ENVIRONMENTAL DYNAMICS OF BENOMYL AND THIABENDAZOLE

by

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(ABSTRACT)

The comprehensive environmental dynamics of the heterocyclic Benzimidazole fungicides, Benomyl and Thiabendazole was investigated. This included examining their fate and distribution in the terrestrial and aquatic phases of a laboratory microcosm comprised of silty clay loam soil and plants. The soil component constituted a major relocation site, with approximately 45 and 75% of initial Benomyl (recovered as MBC) and Thiabendazole concentrations being recovered from the soil component of the microcosm, respectively, while 53 and 27% translocated into corn plants. The adsorption mechanism/s of these fungicides onto soil components were investigated using silty clay loam, silty loam and sandy soils as well as Ca-bentonite. These studies indicated that both fungicides were adsorbed to the highest degree on silty clay loam, followed by silty loam and sandy soils. Their adsorption on Ca-bentonite was found to be a function of the pH of the suspension, suggesting that in the presence of increasing H^+ activity on the clay surfaces, Benomyl and Thiabendazole become protonated to form positively charged molecules. These may then react with the clay surfaces forming Fungicide-clay complexes. The effect of different $CaCl_2$ concentrations on the adsorption process demonstrated that an increase in the salt concentration, at a constant pH resulted in a decrease in the amounts of adsorbed fungicide. The transport of the fungicides (adsorbed onto soil particles) as a consequence of sediment runoff into aquatic systems was also estimated. Results of the simulation of overland sediment runoff from sections of the

Chowan river basin into the Meherrin river following a rainstorm, indicate that significant quantities of Benomyl and Thiabendazole could be transported into aquatic systems. Adsorption studies also indicated that the adsorption process is reversible. Thus, any significant increases in the pH of receiving bodies of water could result in the release of Benomyl and Thiabendazole from sediment causing a contamination of the aquatic system.

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Sincere thanks to for her advise and help in the labs.

Finally, I wish to dedicate this work to the memory of my mother, who would have been proud.

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1.0 Introduction

Modern agriculture is inextricably linked to the widespread use of a variety of pesticides. These synthetic compounds are used as purposeful environmental contaminants, and the user is generally confident that the fragile balance between benefit and risk is decidedly tilted toward the benefit side. This is, however, not always the case, and the unbridled use of fungicides, insecticides and herbicides has come to be considered a major deterrent to environmental quality. The research project described herein deals with the environmental dynamics of the systemic Benzimidazole fungicides, Benomyl and Thiabendazole.

Fungicides may be broadly defined as compounds which kill or inhibit the growth of fungi, and are classified as follows:

Protective fungicides that provide protection against infection at the site of applcation.

Eradicant fungicides that cure an infection at the site of applcation.

Systemic fungicides that can prevent the development of disease on regions of the plant away from the site of application.

Field applications of fungicides are made in the form of soil-drenches, foliar sprays and field dressings. A majority of the fungicides when applied in this way do not penetrate the underlying plant tissue in effective quantities. Systemic fungicides, however, are capable of not only penetrating underlying tissue, but of translocating within the plant body to regions of the plant away from the site of application.[35] Systemic fungicides for example, translocate from the roots to upper regions of the plant when applied as soil drenches, or from the foliage to the stems and roots when applied as foliar sprays.

The systemic heterocyclic benzimidazole fungicides, Benomyl and Thiabendazole, are commonly used compounds effective against a wide variety of fungal diseases affecting crops such as wheat, rice, cotton and tobacco, as well as fruit and vegetable crops. Various studies have described the dynamics of Benomyl and Thiabendazole in the soil environment, and their uptake, distribution and metabolism in plants. These studies address ecosystem components on an individual basis. No attempt has been made, however, to address the comprehensive fate of these compounds in the natural ecosystem. Ecosystems can be conceived of as highly complex matrices consisting of biotic and abiotic components. The biotic components include plants, animals and microorganisms, which form intricate networks within the physical environment. The abiotic components include the physical environment (constituted of air, water, soil and sediment) and other non-biological material. An ecosystem is not merely a grouping of these various components, but a product of the complex interactions between and among them. These interactions have identifiable pathways and functions. Thus, the effects upon an ecosystem's ability to compensate for, and recover from, chemical stress, cannot be inferred from single component studies, since the interconnections between individual components are not additive.[39]

The use of laboratory simulation models or microcosms to study the comprehensive environmental fate of toxic compounds has gained considerable interest over the past decade. A microcosm may be defined in simple terms as a controlled, reproducible laboratory system that contains surrogate components and processes representing specific origins, flows, transformations and effects in the natural environment. The gamut of experimental units, then, runs from pure cultures to excised intact portions of terrestrial landscapes. The components that comprise a

microcosm are selected from within a specific range of parameters that reflect the diversity one may encounter in the natural environment under investigation.

The high degree of adsorption of Benomyl and Thiabendazole to soil components has previously been determined by various researchers. However, the mechanism of this adsorption process has not been qualified. There is also considerable evidence of the long term persistence of both Benomyl and Thiabendazole in soils. These compounds are characterized by low solubility and insignificant volatilization rates. Thus, it is important to consider the transport of these compounds (adsorbed onto soil components) as a consequence of soil erosion and runoff from agricultural areas. Laboratory data from adsorption studies were abstracted into a computer simulation model. This model, taking into account factors such as precipitation, infiltration, soil characteristics and surface topography, attempts to quantify the transport of Benomyl and Thiabendazole as a function of sediment fluxes into aquatic systems.

The objectives of this study were threefold:

1. To determine the comprehensive fate of Benomyl and Thiabendazole in the aquatic and terrestrial phases of a laboratory microcosm,

2. To determine the predominant mechanism(s) involved in the adsorption of these compounds to soil components, and finally,

3. To quantify the transport of Benomyl and Thiabendazole as a result of soil erosion and surface runoff into aquatic systems using a computerized simulation model.

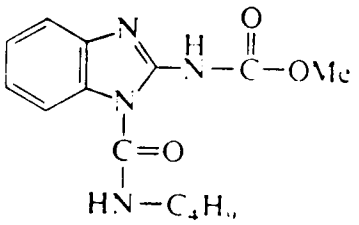
2.0 Literature Review

2.1 Profile of Benomyl and Thiabendazole

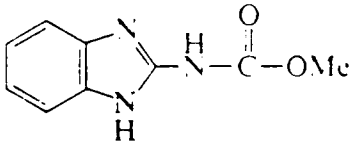
Benomyl is a protective and eradicant fungicide with systemic activity effective against a wide range of fungi affecting field crops. Pure Benomyl (IUPAC: Methyl 1 - (butylcarbamoyl) benzimidazol - 2 - ylcarbamate) is a colorless crystalline solid, with a molecular weight of 290.3. Its fungicidal activity was first described by Delp *et al.* [30] Benomyl was orginally introduced by E.I. Du Pont de Nemours & Co. (Inc.) as *Benlate™* fungicide.

On heating, Benomyl decomposes without melting. Its vapor pressure is negligible at room temperature. Benomyl is soluble at levels of 2 mg/l water at *pH* 7, 18 g/kg acetone, 94 g/kg chloroform and 4 g/kg ethanol. In dilute aqueous solutions, or in organic solvents, Benomyl rapidly loses the butylcarbamoyl group, forming Methyl benzimidazol-2-ylcarbamate (Carbendazim, MBC).[9] [10] Carbendazim is also formed in soil, plants and animals under certain conditions, and is the principle degradative product of Benomyl.

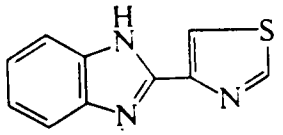
Figure 1 shows the structure of Benomyl, and its principle degradative product, Carbendazim.



Benomyl



Carbendazim



Thiabendazole

Figure 1. Structures of Benomyl, Carbendazim, and Thiabendazole.

Thiabendazole (TBZ) is a systemic fungicide effective against fungal diseases affecting crops such as rice, wheat, cotton and tobacco, as well as fruit and vegetable crops. Thiabendazole, (IUPAC: 2 - (thiazol-4-yl) benzimidazole) is a colorless powder, with a molecular weight of 201.2. Its fungicidal activity was first described by Staron *et al.*[61] It was originally introduced by Merck & Co. (Inc.) as *Mertect™* fungicide.

Thiabendazole is non-volatile at room temperature and has a melting point of 304-305 °*C*. Its solubility at 25 °*C* is 10 g/l water at *pH* 2, < 50 mg/l at *pH* 5-12, and > 50 mg/l at *pH* 12. At room temperature it is soluble at levels of 80 mg/l chloroform and 9.3 g/l methanol. Under normal conditions it is stable to hydrolysis, light, and heat.

Figure 1 shows the structure of Thiabendazole.

2.2 Dynamics of Benomyl and Thiabendazole in the Soil

In a terrestrial environment, the soil comprises a major component and in many instances acts as a sink for environmental contaminants. In order to comprehend the fate and effects of Benomyl and Thiabendazole in the terrestrial ecosystem as a whole, it is necessary to examine their dynamics in the soil. The five major processes affecting the behavior of a contaminant in the soil environment are:

1. Adsorption/desorption,
2. Decomposition,
3. Movement,
4. Plant or organism uptake, and,
5. Vaporization.

The phenomenon of adsorption/desorption directly or indirectly influences the magnitude of the effect of the other factors.

2.2.1 Adsorption/Desorption

The process of adsorption involves the solid phase of the soil, consisting of both inorganic and organic components. The inorganic fraction is composed of crystalline clay minerals, as well as crystalline and amorphous oxides and hydroxides, ranging in size from tiny colloids (< 2 μm), to large gravel (> 2 mm) and rocks. Clay minerals consist of layers of silica and aluminum sheets. Silica is comprised of a silicon atom surrounded by four oxygen atoms in a tetrahedral symmetry, while alumina represents aluminum atoms coordinated by six oxygen or hydroxyl groups in an octahedral fashion. In many cases, the aluminum and silicon atoms are replaced by such atoms as iron, manganese and magnesium.

The organic fraction consists of plant and animal residues at various stages of decomposition, cells and tissues of soil organisms, and substances synthesized by the soil microflora. The organic or humic fraction has not been completely characterized, although it appears that much of the reactivity of this fraction is embodied in a constituent called humic acid. Humic acids have been described by Van Dijk as being globular polybasic acids, with at least two kinds of acid groups—carboxyl and phenolic-hydroxyl groups.[62] Functional groups such as carboxyl, amino, phenolic-hydroxyl and alcoholic-hydroxyl, in addition to directly affecting the adsorption of cationic and anionic compounds by the humic acid, may also provide sites for hydrogen bonding interactions with the compounds. However, due to the complexity of humic acid and the experimental difficulties involved in determining fungicide interactions with organic matter, very little information exists in available literature on this subject.

The adsorption of non-ionic species can rarely be identified with only one mechanism, although the predominant mechanism can often be determined. Molecular characteristics such as 1) chemical character, shape and configuration, 2) acidity or basicity, 3) water solubility, 4) charge

distribution, 5) polarity, 6) size and 7) polarizability, all influence the adsorption of non-ionic compounds by the soil.

Adsorption isotherms, describing the amount of adsorbate (solute) adsorbed by an adsorbent (soil particles) as a function of the equilibrium concentration of the adsorbate in soil water, are used to describe fungicide behavior in soils. The two adsorption isotherms widely used to describe adsorption/desorption phenomena are:

1. Freundlich's isotherm: $\frac{x}{m} = KC^{1/n}$

2. Langmuir's isotherm : $\frac{x}{m} = \frac{abC}{1 + aC}$

In the above equations, x = amount of chemical sorbed; m = weight of the soil; C = equilibrium concentration of the fungicide in solution; and K, n, a, and b are constants. Rhodes *et al.*[52] have described the use of Freundlich isotherms along with soil thin layer chromatography to determine the mobility and adsorption of pesticides such as Bromacil, Diuron and Chloroneb on silt-loam, loam-sand and mucky soils.

The application of Benomyl and Thiabendazole for the control of vascular fungal diseases of plants was found to require extremely large doses, which was not very economical for many crops.[17] Baude *et al.*[2] have suggested that this might be due to the tight adsorption of the Benzimidazole fungicides to the soil. The half-life of total Benzimidazole-containing residues was found to be between 3 and 6 months on turf, and between 6 and 12 months on bare soil from different agricultural areas of the United States. More Benomyl was taken up by plants from sandy soils than from clay soils, and the rate of Benomyl uptake by plants was found to be higher when they were grown in soils with a low organic matter and a high *pH*.[50] Hewleg[24] observed an increasing adsorption of Carbendazim in soil within a few weeks of incubation, and also found that adsorption was the highest in soil with a high organic matter content. Thus, high organic matter and clay content, coupled with low *pH* conditions in the soil environment, seem conducive for the increased adsorption of Benomyl and Thiabendazole.

None of the studies mentioned above have attempted to identify the predominant mechanism(s) of adsorption involved. Mortland,[36] in his discussion on clay-organic complexes and interactions, has shown that, for most organic pesticides which are weak bases, their existence as cations and therefore their ability to exchange with metal ions on the clay, will depend upon their ability to accept a proton from the surrounding medium, which in turn is determined by the *pH*. He suggested that the surface activity of clay minerals may be the source of H^+ for protonating pesticides. Weber[64] demonstrated for a series of *s*-triazine compounds that the maximum adsorption on montmorillonite clay occurred at a *pH* in the vicinity of the pK_a value of each compound, or in other words, the *pH* at which the compound became protonated. A further lowering of the *pH* resulted in some desorption of the *s*-triazine compounds, which was attributed to the competition of the protonated species with H^+. An alternative explanation would be that the low *pH* released Al^{3+} from the clay lattice, which would be a much better competitor than H^+ to displace the protonated organic cation from the exchange complex.

2.2.2 Decomposition

Benomyl and Thiabendazole are susceptible to three major processes of decomposition in the soil which could alter their chemical structure and/or composition. They are 1) purely chemical decomposition, 2) decomposition by soil microorganisms, and 3) photodecomposition.

2.2.2.1 Decomposition of Benomyl

In dilute aqueous solutions or in organic solvents, Benomyl rapidly loses the butylcarbamoyl group, forming Methyl benzimidazol-2-ylcarbamate (Carbendazim, MBC).[9,10]

Carbendazim is rather persistent in soil, the half-life of 0.5-1 year of the total Benzimidazoles in Benomyl-treated soil being attributable to it.

2-amino benzimidazole is formed by the degradation of Carbendazim, and/or Benomyl in the soil. Siegel[56] has shown that sterilization of soils greatly reduced the dissapearance of Carbendazim, and suggested that the ring cleavage of the Benzimidazole nucleus and the metabolism of this, as well as the methyl carbamate moiety, to CO_2, was related to the presence of soil microorganisms. Hewleg[24] observed that after 250 days of incubation of Carbendazim in unsterilized sandy loam and clay loam soils, 13% and 15%, of added Carbendazim was recovered, compared to 70% and 50%, respectively, from sterile soils. Between 4 and 8% of added Carbendazim was recovered as 2-amino benzimidazole from both sterilized and unsterilized soils. In soils with a high humus content, the mobility of 2-amino benzimidazole was found to be very low,[52] which suggests that 2-amino benzimidazole is adsorbed on organic matter, and consequently unavailable for decompositon. Several organisms were isolated from treated soil which degraded Benomyl or Carbendazim,[63] and 2-amino benzimidazole and 5-hydroxy carbendazim were identified as metabolites. However, it is important to note that Carbendazim and 2-amino benzimidazole are poor energy sources for microorganisms as attested by the extremely low evolution of CO_2 from soil amended with Carbendazim.[24] Large scale changes in gross soil microbial populations, which play an important role in soil fertility were not observed in Benomyl-soil experiments by Peeples.[43]

The decomposition of Benomyl to Carbendazim is also accelerated by sunlight.[32] Photo-oxidation of the benzene ring of Carbendazim was the predominant reaction detected by Fleeker and Lacy[19] when the compound was exposed to sunlight for 40 hours as a residue on silica gel, although less than 20% of the Carbendazim was decomposed. Guanidine, Carbomethoxy-guanidine and Carbomethoxy urea were detected among the photolysis products. Figure 2 summarizes all known decomposition pathways of Benomyl in the soil environment.

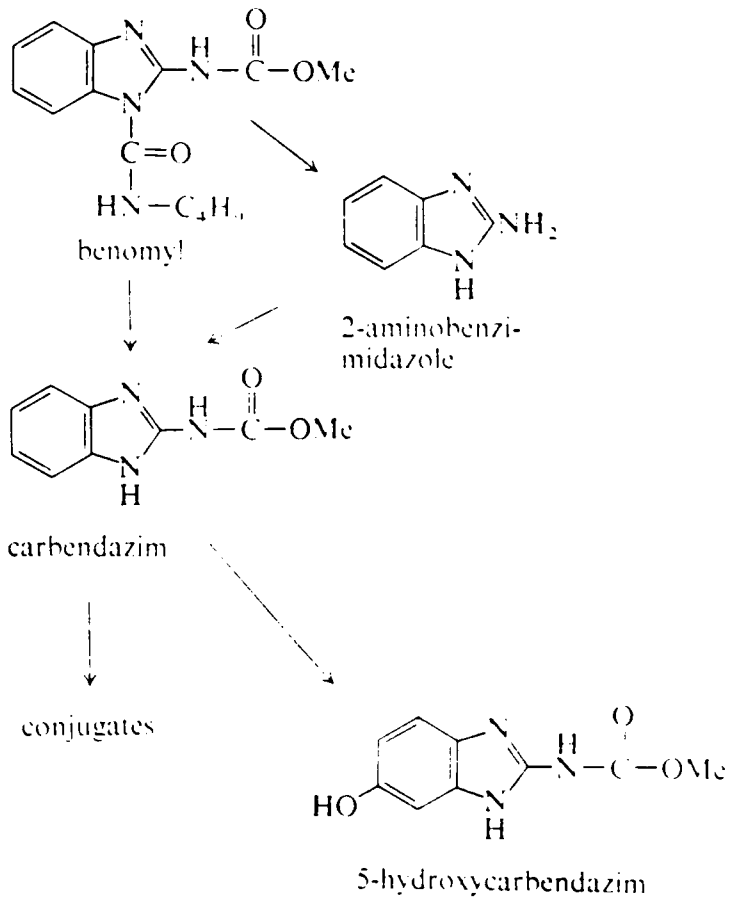
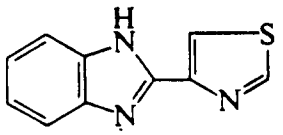
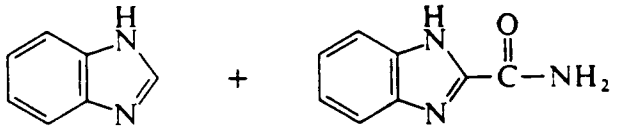


Figure 2. Decomposition pathways of Benomyl in the soil environment.



thiabendazole



benzimidazole + benzimidazole-2-carboxamide

Figure 3. Decomposition pathways of Thiabendazole in the soil environment and in plants.

2.2.2.2 *Decomposition of Thiabendazole*

The transformation of Thiabendazole has not been researched as extensively as that of Benomyl, probably because its practical application is less extensive. There is no specific information on the breakdown of Thiabendazole by microorganisms. Hine *et al.*[28] have shown that Thiabendazole is less persistent in the soil than Carbendazim and that its fungistatic activity dissappeared in 12-14 weeks in soil. Dissappearence from a sandy loam soil was reported by Erwin *et al.*[13] Jacob *et al.*[24] found only unchanged Thiabendazole in plants grown in artificial light, whereas with plants grown in sunlight, 78% of the recovered compound was identified as the initial compound. They also found that Benzimidazole and Benzimidazole-2-carboxamide were the degradative products when Thiabendazole was exposed on glass plates to sunlight. They concluded that degradation appeared to arise from photolysis rather than plant induced metabolism. Figure 3 shows all known decomposition pathways of Thiabendazole in the soil environment.

2.2.3 Movement Characteristics

Soil run-off, leaching and diffusion characteristics of agricultural chemicals and their metabolites are important environmental concerns. The movement of fungicides in soils have been studied by the use of adsorption isotherms,[52] soil columns, analysis of treated fields,[2 51] and more recently by soil thin layer chromatography.[25] The movement of a fungicide in the soil is governed by processes such as adsorption/desorption, diffusion, rate of degradation, hydrodynamic dispersion and solubility. Rhodes and Long,[51] in run-off and leaching studies under greenhouse conditions, have shown that Benomyl and its soil degradation products are highly immobile in the soil. Less than 0.1% of the initial Benomyl concentration of 10 ppm, or < 0.01 ppm of Benomyl in solution was detected in runoff and percolation water when a total of 10.8 cm of artificial rain was applied in 7 days. Greater than 95% of the applied compound remained in the top 0-8 cm depth, indicating that Benomyl has little or no tendency to move downward in the soil. The soil retention factor

(R_f) values for Benomyl, Carbendazim, and 2-amino benzimidazole as determined by soil thin layer chromatography have also demonstrated the relative immobility of these compounds. R_f data were obtained using four different soils representing different soil types from various geographic locations. The R_f values for these compounds on Keyport silt loam were 0.10, 0.05 and 0.12, respectively. These R_f values would place Carbendazim in mobility class 1 (immobile compounds, R_f = 0.0-0.09), and Benomyl and 2-amino benzimidazole in mobility class 2 (R_f = 0.10-0.34), according to the mobility classification suggested by Helling and Turner.[23] Helling and Turner's classification method consists of 5 groups, with class 5 (R_f = 0.90-1.00) being the most mobile. It was shown earlier that the R_f values of compounds on Keyport silt loam and Helling's soils (Hagerstown silty clay loam and Chillum silt loam) are almost identical.

However, processes such as erosion of soil particles on which Benomyl and Thiabendazole have been adsorbed, and desorption of these compounds from soil particles into solution could play a role in the transport into aquatic systems and the accumulation of these fungicides therein.

2.2.4 Vaporization

The vaporization of Benomyl and Thiabendazole from soil surfaces can be considered insignificant for the following reasons:

1. Their high degree of adsorption to soil components. It has been shown that adsorption of a compound to any surface retards vapor loss, and,

2. The insignificant vapor pressure of these compounds.

2.2.4.1 *Transport of Benomyl and Thiabendazole Adsorbed on Soil Particles*

Considering evidence of the long term persistance of Benomyl and Thiabendazole in soils, their low water solubility, relative immobility and insignificant volatilization rates, it is important to consider the transport of these compounds (adsorbed on soil particles) as a result of soil erosion. Erosion can be brought about by the action of flowing water which washes the particle away, by the action of wind, or by the movement of a whole mass of soil slipping down a gradient.[26]

Erosion by water involves two separate processes. First, soil aggregates must be broken down into smaller particles. This requires energy which is normally supplied by the impact of raindrops. The kinetic energy of the raindrops depends on their intensity and the drop size distribution, but can be considerable in heavy storms, reaching several hundred thousand ergs/cm^2 per cm of rain. The second process is the transport of the fine particles as a suspension by the water running over the surface of the soil. The rate at which soil is eroded is clearly very variable, and depends on the climate, structure and texture of the soil and the stability of the aggregates. The topography of the area as well as the nature of the plant cover are also important factors. Loss of surface soil can be considerable on sloping land even where crops are grown, easily reaching 10 tons/hectare/annum, equivalent to 1 mm of topsoil at a bulk density of 1 g/cm^3.

Transport of soil particles by wind involves three processes. The smallest particles can be carried as a dust or suspension often over very great distances, the coarser particles are rolled along the surface, while the particles of intermediate size are transported by the process known as saltation. In this process, eddies of wind lift suitably sized particles from the soil surface to a height of a few centimeters where the air velocity is much greater than at the surface. The particles thus acquire a considerable momentum, and when they fall back to the surface as the eddy dies away, the impact may throw other particles a short distance upward. These are in turn accelerated, thus, repeating the process continually along the exposed length of soil.

In most areas where fungicides are used, erosion by water is more significant than wind erosion.

2.3 *Translocation and Metabolism in Plants*

2.3.1 Translocation

There are a number of general descriptions of pesticide translocation in plants,[34 50] including recent reviews of more specialized aspects. Data relating to systemic fungicides has been reviewed by Erwin.[16] The movement of chemicals in plants can be considered in two stages:

1. Entry into the free spaces within the tissues.

2. Movement in the symplast, which is within the living parts of the cell. This is active, and requires the expenditure of energy. Long distance transport takes place in the phloem, within specialized cells known as sieve tubes.

Solel[55] has discussed in detail the systemic fungicidal effects of the Benzimidazole fungicides. Peterson and Edgington[46] have shown that Benomyl rapidly decomposes to its fungicidally active metabolic product, Carbendazim, and that this compound was mainly transported in the apoplast and accumulated in the leaf tips and margins. In a subsequent study,[47] the authors suggested that the capacity of a specific plant organ to transpire apparently governed its ability to accumalate Carbendazim when used as a systemic fungicide. They were able to mimic the marginal and apical accumulation of Benomyl observed in their earlier study by observing the movement of eosin dye. They explained the distribution patterns observed as a consequence of physical forces alone. Similar studies by Siegel[57] and Solel,[54] have attested to the apoplastic movement of Carbendazim. Staron[61] demonstrated systemic activity following the apoplastic movement of Thiabendazole. Thiabendazole translocated from roots in treated soils to stems and leaves, although concentratations in upper parts of the plants were much less than in the lower parts.[13] Symplastic movement from treated leaves back into the rest of the plant was also reported

for both Benomyl and Thiabendazole. Solel *et al.*[54] have provided more conclusive evidence of the symplastic movement from treated coyledons or leaves to untreated parts of the plant, including the roots, stem and shoot apex.

2.3.2 Metabolism

As mentioned earlier, in dilute aqueous solution or in organic solvents, Benomyl rapidly loses the butylcarbamoyl group, forming Methyl benzimidazol-2-ylcarbamate.[9 10] This compound is also formed from Benomyl in plants. However, when applied to plants by spraying, Benomyl was found to be more stable and was shown to constitute a major part of the spray deposit for extended periods of time.[1] Carbendazim is quite stable in plants. Siegel[57] found no traces of Carbendazim in products of intermediary metabolism after 88 days in strawberry plants, and only 1.5% of initial Carbendazim was respired as CO_2 after 14 days in cucumber plants.[54] Although the Benzimidazole nucleus thus appears stable, small amounts of the non-fungitoxic 2-amino benzimidazole were observed by Siegel,[57] and certain products resulting from the ring cleavage of the Benzimidazole nucleus, via 2-aminobenzonitrile and aniline were detected by Rouchaud *et al.*[49] after 2 months, in addition to Benzimidazole in lemon plants. These latter products might be the result of photodecomposition. Figure 4 shows all known pathways of decomposition of Benomyl in plants.

Erwin *et al.*[13] have studied the fate of Thiabendazole in cotton plants and speculated that congugates of metabolites are formed. The unchanged parent compound was also detected in plants after uptake via the roots. In pepper leaves, Thiabendazole dissappeared faster than Carbendazim.[5] After leaf application on sugar beet, no transformation of Thiabendazole occured under artifical light, while on plants exposed to sunlight, small amounts of Benzimidazole and Benzimidazole-2-carboxamide were formed, obviously by photodecomposition. Figure 3 shows all known pathways of decomposition of Thiabendazole in plants which are similar to the pathways in the soil environment.

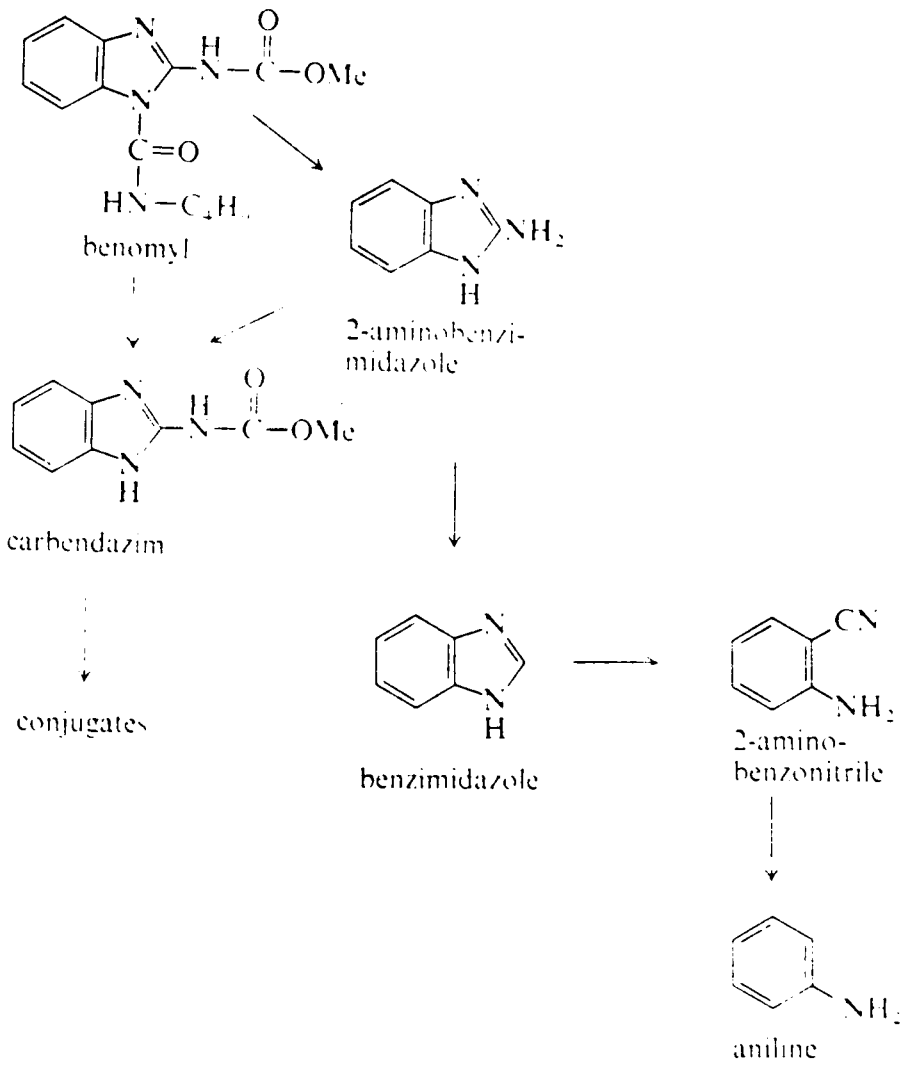


Figure 4. Decomposition pathways of Benomyl in plants.

It is obvious that both Benomyl, and to a lesser extent, Thiabendazole, have been extensively studied in individual components of the ecosystem. However, no attempts have been made to examine their comprehensive fate in the natural ecosystem. Laboratory microcosms could help address this void in our understanding of the fate and distribution of Benomyl and Thiabendazole.

2.4 *Laboratory Microcosms*

Experimental microcosm studies used to evaluate the fate and/or effects of toxicants on ecosystems are quite diverse. Table 1 lists the chief characteristics of some of the microcosms in use today.

Gillett and Gile[20] examined the disposition of Dieldrin in a terrestrial microcosm chamber consisting of a soil medium, agricultural crops and a few invertebrates, and have shown that the microcosm represented field experience generally with regard to the major pathways of transformation and transport, although the photodecomposition process was inadequately represented. Nash and Beall[38] developed a micro-agroecosystem that simulated field conditions to monitor pesticides in four environmental phases: soil, plant, water and air. Their results indicated that the system could be used to obtain preliminary information before more elaborate testing procedures are undertaken.

Metcalf *et al.*[37] have extensively reviewed the environmental toxicology of 15 fungicides, insecticides and herbicides with regard to toxicity, degradation, accumulation and distribution. These parameters were examined in the air, soil, surface water, sediment, leachate, and in aquatic and terrestrial biota. Widely used compounds such as DDT, Aldrin, Dieldrin, Captan and Hexachlorobenzene were used to facilitate a comparison of the results obtained, with the extensive data available in literature from actual field studies of these compounds. The authors concluded that the model results agreed very closely with existing field data.

Table 1. Major characteristics of some of the laboratory microcosms in use today.

Characteristic	System					
	Plant/soil [33]	Terrestrial monoculture system [37]	Microagro-ecosystem [38]	Terrestrial Microcosm Chamber [20]	Soil core [12]	Soil/litter ecosystem respirometer [6]
Unit size	1.0 liter	19 l.	863 l. (1.5×0.5×1.15m)	458 l. (1.0×0.75×0.6m)	40 cc	500 cc
Mass of soil (kg)	0.7	0.4 (vermiculite) 3.0 (Drummer)	165	150	80g	100g
Type of soil(s)	silty loam; sandy; quartz sand	vermiculite; silty clay loam	sandy loam	synthetic potting mix; silty clay loam	various forest and grassland types	(Douglas fir, red alder litter)
Temperature (C)	28/20	26/19	ambient[a]	30/19	26/20	19
Light/dark (hrs)	12/12	12/12	ambient	16/8	12/12	0/24
Air flow rate (l./min)	ambient	ambient	2500	10, 50	ambient	0- by demand
Water inputs	Addition to weight; percolation	addition to weight; post-terrestrial aquatic study	"rain" to set humidity or excess for percolation	"rain to set humidity; "spring"	fixed volume on weekly basis for per-percolation	none
Plants	Corn	Corn; soybeans	Corn; cotton; tomatoes; tobacco; cereals and grasses	Alfalfa/ryegrass; Douglas fir/red alder/ryegrass	Endemic plant types (e.g., fescue meadow plants)	None
Invertebrates added	None	Caterpillar, slugs, pillbugs, earthworms	None	*Tenebrio* larvae, snails, pillbugs, earthworms, crickets, *Collembola* spp., nematode spp.	None (endemic fauna)	None (endemic fauna)
Vertebrates	None	Prairie vole	None	Gray-tailed vole	None	None
Microbiota	Ambient	Ambient	Ambient	Ambient	Ambient	Ambient
Operating time (per experiment)	up to 200 days	30 days as terrestrial; 27 days days as aquatic	60-90 days	60-90 days	6 to 9 weeks (including pre-equilibration time of 5 to 7 weeks)	60 days (including pre-treatment equilibration of about 30 days)

2.4.1 Residue Analysis

Residue analysis is comprised of two steps. Extraction of the compound from the sample matrix, and its identification and estimation. Baker and Hoodless[3] have extensively reviewed analytical methods for the detection and determination of systemic fungicide residues.

Fluorimetric and colorimetric procedures for residual determination of Benomyl in plant and animal tissues and in soils have been described by Pease and Gardiner.[41] The minimum detectable level using this procedure is 0.1 ppm. Extraction with ethyl acetate, followed by both acid and alkaline hydrolysis, converted both Benomyl and Carbendazim to 2-amino benzimidazole, which was determined by fluorescent spectrophotometry or after reaction with bromine, by colorimetry. Pease and Holt[40] described a modification of this procedure, although the minimum detectable limit remained about the same. Kirkland *et al.*[31] have used high speed liquid chromatography for the analysis of Benomyl in soil and plant tissue using an ultra-violet spectrophotometric detector to monitor the eluate at a fixed wavelength of 254 nm. The minimum detectable level was 0.05 ppm.

A number of methods for the determination of Thiabendazole are based on those presented by the manufacturers.[48] [Merck & C0. (Inc.)] Extraction with ethyl acetate is followed by clean-up and final quantitative measurement in 0.1N HCl is made using a fluorescent spectrophotometer. Thiabendazole in cotton plants to a limit of 0.1 ppm has also been determined spectrophotometrically. Szalkowski[53] described a method which involves extraction with dilute HCl, addition of *p*-phenyldiamine, reduction with zinc dust and oxidation to form a colored complex. This complex is extracted with butanol, and the absorbance measured in a spectrophotometer. Concentrations as low as 0.2 ppm were detected by this method.

2.5 *Theoretical Considerations of Surface Runoff*

When rainfall occurs in a given region, its rate often exceeds the infiltration rate into the soil. If this is the case, water will accumulate on the ground surface until the gravitational forces overcome the forces resisting motion, and flow begins to take place. The nature of this flow depends upon the geometry of the terrain. In relatively small and flat catchments, the predominant phenomenon is the thin sheet flow generally designated as overland flow. Usually, the outflow from these catchments is routed to small streams and subsequently to higher order streams and standing bodies of water.

The mathematical formulation of overland flow is based on Eagleson's kinematic wave relationships.[14] The overland flow formulation is that for steady uniform flow in a wide channel:

$$\tau_0 = \gamma y \sin\theta,$$

where τ_0 = bottom shear stress, lb/ft^2
γ = unit weight of water, lb/ft^3
y = water depth, ft
θ = angle of bottom slope.

In turn, τ_0 is a function of the Reynolds number and of the relative surface roughness factor, in a manner depending upon whether the flow is laminar or turbulent.

The formula used to compute the flow at a given location in a catchment is given by:

$$q = \alpha y^m,$$

where q = flow per unit catchment width, $ft^3/sec/ft$
m = constant, found to be $\frac{5}{3}$ for turbulent flow
$\alpha = \frac{1.49}{n}(\sin\theta)^{1/2}$ for the above value of m, $ft^{1/3}/sec$
n = Mannings roughness coefficient.

The value of n can be estimated from tabulated values for different types of land surfaces.[27] The mean velocity of flow (ft/sec), can be obtained by dividing the flow per unit width of the catchment by the water depth. Thus:

$$V = \alpha y^{m-1}.$$

It follows from the above that it is necessary to determine the water depth prior to computing velocity and flow. Thus, preliminary calculations must be made to obtain time averaged values for rainfall rates, infiltration rates and ponding depths. The first step is to inspect ponding depth values to determine the time at which maximum depth occured. This time is then assumed to be the duration of a simplified rainstorm, t_r. Next, the total rainfall R_T (in inches), must be computed. The rainfall intensity is given by:

$$i = \frac{R_T}{t_r} \text{ in/min.}$$

For the infiltration calculations it can be assumed that the time, t_f, at which ponding disappears constitutes the end of the infiltration period. Next, the total amount of infiltration, I_T, must be computed. The infiltration rate is given by:

$$f = \frac{I_T}{t_f} \text{ in/min.}$$

Two main cases arise depending on the relative values of the storm duration, t_r, and the time of concentration of rainfall, t_c. The latter is computed from:

$$t_c = \left[\frac{Li^{1-m}}{\alpha}\right]^{\frac{1}{m}},$$

where L = catchment length, ft

i = rainfall excess (rainfall less infiltration), ft/min.

The flow depths can be computed from:

$$y_L = (i - f)t \quad 0 \le t \le t_c$$
$$y_L = (i - f)t_c \quad t_c \le t \le t_r.$$

These values can be used in the velocity equation, $V = \alpha y^{m-1}$, to compute the mean velocity of flow. The resulting catchment outflow, Q, is given by:

$$Q = qw,$$
where w = width of catchment outflow, ft.

The sediment transport formula as defined by duBoys[15] is given by:

$$q_s = \psi \frac{\tau_o}{\gamma}\left[\frac{\tau_o}{\gamma} - \frac{\tau_{cr}}{\gamma}\right],$$
where q_s = flux of sediment, lb/sec/ft of width
ψ = a constant for a given bed composition,
τ_o = bed shear stress, lb/ft^2
τ_{cr} = critical shear stress, lb/ft^2
γ = unit weight of water, lb/ft^3.

The bed shear stress can in turn be expressed as:

$$\tau_o = \gamma y S_b,$$
where y = flow depth, ft
S_b = slope of bed.

Thus $$q_s = \psi y S_b\left[y S_b - \frac{\tau_{cr}}{\gamma}\right].$$

The values of ψ and τ_{cr} are tabulated for various grain sizes.[15] The total catchment sediment load is given by:

$$Q_s = wq_s,$$
where w = width of catchment outflow, ft
q_s = flux of sediment, lb/sec/ft of width.

3.0 Methods and Materials

3.1 Laboratory Microcosm Phase

The basic microcosm unit was a 25-l glass aquarium. Each unit contained 2500 g of silty clay loam soil, classified as a McGary and Purdy soil.[55] The soil was obtained from the area around Stroubles Creek, Blacksburg. The general soil characteristics were: sand, 10%; silt, 60%; clay, 30%; and organic matter, 2%. Fifty corn seeds (*Zea mays*) were uniformly planted in each unit at a depth of 1 cm. The height of the soil within each unit was 10 cm on an average. Pre-emergent applications at the rate of 5 mg of Benomyl and Thiabendazole in 1 ml of acetone were made in two individual units. This formulation was injected at 20 µl per injection, at a depth of 1 cm beside each of the seeds. This rate simulated a 0.45 kg active ingredient per acre application, which is the commonly used treatment rate in the field. The units were initially sprinkled with 1 liter of distilled water. The units were weighed after planting and watering, and again after 7 and 14 days, at which time enough distilled water was sprinkled to restore the initial wet weight, thus simulating two rains and compensating for the evaporation of water.

The units were operated under the following conditions:

- light/dark phase, 12/12 hours;
- day/night temperature, 26 °C/19 °C;
- day/night substrate temperature, 24 – 26 °C/20 – 21 °C;
- relative humidity, 50%;
- light source, 75 watt plant growth regulators;
- unrestricted air circulation.

The corn plants were sampled on days 10, 12, 14 and 18, and analyzed for Benomyl and Thiabendazole residues as described in Sections 3.2.1 and 3.2.3, respectively. All visible debris was removed and discarded on day 18, after which the substrate was thoroughly mixed, sampled on days 18, 19 and 20, and analyzed for Benomyl and Thiabedazole residues as described in Sections 3.2.2 and 3.2.4, respectively. The microcosms were then flooded with 7 liters of distilled water, and the surface water was subsequently sampled and analyzed on days 21 through 28 as described in Section 3.2.5. The water was decanted on day 28, and the wet sediment left in the aquarium for 5 days, after which it was thoroughly mixed, sampled and analyzed as described for soils. Figure 5 shows the time sequence for the sampling and maintenance of the microcosm units.

3.2 Residue Extraction and Analysis Methods

3.2.1 Extraction of Benomyl Residues from Plant Tissue

A representative sample of the corn plant including the roots was weighed into a blender jar. The mixture was then blended with 150 ml of ethyl acetate at high speed for 10 minutes. The

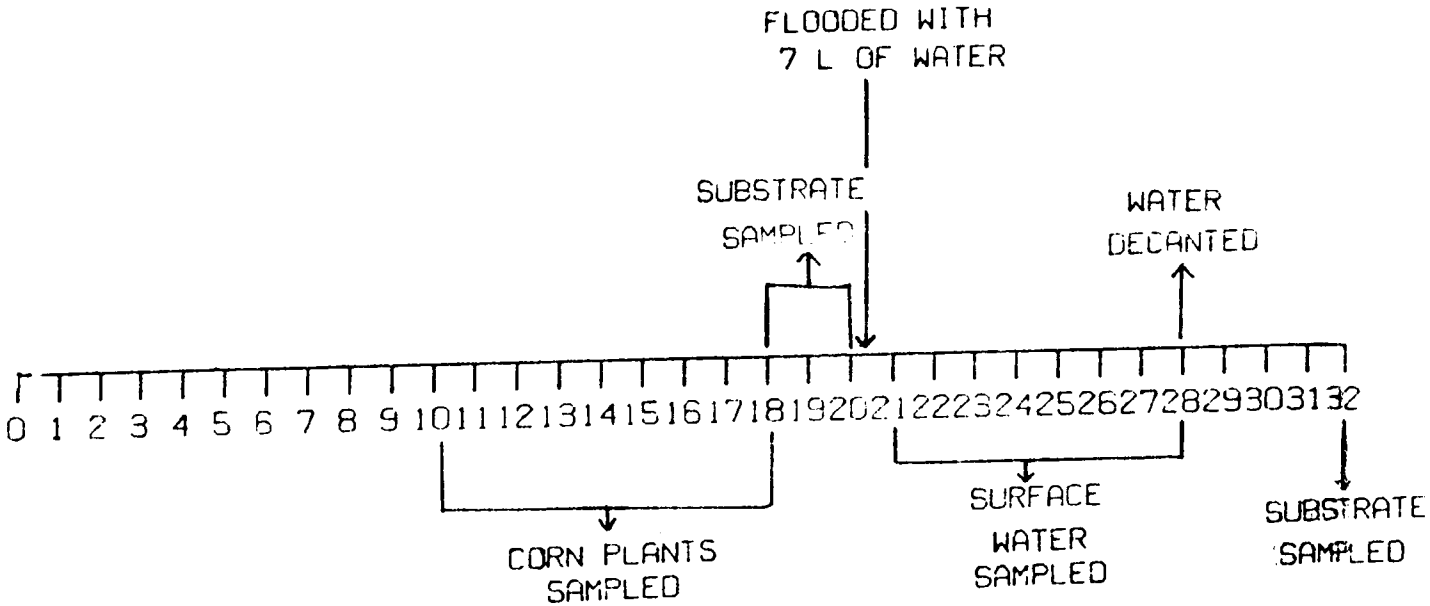


Figure 5. Time sequence for the sampling and maintainance of microcosm units.

blended sample was centrifuged at 2000 rpm for 10 minutes and filtered through a cotton plug. This procedure was repeated using another 100 ml of ethyl acetate, and 12.5 ml of 0.1N HCl was added to the extract. The mixture contained in a beaker was placed on a steam bath at 100 °C under a ventilated hood to evaporate the ethyl acetate. The volume, reduced to approximately 10 ml was transferred to a separatory funnel using small volumes of hot distilled water as wash. The extract was cooled to room temperature, 50 ml of *n*-hexane was added and the funnel was shaken for 2 minutes. After the phases separated, the hexane layer was discarded. The hexane wash was repeated twice, using an additional 50 ml of solvent each time. The aqueous phase was transferred to a separatory funnel along with 15 ml of 6.5N NaOH, the mixture was cooled to room temperature, and extracted with four 75 ml portions of ethyl acetate using 2-3 minute shaking periods for each extraction. After the separation of the layers, the ethyl acetate was filtered through cotton into a beaker and concentrated to about 50 ml by evaporation at room temperature under a ventilation hood.

The concentrated extract was transferred to a separatory funnel, 10 ml of 0.1N HCl was added and the funnel was shaken for 2 minutes. The phases were allowed to separate, and the aqueous phase drained into a second separatory funnel. The *pH* of the extract was checked to verify its acidity, and 1 ml of 1N HCl was added when required. The ethyl acetate was extracted with a second 10 ml portion of 1.0N HCl, and the acid phases combined. A 2 ml aliquot of 6.5N NaOH was added and the *pH* checked to verify the basicity of the solution, which was then extracted with four 50 ml portions of ethyl acetate, involving 2-3 minute shaking periods. After the phases separated, the ethyl acetate extract was filtered through cotton and concentrated to about 5 ml under a ventilation hood, and made up to the required volume with 0.1N H_3PO_4.

3.2.2 Extraction of Benomyl Residues from Soils

A representative soil sample was placed in a 1 liter flask, 100 ml of a 83% methanol-17% 1N HCl solution, and several boiling chips were added, and the mixture was re-

fluxed for 4 hours on a heating mantle, with a water cooled condenser attached in position. The solution was then cooled to room temperature. Approximately 200 ml of the aqueous phase was withdrawn using a syringe, and filtered through a cotton plug into a beaker. The extract was concentrated to about 20 ml by allowing it to stand under a ventilation hood overnight at room temperature. A 10 ml aliquot of 6.5N NaOH was added, and the solution was transferred to a separatory funnel containing 50 ml of chloroform. The funnel was then shaken for 2 minutes. The phases were allowed to separate and the chloroform layer was discarded.

The aqueous phase was extracted with four 75 ml portions of ethyl acetate using 2-3 minute shaking periods. The upper ethyl acetate layer was withdrawn using a syringe and concentrated until the volume was reduced to about 5 ml. The extract was diluted to volume with 0.1N H_3PO_4.

3.2.3 Extraction of Thiabendazole Residues from Plant Tissue

A representative sample of the corn plant including the roots was weighed, transferred into a blender jar, and blended at high speed for 5 minutes. A 100 ml aliquot of 0.1N HCl was added to the blended sample in a flat bottomed flask which was connected to a reflux condenser and placed on a magnetic stirrer hot plate. The mixture was heated for 30 minutes while stirring to obtain gentle refluxing. The sample was cooled to room temperature and centrifuged at 2000 rpm for 5 minutes. A 15 ml aliquot of the supernatant was transferred to a 250 ml flask, and 0.05 ml methyl-red solution (100 mg Me-red in 100 ml alcohol), and 0.5N NaOH were added dropwise until the red color was just discharged. The *pH* of the solution was adjusted to between 6.2 and 8.0. A mixture of 5 g NaCl and 20 ml CH_3Cl was added to the flask which was then shaken on a mechanical shaker for 5 minutes. The solution was then centrifuged for 5 minutes and the top layer was discarded. A 15 ml aliquot of the CH_3Cl extract (the bottom layer) was transferred to another 250 ml flask, 20 ml of 0.1N HCl was added, and the flask shaken for 5 minutes and centrifuged. Next, 15 ml of the clear top solution was transferred to a 25 ml volumetric flask and placed in a

water bath for 20 minutes. The solution was cooled to room temperature, the volume adjusted to 25 ml with 0.1N HCl and mixed thoroughly.

A 15 ml aliquot of the acid extract was transferred to a 250 ml flask, 5 ml of *p*-phenyldiamine solution, and 150 mg zinc dust were added, and the flask was stoppered and gently inverted to suspend the zinc dust. The flask was allowed to stand for 2 minutes to facilitate the settling of the zinc dust. The colored solution was decanted through a cotton plug into a flask and allowed to stand for 45 minutes. A 20 ml aliquot of the clear solution was pipetted into a centrifuge tube, and 5 ml of *n*-butanol and 4 g anhydrous Na_2SO_4 were added. The tube was shaken until the Na_2SO_4 had dissolved. Finally the solution was centrifuged and the clear butanol top layer was withdrawn for analysis on an ultraviolet spectrophotometer.

3.2.4 Extraction of Thiabendazole Residues from Soils

A representative sample of the soil was air dried, and extracted for 4 hours in an extractor using hot methanol as the solvent. The crude extract was removed and cooled in the rear of a well ventilated hood, and brought to a volume of 250 ml with methanol.

A 15 ml aliquot was removed and evaporated to dryness in a 100 ml beaker placed in a water bath at 100 °*C*. To the dried material, 15 ml of a buffer (13.3% anhydrous sodium acetate adjusted to *pH* 4.5 with HCl) and 15 ml of ethyl acetate was added and shaken for 5 minutes. The mixture was then centrifuged for 5 minutes at 5000 rpm, and the ethyl acetate layer was transferred to a 250 ml Erlenmeyer flask and shaken with 10 ml of 0.1N HCl for 5 minutes in a mechanical shaker. The final acid extract was then analyzed on an ultraviolet spectrophotometer.

3.2.5 Extraction of Benomyl and Thiabendazole Residues in Surface Water

A representative sample was placed in a separatory funnel and the sample container rinsed with small volumes of CH_3Cl. The *pH* of the mixture was adjusted to between 2 and 4 with 50% H_2SO_4. A 10 g portion of Na_2SO_4 was added to the solution and the sample extracted with CH_3Cl (1/4-1/10 volume of sample) by shaking the separatory funnel for 3 minutes. The phases were allowed to separate, and the CH_3Cl extract was evaporated for concentration under a ventilation hood.

3.2.6 Analysis of Residues

The analytical procedure for the determination of Benomyl was based upon the relative ease with which the parent compound benomyl degrades to the more stable Carbendazim. Quantitative determinations of Benomyl measured as Carbendazim were performed on a high performance liquid chromatographic system comprised of: 1) Beckman 110B and 114M solvent delivery modules, 2) a Beckman 340 organizer, 3) an Alltech C-18 reverse phase column (25 cm × 4.6 mm, 10 micron), 4) a Beckman 160 Ultraviolet Absorbance Detector and 5) a SpectraPhysics SP 4270 Integrator. The following conditions were used: mobile phases, HPLC grade acetonitrile and water; total carrier flow rate, 1.0 ml/min at 50:50—acetonitrile:water; wavelength, 254 nm.

Calculations were based on linear calibration curves obtained by plotting peak area vs. concentration of known standards. The concentration of Benomyl can be obtained from the following formula:

$$\text{ppm Benomyl} = \frac{\mu\text{g Carbendazim} \times 1.53}{\text{g of sample}} ,$$

where 1.53 is the ratio of the molecular weight of Benomyl (290.3) to that of Carbendazim (191). However, since Carbendazim (MBC) is the principle degradative product of Benomyl, as well as its principle fungicidal agent, all results were reported in terms of MBC.

Quantitative determinations of Thiabendazole residues were performed on a Beckman DU 6 Spectrophotometer. The UV absorbance was directly proportional to the concentration of thiabendazole in the standards. A calibration curve of absorbance vs. concentration was used to determine concentrations in the samples.

3.3 Adsorption Measurements

3.3.1 Adsorption of Benomyl and Thiabendazole on Ca-Bentonite

Solutions containing various concentrations of Benomyl and Thiabendazole (0.5-10 ppm) in 0.01M $CaCl_2$ were placed in 250 ml Erlenmeyer flasks and diluted to a volume of 150 ml with distilled water. Known amounts of bentonite clay were added to these solutions and the flasks were covered with aluminum foil and sealed with parafilm. The flasks were shaken on a mechanical shaker at room temperature for a period of 10 hours to facilitate equilibration. The equilibrated suspension was then centrifuged for 15 minutes at 10,000 rpm and filtered through a Whatman no. 1 filter paper. The clear solution was analyzed as described in Section 3.2.

3.3.2 Adsorption on Silty Clay Loam Soil

Air dried soil samples were passed through a 0.5 mm sieve and placed in a 250 ml Erlenmeyer flask. Solutions containing various concentrations of Benomyl and Thiabendazole

(0.5-10 ppm) in redistilled water were added to the soil, and the contents of the flask diluted to a volume of 150 ml with redistilled water. The flasks were covered with aluminum foil, sealed with parafilm and shaken on a mechanical shaker at room temperature for a period of 10 hours to facilitate equilibration. The equilibrated suspension was centrifuged for 15 minutes at 10,000 rpm, and the supernatant was filtered through a Whatman no. 1 filter paper. The clear solution was analyzed as described in Section 3.2.

3.3.3 Release of Benomyl and Thiabendazole from Soil/Bentonite to Water

Air dried soil/clay samples were treated with an ethyl acetate solution (0.1-1 ml/25 g soil or bentonite) of the fungicide (0.5-10 ppm). Aliquots (25 g) of soil/bentonite were placed in 250 ml Erlenmeyer flasks and 25 ml of redistilled water was added to each flask. The flasks were covered with aluminum foil and sealed with parafilm, and shaken on a mechanical shaker for 10 hours to facilitate equilibration. The equilibrated suspension was centrifuged for 15 minutes at 10,000 rpm, and the supernatant filtered through a Whatman no. 1 filter paper. The clear solution was analyzed as described in Section 3.2.

3.3.4 Determination of Adsorption Isotherms

Adsorption partition coefficients were determined for the fungicides using the Freundlich isotherm:

$$\frac{x}{m} = KC^{1/n},$$

where K and $\frac{1}{n}$ are constants; x = amount of fungicide sorberd in μg; m = weight of substrate in grams; and C = equilibrium concentration of the fungicide in solution in μg/ml. In the log form the above equation becomes:

$$\log \frac{x}{m} = \frac{1}{n} \log C + \log K.$$

Thus, the plotted isotherm becomes a straight line, and can readily be solved graphically for the constants K and $\frac{1}{n}$. K is the intercept and $\frac{1}{n}$ the slope of the line. When the equilibrium concentration in solution is 1 ppm, the equation reduces to the following:

$$\log \frac{x}{m} = \log K,$$

where $\frac{x}{m}$ is the concentration of the fungicide adsorbed to the substrate in ppm. A value for $\frac{1}{n}$ of less than unity indicates that the relative adsorption decreases with increasing concentration.

3.4 Details of Surface Runoff Model

Perez *et al.* [44] have formulated a comprehensive water quality model for a conjunctive surface-ground water system. The main emphasis of their modeling efforts were to simulate nitrogen and phosphorus pollution on surface and groundwater systems. Considered in their system were both flow and water quality processes occuring on the ground surface, in the unsaturated zone and in the saturated or groundwater zone.

The model formulated in the present project was an adaptation of the surface water sub-model described by Perez *et al.* Previous researchers have determined that both Benomyl and Thiabendazole are highly immobile, remaining within the top few centimeters in most soils.[51] Hence, the movement of these compounds into groundwater systems is not a major concern. However, there is considerable evidence of the high degree of adsorption onto soil components by

Benomyl and Thiabendazole. The simulation model described below emphasizes the transport of these compounds into aquatic systems as a result of rainfall, and consequent soil erosion and runoff.

3.4.1 Sample Calculations

3.4.1.1 Catchment Geometry

The geometric characteristics of a hypothetical catchment area are illustrated in Figure 6. Part A of this figure is a plan view of the catchment. Its boundaries and assumed dimensions are indicated. A side view of the catchment is presented in part B, on which the slope is shown.

3.4.1.2 Hydraulic Parameters

The flow rate at the catchment outlet can be computed from the formula:

$$q = \alpha y^m,$$

where q = discharge per unit width , $ft^3/sec/ft$

y = depth of water, ft

α and m are constants,

$m = \frac{5}{3}$, assuming that the flow is turbulent

$$\alpha = \frac{1.49}{n} (\sin\theta)^{1/2},$$

where θ = catchment slope angle,

n = Mannings roughness coefficient.

In this case the units of α are $ft^{1/3}/sec$. The value of n can be estimated from tabulated values of different land surfaces.[27] For simplicity, a fixed value of $n = 0.05$ was assumed for the hypothetical catchment.

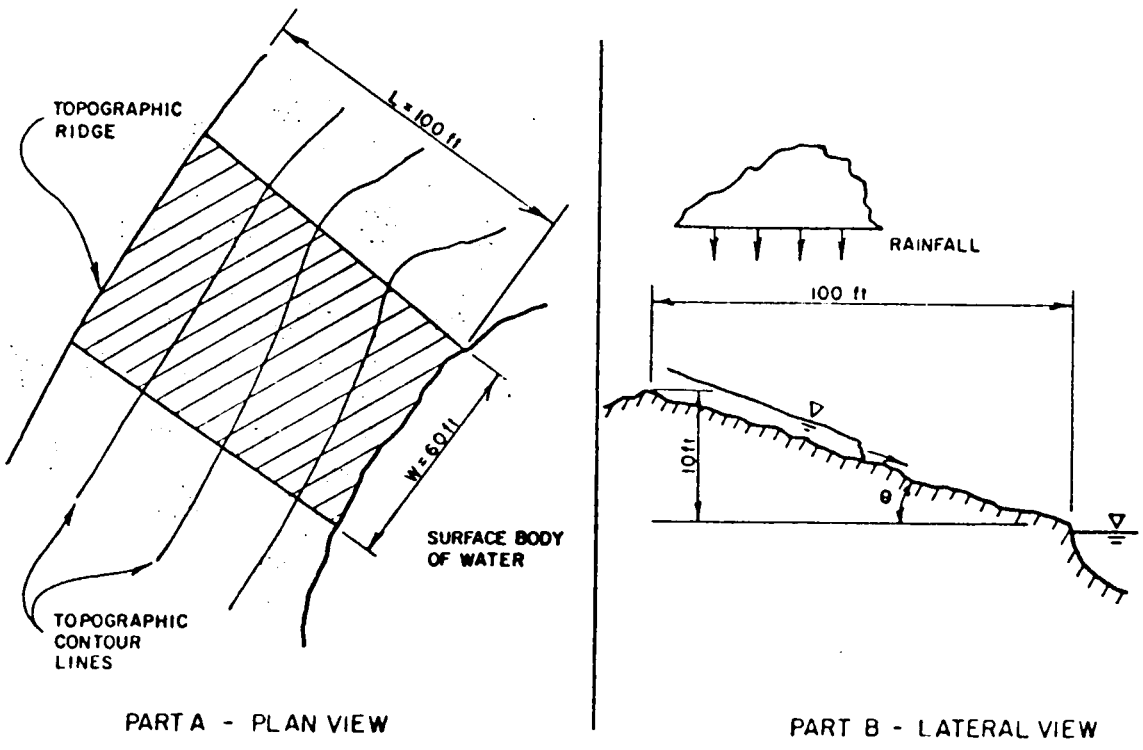


Figure 6. Plan and lateral view of a hypothetical catchment.

3.4.1.3 *Hydrologic Input Conditions*

The hydrologic inputs required to perform the overland flow calculations are rainfall rates, infiltration rates and ponding depths.

3.4.1.4 *Preliminary Calculations*

Since the analytic wave formulation requires the usage of constant rainfall and infiltration inputs, preliminary calculations must be conducted to obtain time averaged values for these variables. The first step is to inspect the ponding depth values to determine the time at which maximum depth occured. This time is then assumed to be the duration, t_r, of the simplified rainstorm and is 15 minutes (Figure 7).

Next the total rainfall, R_T, is computed as follows:

$$R_T = \frac{[8(2.5) + 7(5) + 4(5) + 2(5) + 1(5) + 0.5(5)]\ \frac{\text{in-min}}{\text{hr}}}{60\ \frac{\text{min}}{\text{hr}}} = 1.54 \text{ in},$$

and the synthetic rainfall intensity becomes:

$$\begin{aligned} i &= \frac{R_T}{t_r}, \\ &= 0.102 \text{ in/min} \\ &= 0.00858 \text{ ft/min} \quad \text{for} \quad 0 \le t \le t_r \\ &= 0 \qquad\qquad\quad \text{for} \quad t > t_r. \end{aligned}$$

Turning to the infiltration calculations, it is assumed that the time at which ponding disappears constitutes the end of the infiltration process. An inspection of Figure 7 reveals that the duration of this process is $t_f = 27.5$ min. The total amount of infiltration for that period is given by:

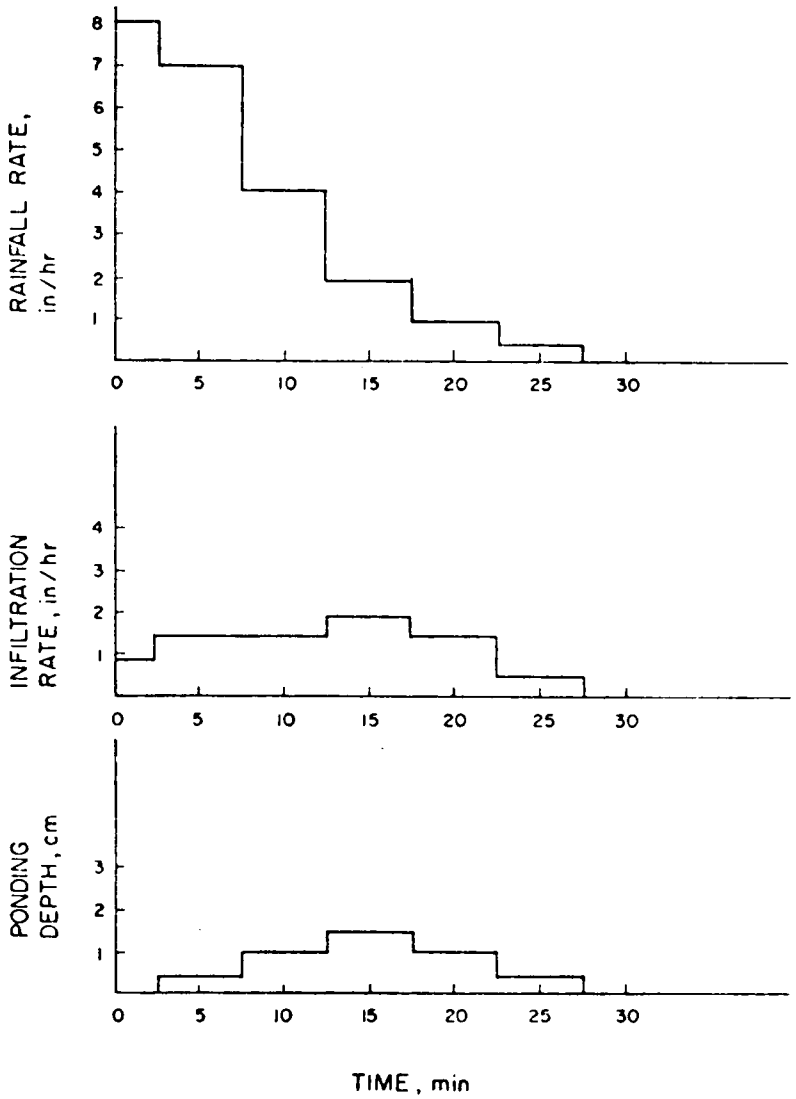


Figure 7. Hypothetical rainfall and infiltration rates, and ponding depths used in sample overland flow calculations.

$$I_T = \frac{[1(2.5) + 1.5(5) + 1.5(5) + 2(5) + 0.5(5) + 0.5(5)]\ \frac{\text{in-min}}{\text{hr}}}{60\ \frac{\text{min}}{\text{hr}}} = 0.538 \text{ in.}$$

Accordingly, the synthetic infiltration rate becomes:

$$f = \frac{I_T}{t_f}$$
$$= 0.0196 \text{ in/min} = 0.00162 \text{ ft/min} \quad \text{for} \quad 0 \le t \le t_f$$
$$= 0 \quad \text{for} \quad t > t_f.$$

3.4.1.5 Overland Flow Calculations

Two main cases arise in the formulation, depending on the relative values of the storm duration, t_r, and the time of concentration of rainfall, t_c. The latter is computed from the formula:

$$t_c = \left[\frac{Li^{1-m}}{\alpha}\right]^{\frac{1}{m}},$$

where L = catchment length, ft

i = rainfall excess (rainfall less infiltration), ft/min.

Substitution of the appropriate parameters in the above equation yeilds a value of 2.6 minutes for t_c. For the catchment and hydrologic conditions in question, t_r exceeds t_c. It is now possible to compute the depths of water, and the corresponding velocities and flows, at various times. These values are computed herein only at the catchment outlet. The calculations for the first time step (t = 5) are given below. The equations used to obtain the flow depth are:

$$y_L = (i - f)t \quad \text{for} \quad 0 \le t \le t_c$$
$$y_L = (i - f)t_c \quad \text{for} \quad t_c \le t \le t_r.$$

A more complex relationship must be used for the case $t > t_r$. Since in this case $t_c \le t \le t_r$, the depth becomes:

$$y_L = (0.00696)(2.6) = 0.0181 \text{ ft.}$$

The corresponding velocity is given by:

$$v = \alpha y^{m-1} = (9.42)(0.0181)^{0.66} = 0.705 \text{ ft/sec,}$$

and the flow per unit width becomes:

$$q = \alpha y^m = vy = 0.01275 \text{ ft}^3/\text{sec/ft.}$$

Multiplying this unit flow by the width (ft), the resulting catchment outflow is:

$$Q = qw = (0.01275)(60) = 0.765 \text{ ft}^3/\text{sec,}$$
$$\textit{where} \quad w = \text{width of catchment outlet, ft.}$$

3.4.1.6 Sediment Load Calculations

The sediment transport formula used in this study (described in detail in Section 2.5) is that developed by duBoys[15]:

$$q_s = \psi y S_b \left[y S_b - \frac{\tau_{cr}}{\gamma} \right] .$$

The values of ψ and τ_{cr} are tabulated.[15] Assuming that the soil in the hypothetical catchment is fine sand, the sediment load at the first time step (t = 5 min) is:

$$q_s = (5.23 \times 10^5)(1.81 \times 10^{-2})(10^{-1})\left[1.81 \times 10^{-3} - \frac{1.62 \times 10^{-2}}{62.4} \right] ,$$
$$= 1.47 \text{ lb/sec/ft.}$$
$$= 0.67 \text{ kg/sec/ft.}$$

Thus, the total catchment load becomes:

$$Q_s = wq_s = 88.3 \text{ lb/sec.}$$
$$= 40.05 \text{ kg/sec.}$$

3.4.1.7 Determination of Benomyl and Thiabendazole Fluxes

Benomyl and Thiabendazole fluxes (adsorbed onto sediment) can be calculated from adsorption data, mobility studies,[2 23 47] and a knowledge of field application rates of these fungicides.

3.4.2 Program description

The overland flow program of Perez *et al* [44] modified to simulate Benomyl and Thiabendazole fluxes, is composed of a main program and several subroutines, AVE, WAVE, RECV, HIDUR, LODUR, RQUAL and WRIT. All these subroutines are involved in quantity computations, with the exception of RQUAL and WRIT. The former handles water quality computations and the latter writes the overall results.

3.4.2.1 MAIN Program

The first task of MAIN is to read in the necessary hydrologic, geometric and quality data. Included among the geometric information is the numbering system that connects the catchments with the receiving elements.

Following the data input, MAIN calls subroutines AVE, WAVE, RECV, RQUAL and WRIT, in that order. Subroutine AVE performs the averaging computations for rainfall, evapo-

ration and infiltration, and thus prepares this data for use in the overland flow calculations. The task of WAVE is to carry out these calculations for all the catchments and time steps. It ultimately computes flows into the receiving elements. Subroutine RECV then computes the total flow into each receiving element from all its feeder catchments. The function of RQUAL and WRIT were explained above.

3.4.2.2 Subroutine AVE

This subroutine determines the mean values of infiltration and rainfall for the time period considered. The stepwise procedure used to obtain these values, discussed below, are also shown in Figures 8 and 9. Beginning with infiltration, AVE first determines the time step after which this process no longer occurs. The method used is to scan the infiltration data and establish when the ponding depth becomes zero. The time interval corresponding to this event is considered to constitute the end of the infiltration process. The scanning process described above is illustrated as Step 1 in Figure 8.

Following determination of the duration of infiltration, AVE computes the time-averaged value of the infiltration rate. This calculation is depicted as Step 2 in Figure 8. Finally, updated values of the infiltration rate are stored for all the time intervals in the study period in the manner shown in Step 3 of the same figure.

Subroutine AVE then considers the rainfall process, and converts the original irregular shaped hyetograph into a step-wise function containing the same amount of rainfall. This conversion process is begun by scanning ponding depths, determining the time at which the maximum ponding depth occurs and arbitrarily setting the duration of the synthetic storm equal to the above time. This process is illustrated in Step 1 of Figure 9. The subroutine then computes the total rainfall from the original record, as shown in Step 2 of the same figure. Finally, it constructs a synthetic step function hyetograph (Step 3) using the duration, t_r, determined above.

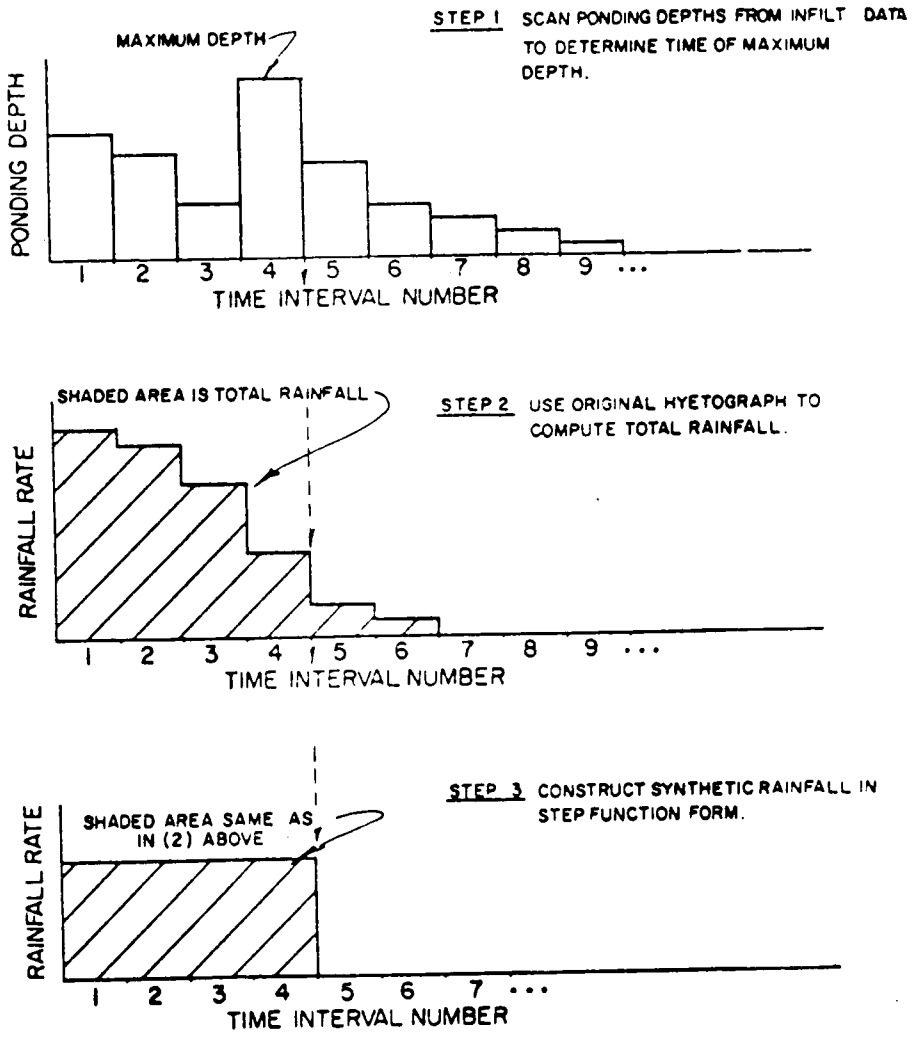


Figure 8. Graphical representation of computational steps in subroutine AVE involving rainfall.

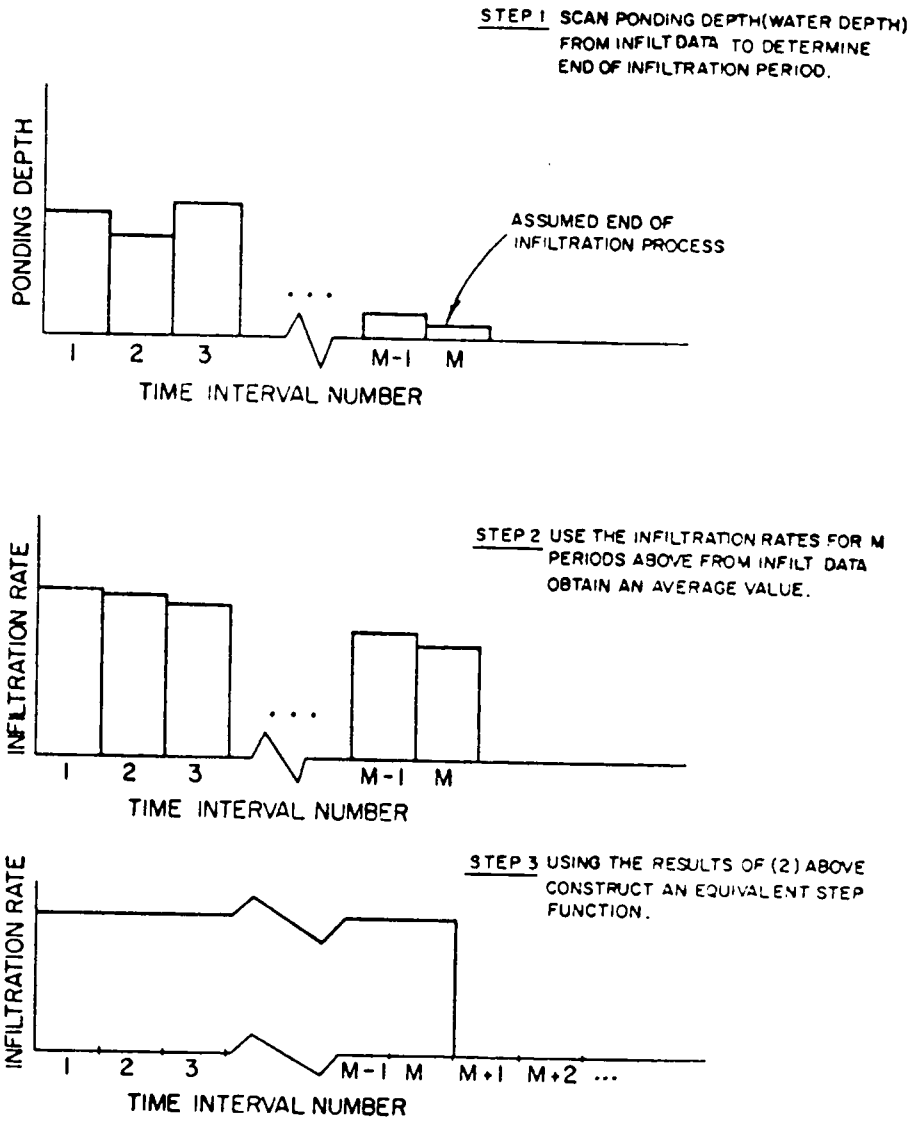


Figure 9. Graphical representation of computations in subroutine AVE involing infiltration.

3.4.2.3 *Subroutine WAVE*

To better represent the overland process, it is desirable to apply the wave relationships not only at each catchment outlet, but also at several points along the length of the catchment. For this purpose each catchment is divided into a given number of intervals, and the formulation is applied to the downstream end of each interval. This division is illustrated in Figure 10. In this study, only one interval comprising the entire catchment was considered. This was acceptable because of the small size of each catchment.

The type of formulae used at each catchment location largely depends on the relative value of t_r, the storm duration as defined in AVE, and t_c, the time of concentration. The latter term can be defined as the maximum amount of time during which an increase of depth can occur on the surface. While t_r is assumed to be the same throughout the catchment, t_c varies with location. At each time step and each catchment interval, WAVE compares these values. If the storm has a relatively high duration, namely t_r exceeds t_c, the subroutine HIDUR is called. Conversely, if t_c is greater than t_r, LODUR is utilized. Each of these two subroutines compute the depth of water at each catchment location.

After the flow depths have been determined, WAVE proceeds to calculate their corresponding velocities and flows. These values are then stored for future use.

3.4.2.4 *Subroutine RECV*

At each time step, this subroutine computes the total flow entering each receiving element from its feeder catchments. To accomplish this, it considers the flows corresponding only to the downstream interval in each catchment.

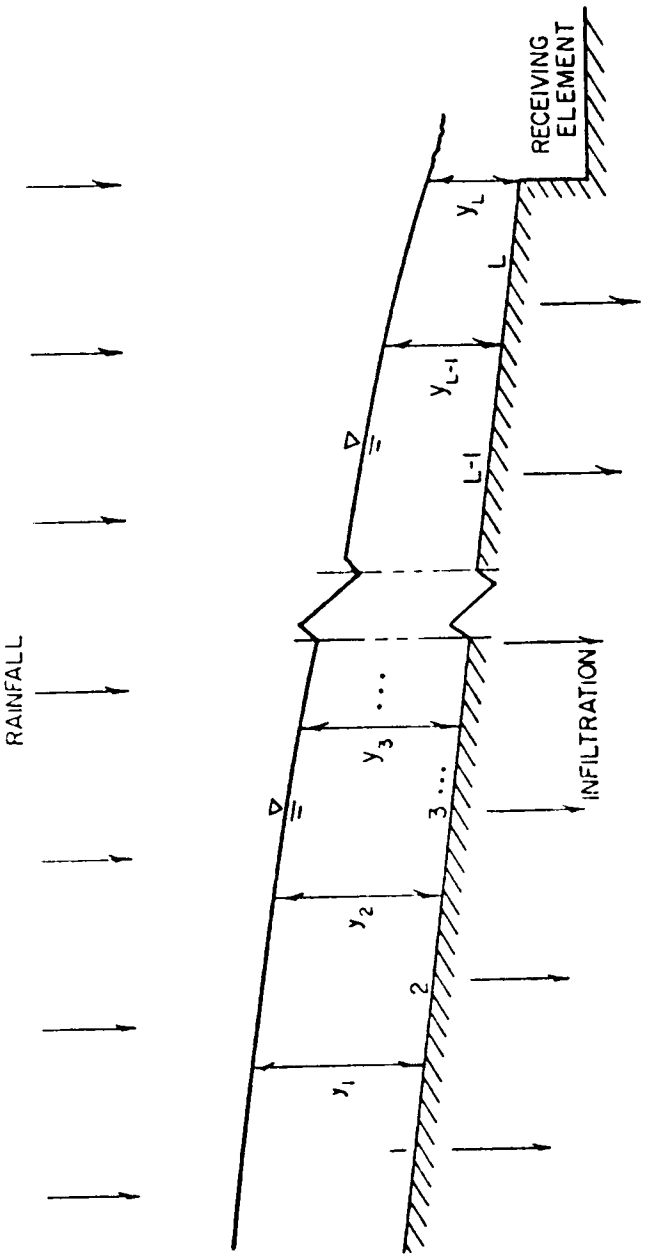


Figure 10. Lateral view of overland flow situation, indicating catchment divisions.

3.4.2.5 *Subroutine HIDUR*

The wave computations carried out in this subroutine correspond to the case $t_r > t_c$ as mentioned above. These computations branch out according to three possible cases. To determine which particular case holds, HIDUR compares the relative values of t, the time corresponding to the time step in question, to three other parameters, t_c, t_r and t_i. The latter parameter is defined as the time at which the depth, y, at a given location vanishes. At the conclusion of these calculations, control is returned to subroutine WAVE.

3.4.2.6 *Subroutine LODUR*

This subroutine is utilized in a relatively low duration situation, namely, $t_r < t_c$. The computations herein are broken down into three classes, depending on the relative values of t_i, defined above, and t_p, which represent the time at which the depth begins to decrease. Each one of these three cases is in turn divided into three sub-cases. As in HIDUR, control is returned to WAVE, allowing for the completion of computations.

3.4.2.7 *Subroutine RQUAL*

This utilizes the duBoys sediment transport equation to compute the suspended solid fluxes at the catchment outlets as outlined in Section 2.5. It also calculates Benomyl and Thiabendazole fluxes at the outlets.

3.4.2.8 Subroutine WRIT

After subroutine RQUAL has completed its calculations, subroutine WRIT is called to print out the results obtained. The most important results are the flows and concentrations at the various catchments, and the total inputs to the receiving elements.

3.4.3 Application of Model to Study Area

3.4.3.1 Description of Study Area

The Chowan river is about 130 miles (209 km) long and drains an area of 4,943 sq. miles (12,802 sq. km) in Southeastern Virginia and Northeastern Carolina. The Chowan river proper is located entirely in North Carolina and flows in a southerly and southeasterly direction from the confluence of the Nottaway and Blackwater rivers at the state line for a distance of 52 miles (84 km) to the entrance of the Albemarle Sound. The three principle tributaries to the Chowan river are the Meherrin, Nottaway and Blackwater rivers. Figure 11 is a schematic of the Chowan river basin.

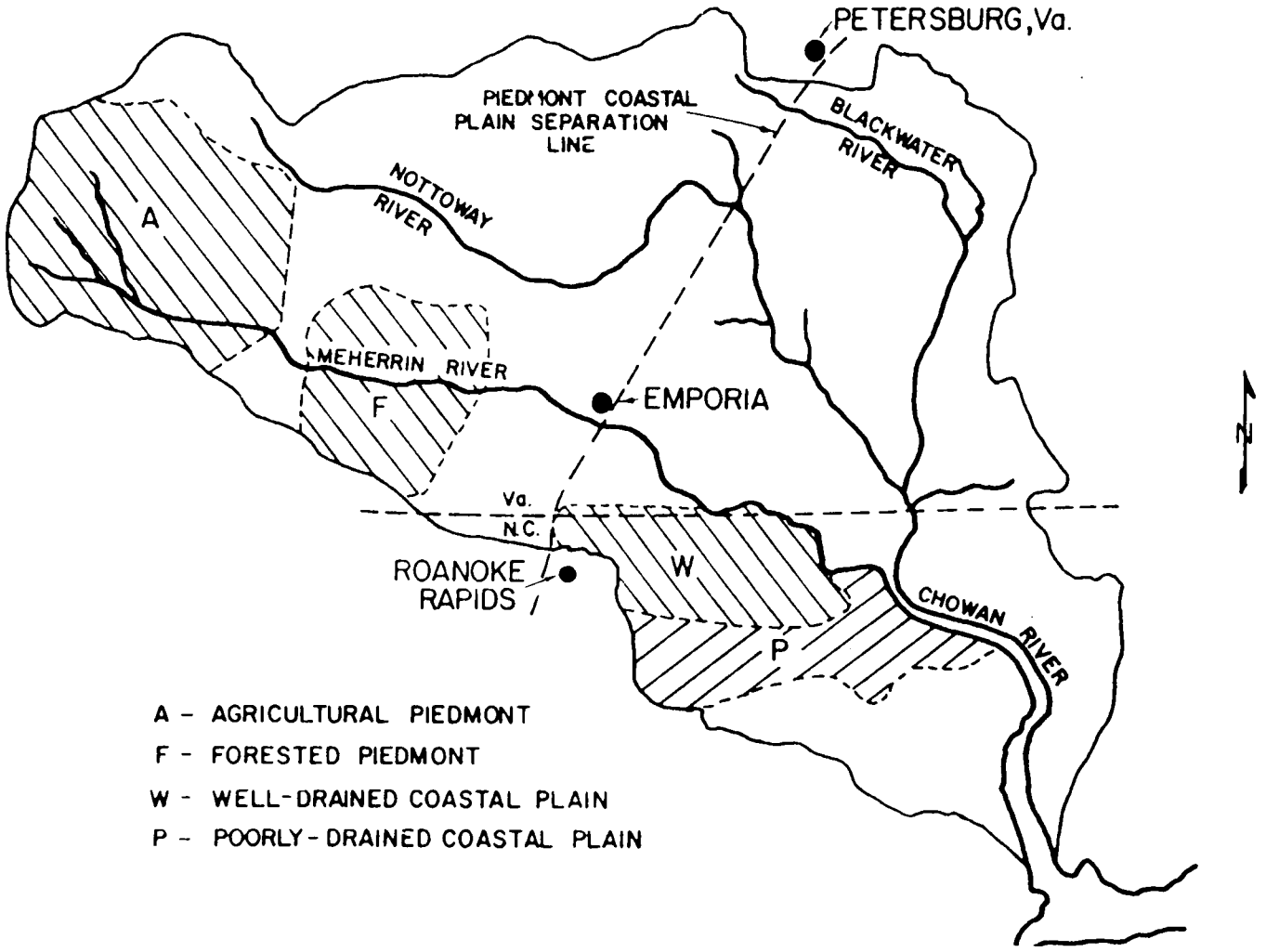


Figure 11. Schematic of the Chowan river basin.

For the purpose of a sample simulation of overland sediment runoff, the basin enclosed by the Nottaway river in the north and the Meherrin river in the south (Lunenburg County, Va), was considered. The Meherrin river rises in Lunenburg County, flows toward the Atlantic coast in a southeasterly direction, and empties in the Chowan river. The Nottaway river also arises in Lunenburg County and flows southeasterly to its confluence with the Blackwater river. Figure 12 is a soil survey map of Lunenburg County, differentiated on the basis of 5 major soil associations. This area is identified as *Agricultural Piedmont* in Figure 11. Figure 13 is an overlay map of the same region showing its division into 37 rectangular sections covering an area of 56.2 sq. km each. Table 2 lists the major characteristics of each of the 5 associations, and identifies catchments which are representative of each.

3.4.3.2 Benomyl and Thiabendazole Routing

Benomyl and Thiabendazole are fixed rapidly to most soils and are consequently capable of being transported with suspended soil particles in overland runoff. For this reason, the weight fraction of the fungicides in the soil had to be determined. Several assumptions (based on results obtained in the present study and on existing literature) were made to estimate the distribution of applied fungicide within the soil proile.

1. Less than 3% and 0.3% of applied Benomyl and Thiabendazole, respectively, is leached into runoff and percolation water (Table 4 and 5, Section 4-1).
2. Greater than 95% of the applied fungicide remains within the top 0-8 cm of the soil profile.[51]
3. It was also assumed that the distribution of fungicide within the soil profile was uniform.
4. Following application, portions of Benomyl and Thiabendazole are slowly translocated into plants. The remaining amount at any time depends, therefore, on time elapsed since application and the growth caracteristics of the crop. A gross assumption was made that on a time-average basis, the amounts of Benomyl and Thiabendazole remaining in the soil were 45 and 70% of the applied amount, respectively (Table 4 and 5, Section 4-1).

5. Field application rates of 0.45 kg active ingredient per acre were assumed for both the fungicides.
6. Since an exact estimate of the annual application rates of these fungicides are difficult to determine, the sample run of the program assumes an individual event comprised of the following sequence of sub-events: 1) field application, 2) plant and organism uptake, and 3) rainall, iniltration, ponding and subsequent overland sediment runoff.

Based on these assumptions, the concentration of MBC within the top 8 centimeters of a sandy loam soil (with a clay content of between 15 and 27%) was determined to be 1.77×10^{-5} kg/ft^3 and the concentration of TBZ was found to be 2.76×10^{-5} kg/ft^3, assuming that 25% of the soil was occupied by voids. Table 3 lists the parameters required in the various formulations of the runoff model for the catchment sections in question. Figure 14 is a graphical representation of rainfall and infiltration rates as well as ponding depths assumed for a hypothetical rainstorm. For simplicity, similar rainfall and infiltration rates as well as ponding depths were assumed for the entire catchment. The Appendix contains an output listing of the model application to the study area.

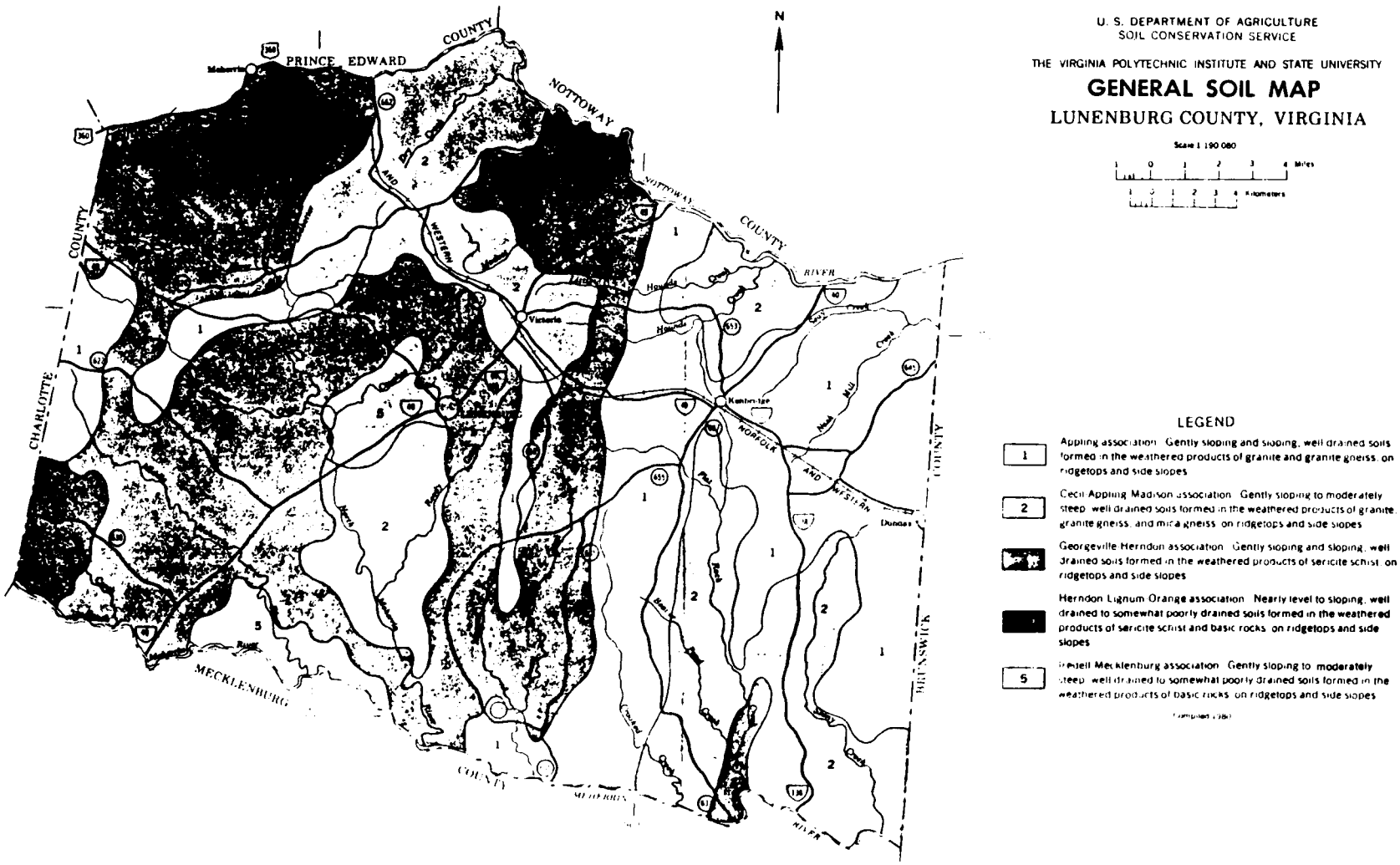


Figure 12. Soil survey map of Lunenburg County.

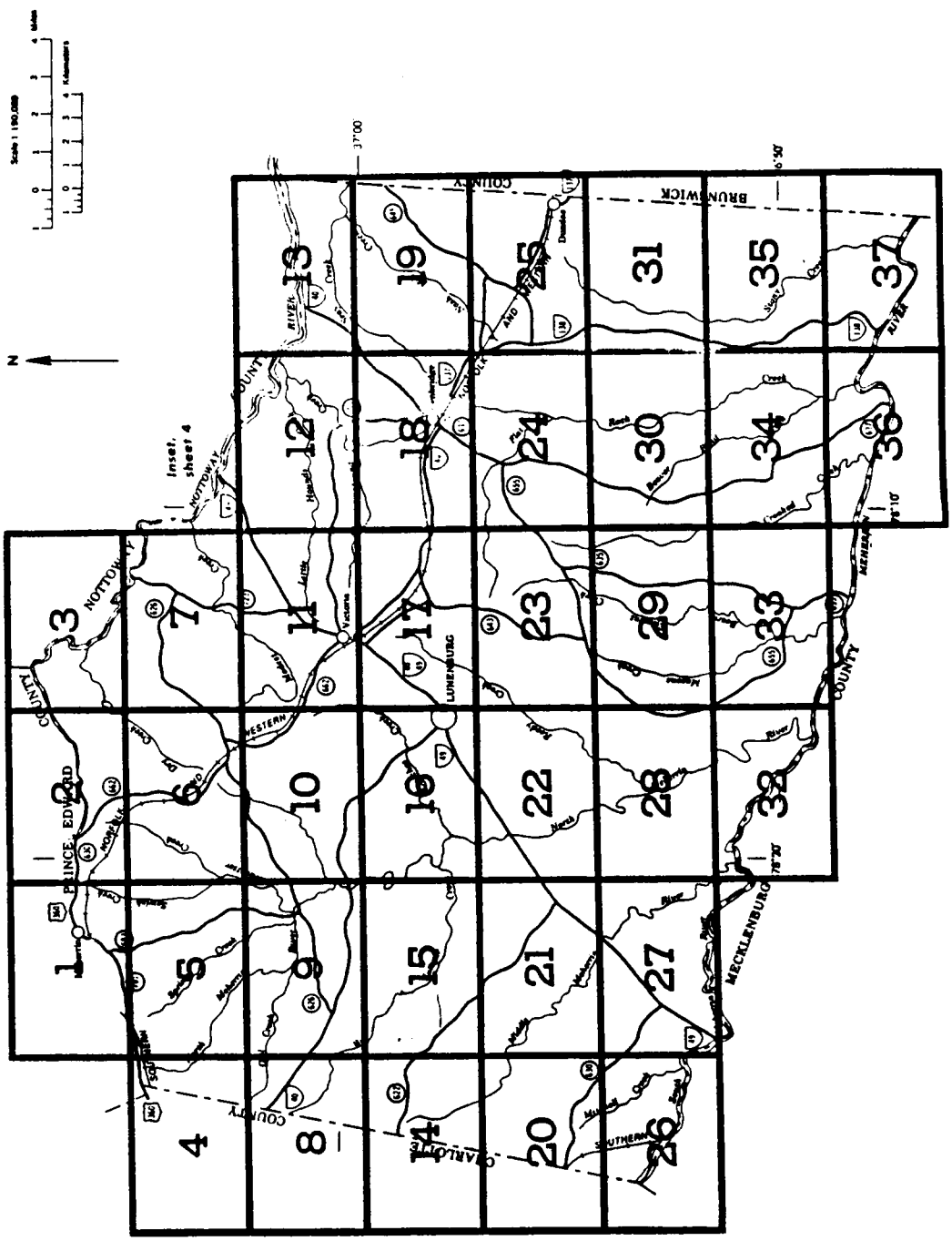


Figure 13. Overlay map of Lunenburg County differentiated into catchments.

Table 2. **Major characteristics of soil associations found in study area.**

Soil Association	**Appling**	**a) Cecil b) Appling c) Madison**	**a) Georgeivlle b) Herndon**	**a) Herndon b) Lignum c) Orange**	**a) Iredell b) Mecklenburg**
Soil texture	*Sandy loam*	*Sandy loam*	*Loam*	*Loam*	*Loam*
Depth, cm	0-15.2	a) 0-15.2 b) 0-17.8 c) 0-10.2	a) 0-12.7 b) 0-12.7	a) 0-12.7 b) 0-30.5 c) 0-25.4	a) 0-22.9 b) 0-12.7
Moist bulk density, G/cm³	1.3-1.55	a) 1.3-1.55 b) 1.0-1.5 c) 1.3-1.6	a) 1.2-1.4 b) 1.2-1.4	a) 1.2-1.4 b) 1.2-1.5 c) 1.25-1.55	a) 1.2-1.4 b) 1.3-1.5
Clay %	5-15	a) 5-15 b) 10-20 c) 5-20	a) 5-27 b) 5-27	a) 5-27 b) 10-27 c) 10-25	a) 15-35 b) 8-25
Organic matter %	0.5-1	a) 0.5-1 b) 0.7-2 c) 0.5-2	a) 0.5-2 b) 0.5-1	a) 0.5-1 b) 0.5-2 c) 1-3	a) 0.5-2 b) 0.5-2
Permeability, cm/hr	5.2-15.2	a) 5.2-15.2 b) 5.2-15.2 c) 5.2-15.2	a) 1.52-5.2 b) 1.52-15.2	a) 1.52-5.2 b) 1.52-15.2 c) 1.52-15.2	a) 0.41-5.2 b) 1.52-5.2
Available water capacity, cm/cm	0.25-0.38	a) 0.25-0.38 b) 0.30-0.35 c) 0.28-0.38	a) 0.38-0.51 b) 0.35-5.2	a) 0.35-0.51 b) 0.35-0.51 c) 0.35-0.51	a) 0.35-0.43 b) 1.52-5.2
pH	4.5-5.5	a) 4.5-6 b) 4.5-6 c) 4.5-6	a) 4.5-6 b) 4.5-6.5	a) 4.5-6.5 b) 4.5-5.5 c) 5.1-6.5	a) 5.6-7.3 b) 5.6-7.3
Representative section No. (fig. 13)	13	37	7	26	27

Table 3. **Parameters required in formulations of runoff model.**

Catchment No. (fig. 13)	28, 32
Soil texture	Sandy loam
Mean particle diameter, mm	0.125
Catchment area, sq.km	56.25
Width of Catchment Outlet(w), ft	24607.5
Slope of catchment, ft/ft Θ	0.0107
Mannings roughness coefficent, n	0.035
Critical shear stress, kg/ft^2	0.007
m	1.66
Ψ	523000
Conc. of adsorbed MBC, kg/ft^3	1.77×10^{-5} kg/ft^3
Conc. of adsorbed TBZ, kg/ft^3	2.76×10^{-5} kg/ft^3

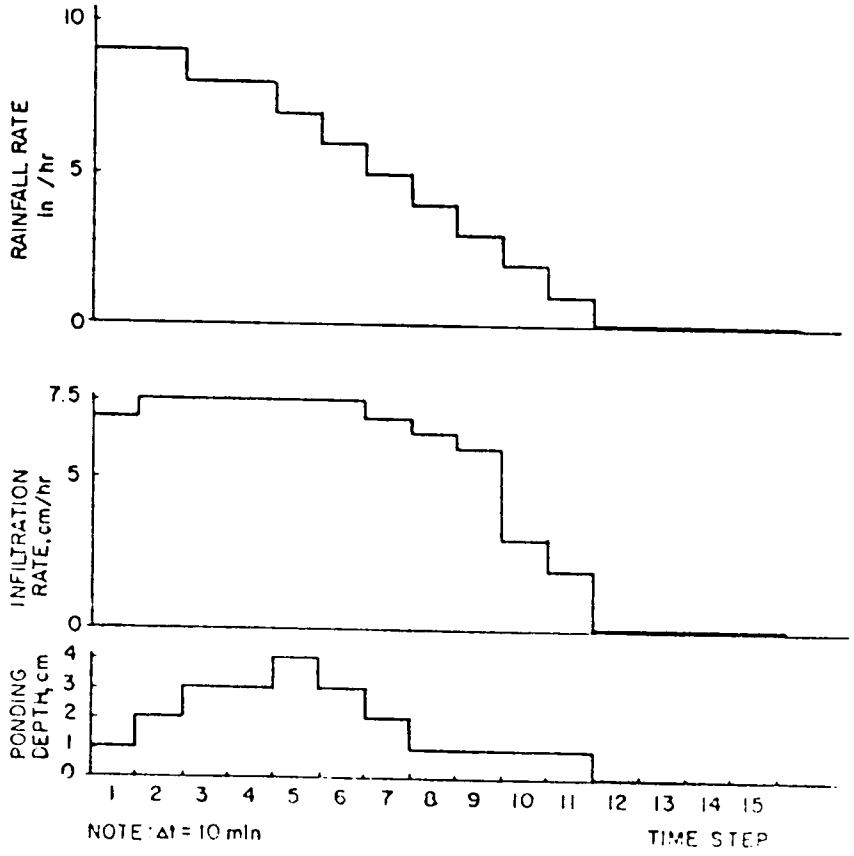


Figure 14. Graphical representation of hypothetical rainfall and infiltration rates, and ponding depths.

4.0 Results and Discussion

4.1 Terrestrial Microcosm Phase

This section presents the environmental fate and distribution of Benomyl and Thiabendazole (TBZ) within a soil-plant terrestrial microcosm. It may be noted that Benomyl decomposes rapidly to its principle degradative product Carbendazim (MBC) in aqueous solutions, soil and plants. Consequently, all Benomyl residue concentrations were recovered as MBC. Tables 4 and 5 summarize the distribution of MBC and Thiabendazole, respectively, in the form of a mass-balance.

4.1.1 Distribution of MBC and TBZ in the Soil

As can be observed in Table 4 and 5, the soil constituted a major relocation site for both TBZ, and to a lesser extent, MBC. The soil component (classified as a McGary and Purdy, silty clay loam soil) was comprised of: silt, 60%; clay, 30%; and organic matter, 2%. MBC and TBZ residues were analyzed 18, 19 and 20 days after initiation of the microcosm experiment, as described

Table 4. Terminal environmental distribution of MBC in a terrestrial soil-plant microcosm.

Ecosystem Component	Total max. mass, g (No.) × mass = total	Mean conc., μg/g	Total resdue, μg (mass)(conc.)	Total residue as a % of applied dose (5000 μg)
1) Corn	(48) × 2.324 = 111.55	23.71	2644.85	52.89
2) Soil	(1) × 2225 = 2225	0.98	2191.62	43.83
3) Surface water	(1) × 7000 = 7000	0.023	161	3.22
4) Air/ Microbial degradation			5000-(1 + 2 + 3) = 2.52	0.05

Table 5. Terminal environmental distribution of Thiabendazole (TBZ) in a soil-plant microcosm.

Ecosystem component	Total max. mass, g (No.) × mass = total	Mean conc., μg/g	Total residue, μg (mass)(conc.)	Total residue as a % of applied dose (5000 μg)
1) Corn	(44) × 2.47 = 108.68	12.22	1327.96	26.66
2) Soil	(1) × 2225 = 2225	1.64	3655.67	73.11
3) Surface water	(1) × 7000 = 7000	0.002	14.7	0.29
4) Air/ Microbial degradation			5000-(1 + 2 + 3) = 1.67	0.03

in Sections 3.2.2 and 3.2.4, respectively. These results are shown in Table 6. The mean concentrations are the average residue levels determined from the analysis of 4 samples per day. Approximately 44% of the initial Benomyl dosage of 5000 μg was recovered from the soil as MBC, 20 days after initiation of the experiment. A much higher percentage of TBZ (74%) was recovered from the soil matrix.

The five major processes affecting the behavior of Benomyl and Thiabendazole in the soil matrix are:

1. Adsorption,
2. Chemical and photodecomposition,
3. Microbial degradation,
4. Vaporization, and
5. Movement.

4.1.1.1 Adsorption

Results obtained from adsorption measurements of both MBC and TBZ on silty clay loam, silty loam and sandy soils are described comprehensively in Section 4.2. A possible mechanism of the adsorption process is also described therein.

4.1.1.2 Chemical and Photodecomposition

As mentioned earlier, Benomyl rapidly decomposes to Methyl benzimidazole - 2 - ylcarbamate (Carbendazim, MBC), in the soil. MBC is also the principle fungitoxic agent of Benomyl. Besides MBC, Benomyl also decomposes to 2-amino benzimidazole, and as a result of photodecomposition, to Guanidine, Carbomethoxy guanidine and Carbomethoxy urea. However, these compounds were in too minute quantities to facilitate their detection. TBZ decomposes to

Table 6. **Benomyl (recovered as MBC) and TBZ residues in the soil.**

Fungicide	Days postplanting	Mean conc., μg/g	Total residue, μg (conc.)(2225 g soil)
MBC	18	0.98	2189.4
	19	0.98	2191.63
	20	0.98	2191.63
TBZ	18	1.64	3655.45
	19	1.64	3655.23
	20	1.64	3655.68

Benzimidazole and Benzimidazole - 2 - carboxamide as a result of photodecomposition. However, photodecomposition may not constitute a major degradative pathway of MBC or TBZ in soils since sunlight is strongly sorbed at the soil surface.

4.1.1.3 Vaporization and Microbial Degradation

Although vaporization could constitute a major route in the loss of contaminants from the soil, it was not found to be the case, for either MBC or TBZ. As shown in Tables 4 and 5, only 0.05 and 0.03% of Benomyl and Thiabendazole, respectively, were either routed into the atmosphere, or underwent microbial degradation. However, considering the negligible vapor pressures of the these fungicides, it is improbable that any significant quantities were routed into the atmosphere. It may be noted that the amounts of fungicide routed into the atmosphere and/or degraded by soil microorganisms were not actually measured but were deduced from the mass-balance summaries.

4.1.1.4 Transport to Surface Water

At the termination of the terrestrial phase (day 20), the microcosms were flooded with 7 liters of water, the mass of which was approximately 3 times greater than that of moist soil. This was a harsh treatment of a land mass with water. However, since the body of water above the soil component was static, as opposed to a natural terrestral environment, a larger quantity of water was flooded into the system. The amounts of MBC and TBZ transported from the soil to the surface water were 3.22 and 0.29% of the initial dose of 5000 µg (7.34% and 0.40% of the concentration in the soil). Figure 15 depicts MBC and TBZ residues in the surface water over a period of 7 days (day 21 to 28 post-planting). Thus, it is evident, that both the fungicides are strongly adsorbed within the soil matrix.

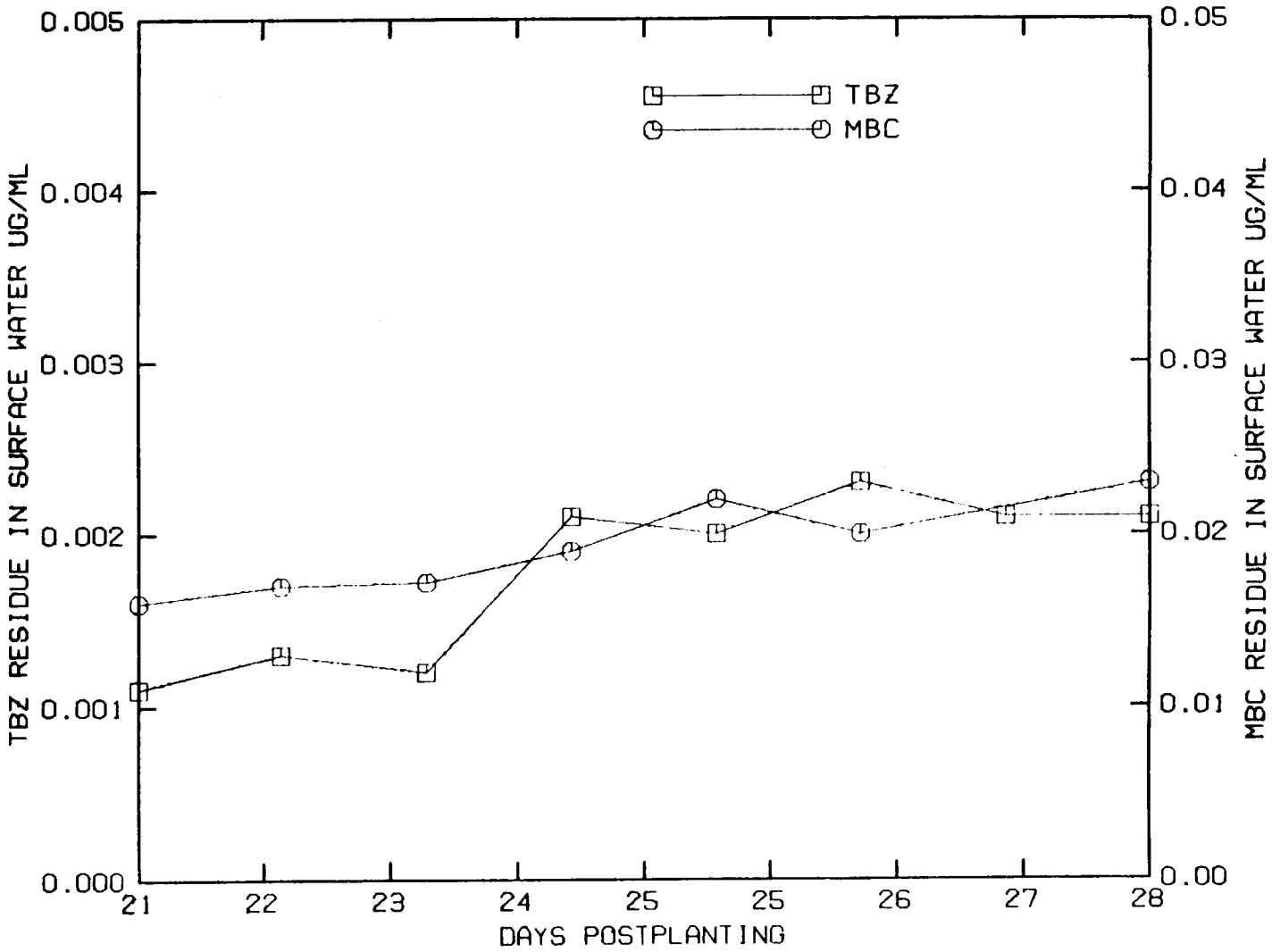


Figure 15. Movement of MBC and TBZ residues from soil to surface water.

4.1.2 MBC and TBZ Residues in Corn Plants

The soil acts as a major sink and consequently, as a reservoir of fungicide, available for uptake by the plants. Approximately 53 and 27% of the initial dose of MBC and TBZ translocated into the plants. This might be expected, since both these fungicides are systemic, i.e., they are capable of translocating to regions of the plant away from the site of application (which, in this case, was the soil). Fungicide concentrations determined by the methods described in Sections 3.2.1 and 3.2.3, on days 10, 12, 14 and 18 post-planting, are summarized in Table 7.

The levels of fungicide found in the corn plants were found to be in agreement with most previously reported investigations. The root system of growing plants, in essence, contribute organic matter to the soil environment, which is an important consideration when examining adsorption. Since the major emphasis of this study was on the fate of MBC and TBZ in agricultural soils, it was quite advantageous to have a growing crop present so as to quantify as closely as possible, the residues one may find in the natural soil environment.

4.2 Adsorption Dynamics of MBC and TBZ in Soils

This section presents the results of investigations into the adsorption of MBC and TBZ on silty clay loam, silty loam and sandy soils, as well as on Ca-bentonite clay.

4.2.1 Adsorption on Silty Clay Loam, Silty Loam and Sandy Soils

The major characteristics of the three soils used in the adsorption experiments are shown in Table 8. Adsorption isotherms for MBC and TBZ on these soils are depicted in Figures

Table 7. Fungicide concentrations in the corn plants.

Fungicide	Days post-planting	Mean concentration, μg/g
MBC	10	19.43
	12	21.17
	18	23.71
TBZ	10	8.72
	12	8.9
	14	-
	18	12.22

16, 17 and 18. TBZ was adsorbed in much larger quantities than MBC, the ratio being between 1:3 and 1:4. An analysis of the adsorption isotherms showed that both TBZ, and to a lesser extent, MBC, were adsorbed in largest quantities to the silty clay loam soil with a clay content of 30%, followed by silty loam soil with a clay content of 20%. Thus, it seems that the clay content plays a major role in the degree of adsorption of MBC and TBZ to soils. On the other hand, the organic matter content of the silty clay loam soil is also higher than in the other soils. The ionized MBC and TBZ molecules could also be adsorbed by the organic fractions. However, due to the complex nature of organic matter (humic acids), and consequent difficulties in experimentally quantifying adsorption phenomena, this possibility was not examined in this study.

4.2.2 Availability of MBC and TBZ to Plants

The differences in the adsorption of MBC and TBZ by the same soil, and the differences in the amount of each fungicide adsorbed on various soils, as observed in the adsorption experiments, may represent the actual variations in the availability of these fungicides to plants. This assumption was examined in the experiment in which MBC and TBZ were adsorbed to the soil, the soil was shaken with water at a ratio of 1:1 by weight, and the fungicide concentrations in the solution at equilibrium were determined. Table 9 summarizes the results of these experiments, which are depicted graphically in Figures 19 and 20.

It can be seen that the concentration of TBZ in the solution amounted to 20% of that of MBC after identical amounts had been applied to the silty loam soil. With the silty clay loam soil, however, this percentage was between 7 and 8. These findings suggest that TBZ is available in the solution in much smaller quantities. The amount of TBZ adsorbed to the soil might be considered as a reservoir of fungicide for plants since the adsorption process was found to be reversible. Attention should be given to the amounts of adsorbent used for MBC and TBZ. This ratio represents the relative strengths of adsorption of these two molecules.

Table 8. **Physical and chemical characteristics of the soils under investigation.**

Soil name	McGary and Purdy	McGary and Purdy	Parker
Depth, cm	0-23	23-94	0-10
USDA texture	Silty loam	Silty clay loam	Sandy loam
Clay%	18-27	30-50	3-10
Moist bulk density, G/cm^3	1.30 - 1.50	1.30 - 1.75	1.30 -1.6
Permeability, cm/hr	0.5 - 5.1	< 0.5	5.1 - 15.2
Available water capacity, cm/cm	0.46 - 0.61	0.28 - 0.46	0.25 - 0.35
Soil pH	3.6 - 7.3	3.6 - 7.8	4.5 - 5.5
Organic matter%	2 - 4	1 - 2	0.5 - 2

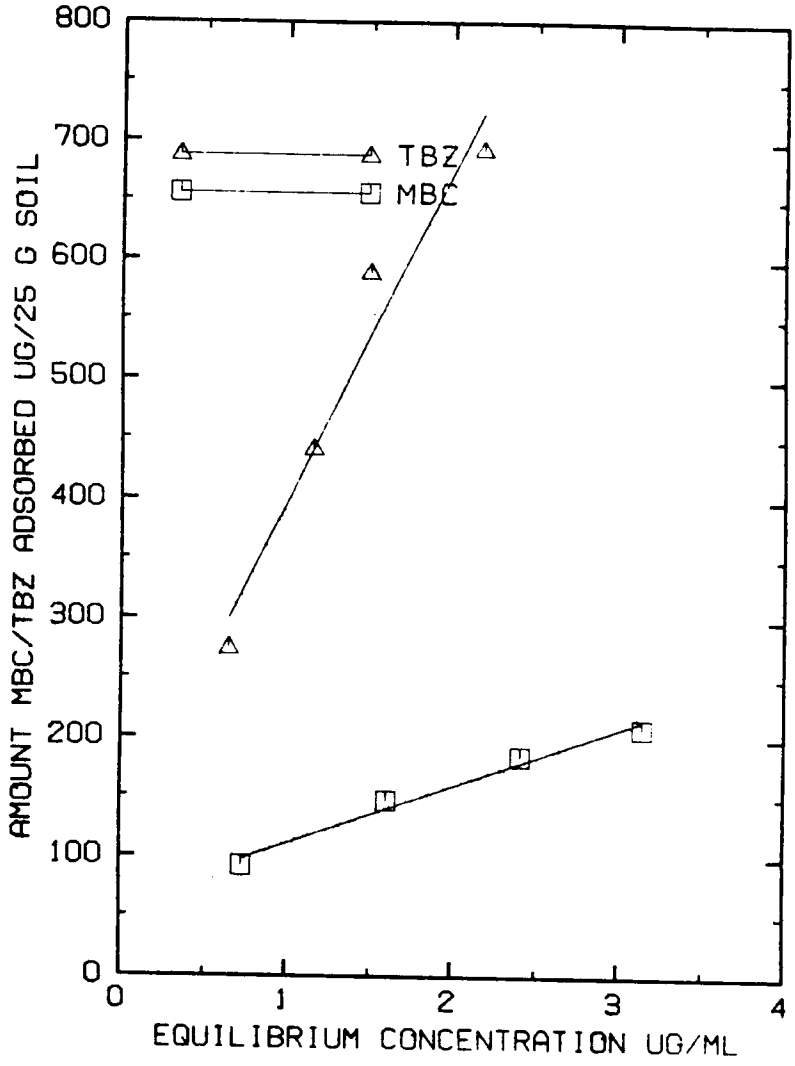


Figure 16. Adsorption isotherms of MBC and TBZ on silty clay loam soil.

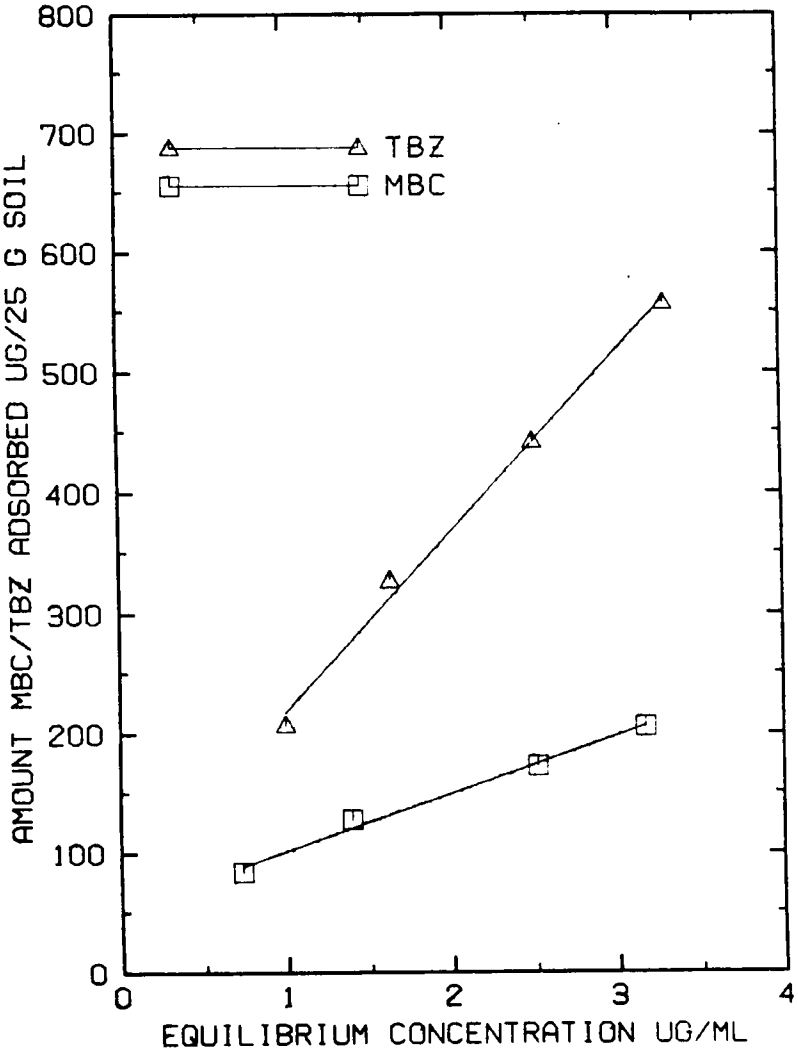


Figure 17. Adsorption isotherms of MBC and TBZ on silty loam soil.

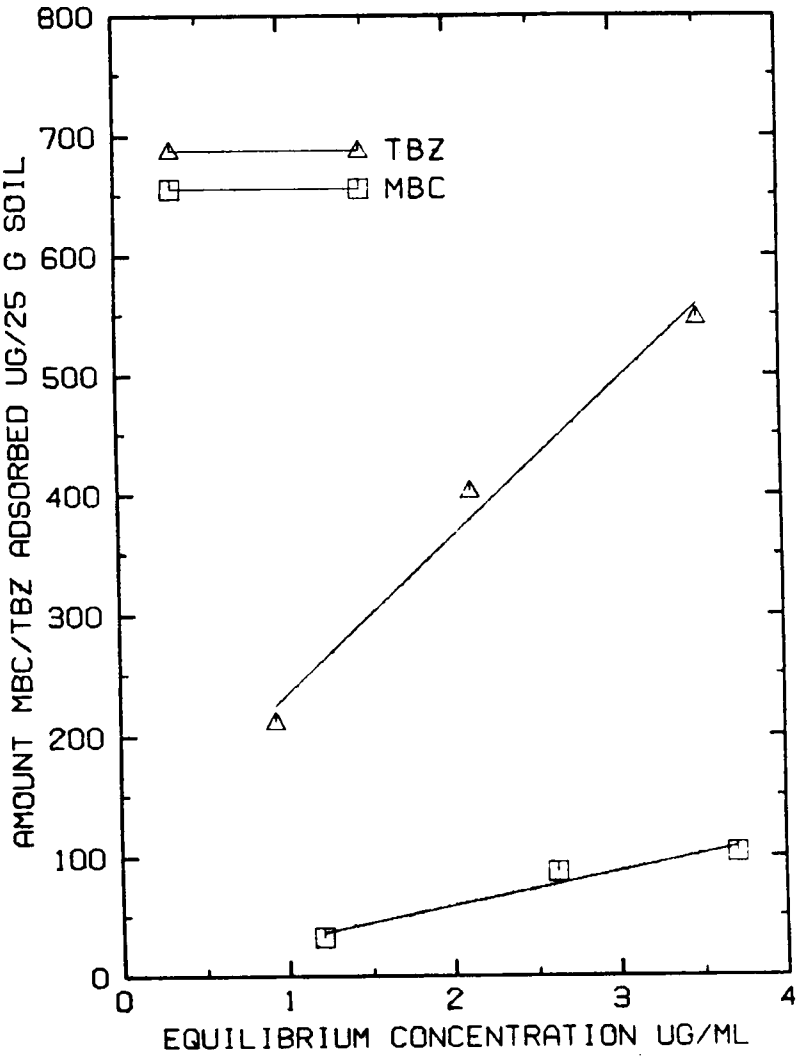


Figure 18. Adsorption isotherms of MBC and TBZ on sandy soil.

Table 9. Concentration of MBC and TBZ in solution at equilibrium as a function of their initial concentrations in the soil.

	Concentration of TBZ in solution at equilibrium, μg/ml		Concentration of MBC in solution at equilibrium, μg/ml	
Quantity of fungicide adsorbed to soil, μg/ml	Silty loam soil	Silty clay loam soil	Silty loam soil	Silty clay loam soil
30	2.4	0.7	12.2	11.2
25	1.7	0.45	9.5	6.25
15	1.2	0.3	5.7	5.5
10	0.4	0.15	2.5	2.3
5	0.25	0.07	1.2	1.0
2	0.1	-	0.5	-
1	0.05	-	0.25	-

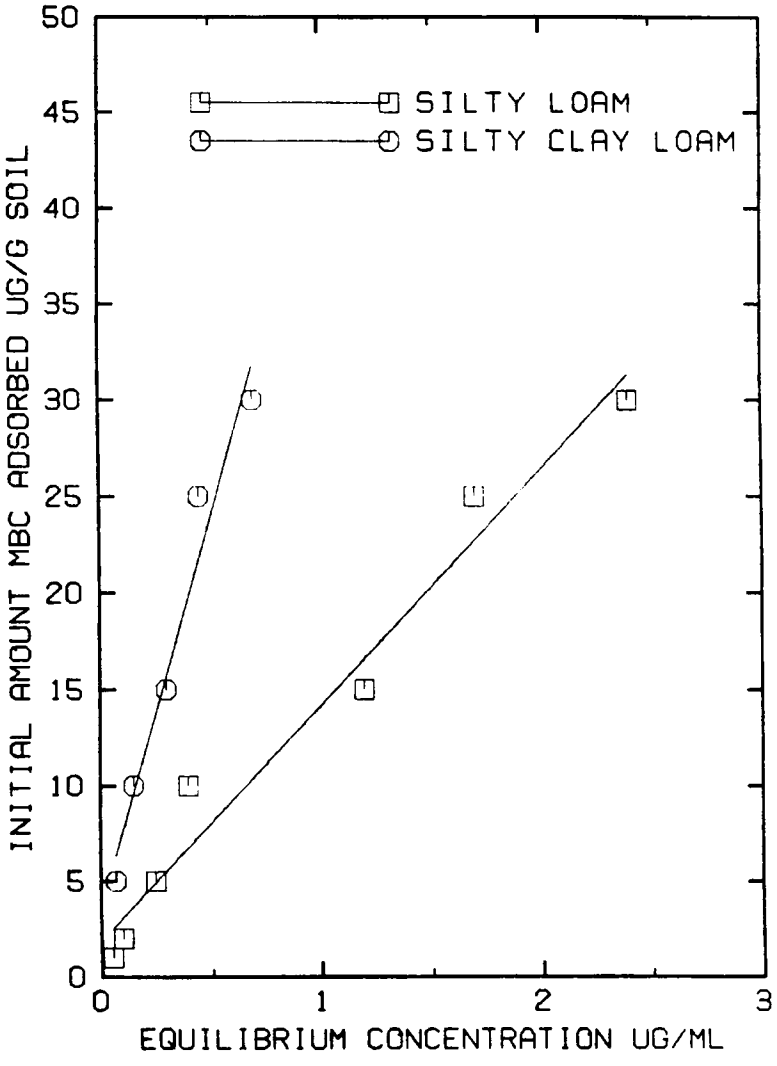


Figure 19. Concentrations of MBC in the soil-water at equilibrium in relation to the initial concentration in the soil.

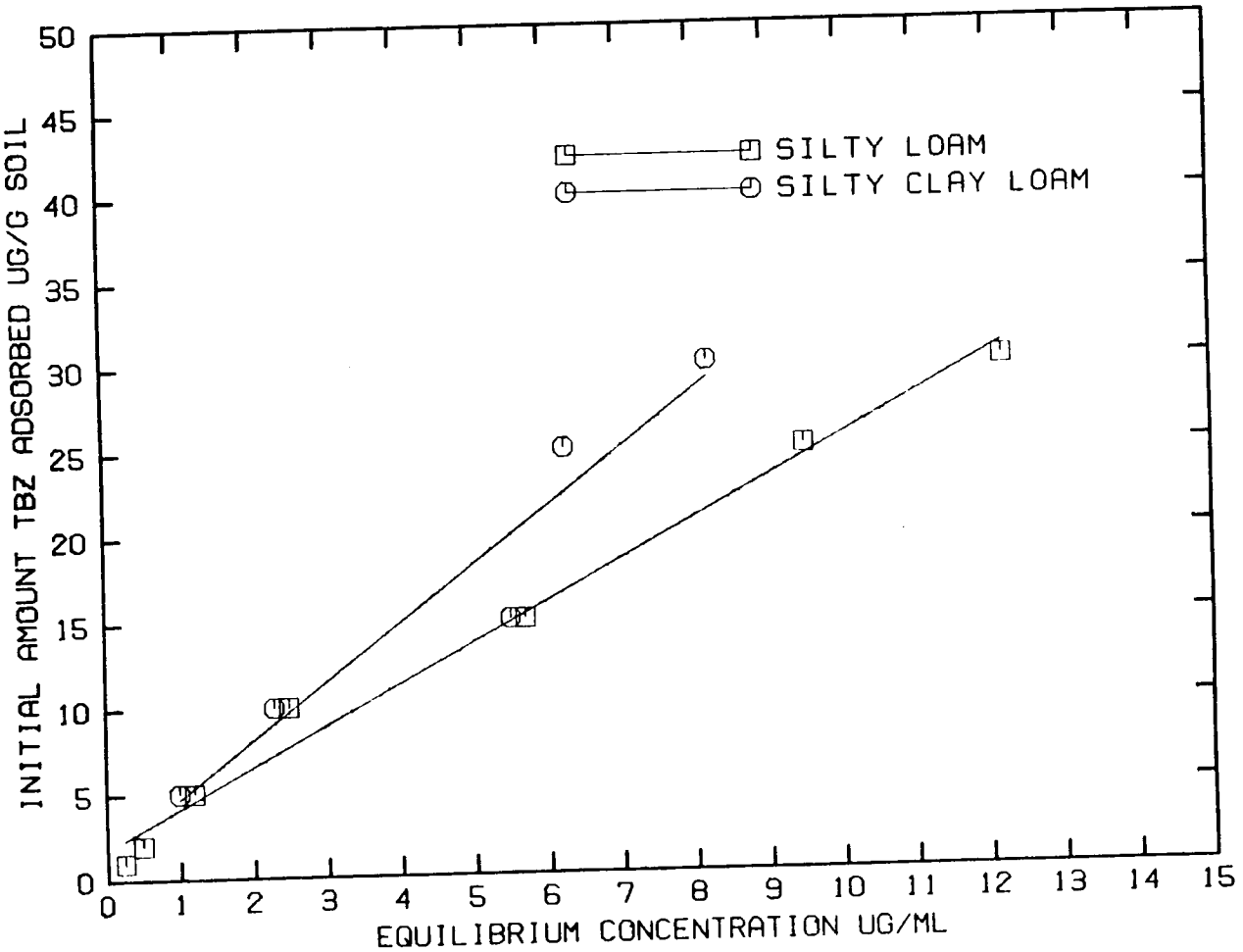


Figure 20. Concentrations of TBZ in the soil-water at equilibrium in relation to the initial concentration in the soil.

4.2.3 Effect of Different Water-Soil Ratios on Adsorption

Table 10 summarizes the concentrations of MBC and TBZ in the water at equilibrium in various water soil ratios. Various concentrations of the fungicides were applied to 50 g of the soil in ethyl acetate, the soil was air dried and the mixture shaken with water for a period of 10 hours. The results obtained indicate that with TBZ and silty loam soil, about 5% of the initial concentration was found in the solution at equilibrium, and less than 5% with the silty clay loam soil. With MBC and the silty loam soil, about 15-20% of the initial concentratation was found in water. It is also evident that at different soil-water ratios, the concentration of the fungicide in the solutions did not vary much. The lower ratio of 2 parts soil to 1 part water by weight might represent the actual concentration of the fungicide in the soil solution under field conditions.

4.3 Adsorption of MBC and TBZ on Ca-Bentonite

4.3.1 Adsorption as a Function of pH

Adsorption isotherms for MBC on Ca-bentonite clay at three different *pH* levels are shown in Figure 21. An increase in the acidity of the solution resulted in a significant increase in the adsorption of the fungicide to the clay. Adsorption isotherms for TBZ (Figure 22) also showed a similar *pH* dependence, although TBZ was adsorbed in much larger quantities per unit of adsorbent. It was also found that the adsorption process could be reversed by changing the *pH* of the solution. It should be stressed, however, that this reversibility was not complete. The amounts of fungicide released from the clay surface was somewhat less than would be expected. It is possible that this might be due to the trapping of portions of the fungicide between layers of the bentonite

Table 10. Effect of different water-soil ratios on the adsorption of MBC and TBZ.

Fungicide	Quantity of fungicide adsorbed to the soil, µg/g	Soil	Water-soil ratio	Concentration in soil solution at equilibrium, µg/ml
MBC	5	*Silty loam*	2:1	0.8
	5	*Silty loam*	3:1	0.7
	5	*Silty loam*	4:1	0.6
	5	*Silty clay loam*	2:1	0.45
	5	*Silty clay loam*	3:1	-
	5	*Silty clay loam*	4:1	-
TBZ	10	*Silty loam*	1:2	0.4
	10	*Silty loam*	2:1	0.55
	10	*Silty loam*	4:1	0.52
	10	*Silty clay loam*	1:2	0.31
	10	*Silty clay loam*	2:1	0.37
	10	*Silty clay loam*	4:1	0.39

clay. However, analytical errors in determining concetrations of fungicide released into solution cannot be completely ruled out.

4.3.2 Possible Adsorption Mechanism of MBC and TBZ

Figure 23 shows the adsorption of MBC and TBZ on Ca-bentonite as a function of the *pH* of the suspension. This *pH* dependence suggests a reaction with the clay surfaces by protonated molecules. The suggested basicity character of the Benzimidazoles is shown in Figure 24. In the presence of increased hydrogen ion activity on the clay surfaces, MBC and TBZ may become protonated to form a positively charged molecule which reacts with the clay surfaces forming Benzimidazole-clay complexes as shown below:

$$\text{Benzimidazole} + H^+ - \text{Clay} = \text{Benzimidazole} - H^+ - \text{Clay}$$

The pK_a of MBC and TBZ are 4.2 and 4.7, respectively. Weber[64] has shown for triazine herbicides that maximum adsorption of these protonated basic molecules occurs in the vicinity of the ionization constant. The decline in adsorption at *pH* values lower than the pK_a was explained by the increase in hydrogen ions activity. The adsorption curves for MBC and TBZ (figure 23) did not show a definite maximum adsorption near the pK_a. The shape of the adsorption curves resemble that of simple titration curves. Almost all the adsorption is confined to four *pH* units which are needed to convert the nonionized molecules to fully ionized species. The fact that the point of 50% adsorption for MBC and TBZ on Ca-bentonite does not correspond to their pK_a values is probably due to the surface acidity of bentonite, which may deviate as much as 3 or 4 *pH* units lower from the measured *pH* in the suspension. The 50% adsorption for TBZ was found to be 1.5 *pH* units higher than that of MBC, whereas the pK_a difference is only 0.5 *pH* units. The adsorption curve for TBZ might be due to two pK_a values, one for the Benzimidazole ring and a second at a lower *pH* for the Thiazole ring (Figure 24).

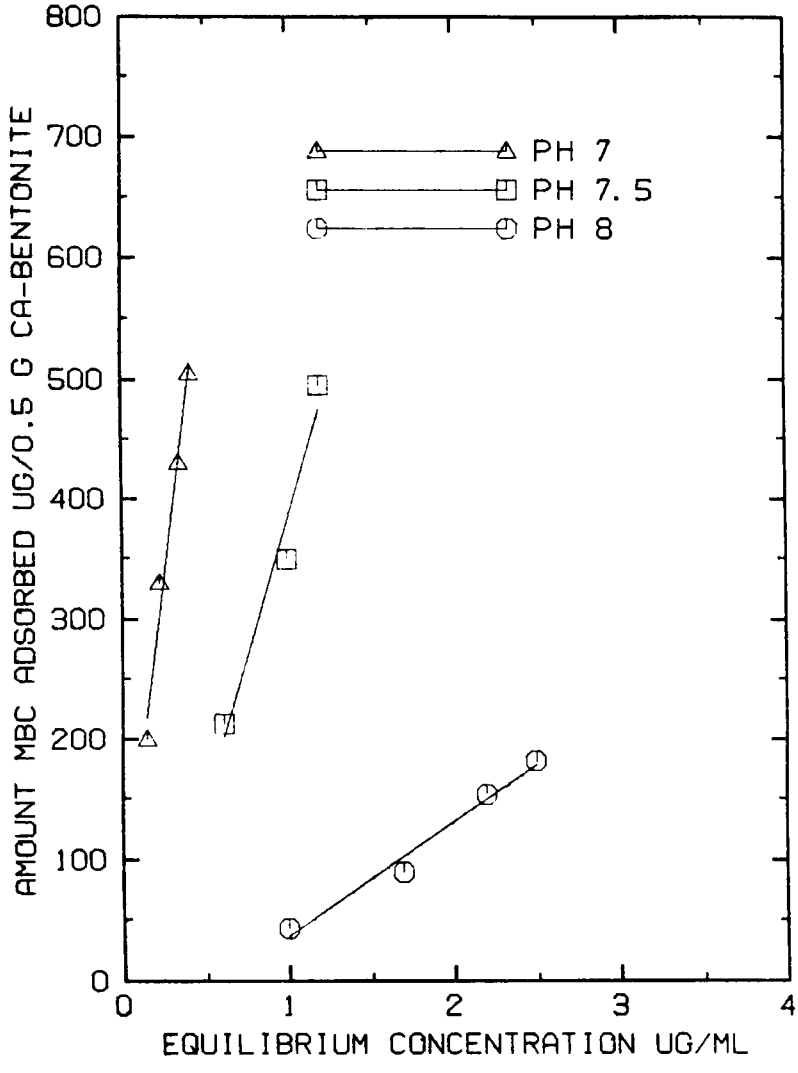


Figure 21. Adsorption isotherms of MBC on Ca-bentonite at different pHs.

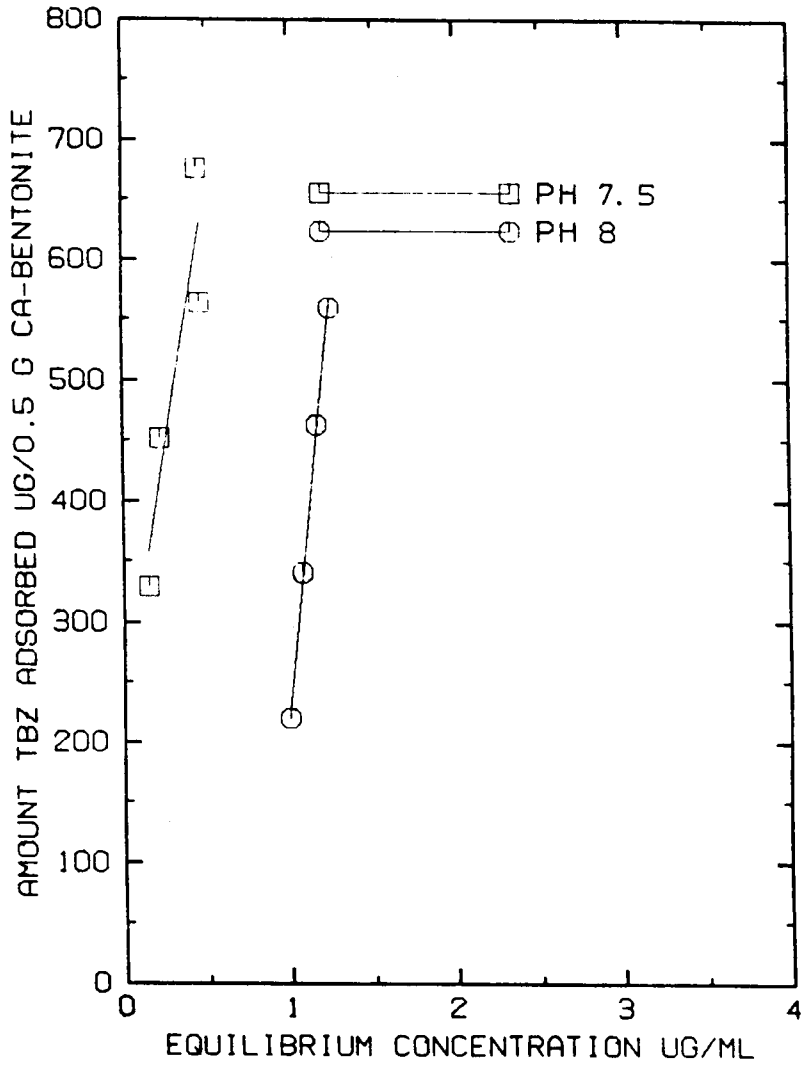


Figure 22. Adsoprtion isotherms of TBZ on Ca-bentonite at different pHs.

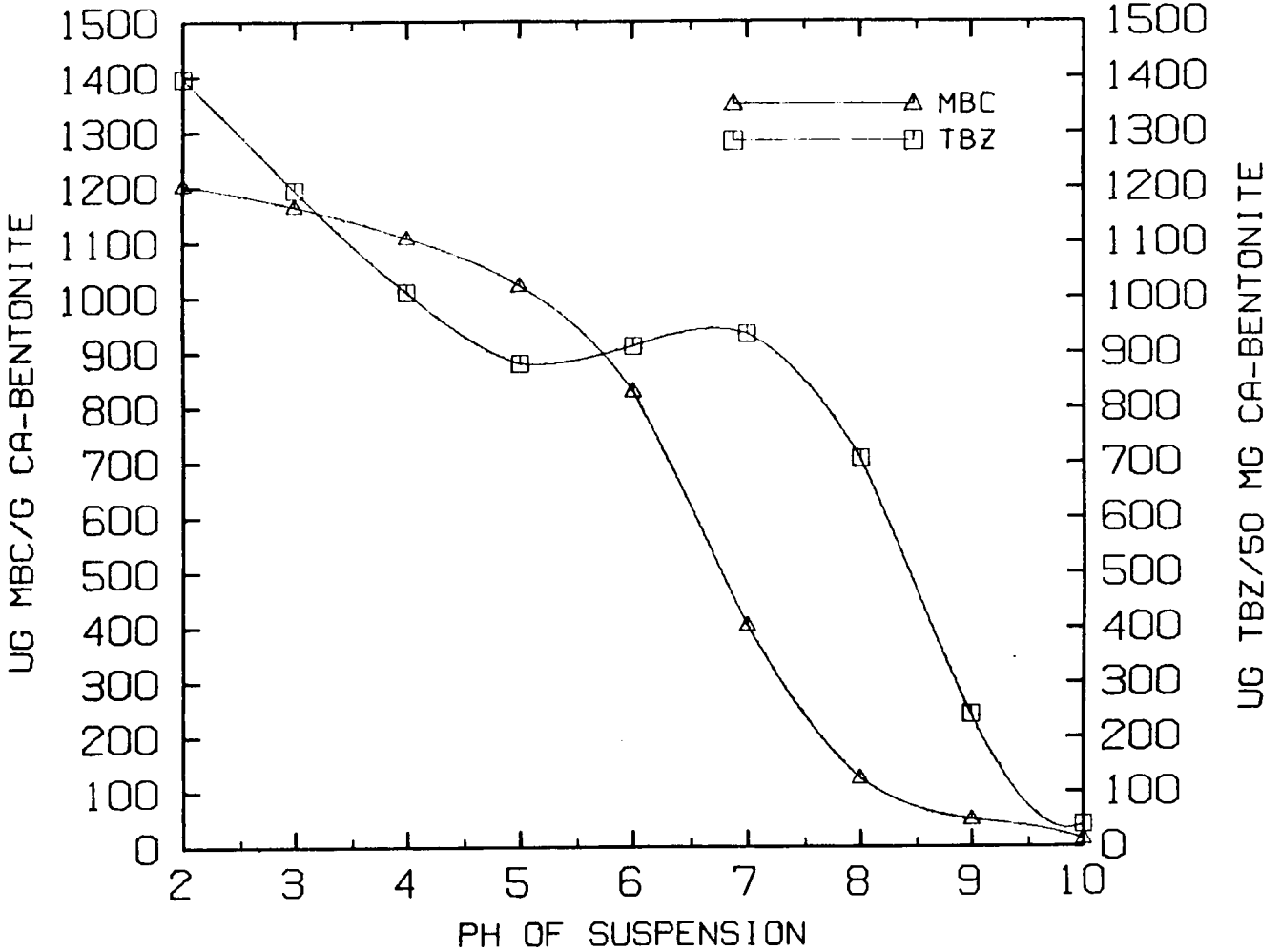
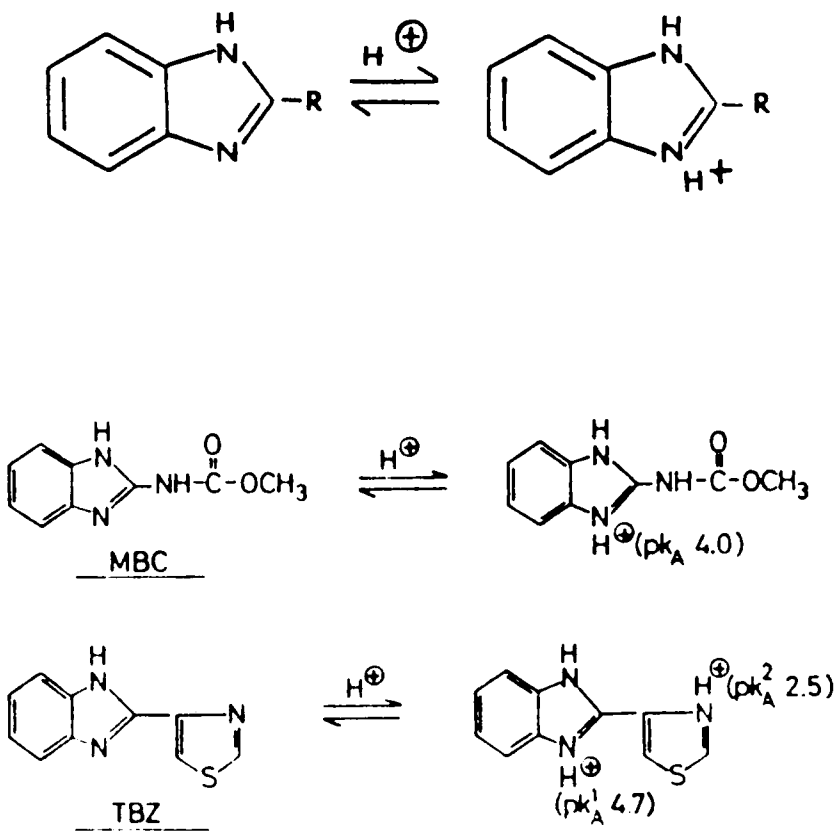


Figure 23. Adsorption of MBC and TBZ on Ca-bentonite as a function of pH.



$$\text{Benzimidazole} + H^{+} - \text{Clay} = \text{Benzimidazole} - H^{+} - \text{Clay}$$

Figure 24. Possible adsorption mechanism of MBC and TBZ on soil surfaces.

4.3.3 Effect of Different $CaCl_2$ Concentrations on Adsorption

The main adsorption mechanism seems to be of a cationic nature. The results of the effect of different concentrations of $CaCl_2$ on the adsorption of MBC and TBZ on Ca-bentonite are shown in Table 11. These results demonstrate, both for MBC and TBZ, that an increase in the salt concentration (keeping the *pH* of the solution constant) caused a decrease in the amount of adsorbed fungicide. However, the affinity of the relatively big TBZ ion to the clay surface is greater than that of Ca^{2+}, since considerable amounts are adsorbed in the presence of 1M $CaCl_2$. Approximately 50% of the total TBZ adsorbed on 150 mg of clay. It is possible that forces other than coulombic are operating in the adsorption process of the Benzimidazole dervatives. However, it is difficult to identify these forces at this point.

4.4 Results of Application of Runoff Model

As outlined in Section. 3.4.3., the model was applied to catchment sections 28 and 32 (Figure 13) of the Chowan river basin. Table 3 lists the major characteristics of the catchments, as well as parameters required in the formulations of the model. Figure 14 depicts the rainfall and infiltration rates, and the resulting ponding depths assumed for the catchments.

Figures 25 and 26 depict the estimated MBC and TBZ loadings (adsorbed onto sediment) into the Meherrin river as a function of catchment outflows at each of the time steps depicted in Figure 14. Significant fluxes of TBZ, and to a lesser extent, MBC, were estimated in the simulation. As mentioned in Section 4.3., the adsorption of MBC and TBZ onto soil particles was found to be reversible. Thus, any significant increases in the *pH* of the water could result in the release of MBC and TBZ from sediments, and contamination of the aquatic environment.

Table 11. Effect of different concentrations of $CaCl_2$ on the adsorption of MBC and TBZ to bentonite clay.

Ca-bentonite mg/150 ml	Amount of fungicide added, μg	Amount of fungcide adsorbed, μg	pH of the suspension	$CaCl_2$ concentation, M
		MBC		
500	1500	942	6.5	0.01
500	1500	529	6.5	0.1
500	1500	501	6.5	1.0
		TBZ		
150	1500	1245	8.0	0.01
150	500	814	8.0	0.1
150	1500	728	8.0	1.0

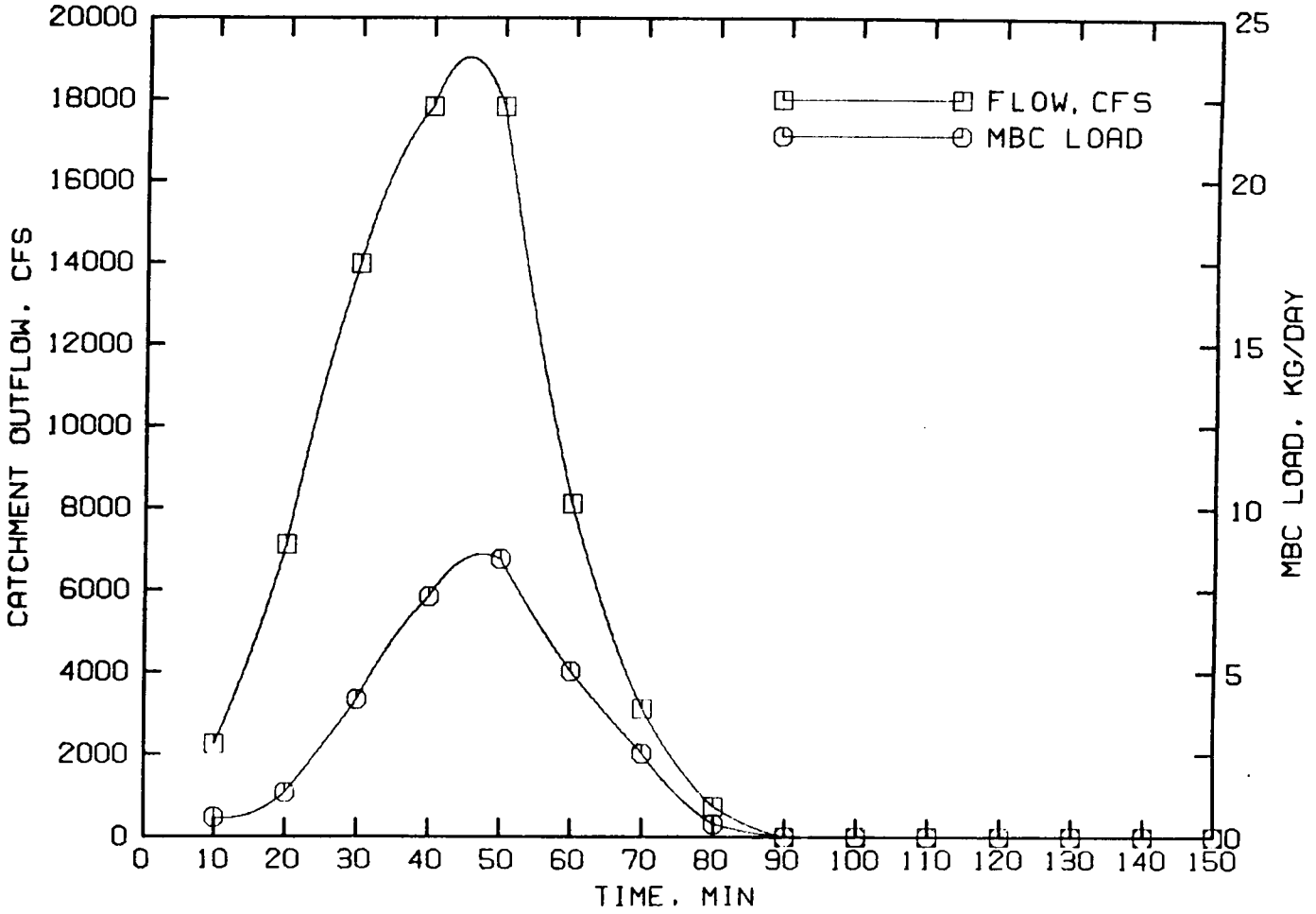


Figure 25. Predicted outflow hydrographs and MBC loadings from catchments 28 and 32 into the Meherrin river.

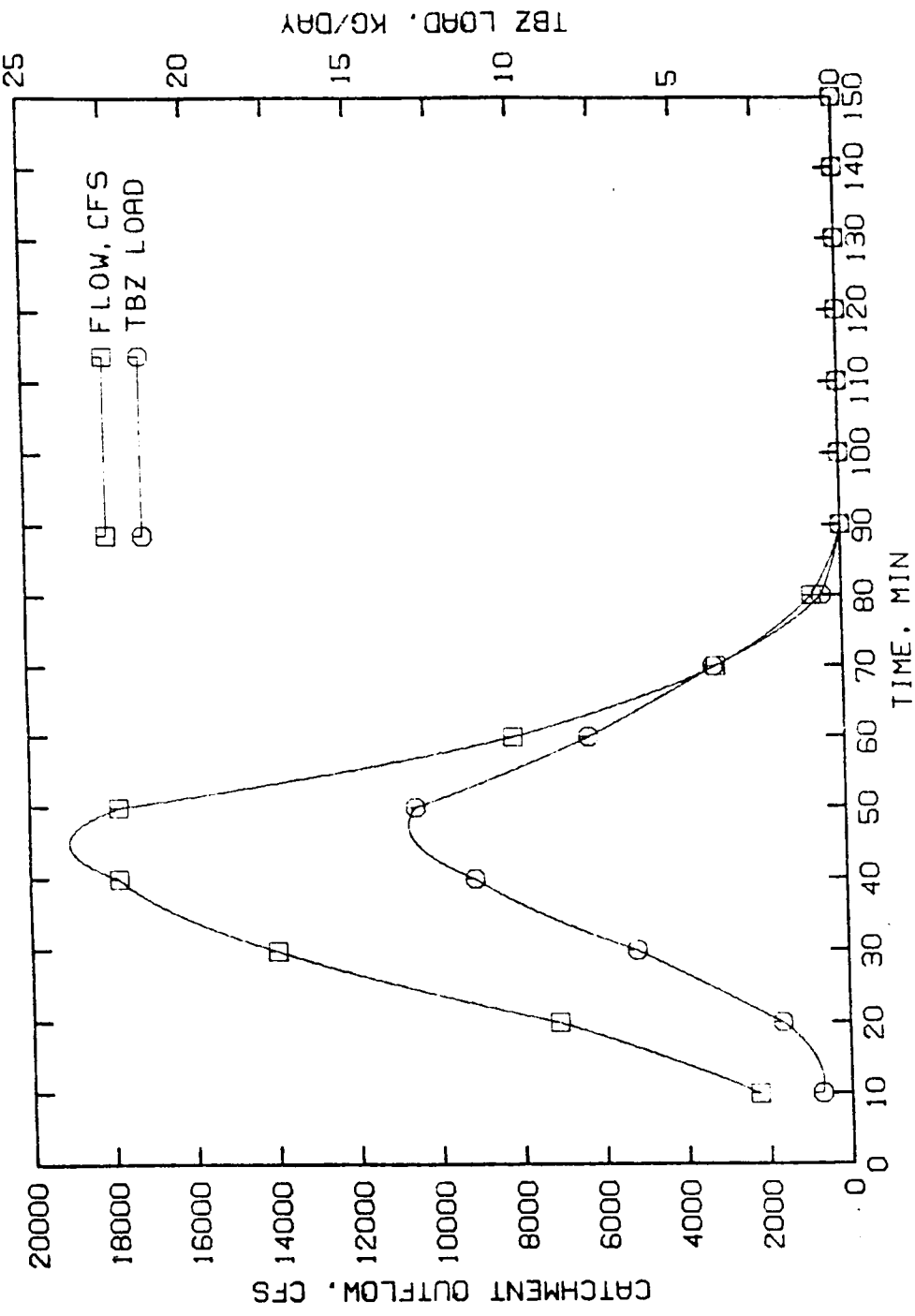


Figure 26. Predicted outflow hydrographs and TBZ loadings from catchments 28 and 32 into the Meherrin river.

5.0 Conclusions

The results presented and discussed in the preceeding sections allow the following conclusions to be drawn:

Terrestrial Microcosm Phase

1. The soil constituted a major relocation site for both Thiabendazole, and to a lesser extent, Benomyl. Approximately 44 and 74% of the initial dosages of Benomyl (recovered as MBC) and Thiabendazole, respectively, were recovered from the soil.
2. Approximately 53 and 27% of the initial dosage of Benomyl (recovered as MBC) and Thiabendazole, respectively, translocated into the plants.
3. Vaporization did not constitute a major route in the loss of either Benomyl or Thiabendazole.
4. The amounts of MBC and Thiabendazole transported from the soil to surface water were 3.22 and 0.29% of their initial dosages, respectively. Both fungicides were quite strongly adsorbed within the soil matrix.

Adsorption Studies

1. Thiabendazole, and to a lesser extent, MBC, were adsorbed in largest quantities to the silty clay loam soil, followed by silty loam and sandy soils. The clay content of these soils were 30, 20 and 10%, respectively.
2. Thiabendazole was available in the soil solution at much smaller quantities than MBC. It was found that at different soil-water ratios, the concentrations of MBC and Thiabendazole did not vary much.
3. An increase in the acidity of the solution resulted in a significant increase in adsorption of MBC and Thiabendazole to Ca-bentonite clay. This *pH* dependence suggests that in the presence of increased hydrogen ion activity on the clay surfaces, MBC and Thiabendazole may become protonated to form positively charged molecules, which react with the clay surfaces forming fungicide-clay complexes.
4. The results of the effect of different concentrations of $CaCl_2$ on the adsorption of MBC and Thiabendazole on Ca-bentonite demonstrated that an increase in the salt concentration (keeping the *pH* of the solution constant) caused a decrease in the amount of adsorbed fungicide, obviously due to the competition for adsorption sites on the clay surface.

Simulation of Sediment Runoff

1. Results of the simulation of sediment runoff from the Chowan river basin into the Meherrin river indicate that significant quantities of MBC and TBZ (adsorbed onto soil particles) could be transported into aquatic systems. Subsequent increases in the *pH* of the aquatic system could result in the release of adsorbed MBC and TBZ into the aquatic environment.

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Appendix

Results of the simulation of MBC loading into the Meherrin river from the Chowan river basin.
Rainfall rate at L-th time step, inches/hour:
0.12E+020.12E+020.10E+020.10E+020.91E+010.78E+010.65E+010.52E+010.39E+010.26E+010.13E+010.00E+00
0.00E+000.00E+000.00E+00
Infiltration rate at L-th time step, cm/hour:
0.70E+010.75E+010.75E+010.75E+010.75E+010.75E+010.70E+010.65E+010.60E+010.30E+010.20E+010.00E+00
0.00E+000.00E+000.00E+00
Ponding depth at L-th time step, cm:
0.10E+010.20E+010.30E+010.30E+010.40E+010.30E+010.20E+010.10E+010.10E+010.10E+010.10E+010.00E+00
0.00E+000.00E+000.00E+00
STORM DURATION = 50.00MIN;
CATCH NO = 1; TIME OF CONC = 34.70MIN;

STEP	CAT	FLOW (CFS)	MBC LOAD (KG/DAY)
1	1	2239.80	0.57
2	1	7110.92	1.32
3	1	13976.91	4.16
4	1	17817.64	7.31
5	1	17817.64	8.45
6	1	8107.74	5.02
7	1	3114.55	2.54
8	1	738.66	0.40
9	1	0.00	0.00
10	1	0.00	0.00
11	1	0.00	0.00
12	1	0.00	0.00
13	1	0.00	0.00
14	1	0.00	0.00
15	1	0.00	0.00

Figure 27. Results of the simulation of MBC loadings into the Meherrin river from the Chowan river basin. (Catchment Nos.28 and 32)

Results of the simulation of TBZ loadings into the Meherrin river from the Chowan river basin.
Rainfall rate at L-th time step, inches/hour:
0.12E+020.12E+020.10E+020.10E+020.91E+010.78E+010.65E+010.52E+010.39E+010.26E+010.13E+010.00E+00
0.00E+000.00E+000.00E+00
Infiltraton rate at L-th time step, cm/hour:
0.70E+010.75E+010.75E+010.75E+010.75E+010.75E+010.70E+010.65E+010.60E+010.30E+010.20E+010.00E+00
0.00E+000.00E+000.00E+00
Ponding depth at L-th time step, cm:
0.10E+010.20E+010.30E+010.30E+010.40E+010.30E+010.20E+010.10E+010.10E+010.10E+010.10E+010.00E+00
0.00E+000.00E+000.00E+00
STORM DURATION = 50.00MIN;
CATCH NO = 1; TIME OF CONC = 34.70MIN

STEP	CAT	FLOW (CFS)	TBZ LOAD (KG/DAY)
1	1	2239.80	0.88
2	1	7110.92	2.06
3	1	13976.91	6.48
4	1	17817.64	11.38
5	1	17817.64	13.17
6	1	8107.74	7.83
7	1	3114.55	3.96
8	1	738.66	0.62
9	1	0.00	0.00
10	1	0.00	0.00
11	1	0.00	0.00
12	1	0.00	0.00
13	1	0.00	0.00
14	1	0.00	0.00
15	1	0.00	0.00

Figure 28. Results of the simulation of TBZ loadings into the Meherrin river from the Chowan river basin. (Catchment Nos.28 and 32)

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