silica sand**

bulk density, $\rho_b = 1.33 \text{ g/cm}^3$

particle density, $\rho_p = 2.75 \text{ g/cm}^3$

porosity, $\Phi = 0.52$

Grain diameter, $d_{50} = 1.0 \text{ mm}$

moister content, $\theta \approx 6.0\%$

organic content ≈ 0

Properties of Vinton soil

Sand= 97.0%

Silt= 1.8%

Clay= 1.2%

bulk density, $\rho_b = 1.34 \text{ g/cm}^3$

particle density, $\rho_p = 2.75 \text{ g/cm}^3$

porosity, $\Phi = 0.51$

moister content, $\theta \approx 23\%$

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