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Department of **SOIL SCIENCE**

The University of British Columbia
Vancouver, Canada

Date **Dec. 21 1995**
ABSTRACT

Soil fumigants have been identified as a potential risk to groundwater quality in unconfined aquifers in the Lower Fraser Valley of British Columbia. Metam-sodium, which converts in soil primarily to the volatile biocidal compound methylisothiocyanate (MITC), has seen increased usage in the area in recent years. The objective of this study was to determine the effects of soil water regime and soil properties on the behavior of MITC in soil. The partitioning of MITC to leaching loss, volatilization loss, soil extractable MITC, and MITC degradation were determined in repacked soil columns under three differing leaching regimes and in four soils with differing clay and organic carbon contents. Degradation of MITC was generally rapid. In the four soil types examined, > 90% of applied MITC was degraded in less than 83 days. Volatilization loss of MITC increased with increasing soil air filled porosity and was inhibited by water application. In another experiment, with no water application in a coarse textured soil, approximately 30% of applied MITC was volatilized over a 35 day period. MITC was very mobile in soil; negligible soil extractable MITC concentrations were measured after completion of the experiments and MITC movement was only slightly retarded compared to bromide, a conservative tracer. The extent of MITC retention compared to bromide increased with increasing soil organic carbon content, suggesting retention by sorption to soil organic matter. The proportion of MITC lost by leaching was dependent on the amount of MITC remaining in the soil after losses by degradation and volatilization processes, and was not related to soil clay or organic carbon content. These results suggest MITC would not normally present a risk to groundwater quality, but because of its high mobility in soil some risk is possible in situations where degradation and volatilization processes are slow in removing MITC from the soil, and water infiltration is high.
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1. INTRODUCTION

Contamination of groundwater with pesticide residues is a significant human health and environmental concern. Contamination of groundwater supplies with pesticides is a problem for many people because groundwater is their sole water source and, particularly for private wells, little or no water treatment is done before consumption. Furthermore, once a groundwater source is contaminated with pesticides, few technologically and economically feasible remediation methods are available, especially when dealing with non-point source contamination over large areas (Scott 1988). Because the chronic health effects of the very low levels of pesticide contamination (low ppb) typically found in groundwater (Leistra and Boesten 1989; Fairchild 1987) are mostly unknown, the public perceives this contamination as a very important human health concern, resulting in intense public pressure to prevent or mitigate pesticide contamination.

The Abbotsford Aquifer area is one example where concerns about groundwater contamination with pesticides have arisen. The Abbotsford Aquifer is the largest unconfined aquifer in the lower Fraser Valley, and is an important source of water for domestic, municipal, and industrial use (Kreye and Wei 1994). The aquifer is also very susceptible to contamination from activities at the surface because of its unconfined nature, the high permeability of the soils above it, and the high annual precipitation received in the area. Intense agricultural land use in the area has contributed to elevated levels of nitrate from both point and non-point sources, as well as trace levels of several pesticides from non-point sources detected prior to 1990 (Leibscher et al. 1992; Gartner Lee Ltd. 1992). A soil fumigant, 1,2-dichloropropane (1,2-DCP) is the most commonly detected pesticide in the Abbotsford Aquifer (Zebarth et al. 1993; Gartner Lee Ltd. 1993). The compound 1,2,2-trichloropropane (1,2,2-TCP), a trace impurity in formulations of the soil fumigant 1,3-dichloropropene (1,3-DCP) was also detected in the Aquifer (Szeto et al. 1994). These
soil fumigants were widely used for control of nematodes in raspberry fields above the Abbotsford Aquifer.

Registration was discontinued in 1985 for products with 1,2-DCP as the active ingredient, and 1,3-DCP formulations were voluntarily withdrawn from the local market in 1993. Subsequently, another soil fumigant, metam-sodium (trade name Vapam) has been substituted for these products in the Abbotsford Aquifer area. Metam-sodium converts almost completely in soil to the volatile biocidal compound methylisothiocyanate (MITC), which is the active fumigant (Smelt et al. 1989).

To date, there have been no reports in the lower Fraser Valley of MITC detections in groundwater (S.Y. Szeto, Pers. Comm.). The susceptibility of the Abbotsford Aquifer to contamination, the detection of other soil fumigants in groundwater, the autumn application of metam-sodium shortly before the high rainfall season, and the low soil adsorption and high volatility of MITC (Gerstl et al. 1977) suggest some risk does exist; however, the magnitude of the risk is unknown at present. This project was therefore initiated as a pro-active effort to gain information about the potential risk posed to groundwater quality in the Abbotsford Aquifer area by MITC generated by soil fumigation with the compound metam-sodium.

To gain insight into potential risks to groundwater quality, the fate of MITC in the environment must be considered. Environmental fate includes degradation, sorption to the soil colloids, transport to the atmosphere via volatilization processes, and transport to the groundwater via leaching processes. The most important environmental factors affecting the fate of MITC in the environment are soil water regime and soil properties. Laboratory soil column systems were used to provide a closed system from which all losses could be measured, and in which environmental factors could be controlled and manipulated.

The specific objective of this study was to use laboratory soil columns to determine the partitioning of MITC to leaching, volatilization, sorption, and degradation processes, and how this partitioning was influenced by soil water regime and soil properties.
2. LITERATURE REVIEW

2.1. Groundwater Quality Concerns With Fumigant Use Over the Abbotsford/Sumas Aquifer

2.1.1. Physical Setting and Characteristics of the Abbotsford/Sumas Aquifer

The Abbotsford/Sumas Aquifer is located in the Fraser Lowland which is part of the lower Fraser River valley of British Columbia and Washington State (Fig. 2.1). The Abbotsford/Sumas Aquifer is the largest unconfined aquifer in both the lower Fraser River Valley of British Columbia and the Nooksack River Valley in Washington. The areal extent of the aquifer is approximately 220 km\(^2\) (Cox et al. 1993), almost evenly divided by the Canada—U.S. international boundary. The aquifer is located on a flat glacial outwash plane extending from the Clearbrook-Abbotsford area of BC, south to Lynden, WA (Cox et al., 1993). The surface boundaries of the aquifer are thought to coincide with the surficial outcrop of the highly permeable deposits in the area known as the Sumas Outwash (Cox et al. 1993). Because this study is primarily focused on the Canadian portion of the Abbotsford/Sumas Aquifer, the aquifer will hereafter be referred to as simply the Abbotsford Aquifer.

Sumas Outwash was formed by meltwater streams flowing southward from a glacial moraine just north of the Canada-U.S. border (Cox et al. 1993). It consists of stratified glaciofluvial sands and gravels with interspersed pockets of glacial till and clayey silt lenses (Halstead 1986). Less permeable glaciomarine silt and bedrock below the outwash deposits determine the lower boundary of the aquifer. The base of the aquifer is known to reach 70 m locally, but typically ranges between 5 and 30 m in thickness (Liebscher et al. 1992).
Figure 2.1. Geographic location and surface boundaries of the Abbotsford/Sumas Aquifer.
Medium textured eolian deposits ranging from 0 to 2 m in thickness cap the gravelly outwash over most of the aquifer area (Luttermerding 1980). The surface soil texture is dominantly silt loam in the areas with the thickest loess deposits, but becomes coarser as the loess thins and gravelly glaciofluvial material is mixed into the surface, grading to gravelly sandy loam textures where the loess cap is thin or absent (Luttermerding 1981). These soils are generally rapidly to well drained and are moderately to rapidly pervious, depending on the surface texture. The majority of the soils above the aquifer are classified as Orthic Humo-ferric Podzols (Luttermerding 1981).

The Abbotsford Aquifer is an unconfined water table aquifer. Groundwater table levels typically range from 3 to 25 m below the land surface (Zebarth et al. 1995a) with an average seasonal fluctuation of 3 m (Cox et al. 1993) which varies with location. The water table is highest in March and lowest in late October, which is directly correlated with precipitation levels (Liebscher et al. 1992). Most recharge to the aquifer occurs as direct infiltration from rain or snow melt during the winter months, but runoff from the clay uplands to the north of the aquifer and seasonal recharge from Fishtrap Creek which flows south across the aquifer (Fig. 2.1) also contribute (Liebscher et al. 1992). The groundwater flow direction in the aquifer is generally south, with some portions flowing southwest and some southeast (Cox et al. 1993). Calculated average linear velocities of water flow range from 5 to 450 m year\(^{-1}\) (Liebscher et al. 1992). This value depends on the measured and assumed values of parameters affecting flow such as the hydraulic gradient, and hydraulic conductivity of the aquifer.

The climate in the Fraser Lowland is characterized by mild, wet winters and warm, dry summers (Fig. 2.2). At the Abbotsford Airport, which is located near the center of the Canadian portion of the aquifer, the 30 year average annual precipitation is 1596 mm (Atmospheric Environment Service 1985). About 70 % of this precipitation falls between October and March. In contrast, potential evapotranspiration is lower from October to March and higher from May to September (Fig. 2.2). The average annual groundwater
Figure 2.2. Mean monthly air temperature, precipitation, and potential evapotranspiration from 1961 to 1990 at Abbotsford, BC. Potential evapotranspiration calculated using method 1 of Baier and Robertson (1965).
recharge for this area, estimated as the difference between total precipitation and potential evapotranspiration for this 30 year data (Zebarth et al. 1995b), is approximately 1000 mm; nearly all of this recharge will typically occur from October to March.

Land use above the aquifer is varied and intensive. Over the past two decades there has been a steady increase in urbanization, in industrial and commercial development, and in the intensity of agricultural and animal husbandry activities in the area (Liebscher et al. 1992). Based on 1991 Census data, the largest use of agricultural land above the aquifer is for raspberry production, which occupies 45% of the cropped agricultural land in the area (Zebarth and Paul 1995).

Groundwater from the Abbotsford Aquifer is an important water source for the area above the aquifer. Groundwater use on the Canadian portion of the aquifer can be broken down as follows (Kohut 1987): industrial 41%, municipal 34%, irrigation 21%, and domestic 4%. There are several major industrial users, with the Fraser Valley trout hatchery the largest single user overall (Kohut 1987). The municipalities of Abbotsford and Matsqui have high capacity production wells, and combined with the trout hatchery, use two-thirds of the groundwater withdrawn on the Canadian side (Liebscher et al. 1992). Almost all irrigation and domestic supply wells are shallow, ranging from 6 to 11 m in depth, and are completed in the Sumas Outwash (Cox et al. 1993). The total number of wells has not been reported in the literature, but Liebscher et al. (1992) estimate there are about 500 wells in the 6 km² area between Abbotsford and the international border.

The quality of groundwater in the Abbotsford Aquifer has declined with the increasing intensity of land use above the aquifer (Liebscher et al. 1992; Zebarth and Paul 1995). The aquifer is susceptible to contamination from activities at the surface for several reasons: 1) the aquifer is unconfined and the overlying glaciofluvial material is highly permeable, 2) the water table is close (< 3m) to the soil surface in some areas, 3) the soils above the aquifer are shallow, relatively coarse textured, and highly permeable, and 4) annual precipitation is high resulting in an intense leaching environment. Nitrates have
been detected in an increasing number of piezometers and wells in the aquifer (Liebscher et al. 1992). Although nitrate contamination of the aquifer will not be discussed here, it can be used as an indicator of the susceptibility of the aquifer to contamination with other compounds such as pesticides (Liebscher et al. 1992).

2.1.2. Detection of Pesticides Including Soil Fumigants in the Abbotsford Aquifer

Several pesticides have been detected in groundwater in the Abbotsford Aquifer. Environment Canada monitored wells and piezometers for selected pesticides from 1984 to 1990 (Liebscher et al. 1992). Groundwater sampling was concentrated in the area south of the Abbotsford Airport where the dominant land use is raspberry production. This area was chosen because it had a high risk for nitrate contamination, as this study also examined nitrate levels in the aquifer. Groundwater samples were analyzed for 23 target compounds selected on the basis of an agricultural pesticide use survey conducted in the area. Twelve of the 23 compounds were detected in the aquifer (Table 2.1). The authors hypothesized that the contamination resulted from field application of the pesticides, i.e., non-point sources.

A soil fumigant, 1,2-dichloropropane (1,2-DCP) was the compound most commonly detected in the study of Liebscher et al. (1992). It was detected in 40 of 139 samples in concentrations up to 5.52 μg L⁻¹. Another soil fumigant, 1,3-dichloropropene (1,3-DCP) was also detected, but only in one sample at a concentration of 3.5 μg L⁻¹. No Canadian Drinking Water Quality Guideline exists for 1,2-DCP or 1,3-DCP. All other ten compounds were detected at concentrations below the Maximum Acceptable Concentration listed in the Canadian Drinking Water Quality Guidelines (Liebscher et al. 1992).

Several soil fumigants have been used over the Abbotsford Aquifer. Soil fumigation in the area is primarily for control of pathogenic nematodes before the
Table 2.1. Pesticides targeted for analysis and pesticide detections (µg L⁻¹) in groundwater samples from the Abbotsford Aquifer by Environment Canada from 1984 to 1990 (Liebscher et al. 1992). Fifty-eight wells and piezometers were sampled for all pesticides, except 1,2-DCP and 1,3-DCP for which 139 wells and piezometers were sampled.

<table>
<thead>
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<th>Pesticide</th>
<th>Number of Positive Detections</th>
<th>Maximum Concentration Detected</th>
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<tbody>
<tr>
<td>1,2-dichloropropane</td>
<td>40</td>
<td>5.52</td>
</tr>
<tr>
<td>Carbofuran</td>
<td>20</td>
<td>12.0</td>
</tr>
<tr>
<td>Atrazine</td>
<td>13</td>
<td>4.0</td>
</tr>
<tr>
<td>Dinoseb</td>
<td>11</td>
<td>1.95</td>
</tr>
<tr>
<td>Simazine</td>
<td>11</td>
<td>1.25</td>
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<td>Diazanon</td>
<td>7</td>
<td>2.0</td>
</tr>
<tr>
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<tr>
<td>Malathion</td>
<td>0</td>
<td>—</td>
</tr>
<tr>
<td>Guthion</td>
<td>0</td>
<td>—</td>
</tr>
<tr>
<td>Carbaryl</td>
<td>0</td>
<td>—</td>
</tr>
<tr>
<td>Dichlobenil</td>
<td>0</td>
<td>—</td>
</tr>
<tr>
<td>Dicamba</td>
<td>0</td>
<td>—</td>
</tr>
<tr>
<td>MCPA</td>
<td>0</td>
<td>—</td>
</tr>
<tr>
<td>2,4-D</td>
<td>0</td>
<td>—</td>
</tr>
<tr>
<td>P, P'-DDT</td>
<td>0</td>
<td>—</td>
</tr>
<tr>
<td>O, P'-DDE</td>
<td>0</td>
<td>—</td>
</tr>
<tr>
<td>P, P'-DDT</td>
<td>0</td>
<td>—</td>
</tr>
</tbody>
</table>

9
establishment of raspberry and strawberry crops. Fumigation is done only when a field is
rejuvenated, typically once every 5 to 15 years (Szeto et al. 1994). In the Abbotsford
Aquifer area the recommended time for fumigation is late August or early September,
following raspberry cane removal (British Columbia Ministry of Agriculture, Fisheries,
and Food (BCMAFF) 1994). Historically, the most commonly used active ingredients for
soil fumigation in the area were a mixture of 1,3-DCP and 1,2-DCP, such as Telone of
Dow Chemical, Agricultural Products Division or D-D of Shell Chemical Company Ltd.,
1,3-DCP alone, such as Telone II of Dow-Elanco Canada Ltd., and 1,2-dibromoethane
(EDB), such as Bromofume of Dow Chemical Company (Szeto et al. 1994).

Soil fumigants as a group have properties that make them prone to leaching. In
order to be effective as a soil fumigant, a compound must have low adsorption, because it
must distribute well throughout the surface soil (Hoffman and Malkomes 1979), and it
must be fairly persistent, because it must be present at toxic concentrations long enough to
kill the target organisms (Cremlyn 1978). Both of these characteristics also increase the
leaching potential of a compound (Jury et al. 1987). In fact, many cases of groundwater
contamination with soil fumigants have been documented worldwide. The soil fumigants
1,2-dibromo-3-chloropropane (DBCP) and EDB have been detected in many areas of the
U.S. (Cohen et al. 1984). In addition, many cases of contamination with 1,2-DCP have
been documented in both the U.S. (Cohen et al. 1984; Ali et al 1986), and western Europe
(Leistra and Boesten 1989; Lagas et al. 1989).

The B.C. Ministry of Health’s Fraser Valley Groundwater Monitoring Program
(Gartner Lee Ltd. 1993) also documented contamination of the Abbotsford Aquifer with the
soil fumigant 1,2-DCP. Groundwater sampling was concentrated in areas of the Lower
Mainland of British Columbia that were delineated as high to medium-high risk areas for
groundwater contamination in a previous report (Gartner Lee Ltd. 1992). Groundwater
samples from 71 wells were analyzed for a total of 54 pesticide compounds, and samples
from 103 wells were analyzed for 1,2-DCP and 1,3-DCP. Overall, only two pesticide
compounds were detected: 1,2-DCP was detected in three wells at concentrations ranging from 0.5 to 1.1 μg L⁻¹, and the pesticide oxamyl was detected in two wells at concentrations of 1.3 and 1.7 μg L⁻¹. Four of the five positive detections were from wells in the Abbotsford Aquifer, just south of the Abbotsford Airport.

A study by Zebarth et al. (1993) screened groundwater samples from 18 piezometers within the study area of Liebscher et al. (1992) for 104 pesticide compounds. These compounds included active ingredients and some breakdown products for most pesticides likely to have been used in significant quantities in the study area. The only compound detected was 1,2-DCP, in 7 of the 18 piezometers.

Subsequently, Zebarth et al. (1993) expanded sampling to 35 piezometers within the same study area, and focused analysis on the soil fumigants 1,2-DCP, 1,3-DCP, and EDB. 1,2-DCP was detected in 27 of the 35 piezometers monitored with a maximum concentration of 7.1 μg L⁻¹. The concentration decreased with increasing depth below the water table which is consistent with a non-point surface source of contamination leaching to the water table.

Zebarth et al. (1993) hypothesized that the 1,2-DCP was from historical use of soil fumigants in agricultural production. There is no known industrial use of 1,2-DCP in the region (S.Y. Szeto, Pers. Comm.). Registrations of fumigants containing 1,2-DCP as the active ingredient were discontinued in Canada during or before 1985 (Szeto et al. 1994), and it is believed local supplies were used up by 1987 (Liebscher et al. 1992). This suggests 1,2-DCP has persisted in the soils or the aquifer since before this date; this is possible since 1,2-DCP is known to be persistent in soils and water (Cohen et al. 1983).

Contamination with 1,3-DCP was also found by Zebarth et al. (1993). 1,3-DCP was detected in only one of 35 piezometers, and the detections were transient in nature and reached a peak concentration of only 0.2 μg L⁻¹. The authors hypothesized that the contamination resulted from treatment of an adjacent field with Telone II and that the
relatively fast degradation rate of 1,3-DCP by hydrolysis in soils and water (Cohen et al. 1983) resulted in the transient nature of the detections.

In the same study, the compound 1,2,2-trichloropropane (1,2,2-TCP) was detected in a large proportion of the groundwater samples (Szeto et al. 1994). The compound was detected in 57% of the piezometers and 44% of the domestic wells sampled with a maximum concentration of 0.62 μg L⁻¹. Szeto et al. (1994) hypothesized that this contaminant originated from past soil fumigation with fumigants containing 1,3-DCP and 1,2-DCP. Analysis of samples of Telone and Telone II revealed they contained approximately 0.1 to 0.3 % by weight of 1,2,2-TCP. In addition, there has been no other known use of this chemical in the Abbotsford Aquifer area (Szeto et al. 1994).

Telone II was voluntarily withdrawn from the local market by the manufacturer in 1993 (S.Y. Szeto, Pers. Comm.), shortly after the detection of 1,2,2-TCP in the Abbotsford Aquifer. Telone II is, however, still registered for use in Canada. Subsequently, most growers now use the soil fumigant metam-sodium (trade name Vapam) for nematode control in raspberry and strawberry production (B.J. Zebarth, Pers. Comm.).

2.2. Metam-Sodium and Methylisothiocyanate (MITC)

2.2.1. Use of Metam-Sodium

Metam-sodium, chemical name sodium methylthiocarbamate, is a general biocide with fumigant action. It is used worldwide for fumigation of field and greenhouse soils to control nematodes and other soil insects, soil fungi, and weeds and weed seeds. In the Netherlands, metam-sodium is used very extensively for soil fumigation, primarily for control of potato-cyst nematodes (Leistra and Boesten 1989). Metam-sodium is applied as a pre-plant soil treatment because of the non-specific nature of its fumigant action, and planting must be delayed until its dissipation from the soil is complete (Worthing 1983).
Metam-sodium is also extensively used as a wood preservative, for example on utility poles (Miller and Morrell 1990).

Metam-sodium was introduced in 1959 by Stauffer Chemical Company and has been marketed under various trade names such as Monam, Nematin, Trimatron, Vapam, and Vitafume (van Berkum and Hoestra 1979). Metam-sodium is currently marketed in Canada by Zeneca Corp. under the trade name Vapam. Vapam is a concentrated aqueous solution of 382 g anhydrous metam-sodium L\(^{-1}\) (Worthing 1983).

Metam-sodium can be applied using several different methods. The undiluted product is commonly either injected into the soil, usually at about 20 cm depth, or sprayed onto the soil surface followed by immediate mixing to 20 or 30 cm depth by rotovation (van Berkum and Hoestra 1979; BCMAFF 1994). In both cases the soil surface is pressed or compacted immediately after application, usually by rolling, to seal or reduce pore space in the surface layer and thus reduce volatilization losses of the fumigant. Alternatively, a light application of water is sometimes used to reduce air filled pore space in the soil surface (Lembright 1990). In greenhouse applications a plastic cover is generally used (van Berkum and Hoestra 1979). Metam-sodium is also commonly applied as a drench, using a sprinkler or trickle irrigation system. In the Abbotsford Aquifer area, metam-sodium is applied by either the injection or rotovation methods followed by rolling of the soil surface (H. Kleindienst, Pers. Comm.).

Recommended application rates of metam-sodium depend on the target organisms and site conditions. Recommended application rates range from 150 to 500 kg metam-sodium ha\(^{-1}\) for field application (Smelt et al. 1989), and up to 1000 kg ha\(^{-1}\) for greenhouse soils (Leistra and Crum 1990).

In British Columbia, metam-sodium is recommended for control of nematodes in raspberry, strawberry, and blackberry production (BCMAFF 1994). For raspberry production, the most common usage, the recommended rate is 450 to 900 L ha\(^{-1}\) of Vapam (BCMAFF 1994), corresponding to approximately 170 to 350 kg metam-sodium ha\(^{-1}\).
The higher rates are for use on soils with heavier texture or high organic matter levels, or where control of soil diseases and weeds is desired (BCMAFF 1994). Metam-sodium is also recommended for pre-plant weed control in strawberries (BCMAFF 1994).

According to a survey of pesticide use in British Columbia for 1991 (British Columbia Ministry of Environment Lands and Parks 1993) metam-sodium application for agricultural purposes by Pest Control Service Licensees in the Lower Mainland amounted to a total of 2124 kg active ingredient. In comparison, 1,3-DCP use for agriculture in the same region was 6711 kg active ingredient. Because metam-sodium was substituted for 1,3-DCP following its withdrawal from this market in 1993, metam-sodium usage after 1993 would probably be substantially higher than the 1991 values.

This survey also reported that over 10,000 kg of metam-sodium were applied by Pest Control Service Licensees in the Southern Interior and Kootany regions of B.C. for wood preservation. In addition, about 14,000 kg of metam-sodium was sold in the Lower Mainland but its use not reported; however, it can be assumed that the majority was used for either soil fumigation or wood preservation.

2.2.2. Conversion of Metam-Sodium to MITC in Soil

It has generally been concluded that the primary breakdown product of metam-sodium is the biocidal compound methylisothiocyanate (MITC), and that this compound is responsible for the fumigant activity of metam-sodium applications (Worthing 1983). This conclusion is a result of research on the breakdown products of metam-sodium in soil and water. At alkaline pH (9.5) metam-sodium was found to convert only to MITC and elemental S by an oxidative reaction (Turner and Corden 1963). However, at acidic pH (5 to 6) metam-sodium underwent several different non-oxidative reactions to produce MITC as well as CS₂, H₂S, N,N'-dimethylthiuram disulfide (DMTD), and methylamine. Methylamine and CS₂ can in turn react to form MITC, which could increase the production
of MITC following non-oxidative decomposition of metam-sodium (Turner and Corden 1963). Wedding and Kendrick (1959) pointed out that isothiocyanates, thiuram disulfides, thiourea, H₂S, CS₂, and ionized or undissociated dithiocarbamic acids had all been implicated as toxicants responsible for the fungicidal activity of metam-sodium at one time or another, but that the trend was to regard MITC as the primary active toxicant produced from metam-sodium. The more recent literature has generally agreed that MITC is the primary degradation product of metam-sodium responsible for its fumigant action (Smelt and Leistra 1974; Gerstl et al. 1977; Worthing 1983; Smelt et al. 1989).

The rate and extent of conversion of metam-sodium to MITC in soil is influenced by several factors. Conversion rates increased with increasing temperature over the 10 to 40 °C range (Gerstl et al. 1977; Smelt and Leistra 1974; Turner and Corden 1963), and increasing pH (Turner and Corden 1963). Higher conversion rates were also seen on finer textured soils compared to coarser textures (Gerstl et al. 1977; Smelt and Leistra 1974), and conversion rates decreased with increases in soil water content from 6 to 20 % (Turner and Corden 1963). Turner and Corden (1963) found more MITC was produced from soil treated with metam-sodium under an air atmosphere than under a nitrogen atmosphere, and therefore suggested that any factor that increased the aeration of the metam-sodium would increase the conversion rate. Low moisture content and finer soil texture would both increase the extent of liquid-air interfaces in the soil, and thus facilitate the oxidation of the metam-sodium to MITC. The authors also used this factor to explain why metam-sodium conversion to MITC is much faster in soils than in aqueous solutions. Gerstl et al. (1977) noted that at low soil moisture contents, the initial metam-sodium concentration applied affected the conversion rate. The conversion of metam-sodium to MITC appears to follow the reaction (Gray 1963; Cremlyn 1978):

\[
\text{H}_3\text{C} \text{N} \overset{\text{C}}{\text{S}} \text{H} \rightarrow \text{H}_3\text{C} \text{N} \overset{\text{C}}{\text{S}} \text{S}^{-} \]

\[
\text{H}_3\text{C} \text{N} \overset{\text{C}}{\text{S}} \text{H} \rightarrow \text{H}_3\text{C} \text{N} \overset{\text{C}}{\text{S}} \text{S}^{-} + \text{SH}^{-}
\]
In all cases, the conversion is a very rapid process, with maximum MITC concentration produced 0.1 to 1 day after initial application, depending on soil characteristics (Smelt et al. 1989). Gerstl et al. (1977) attributed a sharp breakthrough curve of MITC from a column treated with metam-sodium to rapid conversion to MITC, or identical adsorption characteristics for metam-sodium and MITC. Furthermore, they found no difference in MITC degradation rates from MITC itself compared to metam-sodium, suggesting the time required for metam-sodium conversion is negligible compared to time for MITC degradation.

A wide range of values is reported in the literature for the extent of metam-sodium conversion to MITC (Ashley and Leigh 1963; Turner and Corden 1963; Smelt and Leistra 1974). However, all fall within measurements by Smelt et al. (1989) of 67 to 96% of the theoretical production of MITC from metam-sodium, for a variety of soil types. In all cases the maximum extent of conversion was achieved in several days.

2.2.3. Chemical and Toxicological Characteristics

The chemical and physical properties of MITC are listed in Table 2.2, along with those for metam-sodium, 1,2-DCP, and 1,3-DCP for comparison purposes. These compounds have significant differences in their aqueous solubilities, vapor pressures, Henry's constants, and toxicities.

Metam-sodium is a salt and accordingly is highly soluble in water. It is unstable in the solid state but stable in concentrated solution which is how the commercial product is formulated; however, when diluted it again becomes unstable and breakdown products are formed (Gray 1963). MITC is less polar than metam-sodium and is therefore far less soluble in water than metam-sodium, but is more soluble than 1,2-DCP and 1,3-DCP (Table 2.2). The octanol-water partition coefficient ($K_{OW}$) for MITC is reported to be 10.5 (Nihon Schering and Shionogi Co. Ltd 1990).
Table 2.2. Selected chemical and physical properties of MITC, metam-sodium, 1,2-DCP, and 1,3-DCP at 20 °C.

<table>
<thead>
<tr>
<th></th>
<th>MITC</th>
<th>Metam-sodium</th>
<th>1,2-DCP</th>
<th>1,3-DCP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular formula</td>
<td>CH₃NCS</td>
<td>CH₃NHCS.SH</td>
<td>C₃H₆Cl₂</td>
<td>C₃H₄Cl₂</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>117-119</td>
<td>N/A</td>
<td>95.4</td>
<td>104</td>
</tr>
<tr>
<td>Aqueous solubility (g L⁻¹)</td>
<td>7.6, 8.9</td>
<td>722</td>
<td>2.7</td>
<td>1.0, 2.75</td>
</tr>
<tr>
<td>Vapor pressure (kPa)</td>
<td>2.7, 1.7</td>
<td>non-volatile</td>
<td>27.9</td>
<td>3.7</td>
</tr>
<tr>
<td>Kₜ/w (Henry's constant) (μg mL⁻¹ water phase/μg mL⁻¹ gas phase)</td>
<td>92, 170</td>
<td>N/A</td>
<td>11</td>
<td>21</td>
</tr>
<tr>
<td>Diffusion coefficient in air (cm² day⁻¹)</td>
<td>7800</td>
<td>N/A</td>
<td>N/A</td>
<td>6900</td>
</tr>
<tr>
<td>Acute oral LD₅₀ male rats (mg kg⁻¹)</td>
<td>175, 97</td>
<td>1800, 800</td>
<td>N/A</td>
<td>250-500</td>
</tr>
</tbody>
</table>

z Worthing (1983)  
y Smelt and Leistra (1974)  
x Goring (1967)  
w Cohen et al. (1984)  
v Reid and Scherwood (1966) in Siebering and Leistra (1979)  
u van Berkum and Hoestra (1979)  
N/A = value not available

MITC has a much higher vapor pressure than metam-sodium (Table 2.2), which results in MITC's fumigant action. The vapor pressure of 1,3-DCP is very similar to that of MITC, while the vapor pressure of 1,2-DCP is approximately one order of magnitude higher. However, mixtures of 1,2-DCP and 1,3-DCP, such as the formulations Telone and D-D have a vapor pressure of 4.6 kPa (Worthing 1983), similar to that of MITC. Other soil fumigants have a wide range of vapor pressures. For example, at 20 °C DBCP
has a vapor pressure of only 0.1 kPa, compared to 185 kPa for methyl bromide (Goring 1967).

The dimensionless Henry's constant, $K_{w/g}$ (Table 2.2), represents the distribution of MITC between water and gas phases at equilibrium (Smelt and Leistra 1974). The $K_{w/g}$ for low concentrations is usually approximated, using Henry's Law, as the ratio of the water solubility to the saturated vapor concentration of the compound at a given temperature (Siebering and Leistra 1979). Goring (1967) calculated a value of 92 for the $K_{w/g}$ at 20 °C using the widely published (e.g., Worthing 1983) values for MITC solubility and saturated vapor pressure of 7.6 g L$^{-1}$ and 2.7 kPa, respectively, and assuming MITC followed ideal gas laws. In contrast, Smelt and Leistra (1974) measured the $K_{w/g}$ values for MITC at concentrations below saturation, and reported the following values: 340 at 4 °C, 250 at 12 °C, and 170 at 20 °C. With decreasing temperature, the vapor pressure of the fumigant decreases sharply, while the water solubility is much less affected (Siebering and Leistra 1979). Smelt and Leistra (1974) also found that the $K_{w/g}$ at a given temperature appeared to be independent of concentration in the 250 to 2000 μg mL$^{-1}$ water range studied, indicating Henry's Law was valid over this concentration range. Furthermore, these authors noted that their measured $K_{w/g}$ for 20 °C agreed well with the $K_{w/g}$ calculated from their reported values of MITC solubility and saturated vapor pressure at the same temperature (Table 2.2).

MITC has a relatively high $K_{w/g}$ value compared to most other fumigants. This is a result of MITC's combination of high solubility and moderate vapor pressure. Although 1,3-DCP has a vapor pressure similar to MITC, its water solubility is lower than that of MITC, resulting in a lower $K_{w/g}$ for 1,3-DCP compared to MITC (Table 2.2). Methyl bromide, on the other hand, has a $K_{w/g}$ of 4.1 (Goring 1967) primarily because of its extremely high vapor pressure relative to its solubility.

The mammalian toxicity of MITC is much higher than metam-sodium, and slightly higher than both 1,2-DCP and 1,3-DCP (Table 2.2). All of these fumigant compounds
cause skin, eye, and respiratory tract irritation (Worthing 1983). The one-hour LC50 for inhalation of MITC for male rats was reported to be 1.9 g m⁻³ (Nihon Schering and Shionogi Co. Ltd 1990). In a two year feeding trial the no effects level (NEL) for MITC in rats was 10 mg mL⁻¹ in drinking water (Worthing 1983).

2.2.4. Soil Fumigant Formulations Containing or Generating MITC

MITC is an active ingredient in several soil fumigant formulations. MITC can be present alone, as it was when first introduced in 1959 by Schering AG under the trade name Trapex. It has also been used in mixtures with other soil fumigants. The products Vorlex and Di-Trapex (Schering AG) are mixtures of 20 % MITC and 80 % 1,3-DCP and 1,2-DCP; Di-Trapex CP (Schering AG) is similar to Di-Trapex but also contains the fumigant chloropicrin (van Berkum and Hoestra 1979).

Dazomet (3,5-dimethyltetrahydro-1,3,5(2H)-thiadiazine-2-thione) is another product that generates MITC. Dazomet is practically insoluble in water, but in contact with moist soil it hydrolyzes to MITC (van Berkum and Hoestra 1979). Dazomet is sold as a powder or finely granulated product under various trade names (e.g., Basamid, Mylone).

The product Basamid is used to a small extent in the Abbotsford Aquifer area (H. Kleindienst, Pers. Comm.). It is recommended for use as a soil fumigant in strawberry production (BCMAFF 1994).

According to a survey of pesticide use in British Columbia for 1991 (British Columbia Ministry of Environment Lands and Parks 1993) MITC and dazomet application for agricultural purposes by Pest Control Service Licensees in the Lower Mainland amounted to a total of 862 and 661.5 kg active ingredient, respectively.
2.3. Environmental Fate of Methylisothiocyanate

The fate of MITC in the soil root zone when applied as a fumigant is determined by its partitioning to the processes of degradation, sorption to soil, volatilization from the soil surface, and leaching from the soil root zone. The relative magnitude of each of these processes will be determined by climatic factors such as temperature and the timing and amount of precipitation, and soil factors such as texture, organic carbon content, water content, pH, total and air-filled porosity, and microbial activity.

These four processes are interrelated in that each process can affect the magnitude of the others. When MITC is degraded it is no longer available for any of the other processes. Sorption of MITC retards movement in the gas and liquid phases if it is reversible, or completely stops movement if it is irreversible; both will affect volatilization and leaching processes. However, sorbed MITC will be available for degradation processes. Volatilization to the atmosphere removes MITC from the soil profile, making it unavailable to the other processes, including leaching.

2.3.1. Degradation in the Soil Root Zone

2.3.1.1. General Processes and Factors Affecting Degradation

Degradation of pesticides can occur by microbial, chemical, and photochemical processes. These processes are dependent on the inherent characteristics of the pesticide and on the site specific characteristics of the soil medium.

Microbial decomposition is the most significant decomposition process for most pesticides under most soil conditions (Saltzman and Yaron 1986). The characteristic disappearance pattern of microbial decomposition, a lag phase followed by rapid degradation, reflects growth and adaptation of the microbial population (Saltzman and
Yaron 1986). The lag phase is attributed to the induction of enzymes capable of degrading a substrate, by the presence of the substrate (Graham-Bryce 1981). There is also evidence of accelerated transformation of frequently applied pesticides, by adapted microbial populations (Smelt et al. 1987). Microbial degradation does not occur uniformly in the soil, but is fastest in regions where microbial populations are large and active, for example in the root rhizosphere, and effectively stops in the subsoil (Graham-Bryce 1981).

The soil is also an effective medium for chemical degradation. It is generally very moist and well aerated, which promotes breakdown of pesticides by hydrolysis and oxidation reactions (Graham-Bryce 1981). In addition, reduction reactions can occur at anaerobic sites within the soil profile. Adsorption catalyzed degradation reactions on reactive clay surfaces have been demonstrated for several pesticides (Saltzman and Yaron 1986). In addition, extracellular enzymes in free and adsorbed forms can catalyze degradation reactions. This type of reaction makes distinctions between microbial and chemical degradation processes unimportant (Graham-Bryce 1981). Photochemical degradation, especially photo-oxidation, can be very important for surface applied pesticides. However, for soil-incorporated pesticides degradation by photochemical processes would be expected to be negligible.

Pesticide degradation rates are often measured by the rate of disappearance of organic solvent-extractable parent compound. Degradation rates are commonly found to be proportional to the pesticide concentration, and thus degradation can be described by first-order kinetics, and a half-life reported (Rao and Davidson 1980).

Pesticide degradation rates in soil are strongly dependent on the inherent stability of the compound. As a result of differing levels of pesticide stability, degradation half-lives in soil for pesticides vary over several orders of magnitude. The relative persistence of different pesticides in soil can be ranked by measuring degradation rates under controlled laboratory conditions. Using this idea, Rao and Davidson (1980) classified common pesticides into three groups: nonpersistent, with half-lives less than 20 days, moderately
persistent, with half-lives between 20 and 100 days, and persistent, with half lives over
100 days.

Soil conditions, however, will also have a great influence on pesticide degradation
rates. Soil properties such as temperature, moisture content, aeration, pH, and the amount
and nature of organic and mineral colloids will affect both chemical and microbial
transformation processes. Degradation rates are directly related to temperature. Increased
temperature will increase the rate of chemical reactions as well as levels of microbial
activity. At very low soil moisture contents microbial activity will be reduced, and
adsorption to soil solids can increase (Rao and Davidson 1980) often decreasing availability
of the compound to degradation reactions. Moisture content and soil porosity will affect
soil aeration, in turn influencing the type and rate of chemical reactions (e.g., oxidation or
reduction) and microbial activity (Rao and Davidson 1980).

The effects of soil pH on degradation are complex. Soil pH affects the diversity,
population, and activity of microorganisms. Soil pH also influences the nature and the rate
of redox and hydrolysis reactions involved in pesticide transformation (Rao and Davidson
1980). The effect of pH on degradation through microbial and chemical processes depends
on the specific pesticide, and therefore generalizations cannot be made. For example, the
effect of pH on hydrolysis reactions will be opposite for acid-catalyzed vs. base-catalyzed
reactions (Nicholls 1988).

Degradation rates will be influenced by the large microbial biomass associated with
high soil organic matter levels (Nicholls 1988). Sorption on organic or clay colloids can
increase or decrease decomposition rates because it can result in a compound becoming
either more or less available to microorganisms (Graham-Bryce 1980). In addition,
sorption on clay mineral surfaces can result in adsorption-catalyzed hydrolysis reactions for
some pesticides (Saltzman and Yaron 1986).
2.3.1.2. MITC Degradation

Degradation rates of MITC in soil have been studied extensively, but only in laboratory experiments. Degradation rates were found to increase with increasing temperature, and were influenced by clay and organic matter content and pH, although no clear relationships with these factors have emerged. Microbial and chemical processes have been implicated, and some evidence suggests microbial processes are more important. In all the studies cited below, MITC degradation followed first-order kinetics and MITC half-lives are reported.

Smelt and Leistra (1974) studied MITC degradation in sealed flasks using several soil types and incubation temperatures. The MITC degradation rate increased with increasing temperature over the 4 to 21 °C range studied, and with increasing clay content. They reported degradation half-lives ranging from 8 to 14 d at 13 °C and 4 to 7 d at 21 °C.

Gerstl et al. (1977) conducted a similar experiment and reported half-lives of 3.3 to 9.9 d for incubation at 20 °C and 20 % soil moisture content. Although Gerstl et al. found no relationship between degradation rate and clay content or pH, they found a weak relationship (r = 0.59) between degradation rate and percent soil organic matter. The authors also found no difference in MITC degradation rate whether the MITC source was MITC itself or metam-sodium (Fig. 2.3).

Ashley et al. (1963) studied the influence of a number of factors on MITC degradation in soil. They reported half-lives of 4 to 10 d at 15 °C, which decreased by 25 to 50 % for incubation at 10 °C. Faster degradation was measured in all textures of mineral soils as compared to peat soils. They found slower degradation in acidic soils (pH < 5.5) and that addition of lime to these soils increased degradation rates. These authors also measured lower degradation rates in heat sterilized soil than in unsterilized soil, leading the authors to conclude microorganisms are primarily responsible for MITC degradation.
However, degradation still occurred at a low rate in the sterilized soil which the authors attributed to chemical degradation processes.

Smelt et al. (1989) found accelerated MITC transformation in 5 of 8 soils from fields frequently treated with metam-sodium. Soils from never-treated fields had an initial lag phase of 3 to 30 d with slow transformation rates, followed by very fast transformation rates, whereas previously treated soils had no lag phase, but immediately had the fast transformation rates. This is consistent with degradation dominated by microbial processes and adaptation of the microbial population in frequently treated soils. They reported half-lives in the range 0.5 to 50 d at 15 °C for all soils studied. Half-lives of 26 to 50 d were
measured in some humic sand soils, which the authors considered to be remarkably high for arable soils.

In contrast, Wambeke et al. (1988) found no influence of microbial activity on MITC degradation. No differences in degradation rates were found between autoclave sterilized and unsterilized soil at either 2 or 25 °C. Degradation in both soils was higher at 25 °C. The authors did not report MITC half-lives.

Boesten et al. (1991) demonstrated that MITC can be very stable in aqueous systems under certain conditions. Half-lives measured in water saturated subsoil materials at 10 °C ranged from 6 to 35 d in stoppered flasks, but for identical materials in flasks sealed by melting a special glass adapter, half-lives ranged from 240 to 540 d. The authors hypothesized that the latter group was exposed to higher temperatures upon sealing which had an effect on microbial activity. High stability of MITC in aqueous solutions was also reported by Ashley and Leigh (1963) who measured 10 % loss of MITC from distilled water after 24 days at room temperature.

Very little information is available on the specific pathways and end products of MITC degradation in soils. Kotter et al. (1961, cited in Hoffman and Malkomes, 1979) found MITC oxidation results in an increasing amount of sulfate in the soil, but no other distinct transformation products were identified.

The compound MITC can be considered relatively non-persistent in soil compared to other pesticides. Reported values of MITC degradation half-lives in soil are predominantly in the range from 5 to 15 d at temperatures from 15 to 21 °C; therefore, MITC would be ranked as a non-persistent pesticide (half life < 20 d) by Rao and Davidson (1980). MITC is one of the least persistent soil fumigants. The soil half-life of 1,3-DCP of 25 d at 15 °C (Siebering and Leistra 1979) is slightly longer, but in the same range as that of MITC. In contrast, the hydrolytic half-life of 1,2-DCP is expected to be six months to several years (Cohen et al. 1984), and the fumigants DBCP and EDB have reported soil half-lives of 225 and 365 d, respectively (Jury et al. 1987).
2.3.2. Sorption to the Soil Solid Phase

2.3.2.1. General Processes and Factors Affecting Sorption

The term sorption is often used to refer to general retention processes, including adsorption, absorption, and precipitation, because experimentally these processes are usually indistinguishable (Koskinen and Harper 1990). Sorption of pesticides by the soil solid components retards transport in aqueous and gaseous phases, influencing not only pesticide fate but also the efficacy of the compounds as agrochemicals. Pesticide sorption can take place by reactions such as electrovalent and covalent bonding, by intermolecular interactions such as van der Waal's forces and hydrogen bonding, or by dissolution in organic solvents formed by degradation of organic matter (Hoffman and Malkomes 1979). The extent of sorption will be influenced by the properties of the pesticide molecule such as lipophilicity, and soil properties such as clay and organic matter content, pH, and water content.

A linear sorption isotherm is most commonly used to describe the relation between sorbed phase and solution phase concentrations at equilibrium. This isotherm describes partitioning between solid and liquid phases that is independent of concentration, which is usually valid over only small concentration ranges (Scheunert 1992). However, several authors (Haque and Freed 1974; Rao and Davidson 1980; Nicholls 1988) agree that the linear isotherm usually fits data well at the dilute pesticide concentrations found in agricultural ecosystems. Although sorption isotherms describe partitioning at equilibrium, equilibrium may not necessarily be achieved under field and laboratory conditions. For example, in soil profiles with pesticide transport downward with water flow the contact time between solid and solution phases may be insufficient for equilibrium sorption to
occur (Rao and Jessup 1983). This would result in actual sorption less than predicted by
the isotherm.

The value of the linear sorption coefficient, $K_d$ or $K_{s/w}$, for a specific pesticide
may vary by an order of magnitude or more for different soils, and varies greatly for
different pesticides in the same soil (Rao and Jessup 1983). Thus, the partition coefficient
will depend on the characteristics of both the pesticide and the soil.

Soil organic matter has been shown to affect sorption of a wide variety of organic
pesticide classes, including cationic, basic, acidic, and nonionic types. For nonionic and
less-polar pesticides, organic matter is the primary sorbing component of soil (Loch 1991).
Multiple regression analysis has indicated that soil organic matter or organic carbon content
may be the single best predictor of $K_d$ values for nonionic and less-polar pesticides (Rao
and Jessup 1983). Nonionic pesticides partition from the highly polar aqueous phase to the
less polar organic carbon phase; this sorption mechanism is called hydrophobic bonding
(Loch 1991). Hoffman and Malkomes (1979) attribute the high sorption capacity of
organic matter to the high availability of sites for covalent bonding, and to the dissolution
into organic solvents formed upon organic matter decomposition.

For a given pesticide, it is often found that the sorption coefficient $K_{d}$ normalized
with respect to soil organic carbon content, denoted $K_{oc}$ (or alternatively with organic
matter content, denoted $K_{om}$) is essentially independent of soil type (Rao and Davidson
1980; Scheunert 1992). However, some variability in $K_{oc}$ values for a specific pesticide
result from interrelationships between adsorption on soil organic and inorganic

Clay minerals are most important for sorption of charged and highly polar pesticide
species through ion exchange mechanisms (Sparks 1989). The effects of clays on nonionic
and less-polar pesticide sorption are more difficult to assess because the presence of clay-
organic matter complexes makes the separations of contributions of each component
difficult, and because of the correlation of clay and organic matter contents in arable soils

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Sorption of non-polar pesticides on clay minerals has been shown to increase with decreasing water content. Hoffman and Malkomes (1979) reported that water on the surfaces of the clay fraction acted as a mechanical barrier to sorption of non-polar pesticides.


Large differences in $K_d$ values among pesticides in the same soil result from differing chemical properties of the pesticides, the most important of which is lipophilicity. The more lipophilic the compound the higher its sorption on soil organic matter by hydrophobic bonding (Loch 1991). The lipophilic or, alternatively, hydrophobic nature of a compound can be expressed by its partition coefficient between 1-octanol and water, the $K_{ow}$. Octanol is used because it is considered to replicate the hydrophobic sorptive properties of soil organic matter (Rao and Davidson 1980). Thus, the $K_{ow}$ of a pesticide is often used to predict its sorption in soil (e.g., Rao and Davidson 1980; Briggs 1981).

### 2.3.2.2. MITC Sorption Characteristics

There are relatively few studies on MITC sorption by soils but all agree that MITC is weakly sorbed. It is also generally concluded that clay and organic matter components of soil are primarily responsible for the sorption that does occur.

Smelt and Leistra (1974) found linear sorption isotherms for MITC in three soils at 20 °C. They reported a sorption coefficient, $K_{s/w}$, ranging from 0.031 to 0.12 mL g$^{-1}$, and calculated $K_{om}$ values of 1.9 to 3.9 mL g$^{-1}$. Thus, the $K_{om}$ was not constant, but increased with increasing soil organic matter content. Gerstl et al. (1977) measured similar


\[ K_{s/w} \] values, and values generally increased with soil clay and organic matter content. Reported \[ K_{s/w} \] values ranged from 0.012 mL g\(^{-1}\) for a soil with 3 % clay and 0.45 % organic matter, to 0.57 mL g\(^{-1}\) for a soil with 65 % clay and 4 % organic matter. The corresponding \[ K_{0m} \] values in these soils range from 2.7 to 14 mL g\(^{-1}\). They measured \[ K_{s/w} \] values in montmorillonite clay, kaolinite clay, and peat of 1.0, 1.5, and 1.8 mL g\(^{-1}\), respectively. The authors noted these values indicated MITC was only slightly sorbed to these three materials.

This low sorption is consistent with what would be expected from the \[ K_{OW} \] of MITC. According to Nicholls (1988), pesticides with \[ \log K_{OW} \] values < 1 would be expected to be "weakly adsorbed" in soils; MITC, with a \[ K_{OW} \] of 10.5 (Nihon Schering and Shionogi Co. Ltd 1990) could be included in this category.

Gerstl et al. (1977) warned that MITC sorption under field conditions may be lower than measured \[ K_{s/w} \] values indicate. These values are measured under equilibrium conditions but in the field water flow rates may be such that sorption equilibrium is not reached. A similar phenomena was demonstrated by Ben-Yepheth and Frank (1985) in repacked soil columns. Deeper and more rapid penetration of a metam-sodium solution was observed in a well-structured clay soil compared to a poorly aggregated loessal soil. They discovered that the longer percolation time in the loess resulted in more MITC adsorption to clay particles and more MITC decomposition, and thus lower MITC concentrations at depth compared to the well aggregated clay.

Very little is known about the effect of soil pH on MITC sorption. Munnecke and Martin (1964) examined the effect of pH on MITC evolution from treated soils. MITC evolution increased linearly from pH 2.5 to 8 which the authors interpreted as a linear decrease in sorption over the pH range.

The sorption of MITC to soil can be considered extremely low relative to other pesticides and soil fumigants. Reported \[ K_{0m} \] values for 1,3-DCP are 14 to 15 mL g\(^{-1}\) (Leistra 1970), and 27 mL g\(^{-1}\) for 1,2-DCP (Cohen et al. 1984), compared to the average
$K_{om}$ for MITC of 2.7 mL g$^{-1}$ reported by Smelt and Leistra (1974). In contrast, the $K_{om}$ for the widely used herbicide atrazine is reported to be 93 mL g$^{-1}$ (Jury et al. 1987).

2.3.3. Volatilization Loss to the Atmosphere

2.3.3.1. General Processes and Factors Affecting Volatilization Loss

Volatilization loss of pesticides from soil refers to movement in the gas phase from plant or soil surfaces to the atmosphere. Only the volatilization loss of soil incorporated pesticides will be considered here.

Spencer et al. (1973) described the factors influencing pesticide volatilization losses from soil to the atmosphere. Volatilization of a pesticide from a surface depends on the vapor pressure of the pesticide and the rate of movement away from the surface. If the surface adsorbs the pesticide, as would occur with application to the soil surface, the vapor pressure would be reduced according to the extent of adsorption. If the pesticide were incorporated into the soil, it would also have to migrate to the soil surface in order to be lost to the atmosphere. Thus, volatilization loss of a soil-incorporated pesticide will depend on the effective vapor pressure of the pesticide, its movement to the soil surface, and its movement away from the soil surface to the atmosphere (Spencer et al. 1973). In turn, each of these processes will be influenced by the characteristics of the pesticide and the soil.

The vapor pressure of a soil-incorporated pesticide will influence both its evaporation from the soil surface and its gas phase diffusion from within the soil to the soil surface. Each pesticide has a characteristic saturation vapor pressure that varies with temperature, but in soil the vapor pressure will be reduced because of partitioning to soil water and solid phases (Spencer et al. 1973; Taylor and Spencer 1990; Petersen et al. 1994). The pesticide will partition from the gas to the water phase according to its
solubility and saturated vapor pressure, which can be described by the Henry's Law coefficient $K_{w/g}$ (Section 2.2.3). The partitioning from the liquid to solid phase depends on sorption and is described by the adsorption coefficient, $K_{S/W}$ (Section 2.3.2.1.) in the case of the linear sorption isotherm. The $K_{w/g}$ is determined by pesticide properties alone but is influenced by temperature, whereas the $K_{S/W}$ is determined by pesticide and soil characteristics (Section 2.3.2.1). These partition coefficients will determine the proportions of pesticide in the solid, water, and gas phases, but the actual concentrations in each phase will depend on the quantity of pesticide applied to the soil (Taylor and Spencer 1990).

For soil incorporated pesticides the movement from within the soil to the soil surface is necessary for volatilization loss to occur. There are two general mechanisms whereby pesticides are transported to the soil surface, diffusion in the gas and/or liquid phases, and mass flow with evaporating water (Spencer et al. 1973; Taylor and Spencer 1990).

Diffusion to the soil surface in gas or liquid phases follow Fick's Law (Mayer et al. 1974), and therefore is proportional to the concentration gradient and a diffusion coefficient for the appropriate phase of the soil medium. For pesticides with high vapor pressures, such as soil fumigants, gas phase diffusion is considered more important than liquid phase diffusion because there is relatively strong partitioning into the gas phase, and diffusion in the gas phase is $10^3$ to $10^4$ times faster than liquid phase diffusion (Hoffman and Malkomes 1979; Siebering and Leistra 1979; Petersen et al. 1994).

Pesticide compounds will diffuse in the gas phase to the soil surface according to the concentration gradient, then as pesticide is depleted from the surface by volatilization loss, additional pesticide will diffuse upward along the concentration gradient to replace it (Spencer et al. 1973). Thus, the concentration of the pesticide in the gas phase, which is influenced by the $K_{w/g}$, is important for gas phase diffusion. For example, Siebering and
Leistra (1979) state that differences in diffusion rates of fumigants in soil are primarily due to differences in their $K_{w/g}$ values.

The rate of gas phase diffusion will also be influenced by the "effective diffusion coefficient" for the pesticide in the soil gas phase, which will be less than the diffusion coefficient of the pesticide in free air (Petersen et al. 1994). The effective diffusion coefficient will be sensitive to temperature as well as the air filled porosity in the soil (Taylor and Spencer 1990), which is in turn determined by soil water content and bulk density. For example, Farmer et al. (1973) found an inverse relationship between soil bulk density and volatilization of the soil applied pesticide dieldrin. They attributed the decrease in vapor phase movement to decreasing air filled porosity with increasing bulk density. The tortuosity of the air filled pore space is also an important factor, and depends on soil geometry and the volumetric air content (Jury et al. 1983). Because of the dependence of the effective gas phase diffusion coefficient on air filled porosity, no single value can characterize behavior of a single pesticide in a specific soil (Taylor and Spencer 1990).

Gas phase diffusion of pesticides is also retarded by partitioning into water and solid phases. As the pesticide diffuses into soil volumes with lower or zero pesticide concentrations, some pesticide will be removed from the gas phase by dissolution in soil water and sorption to soil colloids according to the specific partition coefficients (Petersen et al. 1994). For soil fumigants, the "fumigant capacity factor", defined as the quotient of fumigant concentration in the soil system (solid and liquid phases) to that in the gas phase, is used to describe the extent to which vapor diffusion is retarded by distribution among the phases (Leistra et al. 1974). However, as shown by Cho et al. (1993) equilibrium partitioning may not occur under conditions where the advective flow of one of the phases becomes a significant factor, such as with water infiltration.

Transport of pesticides to the soil surface will be significantly affected by application procedures (Cohen et al. 1984). For example, the length of the diffusion path to the soil surface will be determined by the depth of injection (Taylor and Spencer 1990).
Treatment of the soil surface after injection, by compaction or irrigation, will also strongly affect transport to the soil—air boundary (van Berkum and Hoestra 1979).

Soil incorporated pesticides can also be transported to the soil surface in water flowing upward in response to evaporation at the soil surface (Spencer et al. 1973; Taylor and Spencer 1990). The magnitude of this effect will depend on the water evaporation rate at the surface and the concentration of the pesticide in the soil water.

The final step in the process of volatilization loss is movement away from the soil surface and dispersion to the atmosphere. The process is similar to that for transfer of water, carbon dioxide, and other gases between soil surfaces and the atmosphere (Taylor and Spencer 1990). However, a critical difference between these gases and pesticides is that there are negligible background concentrations of pesticides in the ambient air, resulting in much higher concentration gradients. Briefly, the process consists of diffusion across the laminar boundary layer above the soil surface, then turbulent mixing with the atmospheric boundary layer. The depth of the laminar boundary layer depends on the air flow rate and the diffusion across it can be described by the vapor pressure gradient and the molecular diffusion coefficient of the pesticide vapor (Spencer et al. 1973). Relatively rapid dispersal of pesticide vapor occurs in the overlying turbulent zone (Taylor and Spencer 1990).

Several simulation models for volatilization loss of soil incorporated pesticides have been developed (Mayer et al. 1974; Jury et al. 1984). These models can be used to discern which processes will be the most important for volatilization loss of a specific pesticide. Mayer et al. (1974) developed models describing two distinct cases for volatilization loss. In the first model air movement over the soil surface was sufficient to maintain a zero pesticide concentration at the soil surface, so volatilization loss was limited by transport to the soil surface. In the second model diffusion of the pesticide through a stagnant air boundary layer over the soil surface limits volatilization losses. Jury et al. (1984) developed similar models and compared maximum volatilization loss rates possible in each
The authors reasoned that the boundary layer would limit volatilization loss only if the maximum flux through the boundary layer was small compared to the rate at which pesticide could be transported to the surface. They found a critical value for the Henry's constant of the pesticide that determined which process would limit volatilization loss under a given set of soil properties. The simulation predicted that for very volatile pesticides, such as soil fumigants, the volatilization loss rate would not be limited by the boundary layer, but only by the rate of transport to the soil surface.

Taylor and Spencer (1990) reviewed a number of field experiments measuring volatilization loss rates of soil applied pesticides. They concluded that volatilization loss rates are determined by supply of the pesticide to the soil surface, which was dependent on soil conditions, especially moisture content. Meteorological conditions such as temperature, radiation input, and wind speed are only important through their effects on soil conditions.

2.3.3.2. MITC Volatilization Loss Measurements

Very little information on MITC volatilization loss rates is available. Van den Berg et al. (1992) measured MITC concentrations in air above a greenhouse soil after injection of 612 kg ha\(^{-1}\) metam-sodium. The MITC concentration in air was 33 to 176 mg m\(^{-3}\) a few hours after injection, and after 3 d decreased to 0.06 to 0.31 mg m\(^{-3}\).

The only field measurements of MITC air concentrations in the literature were reported by Van den Berg (1993). Metam-sodium was applied to two fields by injection to a depth of 18 cm at a rate of 153 kg ha\(^{-1}\). In one field, the maximum measured MITC air concentration at 1.5 m above the soil surface was 3.1 \(\mu\)g m\(^{-3}\), measured 1 d after treatment and 50 m downwind from the field. In a second field, the maximum concentration at 1.5 m height was also 3.1 \(\mu\)g m\(^{-3}\) but it occurred 2 d after treatment and 190 m downwind. The fact that the maximum air concentrations were measured downwind from both fields could
be due to the considerable height of measurement. For the second field, the authors noted that an adjacent field that had been fumigated one day after the experimental field contributed significantly to the downwind MITC air concentration.

Van den Berg (1993) also used a model to predict MITC volatilization loss fluxes in the same two fields. Maximum computed MITC fluxes ranged from 1.37 \( \mu g \, m^{-2} \, s^{-1} \) at 3.4 d after treatment to 0.96 \( \mu g \, m^{-2} \, s^{-1} \) at 5.8 d after treatment. The predicted total volatilization loss was 10% for the three weeks following treatment. By comparison, a model developed by Leistra and Crum (1990) computed much higher volatilization losses. They simulated injection of metam-sodium into a greenhouse soil at a depth of 5 to 10 cm. Predicted total volatilization losses over the 2 weeks following application ranged from 50% to 64% depending on the MITC degradation rate used in the model.

MITC is generally considered to have a lower diffusion rate in soil compared to other common soil fumigants such as 1,2-DCP, 1,3-DCP, and methyl bromide (Leistra et al. 1974; van Berkum and Hoestra 1979), and would therefore be expected to have a lower volatilization loss rate as well. Smelt and Leistra (1974) computed a fumigant capacity factor (Section 2.3.3.1) of 78 for MITC compared to 20 for 1,3-DCP in the same loam soil, indicating comparatively slower gas phase diffusion for the MITC. However, comparison of experimental volatilization loss rates is inconclusive. For example, Van den Berg et al. (1992) measured 1,3-DCP air concentrations above treated fields and found maximum concentrations of up to 506 \( \mu g \, m^{-3} \), much higher than the maximum concentration of 3.1 \( \mu g \, m^{-3} \) for MITC by Van den Berg (1993). On the other hand, in a laboratory experiment less than 5 to 10% volatilization loss of 1,2-DCP was measured from a sandy loam soil treated at 30 cm depth (McKenry and Thomason 1974, cited in Cohen et al. 1984); this is similar to the 10% total MITC volatilization loss predicted by Van den Berg (1993). However, this variation in experimental volatilization losses may be due to other differences in soil and micrometeorological factors.
2.3.4. Leaching Below the Soil Root Zone

Processes in the root zone strongly affect pesticide leaching behavior. Pesticide degradation rates are highest near the soil surface, but decrease with depth as temperatures and microbial activities decrease. Similarly, pesticide sorption is greater at the surface where organic matter contents are highest, but decrease with depth (Nicholls 1988). Once a pesticide moves below the root zone, the rate or extent of these processes will be drastically reduced; the compound can persist for longer durations and has a higher mobility, leading to a high potential to contaminate groundwater. Thus, the ultimate potential for a pesticide to contaminate groundwater will be strongly affected by its behavior in the soil root zone.

2.3.4.1. General Processes and Factors Affecting the Leaching Process

Transport of pesticides down the soil profile occurs by a combination of convection, dispersion, and diffusion processes. The term mass flow is often used to include both convection and dispersion components of transport (Scheunert 1992). Transport by mass flow depends on the movement of soil solution, while diffusion is independent of water movement.

Transport by convective mass flux will depend only on the rate of water flow and sorption onto the soil solid phase (Saltzman and Yaron 1986). However in soils, dispersion will occur due to the effects of differing soil pores sizes on water flow velocities. As a result of dispersion, a pesticide applied to the soil surface or injected into the soil on a plane will spread to form a bell shaped pulse as it is transported down the soil profile (Graham-Bryce 1981). The extent of the spreading and the shape of the pulse will be affected by a number of factors (Graham-Bryce 1981): the amount of water required to initially dissolve the compound, the nature of the sorption isotherm, the soil pore size
distribution and tortuosity, longitudinal diffusion in the soil pores, and the rate of sorption equilibria in relation to the rate of water flow.

Dispersion can be significant in well aggregated soils with large macropores and in soils with large cracks or earthworm and root channels. Water can move rapidly down these macropores and channels, bypassing soil aggregates and much of the sorbing surfaces (Saltzman and Yaron 1986). These preferential paths for water flow are very important for pesticide leaching (Parlange et al. 1988).

Transport of pesticides down the soil profile can also occur by diffusion in the gas and liquid phases (Section 2.3.3.1). Although the slow diffusion of pesticides in soil solution is rarely an important mechanism when considering groundwater contamination (Graham-Bryce 1981), the rapid diffusion in the soil gas phase can be important (Helling and Dragun 1981). For volatile pesticides, the gas phase diffusion that transports material to the soil surface for volatilization occurs in three dimensions. Thus, the rapid diffusion of pesticide to the soil surface, indicated by high volatilization rates, also means rapid diffusion down the soil profile (Loch 1991), although actual rates will be affected by differences in soil porosity, water content, and temperature.

The soil fumigant methyl bromide, for example, has been shown to diffuse from a surface application to a depth of 1 m in 6 h (Hoffman and Malkomes 1979). MITC injected at 20 cm was shown to have effective fumigant action to a depth of 40 cm (Hoffman and Malkomes 1979), indicating trace amounts would have diffused even further down the soil profile.

The amount of pesticide leached from the root zone will depend on the interaction among pesticide characteristics and use patterns, soil properties, and climatic factors. These factors will determine leaching through effects on the amount of pesticide present in the soil and its persistence, the extent of retention of the pesticide by sorption to soil solids, and the amount, rate, and timing of water flow through the soil profile.
The potential for a pesticide to leach from the root zone will be related to the amount present in the soil. The rate and frequency of pesticide application will determine the amount added to the soil; the rates of degradation and volatilization loss to the atmosphere will determine the rate at which the pesticide is removed from the soil. Removal from the soil by these processes means the pesticide is no longer available for leaching processes. Thus, degradation and volatilization processes (Sections 2.3.1 and 2.3.3) have a very important influence on leaching potential (Helling and Dragun 1981).

The transport of pesticides down the soil profile will be retarded by sorption to the soil solid phase. In terms of leaching, the rates of sorption and desorption in relation to water flow are important; at high water flow rates, equilibrium sorption or desorption may not occur (Graham-Bryce 1981).

The amount, timing, and rate of water movement through the soil profile depends on soil properties and climate. The proportion of pesticide which is present within the soil that will leach will increase with the amount and rate of water flow through the soil profile. The amount of groundwater recharge indicates the net water flow through the profile, and depends primarily on the balance between precipitation and evapotranspiration levels (Nicholls 1988). Recharge will be greater where water holding capacity is low and permeability is high, indicating the importance of soil texture and structure (Helling and Dragun 1981). Higher rates of water flow will result in shorter residence time of the pesticide within the soil root zone; there will be less opportunity for loss by volatilization and degradation, and equilibrium sorption may not occur. The water flow rate will depend on the frequency and amount of precipitation events, and the effects of soil texture and structure on soil hydraulic conductivity.

The timing of water flux through the profile relative to pesticide application significantly effects the leaching of the pesticide through the root zone. For example, Oki and Giambelluca (1989) found that rainfall-induced recharge events immediately following application of soil fumigants were important for determining the extent of leaching from the
soil root zone. They concluded that transport away from the soil surface by percolating water reduced the extent of volatilization, degradation, and sorption of the fumigants, leaving greater amounts available for leaching.

Considering all the above factors influencing pesticide leaching through the soil root zone, several authors have described scenarios where leaching potential is high. Cohen et al. (1984) summarized pesticide properties associated with high leaching potential, which included a $K_{OC}$ value less than 300 to 500, low volatility, and a soil half-life greater than 2 to 3 weeks. Soil and climatic factors that result in a high leaching potential include highly permeable sandy or sandy loam soils with low organic matter content, high total precipitation and irrigation recharge rates (> 25 cm year$^{-1}$), and a soil pH under which the pesticide residue is stable (Cohen et al. 1984; McRae 1991). Nicholls (1988) described the importance of seasonal timing of pesticide application to leaching potential. Where winters are cold and have high precipitation levels compared to evapotranspiration, pesticide degradation rates will be low and recharge rates high. Pesticides applied in autumn will, under these climatic conditions, have a significantly higher leaching potential than those applied in spring.

Although migration of pesticides to below the soil root zone drastically increases the potential for leaching to groundwater, transport to groundwater will also depend on the permeability of the vadose zone material and the depth to the water table (Pfannkuch et al. 1993). In general, groundwater supplies in shallow, unconfined aquifers are the most susceptible to contamination (McRae 1991). High nitrate levels in groundwater are also indicative of high susceptibility to contamination by pesticides (Cohen et al. 1984; Liebscher et al. 1992).
2.3.4.2. MITC Leaching Behavior

MITC is expected to have a relatively high leaching potential based on its degradation and sorption behavior in soil. Gustafson (1989) developed a pesticide screening procedure for groundwater contamination potential. The groundwater contamination potential of a pesticide was estimated using only its soil half-life and $K_{oc}$ value. Pesticides that had contaminated groundwater could be separated from those that had not by a value called the Groundwater Ubiquity Score (GUS) which was calculated for each pesticide as:

$$GUS = \log(\text{half-life (d)}) \times (4.0 - \log(K_{oc}))$$

It was found a GUS of 2.3 separated pesticides that were "leachers" from those that were "non-leachers". For MITC, assuming a half-life of 10 d and a $K_{oc}$ of 5.2 ($K_{om}$ of 3), the GUS value is 3.3; according to Gustafson's scheme, MITC would be classified as a "probable leacher".

According to Boesten et al. (1991), the leaching behavior of MITC can be expected to be similar to that of 1,3-DCP. The authors based this on the similar $K_{om}$ values and soil half-lives of the two compounds. They cited a model prediction of 1,3-DCP leaching which estimated 0.1 to 4% of the dose leached below 1 m depth, and assumed calculations for MITC would be approximately the same. This prediction is supported by occasional detections of 1,3-DCP in groundwater in Western Europe. Leistra and Boesten (1989) cited several studies with detections of 1,3-DCP in shallow groundwater in the Netherlands and West Germany. Groundwater samples were analyzed for MITC in one study, but no positive detections were reported.

In the literature, the only report of detection of MITC in groundwater is by Lagas et al. (1989). These authors detected MITC in shallow groundwater (< 6 m) in the
Netherlands, below fields used for potato and flower bulb cultivation. Below potato fields only 1 out of 10 samples had a detectable MITC concentration, which was 0.1 µg L\(^{-1}\); below flower bulb fields all 8 samples analyzed had detectable MITC, with concentrations ranging from 0.06 to 0.3 µg L\(^{-1}\). The maximum concentrations were therefore above the European Community drinking water standards guideline of 0.1 µg L\(^{-1}\) maximum admissible concentration (Lagas et al. 1989).

Under a joint Environment Canada and Agriculture and Agri-Food Canada project, more than 2000 groundwater samples from the Abbotsford Aquifer were analyzed from 1990 to 1994 for a variety of pesticides, including MITC. There were no positive detections (detection limit 0.1 µg L\(^{-1}\)) of MITC (S.Y. Szeto, Pers. Comm.).
3. MATERIALS AND METHODS

Laboratory soil column systems were used to determine the partitioning of methylisothiocyanate (MITC) among the processes of leaching, volatilization, degradation, and sorption, and to determine how these processes are influenced by soil water regime and soil properties. Three main experiments were used, the first two examined the effects of leaching regime and soil properties on MITC partitioning, and the third compared the mobility of MITC to bromide, a conservative tracer. This section contains the details describing these experiments, including construction, testing, and function of the soil column systems, the measurement of MITC volatilization loss, leaching loss, and MITC extractable from soil, as well as soil characterization.

3.1. EXPERIMENTAL DESIGN

The three main experiments were conducted in identical soil column systems, under similar laboratory temperatures. The average temperature for all experiments was approximately 21°C, and temperature varied similarly for each experiment with normal laboratory temperature fluctuations of approximately ± 3°C.

3.1.1. Soil Water Regime Experiment

The soil water regime experiment was conducted to determine the effects of soil water regime or leaching regime on MITC behavior in soil columns. Three leaching regime treatments were each replicated twice where the experimental unit was a soil column as described in Section 3.2.1. A soil of the Monroe series (Luttermerding 1981) was selected for all soil water regime experiments because of its coarse texture and low organic carbon.
content, which would be expected to maximize MITC leaching and volatilization from the soil columns.

The three leaching regimes, referred to as high, moderate, and low intensity, consisted of variable timing of "leaching events" following injection of MITC into the soil columns (Table 3.1). Each leaching regime consisted of the application of 2.5 cm of water to each column over a four hour period (Section 3.2.3.). The high intensity leaching regime was run first, followed by the moderate and high intensity leaching regimes which were conducted simultaneously.

Table 3.1. Description of experimental leaching regimes.

<table>
<thead>
<tr>
<th>Treatment or Experiment</th>
<th>Days After Injection To First Leaching</th>
<th>Leaching Frequency</th>
<th>Number of Leaching Events</th>
<th>Total Water Applied (mm)</th>
<th>Total Duration (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HILR(^Z)</td>
<td>1</td>
<td>daily</td>
<td>10</td>
<td>250</td>
<td>11</td>
</tr>
<tr>
<td>MILR(^Z)</td>
<td>1</td>
<td>every 4th day</td>
<td>18</td>
<td>450</td>
<td>70</td>
</tr>
<tr>
<td>LILR(^Z)</td>
<td>35</td>
<td>daily</td>
<td>18</td>
<td>450</td>
<td>53</td>
</tr>
<tr>
<td>Soil Type and Bromide</td>
<td>14</td>
<td>every 4th day</td>
<td>18</td>
<td>450</td>
<td>83</td>
</tr>
</tbody>
</table>

\(^Z\) HILR, MILR, and LILR are High, Moderate, and Low Intensity Leaching Regimes, respectively.

The high intensity leaching regime consisted of one leaching event each day for 10 consecutive days, starting one day after MITC injection (Table 3.1). The moderate intensity leaching regime consisted of one leaching event every four days starting one day after MITC injection, for a total of 18 leaching events over 69 days. The low intensity leaching regime consisted of no leaching events for the first 34 days after MITC injection,
followed by one leaching event each day for the next 18 days, for a total of 18 leaching
events.

The leachate was collected from each leaching event, and total volume and MITC
concentration determined (Section 3.4.3). In addition, daily total MITC volatilization from
the soil column surface was measured using activated charcoal traps (Section 3.3). At the
end of each leaching regime treatment the soil columns were sectioned by depth and the
MITC in each column section determined (Section 3.5). MITC degradation was calculated
by mass balance by subtracting the total MITC leaching and volatilization losses and MITC
extracted from soil from the amount of MITC applied. Selected physical characteristics of
each column section were also measured (Section 3.6.2).

The high intensity leaching regime was chosen to represent a worst-case scenario
for leaching. A total equivalent of 250 mm of precipitation was applied over a 10 day
period. The moderate intensity leaching regime was chosen to represent a more realistic
situation. A total equivalent of 450 mm precipitation was applied over the 70 days of the
experiment, or approximately 200 mm of precipitation per month. This is comparable to
the amount of precipitation received in the Lower Fraser Valley in October or November,
several weeks after Vapam application which usually occurs in late August or in
September. For example, at Abbotsford, B.C. the 30 year (1960-1991) mean monthly
precipitation and highest recorded monthly precipitation are 88 and 202 mm for September,
155 and 381 mm for October, and 224 and 391 mm for November (Atmospheric
Environment Service 1985). The low intensity leaching regime was chosen to represent a
situation where volatilization losses would be maximized: no precipitation for one month
following application. This was followed by leaching in order to determine the extent of
MITC degradation, retention, and redistribution by diffusion over the first 34 days.

3.1.2. Soil Property Experiment
The soil property experiment was conducted to determine the effects of soil texture and organic carbon content on MITC behavior in soil columns. A completely randomized experimental design with four treatments and two replicates was used. Treatments included four soils with varying clay and organic carbon contents (Section 3.6.1.).

The leaching regime used was intermediate to the moderate and low intensity leaching regimes of the soil water regime experiments (Table 3.1). It consisted of no leaching events for the first 14 days after MITC injection, followed by one leaching event every 4 days starting on day 15 for a total of 18 leaching events giving a total duration of 83 days for the experiment. This regime was selected to maximize volatilization losses over the first 14 days, followed by measurement of leaching behavior thereafter. This leaching regime simulates a realistic scenario consisting of a 2 week period with no precipitation after fumigant application, followed by total precipitation equivalent to 450 mm over 72 days, or about 200 mm per month over 2.5 months.

MITC leaching and volatilization losses from the soil columns, MITC extracted from soil at various depths in the soil columns, MITC degradation, and selected soil physical properties were determined as for the soil water regime experiment (Section 3.1.1).

3.1.3. Bromide Tracer Experiment

The bromide tracer experiment was conducted to compare MITC and bromide mobility in the different soils used in the soil property experiment. The experimental design was the same as that used for the soil property experiment, and soil columns were packed identically to the columns used in the soil property experiment. The experimental protocol was identical to the soil property experiment, including an identical leaching regime (Table 3.1), with two exceptions. First, potassium bromide solution was injected into the columns at a rate of 100 kg Br⁻ ha⁻¹ using the same procedure as for MITC in the
other experiments (Section 3.2.3). Second, because bromide does not volatilize, air flow was adjusted to the same rate used in the other experiments but was not passed through charcoal traps.

The leachate was collected from each leaching event and its volume recorded and bromide concentration determined (Section 3.4.4).

3.1.4. Statistical Analyses

All one-way analyses of variance were carried out using Statworks software (Cricket Software Inc., Philadelphia, PA). The analysis of variance for factorial experiments was conducted manually, as described by Hicks (1993). All regression equations were fit using Cricket Graph software (Cricket Software Inc., Philadelphia, PA). The Least Significant Difference (LSD) test (Sokal and Rohlf 1981) was used for multiple comparisons of treatment means where the main effect was significant.

3.2. CONSTRUCTION AND OPERATION OF SOIL COLUMN SYSTEMS

3.2.1. Column Construction

Each soil column system consisted of 3 main sections: a column of soil, a volatilization chamber, and a leachate collection system (Fig. 3.1). Characteristics of soil column systems used by several other authors (Alhajjar et al. 1990; Cho and Jaffe 1990; Fermanich et al. 1991) were incorporated in the design.

Each soil column was constructed of 10 cm i.d. polyvinylchloride (PVC) pipe with 3 mm (1/8") wall thickness, cut into 31 cm lengths. The bottom end of each pipe was fitted with a PVC end cap which was sealed to the pipe with silicone sealant (Silicone II, General Electric). A 6 mm diameter hole was drilled in the center of each end cap to allow leachate
Figure 3.1. Schematic representation of soil column system. (See Figure 3.2 for volatilization chamber detail.)
to drain. A small amount of coarse glass wool was placed at the bottom of each column to support the soil. Four 13 mm diameter holes were drilled evenly spaced around the column circumference at 11 cm from the top of the column (10 cm below the soil surface). The holes were fitted with neoprene septa (Bittner Corp., Alpharetta, GA) for MITC injection and sealed to the pipe with silicone.

Each volatilization chamber consisted of a 15 cm length of 10.8 cm (4-1/4") i.d. cast acrylic (Plexiglas) tube with 3 mm (1/8") wall thickness (Fig. 3.1). The top of the chamber was capped with a flat Plexiglas plate (12 cm x 12 cm x 0.5 cm thickness) sealed to the acrylic tube with silicone. The chamber was silicone sealed over the PVC soil column with 4 cm overlap so that 11 cm of the acrylic tubing extended above the PVC. Six pieces of glass tubing were inserted into the chamber through holes in the top plate and sealed in place with silicone: one air inlet, one air outlet, and four water inlet tubes (Fig. 3.2).

Water was supplied to the top of the soil column with four 1.5 mm (1/16") i.d. Tygon tubing which entered the chambers through the four 5 mm i.d. glass water inlet tubes (Fig. 3.2). The Tygon tubing was sealed to the glass tubes at both ends with silicone. A short length (∼1 cm) of Tygon tubing extended past the end of the glass tube to drip water directly onto the soil surface in order to eliminate splashing and soil surface disturbance. A 16-channel peristaltic pump (Lachat Instruments, Mequon, WI) supplied a constant water flow to each tube using 0.38 mm i.d. peristaltic pump tubing. Using all channels the pump supplied four soil columns with water simultaneously.

The 6 mm i.d. glass air outlet tube was connected to two charcoal filled glass tubes, hereafter referred to as charcoal traps, in series (Fig. 3.2). The air outlet tube and the two charcoal traps were all connected with polypropylene "quick disconnect" glass tubing connectors (Cole-Parmer Ltd., Niles, IL). Air was drawn out of the chamber through the charcoal traps with an 'Air-Cadet' vacuum/pressure pump (Cole-Parmer Ltd., Niles, IL). One pump was connected to four columns with 8 mm (5/16") i.d. Tygon tubing through a
Figure 3.2. Schematic representation of soil column system volatilization chamber, including air and water flows into and out of the chamber.
manifold with ball valves to adjust air flow rates (Fig. 3.2). A Gilmont variable area flowmeter was used to measure air flow into each column through its air inlet. The 5 mm i.d. glass air inlet tube was fitted with a 10 cm length of 6 mm (1/4") i.d. Nalgene tubing to allow connection to the flowmeter. The flowmeter was calibrated with a film flowmeter (Fig. 3.3) prior to use.

![Calibration curve of Gilmont variable area flowmeter against a film flowmeter. Five film flowmeter readings taken at each calibration level on Gilmont flowmeter.](image)

\[ Y = 5.34 + 0.675X - 3.41 \times 10^{-1}X^2 + 1.27 \times 10^{-4}X^3 \]

\[ r^2 = 0.998 \]

Air flow through the volatilization chamber was accomplished by applying a vacuum to draw air into the chamber and out through the charcoal traps. This arrangement minimized the difference between air pressure in the chamber and ambient air pressure. Large differences in air pressure could potentially interfere with gas and water movement in the soil column, particularly when the bottom of the column was open to atmospheric
pressure during leaching. The air pressure drop in the chamber was minimized because the air encountered the major resistance to flow, the charcoal traps, after the chamber. Forcing air out of the chamber through the charcoal traps would have required a significant increase in air pressure inside the chamber. Furthermore, drawing air out of the chamber with a vacuum minimized MITC loss from the volatilization chamber by leakage.

The leachate collection system consisted of a glass funnel with a 2 cm long stem connected to a glass "U"-tube (5 mm i.d. glass tubing) with a 4 cm length of 6 mm (1/4") i.d. Nalgene tubing. The funnel was sealed with silicone to the center of the soil column end cap. The glass "U"-tube maintained a small volume of liquid at all times to reduce MITC gas phase losses from the bottom of the column. After a leaching event, the bottom of the column was sealed by clamping the Nalgene tubing, the "U"-tube was removed and the liquid from the "U"-tube was added to the leachate collection flask. At the next leaching event, the clamp was not removed until a small amount of liquid had accumulated in the glass funnel, which would then fill the "U"-tube when the clamp was removed.

A 250 mL Erlenmeyer flask was placed under the "U"-tube to collect the leachate. The flask was placed in an insulated ice bath to reduce MITC volatilization losses from the leachate (see Section 3.4.1). Prior to use, the flasks, as well as all glass used in construction of the soil column system, was washed, rinsed with distilled water, then acetone, and heated at 130 °C for at least 4 hours.

An experiment was conducted to determine the extent of MITC adsorption from aqueous solution onto the materials used to construct the soil column systems. A two factor factorial arrangement of treatments was used in a completely randomized design with two replicates. One factor was type of material which included PVC, Teflon, Nalgene tubing, and a control with no added material. The second factor was the length of time the materials were in contact with the MITC solution, either one or four days. Nalgene tubing and PVC were used in column construction, and Teflon, which has been shown to have low adsorption of organic compounds (Barcelona et al. 1985), was used for comparison.
purposes. Pieces of Teflon, PVC, and Nalgene tubing were cut into specified sizes (Table 3.2), and rough edges on the Teflon and PVC pieces sanded smooth. The pieces were washed with soap and water, rinsed well with distilled water, then methanol, and dried in an oven at 60°C for 12 hours to clean the surfaces and remove residues of other organic compounds. Two pieces of each material were placed in 125 mL amber glass bottles with Teflon-lined screw caps. The bottles were completely filled with 5 µg L⁻¹ MITC solution to eliminate any headspace, capped, and stored in the dark in an incubator at 20 °C. The MITC concentration in the solution was analyzed using the methods described in Section 3.4.3.

Table 3.2. Dimensions and surface area of materials tested for MITC adsorption from aqueous solution.

<table>
<thead>
<tr>
<th>Material</th>
<th>Dimensions of Each Piece</th>
<th>Surface Area per Piece</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC</td>
<td>70 x 10 x 3</td>
<td>18.8</td>
</tr>
<tr>
<td>Teflon</td>
<td>70 x 10 x 6.5</td>
<td>24.4</td>
</tr>
<tr>
<td>Nalgene Tubing</td>
<td>6.4 i.d. x 9.5 o.d. x 70 length</td>
<td>25.7</td>
</tr>
</tbody>
</table>

² Two pieces placed in each sample bottle.

There was a significant effect of material, but not of storage time, on MITC concentration in solution (Table 3.3). There was, however, a significant interaction between material and storage time. From one to four days storage time, MITC concentration in solution increased for the Teflon and Nalgene tubing, decreased for the PVC, and stayed about the same for the control (Table 3.4). The interaction is most likely
an artifact of variability because an actual increase in MITC concentration over time is improbable.

Table 3.3. Analysis of variance for results presented in Table 3.4.

<table>
<thead>
<tr>
<th>Source</th>
<th>df</th>
<th>Sum of Squares</th>
<th>Mean Square</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>3</td>
<td>2.548</td>
<td>0.8495</td>
<td>5.92*</td>
</tr>
<tr>
<td>Storage Time</td>
<td>1</td>
<td>0.013</td>
<td>0.0131</td>
<td>0.09</td>
</tr>
<tr>
<td>Material x Time</td>
<td>3</td>
<td>2.811</td>
<td>0.9369</td>
<td>6.53*</td>
</tr>
<tr>
<td>Error</td>
<td>8</td>
<td>1.147</td>
<td>0.1434</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>15</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* P < 0.05.

Table 3.4. MITC concentration in aqueous solution in contact with materials used for soil column system construction for two storage times (μg L⁻¹ ± 1 SE, n=2). Original MITC concentration was 5 μg L⁻¹.

<table>
<thead>
<tr>
<th>Material</th>
<th>Storage Time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 Day</td>
</tr>
<tr>
<td>Control (no material)</td>
<td>3.67 ± 0.27a</td>
</tr>
<tr>
<td>PVC</td>
<td>3.86 ± 0.22a</td>
</tr>
<tr>
<td>Teflon</td>
<td>3.30 ± 0.49ab</td>
</tr>
<tr>
<td>Nalgene Tubing</td>
<td>2.67 ± 0.12b</td>
</tr>
</tbody>
</table>

² Means within storage times without the same letter are significantly different (P < 0.05) using LSD test.

Within the one day storage time only the Nalgene tubing had a significantly lower MITC concentration than the control with no added material (Table 3.4). Within the four day storage time only the PVC was significantly lower than the control. However, these
differences are relatively small in magnitude and may be due at least in part to the high variability in the results. Since little adsorption to the Nalgene tubing and PVC was measured, these materials should have little effect on MITC behavior within the soil column system, and were deemed suitable for use in construction of the soil column systems.

3.2.2. Soil Preparation, Packing, and Pre-Treatment

Bulk soil samples were collected from the field, air dried, ground using a wooden rolling pin to pass a 2 mm sieve, and mixed thoroughly. Water was added to the air-dry soil in increments until the soil was moist enough to stick together when squeezed in the hand. Two sub-samples were taken for determination of gravimetric moisture content.

Increments of 350 g moist soil were added to each column and packed using a wooden piston-type plunger which fit snugly inside the PVC column. A consistent number of plunger strokes were used to pack each 350 g increment. Near the top of the column 100 g then 50 g increments were packed to bring the soil to within 1 cm of the top of the 31 cm PVC column, thus giving a 30 cm soil column. When packing near the top of the columns, another piece of PVC tubing was used as an extension to allow smooth plunger movement.

Packed columns were then fitted with volatilization chambers and leachate collection funnels and placed in a support rack. Water was supplied to the columns using the leaching system in order to saturate the soil. Leaching continued until approximately 1 L of leachate was collected from each column. The final 200 mL of leachate was retained for MITC background residue analysis. The columns were allowed to drain for approximately 2 days after leaching, prior to MITC injection.

During this pre-treatment, air was circulated through the volatilization chambers at 50 mL min\(^{-1}\) to prevent condensation on the inside of the volatilization chambers, and to
facilitate drying of the soil surface. Air was passed through charcoal traps for the 24 hours prior to MITC injection, and these traps analyzed for background MITC concentrations.

No MITC background concentrations were detected in any leachate samples or charcoal trap samples taken before MITC injection. This confirms that there were no detectable MITC residues present in the soil columns prior to the start of each experiment.

3.2.3. Experimental Protocol

Upon completion of column pre-treatment, MITC was injected into the soil columns to simulate the shank injection method of field application of metam-sodium. The mass of MITC injected into each column was selected based on the maximum recommended field application rates of Vapam for raspberry production in British Columbia of 450 to 900 L ha$^{-1}$ (BCMAFF 1994). The Vapam formulation contains 382 g L$^{-1}$ of its active ingredient metam-sodium (Worthing 1983). A 100% stoichiometric conversion rate from metam-sodium to MITC is assumed. Thus, the highest Vapam application rate is equivalent to 343.8 kg ha$^{-1}$ metam-sodium and assuming 100% conversion, 194.5 kg ha$^{-1}$ MITC. This application rate is equivalent to 144 mg MITC for the 10 cm diameter soil columns used in this study.

The MITC was applied in a volume of liquid similar to the volume of Vapam applied in the field. The 900 L ha$^{-1}$ rate is equivalent to 0.707 mL column$^{-1}$, so a 200 mg mL$^{-1}$ MITC solution was prepared, for which 144 mg MITC could be delivered in 0.720 mL of liquid. Only 124 mg of MITC was injected into the soil columns used in the HILR treatment of the soil water regime experiment, which corresponds to a field application rate of 730 L ha$^{-1}$ Vapam.

The 200 mg mL$^{-1}$ MITC solution was prepared in methanol from 97% pure MITC (Aldridge Chemical, Milwaukee, WI). Based on this purity, an appropriate amount of MITC was weighed in a small beaker with an analytical balance, then dissolved in a small
amount of methanol and transferred to a ten mL volumetric flask. The beaker was thoroughly rinsed several times with methanol to dissolve any remaining MITC, and the methanol added to the flask, and the flask then made up to volume with methanol.

MITC was injected into the soil columns through the four neoprene septa spaced evenly around the column at 10 cm below the soil surface. The desired mass of MITC was delivered to each column by 12 injections of 60 \mu l each, using a 100 \mu l Hamilton syringe. Three injections were made through each septa, one straight in, and one to each side at a 45° angle. Multiple injections were used in order to distribute the MITC as evenly as possible across a horizontal injection plane. When injecting, the needle was inserted all the way, then the plunger slowly pushed in as the needle was slowly withdrawn, in order to distribute the MITC uniformly along the needle path. A side-port needle was used to prevent clogging of the port with soil particles. The needle was 5.2 cm in length which allowed injection to the center of the 10 cm diameter columns.

In the bromide tracer experiment potassium bromide solution was injected, instead of MITC solution, at a rate of 100 kg ha\textsuperscript{-1} Br\textsuperscript{-}, or 0.0786 g Br\textsuperscript{-} (0.1170 g KBr) per soil column. This was injected using the same procedure and in the same volume of liquid as for MITC in the other experiments. Thus, 0.720 mL of 0.1625 g mL\textsuperscript{-1} (1.365 M) aqueous KBr solution was injected into each column.

The primary and backup charcoal traps were changed just prior to the MITC injection, and the air flow adjusted to the prescribed rate of 50 mL min\textsuperscript{-1} (Section 3.3.1). Both primary and backup charcoal traps were changed every 24 hours for the duration of the experiments, except near the end of some experiments when volatilization fluxes were very low, when traps were changed every 2 to 4 days. Air flow rates were checked and adjusted whenever charcoal traps were changed.

The soil columns were leached intermittently. During each "leaching event" 200 mL of leaching solution was applied to each column over a period of approximately four hours, which corresponds to a flow rate of about 0.21 mL min\textsuperscript{-1} for each of the four tubes.
supplying a column. Exactly 200 mL was always applied since this amount was measured into an Erlenmeyer flask from which the solution was drawn by all four tubes for a single column, until the flask was empty. Slight variations in pumping rates caused by progressive wear on peristaltic pump tubes and variations in pump motor speed caused the actual delivery time to range from about 3.5 to 5.0 hours.

The amount and duration of water application for each leaching event was selected for several reasons. Two hundred mL of water is equivalent to about 2.5 cm of precipitation over the surface of the soil column, a large but realistic precipitation event in the lower Fraser Valley of B.C. Applying the 200 mL over four hours allowed the solution to infiltrate as it was applied, preventing ponding on the soil column surface in most cases. Surface ponding was avoided as much as possible because it could result in enhanced side-wall flow, or preferential flow down macropores. The application time was limited to 4 hours to allow the soil columns to drain between leaching events when they occurred daily.

To prevent soil dispersion, the soil columns were leached with 0.01 M Ca(NO₃)₂ solution prepared with distilled water. Other soil column leaching studies have used 0.003 M CaCl₂ (Comfort et al. 1992; Veeh et al. 1994), 0.01 M CaCl₂ (Gerstl et al. 1977), and 0.005 M CaSO₄ (Bowman 1994) solution. However, CaCl₂ was not used because of the possible anti-microbial effects of Cl⁻, and CaSO₄ was not used because of possible increases in volatilization of sulfur containing compounds, which would be trapped by the charcoal and possibly interfere with the sulfur-specific flame photometric detector used for MITC determination in the charcoal extracts.

The leachate was collected in the leachate collection flasks for about 24 hours from the start of the leaching event. Each flask was then weighed to determine the mass of leachate collected, which was later converted to volume assuming a density of 1.0 g mL⁻¹. Leachate volumes were used to calculate the pore volumes of leachate collected, and to calculate the mass of MITC collected in the leachate using leachate MITC concentrations determined by gas chromatography and mass spectrometry (GC/MS) analysis (Section
3.4.3). A 125 mL amber glass bottle with a teflon lined screw cap was filled to the brim with a sub-sample of the leachate, and stored at 4 °C in the dark for a maximum of three weeks before analysis. For the bromide tracer experiment leachate subsamples were taken in 150 mL Nalgene screw-cap bottles and frozen until analysis.

Upon completion of the soil water regime and soil properties experiments the soil column systems were disassembled and the PVC columns were covered at the top and bottom with aluminum foil, sealed in individual plastic bags, and frozen at -20 °C to await sectioning and MITC extraction.

3.3. VOLATILIZATION MEASUREMENT USING CHARCOAL TRAPS

3.3.1. Selection of Air Flow Rate

The air flow rate through the volatilization chambers and charcoal traps was selected to be 50 mL min~1. This rate was chosen based on two factors: 1) the air exchange in the volatilization chamber needed to be rapid enough to quickly remove MITC so that a high MITC air concentration would not build up inside the chamber and cause volatilization to be limited by the rate of diffusion from the soil surface to the air (Section 2.3.3.1); and 2) the air flow rate must be low enough to avoid MITC breakthrough from the primary charcoal traps over the 24 hour sampling period. Several interacting factors influence analyte breakthrough in charcoal traps, including sampling time, flow rate, relative humidity, temperature, analyte concentration, and the quantity of charcoal in the trap (Tuinstra et al. 1988). Van den Berg et al. (1992) detected no MITC breakthrough from 100 mg charcoal traps when sampling air volumes of up to 60 L. Thus, the 72 L of air sampled from the volatilization chambers at a flow rate of 50 mL min~1 over 24 hours was deemed a reasonable sampling volume considering 400 mg charcoal traps were being used. In addition, the charcoal recovery experiments (Section 3.3.4.) indicated no MITC
breakthrough from the primary charcoal traps at a 50 mL min\(^{-1}\) flow rate for 24 hours, even for the 5000 \(\mu\)g MITC loadings. To confirm breakthrough from primary traps was not occurring under experimental conditions, backup traps were analyzed whenever >1500 \(\mu\)g MITC was recovered from the primary trap and whenever traps were used for more than 24 hours. No MITC was detected in the backup traps analyzed.

3.3.2. Manufacture of Charcoal Traps

Each charcoal trap consisted of activated charcoal packed into a glass tube. The glass tubing (6 mm i.d.) was washed, rinsed with distilled water, then acetone, and baked at 130 °C for at least 4 hours prior to packing with the charcoal. Petroleum based charcoal (Lot 208, SKC Inc., Eighty-Four, PA) was used, rather than coconut based charcoal, because MITC was found to have higher stability and higher desorption efficiency on petroleum based charcoal. Gan et al. (1994) reported coconut charcoal had a higher reactivity with MITC than petroleum based charcoal, and Tuinstra et al. (1988) found a 65 \% desorption efficiency for petroleum based charcoal, versus only 20 \% for coconut based charcoal.

Two types of traps were used: "Primary" traps where volatilization chamber air passed through first and all MITC should have been adsorbed, and "back-up" traps which were placed in series behind the primary trap to check for MITC breakthrough from the primary trap (Fig. 3.2). Primary charcoal traps consisted of 400 ± 3 mg charcoal packed in 10 cm lengths of glass tubing, whereas back-up traps consisted of 100 ± 3 mg charcoal packed in 7 cm lengths of tubing.

Separate primary and backup traps were used rather than combining both sections in a single glass tube, as in most commercially available traps. Separate traps allow identification of actual breakthrough from the primary to backup traps, whereas with combined sections, diffusion between sections during storage can obscure results. For
example, Tuinstra et al. (1988) measured 5% transfer of MITC from primary to backup charcoal sections in tubes stored for 10 days at 4°C.

Silanized glass wool plugs were used to hold the charcoal in the glass tubes. The charcoal was slowly and evenly poured into the glass tubing with one glass wool plug in place to support the charcoal; the other glass wool plug was then inserted and both ends lightly tamped with a thin glass rod to evenly compress the glass wool plugs. Packed traps were then cleaned by eluting with 5 mL pesticide-grade acetone for primary traps, or 3 mL for backup traps. After evaporating the remaining acetone from the traps in a fumehood, they were baked at 130°C for exactly 24 hours to drive off all acetone and other volatile organics. Traps were then cooled and immediately sealed at both ends with plastic end caps (SKC Inc., Eighty Four, PA).

3.3.3. MITC Desorption from Charcoal Traps

After use, charcoal traps were immediately re-capped and stored in a sealed container at -30°C for a maximum of 2 weeks before extraction. Charcoal traps used for MITC monitoring have been shown to be stable at low (< -20°C) temperatures (Van den Berg et al. 1992; Van den Berg 1993). For MITC extraction one glass wool plug was removed and the charcoal transferred directly to a 16 x 100 mm test tube with a Teflon-lined screw cap, which were washed, rinsed with distilled water, then acetone, and baked at 130°C for at least 4 hours prior to use. Immediately, 5.0 mL pesticide grade acetone was added, and the tubes were placed in an ultrasonic bath for exactly 1 hour, then centrifuged for 5 minutes at 2000 rpm to settle the charcoal. Both acetone and carbon disulfide have been shown to be effective solvents for desorbing MITC from petroleum based charcoal (Tuinstra et al. 1988), but acetone was chosen because carbon disulfide was unacceptable to the sulfur-specific flame photometric detector. The samples were stored at
4 °C for a maximum of 3 days before analysis of the supernatant acetone by the method described in Section 3.3.5.

3.3.4. Collection and Desorption Efficiency of MITC from Charcoal Traps

When sampling organic vapors from the air using solid sorbents, collection efficiency refers to the efficiency (percentage) with which a compound can be trapped on the sorbent from the air, which depends on the affinity of the organic vapor for the sorbent. Desorption efficiency refers to desorption from the sorbent with a particular solvent (Hertlein 1980). The sum of collection and desorption efficiencies is referred to as the 'overall' efficiency (Hertlein 1980). Overall efficiency is measured by introducing a known amount of sample into the air stream moving through the sorbent, and measuring the amount recovered (this includes desorption efficiency); desorption efficiency, however, is measured by simply applying a known sample amount directly to the sorbent, then extracting (Hertlein 1980; Voborsky 1980). Thus, collection efficiency can then be calculated as the difference between overall and desorption efficiencies (Hertlein 1980).

The overall efficiency of MITC recovery on petroleum based activated charcoal was determined using the apparatus shown in Figure 3.4. The apparatus was designed to simulate air flow through the charcoal traps from the column volatilization chamber; the air pump, manifold, and valves were the same as those used on the columns, and the air flow rate and time, i.e., 50 mL min⁻¹ for 24 hours, were identical to those used on the soil columns.

The overall recovery efficiency for four MITC loading rates was tested in an experiment using a completely randomized design with four replicates. Treatments of 10, 100, 1000, and 5000 µg of MITC in small quantities of methanol (10, 10, 10, and 25 µL, respectively) were applied to the glass wool plugs in front of the charcoal tubes, using a 100 µL Hamilton gas-tight syringe. As the MITC evaporated it was drawn by the air flow
into the charcoal traps. After 24 hours of air flow the traps were extracted as described in Section 3.3.3.

Back-up traps were used to determine if the primary traps quantitatively retained all MITC, or if MITC breakthrough occurred. This provided information on the maximum amount of MITC that could be collected on the primary traps without breakthrough under experimental conditions.
Four blank charcoal traps which had air drawn through for the prescribed rate and time but had no MITC applied were extracted and analyzed. No background MITC or other interfering compounds were detected on the four traps. The glass wool plugs onto which the 1000 $\mu$gMITC loadings were applied were also extracted with acetone, and no MITC residue was detected, indicating all applied MITC evaporated and was drawn into the charcoal traps.

The overall recovery efficiencies for MITC from the primary charcoal traps for the four MITC loading rates are given in Table 3.5. One-way analysis of variance indicated that the loading rate had a significant effect on overall recovery over the range of loading rates tested (Table 3.6). However, the recoveries in the range 10 to 1000 $\mu$g were not significantly different (Table 3.5). Since nearly all experimental charcoal trap samples had MITC loading rates below 1000 $\mu$g, the mean overall recovery in the range 10 to 1000 $\mu$g of 71% was used as a correction factor for all experimental volatilization measurements. No MITC breakthrough from the primary traps was observed under the experimental conditions for the MITC loadings tested, indicating MITC was quantitatively trapped by the primary traps. Thus, the collection efficiency of the primary traps was 100% for the range of MITC loadings tested, and the overall recovery efficiency was equivalent to the desorption efficiency.

3.3.5. Determination of MITC Concentration in Charcoal Trap Extracts

Following the charcoal solvent extraction procedure, MITC in the solvent extract was determined by gas chromatography and flame photometric detection. The system consisted of a Hewlett-Packard 5880A capillary gas chromatograph and a Hewlett-Packard flame photometric detector, operating in sulfur mode (394 nm).

The operating parameters for the Hewlett-Packard 5880A were: sample volume injected, 1 $\mu$l; cool on-column injection; column, J & W DB-624-30W (30 m x 0.32 mm...
Table 3.5. Overall recovery efficiencies for MITC from 400 mg petroleum based charcoal traps for different quantities of MITC applied, with 50 mL min\(^{-1}\) air flow rate for 24 hours (mean ± 1 SE, n=4).

<table>
<thead>
<tr>
<th>MITC Applied ((\mu g))</th>
<th>Overall Recovery Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>69.6 ± 1.31b(^z)</td>
</tr>
<tr>
<td>100</td>
<td>72.8 ± 0.74b</td>
</tr>
<tr>
<td>1000</td>
<td>70.8 ± 1.21b</td>
</tr>
<tr>
<td>5000</td>
<td>86.1 ± 1.09a</td>
</tr>
</tbody>
</table>

\(^z\) Means without the same letter are significantly different (P < 0.05) using LSD test.

Table 3.6. Analysis of variance for results presented in Table 3.5.

<table>
<thead>
<tr>
<th>Source</th>
<th>df</th>
<th>Sum of Squares</th>
<th>Mean Squares</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loading Rate</td>
<td>3</td>
<td>704.88</td>
<td>234.96</td>
<td>42.75*</td>
</tr>
<tr>
<td>Error</td>
<td>12</td>
<td>65.95</td>
<td>5.50</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>15</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* P < 0.005.

i.d., 1.8 \(\mu\)m thick); carrier gas, helium at 85 kPa. The column temperature program was: initial temperature 35 °C for 5 min; first program rate 6 °C min\(^{-1}\) to 80 °C; second program rate 25 °C min\(^{-1}\) to 220 °C. The flame photometric detector was operated at 200 °C and the detector gas consisted of 120 mL min\(^{-1}\) hydrogen, 100 mL min\(^{-1}\) air, and 30 mL min\(^{-1}\) nitrogen.

An authentic reference standard of MITC (97 % pure) was obtained from Aldridge Chemical (Milwaukee, WI). A primary stock solution of 1000 \(\mu g\) mL\(^{-1}\) MITC was
prepared in pesticide-grade methanol and kept in a freezer. This solution was used to prepare a 10 μg mL⁻¹ working stock solution in pesticide-grade methanol. This was appropriately diluted in pesticide-grade acetone to produce 0.50, 0.75, and 1.00 μg mL⁻¹ analytical standards. The detector was calibrated at the beginning of each day using the 0.50 and 1.00 μg mL⁻¹ standards; quantification was based on peak area. In addition, the 0.50 or 0.75 μg mL⁻¹ standards were run after every 5 to 7 samples, and the 0.75 μg mL⁻¹ standard was run at the end of each day to check the stability of detector response. Typically, the variation in standard concentration was < 5 % of the nominal standard concentration. Results were accepted only when variability in standard concentration was < 10 % of the nominal standard concentration. Under the given conditions, the retention time of MITC standard peaks ranged from 11.29 to 11.31 minutes (Fig. 3.5).

For quantification, a curvilinear standard curve was prepared because the detector response was curvilinear over the working concentration range (0 - 1.00 μg mL⁻¹). For each daily standard curve, the best fit quadratic regression curve was established based on standards with MITC concentrations of 0, 0.5, 0.75, and 1.0 μg mL⁻¹. When more than one run was done for the 0.5 or 0.75 μg mL⁻¹ standards in a day, all area counts were used in the regression. The regression equation for each day was used to calculate the unknown concentrations for samples run that day. The r² values for all days of analysis ranged from 0.985 to 1.000. A typical standard curve with its best-fit regression equation is shown in Figure 3.6.

3.4. MEASUREMENT OF MITC AND BROMIDE CONCENTRATIONS IN COLUMN LEACHATE

3.4.1. Volatilization Losses of MITC During Leachate Collection
Figure 3.5. Example of chromatograph output from flame photometric detector used to quantify MITC in charcoal trap extracts. The peak at 11.30 minutes retention time is MITC at a concentration of 0.5 μg mL⁻¹.
This experiment was conducted to determine the magnitude of MITC volatilization losses from the soil column leachate collection flasks. Duplicate 250 mL Erlenmeyer flasks were filled with 200 mL (the amount of leachate collected from a typical leaching event) of 5 µg L⁻¹ MITC solution and placed in an open ice bath for 24 hours to simulate collection of leachate from the columns. The flasks were weighed at the beginning and end of the 24 hour period to verify that evaporation losses were negligible. The solution was immediately analyzed to determine MITC concentration according to the method described in Section 3.4.3.

The MITC concentration was 5.6 µg L⁻¹ (SE = 0.29, n=2) at the start of the experiment, and was 5.2 µg L⁻¹ (SE = 0.5, n=2) after 24 hours. A two-tailed Student's t test between MITC concentration means at the start and end of the experiment showed that
the difference was not significant (P < 0.05). Thus, MITC volatilization losses from the leachate collection flasks were considered to be negligible under experimental conditions.

3.4.2. MITC Stability During Leachate Sample Storage

This experiment measured the stability of MITC in water samples stored for various periods of time at 4 °C. This information was needed to determine the maximum length of time leachate samples could be stored before analysis, without significant decreases in MITC concentration. The experiment used a completely randomized design with five treatments, replicated twice. Treatments consisted of 5 µg L⁻¹ MITC solution analyzed immediately after preparation (time zero) or after storage at 4 °C for 7, 17, 29, and 67 days. The solution was stored in completely filled 125 mL amber glass bottles with Teflon-lined screw caps. The solution was analyzed to determine MITC concentration according to the method described in Section 3.4.3.

Storage time had a significant effect on MITC concentration over the range of storage times tested (Table 3.7). There was no significant decrease in MITC concentration in samples stored for up to 29 days, but a significant decrease was seen for the 67 day storage time (Table 3.8). Therefore, samples could be stored for up to four weeks before a significant decrease in MITC concentration would occur. In this study a maximum storage period of only three weeks was used.

Table 3.7. Analysis of variance for results presented in Table 3.8.

<table>
<thead>
<tr>
<th>Source</th>
<th>df</th>
<th>Sum of Squares</th>
<th>Mean Square</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Storage Time</td>
<td>4</td>
<td>6.5861</td>
<td>1.6465</td>
<td>5.93*</td>
</tr>
<tr>
<td>Error</td>
<td>5</td>
<td>1.3874</td>
<td>0.2775</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>9</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* P < 0.05.
Table 3.8. MITC concentration in aqueous solution as affected by storage time at 4°C.

<table>
<thead>
<tr>
<th>Storage Time (days)</th>
<th>MITC Concentration (μg L⁻¹ ± 1 SE, n=2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.80 ± 0.22a</td>
</tr>
<tr>
<td>7</td>
<td>4.33 ± 0.00a</td>
</tr>
<tr>
<td>17</td>
<td>4.61 ± 0.15a</td>
</tr>
<tr>
<td>29</td>
<td>4.24 ± 0.63a</td>
</tr>
<tr>
<td>67</td>
<td>2.53 ± 0.47b</td>
</tr>
</tbody>
</table>

*Means without the same letter are significantly different (P < 0.05) using LSD test.*

**Y** Analyzed immediately after solution prepared.

3.4.3. Determination of MITC Concentration in Leachate

MITC concentration in leachate samples was determined by purge and trap capillary gas chromatography and mass spectrometry. The system consisted of a Tekmar LSC 2000 purge and trap with capillary interface and cryogenic focusing, a Hewlett-Packard 5990 gas chromatograph, and a Hewlett-Packard 5970 mass selective detector.

The operating parameters for the Tekmar LSC 2000 purge and trap were: trap composition, Tekmar no. 1 Tenax; initial trap temperature 30 °C; purge time 11 minutes using helium at 40 mL min⁻¹; moisture control module cooldown temperature 8 °C; heat up temperature 86 °C; capillary interface cooldown temperature -150 °C; desorb preheat at 195 °C; desorb temperature 200 °C for 4 minutes; inject temperature 200 °C for 1.50 minutes; bake temperature 225 °C for 20 minutes; valve temperature 100 °C; line temperature 100 °C; mount temperature 40 °C; capillary interface union temperature 200 °C; and sample size 25 mL.

The operating parameters for the Hewlett-Packard 5990 capillary gas chromatograph were: injection port temperature 225 °C; mass selective detector interface
temperature 250 °C; column, J & W DB-624-30W (30 m x 0.32 mm i.d., 1.8 µm thick); carrier gas, helium at 30 kPa. The column temperature program was: initial temperature 35 °C for 5 minutes; first program rate 6 °C min⁻¹ to 160 °C; second program rate 20 °C min⁻¹ to 220 °C and hold for 5 minutes.

The operating parameters for the Hewlett-Packard 5970 mass selective detector were: solvent delay 6.8 minutes; mass range 55 to 200 amu; scan speed 0.74 scan s⁻¹.

The 1000 µg mL⁻¹ MITC primary stock solution was used to prepare a 125 µg mL⁻¹ working stock solution in pesticide-grade methanol, 10 µl of which was diluted in 250 mL deionized distilled water to give an aqueous analytical standard solution containing 5 µg L⁻¹ MITC. Fresh aqueous standard was prepared every 2 days and stored in the refrigerator (< 4 °C).

Identification of MITC was based on its retention time (Fig. 3.7) and confirmed by full scan mass spectrum (Fig. 3.8). Quantification was based on the mean total ion count of the external standards injected before and after the samples each day. Results were accepted only when the standard deviation of the responses of the external standards was less than 15% of the mean.

3.4.4. Determination of Bromide Concentration in Leachate

The bromide concentration in the leachate samples was determined by the phenol red spectrophotometric method using flow injection analysis (Anfalt and Twengstrom 1986). This method is based on the bromination of phenol red to bromophenol blue after oxidation of bromide to bromine. A Tecator 5020 Flow Injection Analyzer with a V-200 double channel, variable volume valve and a Chemifold II manifold was used. A Tecator 5023 spectrophotometer was used as a detector at 590 nm. The method of Anfalt and Twengstrom (1986) was followed with the exception that one rather than two carrier streams was used. The detection limit was 0.1 mg L⁻¹.
Figure 3.7. Example of total ion chromatograph used to quantify MITC concentration in leachate samples. Peak shown is MITC with a retention time of 12.382 minutes.
3.5. SOIL COLUMN SECTIONING AND MITC EXTRACTION FROM SOIL

3.5.1. Soil Column Sectioning

The soil columns from the MILR and LILR treatments of the soil water regime experiment and from the soil property experiment were sectioned prior to MITC extraction.
The columns used in the HILR treatment of the soil water regime experiment were not frozen immediately after completion of the leaching regime and thus could not be included in this analysis.

Each soil column was cut into four sections, 0 - 7, 7 - 13, 13 - 21.5, and 21.5 - 30 cm, measured from the soil surface. These lengths were chosen in order to center one section on the 10 cm injection plane, to allow a separate section for the soil surface, and to have some division of the lower half of the column.

Soil columns were cut with a hacksaw while still frozen to ensure the soil would stay in place during cutting. The outer PVC was first cut around the entire circumference at the appropriate measurement, then the frozen soil was cut. Individual section lengths were measured after cutting and were generally ± 1 mm of the desired length. The hacksaw blades were washed and rinsed with acetone between cuts to eliminate cross contamination of column sections.

The column sections were allowed to thaw slightly around the circumference so that the soil could be pushed out into a plastic bag, which was immediately sealed. Individual sections were immediately weighed and re-frozen until extraction.

3.5.2. MITC Extraction from Soil

Soil column sections were thawed immediately before extraction. Each section was thoroughly mixed by shaking and kneading in a plastic bag for approximately 5 minutes. Two subsamples of about 50 g were taken from each section for determination of gravimetric moisture content.

A 1:1 soil:solvent ratio was chosen for the extractions on the basis of two factors: a minimal solvent volume was desired in order to minimize dilution of MITC in the solvent and therefore improve detection limits, and a large enough volume of solvent was needed to provide adequate supernatant for analysis or further dilution. Two soil subsamples from
each column section were extracted. Soil subsamples of 5 to 6 g wet weight were weighed into 15 x 150 mm acetone rinsed test tubes and exact weights recorded (0.01 g accuracy); these wet weights were approximately equivalent to the desired mass of 4 to 5 g oven dry soil. Immediately 4.0 mL pesticide grade ethyl acetate was added and the tube capped with an aluminum foil-lined rubber stopper. Ethyl acetate was chosen over acetone as the solvent because of its lower miscibility with water. Each tube was then agitated on a vortex mixer for 1 minute then placed in an ultrasonic bath for 5 minutes; this procedure was repeated twice more. The supernatant solution in the test tube was pipetted into an acetone-rinsed 16 x 100 mm test tube with a teflon-lined screw cap, which was then capped and centrifuged for 5 minutes. Finally, approximately 1 g anhydrous granular NaSO₄ was added to each tube for moisture removal. The ethyl acetate extract was then analyzed following the same procedure as the acetone extract from the charcoal traps (Section 3.3.5.), with the exception that MITC standard solutions in this case were made in ethyl acetate. In addition, the retention time for MITC standards in ethyl acetate was 11.36 to 11.38 minutes, slightly longer than those in acetone.

MITC concentrations in soil were calculated based on oven dry soil weight. With a detection limit of 0.2 μg mL⁻¹ in the ethyl acetate extract, the soil detection limit ranged from 0.2 μg g⁻¹ for 4 g oven dry soil to 0.16 μg g⁻¹ for 5 g oven dry soil.

3.5.3. Efficiency of MITC Recovery from Soil

An experiment was conducted to determine if the efficiency of MITC recovery from soil was dependent on the length of time of equilibration of MITC with the soil or, in other words, if MITC residues became irreversibly bound or non-extractable with time. The experiment used a completely randomized design with two treatments and four equilibration times of 0, 1, 4, and 24 h, replicated 4 times. The treatments consisted of 2 mL of 1 μg mL⁻¹ aqueous MITC solution added to a 15 x 150 mm test tube which contained either 0 or
4 g (oven dry basis) of air-dry Monroe soil (from the soil water regime experiment). The tubes were capped with an aluminum foil-lined rubber stopper and equilibrated for the appropriate time in the refrigerator at 4 °C. Both treatments were extracted and analyzed following the soil extraction procedure outlined in Section 3.5.2.

MITC recovery efficiency from both water and soil decreased with length of equilibration time (Table 3.9). With zero equilibration time, the MITC recovery efficiencies from water and soil were similar. At longer equilibration times, MITC recovery efficiency was consistently lower from the soil compared to the water. However, the recovery from soil was an essentially constant proportion of the recovery from water, at an average of 90 %, over the 1 to 24 hour equilibration times (Table 3.9).

Table 3.9. Recovery efficiency of MITC from water and Monroe soil by ethyl acetate extraction after varying sample equilibration times.

| Equilibration Time (h) | Water (% recovery ± 1 SE, n=4) | Monroe Soil (% recovery ± 1 SE, n=4) | Monroe Soil Recovery as a Percentage of Recovery from Water (%)
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>95.2 ± 1.0</td>
<td>95.6 ± 0.6</td>
<td>100</td>
</tr>
<tr>
<td>1</td>
<td>90.2 ± 0.8</td>
<td>83.3 ± 1.1</td>
<td>92</td>
</tr>
<tr>
<td>4</td>
<td>87.9 ± 3.9</td>
<td>77.1 ± 1.2</td>
<td>88</td>
</tr>
<tr>
<td>24</td>
<td>68.0 ± 8.4</td>
<td>60.8 ± 6.0</td>
<td>89</td>
</tr>
</tbody>
</table>

The reduction in recovery from the water with increasing equilibration time is most likely due to volatilization to the test tube headspace and/or degradation. Considering the results of the MITC leachate sample storage experiment, it seems probable that the majority of MITC loss from the test tubes was due to volatilization. The larger drop in recovery from the 0 to 1 hour equilibration time for the Monroe soil compared to the water is
probably due to a fraction of the MITC becoming irreversibly bound or non-extractable in the soil over this time. However, the reduction in recovery from soil from the one hour to the four and 24 hour equilibration times is similar to the reduction in recovery from water over the same time period, as illustrated by the essentially constant recovery from soil calculated as a proportion of recovery from water for these equilibration times. This suggests the fraction of MITC irreversibly bound or non-extractable from the soil remained constant for equilibration times greater than one hour.

Since changes in recovery were negligible for sample equilibration times of one hour or greater, the Columbia, Lehman Surface, and Lehman Subsurface soil recoveries were determined in quadruplicate for this time only (Table 3.10), following the procedure described above. In addition, a single subsample blank (with no MITC added) of each soil type was extracted. For all soils, MITC levels in the blanks were below detection limits.

Table 3.10. Recovery efficiency of MITC from the Columbia, Lehman Surface, and Lehman Subsurface soils by ethyl acetate extraction after one hour sample equilibration time.

<table>
<thead>
<tr>
<th>Soil Type</th>
<th>Recovery Efficiency from Soil</th>
<th>Soil Recovery as a Percentage of Recovery from Water$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(% recovery ± 1 SE, n=4)</td>
<td>(%)</td>
</tr>
<tr>
<td>Columbia</td>
<td>86.2 ± 1.9</td>
<td>96</td>
</tr>
<tr>
<td>Lehman Surface</td>
<td>82.3 ± 1.1</td>
<td>91</td>
</tr>
<tr>
<td>Lehman Subsurface</td>
<td>84.5 ± 3.1</td>
<td>94</td>
</tr>
</tbody>
</table>

$^2$ Recovery from soils as a percentage of recovery from water for one hour equilibration time (Table 3.9).

For calculating the mass balance of MITC in the soil columns, the MITC soil concentrations ($\mu$g g$^{-1}$ oven dry soil) were corrected using soil recovery efficiencies with 1
h sample equilibration times corrected for loss from water (Tables 3.9 and 3.10). The corrected soil concentrations were multiplied by the oven dry weight of the soil in the corresponding column section to give the mass of MITC present in the column section.

3.6. SOIL AND SOIL COLUMN CHARACTERIZATION

3.6.1. Soil Properties

Four soils were selected in order to have a range of clay and organic matter contents (Table 3.11). The Monroe soil was collected from a field at the Pacific Agriculture Research Center at Agassiz, and the remaining soils were collected from farm fields in the Abbotsford Aquifer area.

Soil particle size distribution was determined using a method similar to the pipette method of Kilmer and Alexander (1949). The total organic-free sample weight was determined using the weight of sand plus a pipette fraction taken immediately after stirring. Carbonates and soluble salts were not removed.

Organic carbon content was estimated from total carbon content, assuming negligible inorganic carbon content in the soils tested. Total carbon content was determined by combustion using a Leco induction furnace (Model 577-100, Leco Laboratory Equipment Corp., St. Joseph, Michigan). Soil pH was measured in 1:1 soil:water suspension (Hendershot et al. 1993).

All the Monroe soil was sampled from the same location in the field and had similar sand, silt, and clay contents (Table 3.11). However, the soil used in the soil water regime experiment was collected in the fall of 1994 whereas that used in the soil type experiment was collected in the spring of 1995, several weeks after liquid manure was applied to the area. The organic carbon content of the collected soils were similar before and after the manure application (Table 3.11).
### Table 3.11. Classification, texture, organic carbon content, and pH of experimental soils (mean ± 1 SD, n=3).

<table>
<thead>
<tr>
<th>Soil</th>
<th>Classification</th>
<th>Sampling Depth (cm)</th>
<th>% Sand</th>
<th>% Silt</th>
<th>% Clay</th>
<th>% Organic Carbon&lt;sup&gt;2&lt;/sup&gt;</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monroe</td>
<td>Eluviated Eutric Brunisol</td>
<td>0-15</td>
<td>78.5 ± 0.5</td>
<td>16.9 ± 0.3</td>
<td>4.7 ± 0.4</td>
<td>0.84 ± 0.06</td>
<td>N/A</td>
</tr>
<tr>
<td>(soil type)</td>
<td>Eluviated Eutric Brunisol</td>
<td>0-15</td>
<td>75.4 ± 0.1</td>
<td>19.7 ± 0.5</td>
<td>4.9 ± 0.3</td>
<td>0.79 ± 0.01</td>
<td>6.2 ± 0.1</td>
</tr>
<tr>
<td>Columbia</td>
<td>Orthic Humo-ferric Podzol</td>
<td>0-15</td>
<td>32.0 ± 0.3</td>
<td>58.3 ± 0.3</td>
<td>9.7 ± 0.5</td>
<td>4.48 ± 0.49</td>
<td>5.5 ± 0.0</td>
</tr>
<tr>
<td>Lehman (surface)</td>
<td>Orthic Humic Gleysol</td>
<td>0-15</td>
<td>28.5 ± 0.3</td>
<td>55.6 ± 0.3</td>
<td>15.8 ± 0.4</td>
<td>2.23 ± 0.08</td>
<td>6.8 ± 0.1</td>
</tr>
<tr>
<td>Lehman (subsurface)</td>
<td>Orthic Humic Gleysol</td>
<td>15-30</td>
<td>28.3 ± 0.2</td>
<td>56.3 ± 0.4</td>
<td>15.5 ± 0.2</td>
<td>1.84 ± 0.10</td>
<td>6.0 ± 0.0</td>
</tr>
</tbody>
</table>

<sup>2</sup> n=2.

N/A = not measured.
3.6.2. Packed Soil Column Characteristics

Gravimetric moisture contents at packing and for each column section were measured in duplicate, after oven drying sub-samples at 105 °C for 24 hours (Table 3.12). Columns with Monroe soils were grouped according to packing date. Data presented for the four soil types is for soil columns used in the soil property experiment only, except for water content at packing which applies to columns used in both the soil property and bromide tracer experiments. Soil bulk density was determined for each column section (Table 3.12). Total porosity for each section was calculated as (Ballard 1994):

\[ f = 1 - \left[ (OM \times BD/d_{om}) + ((1-OM) \times BD/d_{m}) \right] \]

where:
- \( f \) = total porosity (cm\(^3\) cm\(^{-3}\))
- \( BD \) = bulk density (g cm\(^{-3}\))
- \( OM \) = organic matter content of soil (g g\(^{-1}\))
- \( d_{om} \) = density of organic fraction = 1.3 g cm\(^{-3}\)
- \( d_{m} \) = density of mineral fraction = 2.65 g cm\(^{-3}\)

Air-filled porosities were calculated as the difference between total porosity and volumetric water content (Table 3.12). Average air filled porosity from the surface to the 10 cm injection depth was calculated using an average of air filled porosities from the 0-7 cm and 7-13 cm depths, weighted according to the proportion of the 10 cm depth occupied by that section, i.e., 70 % of the 0-7 cm section value plus 30 % of the 7-13 cm section value.
Table 3.12. Selected properties of packed soil columns.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Gravimetric Water Content at Packing</th>
<th>Gravimetric Water Content at FC</th>
<th>Bulk Density</th>
<th>Total Porosity</th>
<th>Air Filled Porosity at FC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(g g⁻¹) (cm)</td>
<td>(g g⁻¹) (g cm⁻³)</td>
<td></td>
<td>(cm³ cm⁻³)</td>
<td>(cm³ cm⁻³)</td>
</tr>
<tr>
<td>HILRX</td>
<td>15.7 N/A</td>
<td>N/A</td>
<td>1.33 ± 0.01</td>
<td>0.49 ± 0.03</td>
<td>N/A</td>
</tr>
<tr>
<td>MILR &amp; LILRX</td>
<td>17.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monroe</td>
<td>19.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Columbia</td>
<td>12.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lehman Surface</td>
<td>24.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lehman Subsurface</td>
<td>17.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Measured from soil surface.

FC= Field Capacity defined as water content in soil columns after 24 hours drainage.

HILR, MILR, and LILR are High, Moderate, and Low intensity leaching regimes, respectively.

\( n=4 \) for MILR and LILR soil columns grouped together.
4. RESULTS

4.1. SOIL WATER REGIME EXPERIMENT

4.1.1. MITC Volatilization Losses

Under the high intensity leaching regime (HILR) volatilization was first detected on the day of MITC injection (day 0) at a flux of 13.9 µg d⁻¹, increased to a maximum of 29.0 µg d⁻¹ one day after MITC injection, then decreased rapidly with time to below the detection limit of 0.5 µg day⁻¹ four days after MITC injection (Fig. 4.1). Volatilization flux remained below the detection limit until the end of the experiment 10 days after MITC injection.

Volatilization was first detected with the moderate intensity leaching regime (MILR) two days after MITC injection at a flux of 1.0 µg d⁻¹, and rapidly increased to a maximum of 16.9 µg d⁻¹ four days after MITC injection (Fig. 4.2). Volatilization dropped rapidly to a flux of 2.7 µg d⁻¹ on day five, after the second leaching event, increased to 3.9 µg d⁻¹ by day eight, then dropped again to 0.9 µg d⁻¹ on day nine, following the third leaching event. Volatilization flux remained at approximately 0.9 µg d⁻¹ until day 12, then dropped to below the detection limit on day 13 after the fourth leaching event, where it remained until 35 days after MITC injection. Charcoal trap samples were not analyzed for MITC after day 35 until the end of the experiment 69 days after MITC injection, but volatilization flux was assumed to remain below the detection limit.

The volatilization flux varied substantially among the duplicate soil columns for the MILR. In one soil column, the only detectable MITC volatilization flux occurred four days after MITC injection, on the same day as the peak mean volatilization flux for the second soil column. Air filled porosity from the 0 to 10 cm soil depth was 9.1 % for the former column as compared to 12.1 % for the latter column.
Figure 4.1. Leaching and volatilization loss of MITC under the high intensity leaching regime. Values are means for duplicate soil columns, bars represent one standard error.
Figure 4.2. Leaching and volatilization loss of MITC under the moderate intensity leaching regime. Values are means for duplicate soil columns, bars represent one standard error.
Under the low intensity leaching regime (LILR) volatilization was first detected one day after MITC injection at a flux of 79.9 μg d⁻¹, increased very rapidly to a maximum of 2563 μg d⁻¹ six days after MITC injection, then declined to 437 μg d⁻¹ at 34 days after MITC injection (Fig. 4.3). The volatilization flux dropped suddenly to 87.9 μg d⁻¹ on day 35 following the first leaching event on that day. From day 35 onward, the volatilization flux gradually declined to 1.3 μg d⁻¹ on the last day of the experiment, 52 days after MITC injection.

Volatilization was detected on the day of MITC injection under the HILR, but not until one day after injection for the LILR. For the MILR, volatilization was not detected until two days after MITC injection, one day after the first leaching event.

The peak volatilization flux in the LILR, in the absence of leaching, occurred six days after MITC injection, and was approximately two orders of magnitude higher than the peak in the HILR and MILR where leaching occurred. Peak volatilization rates occurred the day before the second leaching events with both the HILR and MILR. The HILR had a peak flux approximately twice as high as the MILR. The volatilization flux dropped to below the detection limit after four leaching events under both the HILR and MILR, but in the LILR volatilization flux was above the detection limit after 18 leaching events.

Total volatilization losses for each leaching regime were calculated as the sum of daily volatilization losses over the duration of each treatment (Table 4.1). There was a significant effect of leaching regime on the total volatilization loss (Table 4.2). Total volatilization loss was small, 0.040 % or less of MITC applied, and similar under the MILR and HILR (Table 4.1). In comparison, total volatilization loss was approximately three orders of magnitude higher under the LILR and accounted for almost one-third of the applied MITC.
Figure 4.3. Leaching and volatilization loss of MITC under the low intensity leaching regime. Values are means for duplicate soil columns, bars represent one standard error.
Table 4.1. Total MITC loss by volatilization and leaching, MITC extracted from soil after completion of each treatment, and MITC degradation for three soil water regimes (% of MITC applied ± 1 SE, n=2)\textsuperscript{z}.

<table>
<thead>
<tr>
<th>Treatment\textsuperscript{y}</th>
<th>Duration \textsuperscript{y}</th>
<th>Volatilization Loss\textsuperscript{x}</th>
<th>Leaching Loss</th>
<th>Total Loss\textsuperscript{w}</th>
<th>Extracted from Soil\textsuperscript{v}</th>
<th>Degradation\textsuperscript{u}</th>
</tr>
</thead>
<tbody>
<tr>
<td>HILR</td>
<td>11</td>
<td>0.040 ± 0.007b</td>
<td>68.6 ± 7.7a</td>
<td>68.6 ± 7.7a</td>
<td>N/A</td>
<td>31.4 ± 7.7a\textsuperscript{t}</td>
</tr>
<tr>
<td>MILR</td>
<td>70</td>
<td>0.026 ± 0.023b</td>
<td>42.5 ± 5.4b</td>
<td>42.6 ± 5.4a</td>
<td>ND</td>
<td>57.4 ± 5.4a</td>
</tr>
<tr>
<td>LILR</td>
<td>52</td>
<td>30.0 ± 0.4a</td>
<td>15.7 ± 0.1c</td>
<td>46.0 ± 0.2a</td>
<td>0.123 ± 0.007</td>
<td>54.1 ± 0.4a</td>
</tr>
</tbody>
</table>

\textsuperscript{z} Means within a column without the same letter are significantly different (P < 0.05) as determined by LSD test.
\textsuperscript{y} HILR, MILR, and LILR are High, Moderate, and Low intensity leaching regimes, respectively.
\textsuperscript{x} Results corrected for 71% recovery efficiency from charcoal traps.
\textsuperscript{w} Total loss = sum of leaching and volatilization losses.
\textsuperscript{v} Results corrected for recovery efficiency.
\textsuperscript{u} Degradation values calculated by mass balance.
\textsuperscript{t} Soil extractable plus degradation.
N/A = not measured.
ND = not detectable; detection limit was 0.10% of applied MITC.
Table 4.2. Analysis of variance for results presented in Table 4.1 (values are mean squares).

<table>
<thead>
<tr>
<th>Source</th>
<th>df</th>
<th>Volatilization Loss</th>
<th>Leaching Loss</th>
<th>Total Loss</th>
<th>Degradation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Leaching Regime</td>
<td>2</td>
<td>601.282**</td>
<td>1398.3*</td>
<td>403.2ns</td>
<td>399.7ns</td>
</tr>
<tr>
<td>Error</td>
<td>3</td>
<td>0.094</td>
<td>58.6</td>
<td>59.0</td>
<td>53.3</td>
</tr>
<tr>
<td>Total</td>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*, **, ns: P < 0.05, P < 0.01, and non-significant, respectively.

4.1.2. MITC Leaching Losses

Leaching losses followed the same general pattern for all water regimes, with the mass leached from a given event increasing rapidly to a maximum, then decreasing more slowly thereafter to very low levels. Under the HILR, MITC was first detected in leachate from the second leaching event at a magnitude of 0.08 mg MITC. The mass leached increased to a maximum of 37.0 mg from the fourth leaching event, then declined with each subsequent leaching event to a loss of 0.95 mg from the tenth and final leaching event (Fig. 4.1).

Under the MILR, MITC was first detected in leachate from the second leaching event five days after MITC injection at a magnitude of 0.23 mg, then increased to a maximum of 15.5 mg from the fourth leaching event 13 days after injection (Fig. 4.2). The mass leached then declined to 0.71 mg by the tenth leaching event 37 days after injection, and to 0.04 mg from the sixteenth leaching event 61 days after injection. MITC was not detected in the leachate from the final two leaching events.

Leaching loss under the LILR was detected from the first leaching event 35 days after MITC injection at a magnitude of 0.47 mg, then rapidly increased to a peak of 4.56 mg from the fifth leaching event 39 days after injection (Fig. 4.3). The mass leached subsequently declined to 0.55 mg from the tenth leaching event 44 days after injection, and
then declined more gradually to 0.14 mg from the final leaching event 52 days after injection.

MITC was first detected in the leachate from the second leaching event for both the HILR and MILR, although the magnitude of loss was over twice as high in the MILR. Leaching loss was detected from the first leaching event of the LILR at a magnitude approximately two and four times as high as the first leaching loss under the MILR and HILR, respectively. The peak mass leached for both the HILR and MILR occurred from the fourth leaching event, but in this case loss from the HILR was over two times that in the MILR. The peak mass leached for the LILR occurred one leaching event later than for the MILR and HILR, and its magnitude was approximately 30 % and 12 % of the peak masses leached for the MILR and HILR, respectively. Leaching loss of MITC occurred from the final leaching events of both the HILR and LILR, but MITC was not detectable in the leachate from the final two leaching events of the MILR.

To more clearly illustrate the pattern of MITC leaching loss under the three leaching regimes the mass of MITC leached from each leaching event was converted to a percentage of the total amount of MITC leached for that treatment, and plotted against the pore volumes of leachate collected (Fig. 4.4). Plotting the amount of MITC leached as a percentage of the total amount leached removes differences in magnitudes of leaching loss, and plotting pore volumes of leachate is important for relating MITC movement to water movement in soil. Leachate pore volume was calculated from the MITC injection plane at 10 cm depth downward, i.e., from 10 to 30 cm depth, using measured bulk densities (Table 3.12).

The peak MITC leaching loss occurred at approximately one pore volume of leachate for all three leaching regimes (Fig. 4.4). However, the magnitude of the peak leaching loss decreased progressively from the HILR to the LILR, and the shape of the peak changed from being quite sharp and narrow for the HILR to progressively more flat and broad in the MILR and LILR. As a result of the broader peak of the LILR,
larger leaching losses occurred with the first small volume of leachate than under the other leaching regimes. In addition, all three curves had an asymmetrical tail after the peak which progressively increased in magnitude from the HILR to the LILR (Fig. 4.4).

There was a significant effect of the leaching regime on the total mass of MITC leached over the duration of each leaching regime treatment (Table 4.2). The mean total leaching losses were significantly different for all three leaching regimes and ranged from nearly 70% of applied MITC for the HILR treatment to approximately 16% of applied MITC for the LILR treatment (Table 4.1).

The sum of leaching and volatilization loss over the duration of each leaching regime, reported as total loss, was not significantly affected by the leaching regime (Table 4.2). The mean total loss for the HILR was approximately 50% higher than total losses for the MILR and LILR, but the HILR and MILR total loss estimates were quite variable (Table 4.1). Under the HILR and MILR the total losses were almost entirely due to leaching, whereas with the LILR leaching accounted for only approximately one-third of the total loss.

4.1.3. MITC Extracted from Soil and MITC Degradation in Soil

MITC extractable from soil was determined for soil columns from the MILR and LILR after the final leaching event of each regime. MITC residues were detected only in the LILR columns, at all depths except 0 to 7 cm, however, concentrations were high enough for quantification only in the 21.5 to 30 cm depth (Table 4.3). The total amount of MITC extracted as a percentage of MITC applied for the LILR was 0.123% (Table 4.1).

MITC degradation was calculated by mass balance by subtracting MITC leaching and volatilization losses over the duration of the treatment and MITC extractable from soil at the end of the treatment from the total MITC applied at the start of the treatment. Thus, it is assumed all MITC that was not recovered had been degraded.
Table 4.3. MITC extracted from soil ($\mu$g g$^{-1}$ ± 1 SE, n=4) with depth in the soil column after the final leaching event of each water regime treatment. Results are presented on an oven dry soil weight basis and are not corrected for MITC recovery efficiency from soil.

<table>
<thead>
<tr>
<th>Leaching Regime</th>
<th>Depth from Soil Surface (cm)</th>
<th>0 - 7</th>
<th>7 - 13</th>
<th>13 - 21.5</th>
<th>21.5 - 30</th>
</tr>
</thead>
<tbody>
<tr>
<td>HILR</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>MILR</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>Trace</td>
<td>0.20 ± 0.01</td>
</tr>
<tr>
<td>LILR</td>
<td>ND</td>
<td>Trace</td>
<td>Trace</td>
<td>Trace</td>
<td>0.20 ± 0.01</td>
</tr>
</tbody>
</table>

N/A = not measured.
ND = not detectable. Quantification limit = 0.16 $\mu$g g$^{-1}$; concentrations < 0.16 $\mu$g g$^{-1}$ which were confirmed by retention time are reported as trace.

Calculated mean MITC degradation was similar for the MILR and LILR treatments, and approximately twice as high as for the HILR (Table 4.1). The variability in calculated degradation was high for the HILR and MILR, however, and the leaching regime had no significant effect on the proportion of MITC degraded (Table 4.2). Since the proportion of MITC extracted from soil was below the detection limit or very small compared to total loss values, differences in degradation values were almost entirely dependent on differences in total loss values.

4.2. SOIL PROPERTY EXPERIMENT

4.2.1. MITC Volatilization Losses

Volatilization flux from the Monroe soil was first detected three days after MITC injection at 7.5 $\mu$g day$^{-1}$ then increased to 550 $\mu$g day$^{-1}$ eight days after injection, and reached a maximum of 611 $\mu$g day$^{-1}$ 11 days after injection (Fig. 4.5). Volatilization flux
Figure 4.5. Volatilization flux of MITC with time for four soils. Arrows indicate leaching events. Values are means for duplicate soil columns, bars represent one standard error.
then decreased to 510 µg day⁻¹ on day 13, and dropped suddenly to only 23 µg day⁻¹ on day 14 following the first leaching event. Volatilization flux continued to drop after day 14 until it reached non-detectable levels 17 days after injection, where it remained until 45 days after MITC injection. Charcoal trap samples from all soil columns in this experiment were not analyzed for MITC after day 45, but volatilization flux was assumed in all cases to remain below the detection limit until the end of the experiment, 82 days after MITC injection.

In the Columbia soil, MITC volatilization flux was first detected four days after MITC injection at a flux of 0.8 µg day⁻¹ (Fig. 4.5). It increased over time to a maximum of 319 µg day⁻¹ 13 days after MITC injection, then dropped to 73 µg day⁻¹ on day 14, after the first leaching event. Volatilization flux remained fairly constant for the next three days until the next leaching event, when it again dropped. Stepwise drops in volatilization flux continued for the next two leaching events until the flux finally dropped below the detection limit 26 days after injection, where it remained until the end of the experiment.

Volatilization flux was first detected with the Lehman surface soil four days after MITC injection at 3.5 µg day⁻¹ (Fig. 4.5). It increased to a peak of 169 µg day⁻¹ at 10 days after injection, decreased until 13 days after injection when the flux was 79 µg day⁻¹, then dropped to only 7.1 µg day⁻¹ on day 14 after the first leaching event. Volatilization flux continued to slowly decline after day 14, reaching levels below the detection limit 17 days after MITC injection, where they remained until the end of the experiment.

With the Lehman subsurface soil, volatilization flux was first detected five days after MITC injection at 2.3 µg day⁻¹, and increased to a maximum flux of 152 µg day⁻¹ at 11 days after MITC injection (Fig. 4.5). It decreased slowly over the next two days to 126 µg day⁻¹ on day 13; the variability in volatilization flux between duplicate soil columns was quite high over this two day period. A large drop in volatilization flux to only 14 µg day⁻¹ on day 14 was observed following first leaching event. Volatilization flux continued to drop in a stepwise fashion with each leaching event to levels below the detection limit 21
days after injection, where it remained for the rest of the experiment. It should be noted that significant swelling of the Lehman Subsurface soil occurred over the first 13 days of the experiment such that the soil surfaces in the columns were raised approximately 0.5 cm above their original level.

The Monroe soil had the earliest detectable volatilization flux three days after MITC injection, while volatilization flux was not detected until four days after injection in both the Columbia and Lehman surface soils, and five days after injection in the Lehman subsurface soil. The rate of increase of volatilization flux from the first detection to the peak was greatest for the Monroe soil, lower for the Columbia soil, and lowest for the two Lehman soils, for which the rate was similar. The magnitude of the peak volatilization flux decreased significantly ($P < 0.05$) in the order Monroe > Columbia > Lehman surface = Lehman subsurface (data not presented), with the Columbia soil at approximately only one-half, and the Lehman soils at approximately only one-quarter of the peak volatilization flux of the Monroe soil.

A substantial decline in volatilization flux occurred in all soils after the first leaching event 14 days after injection. In most soils volatilization flux was at or near the peak when this decrease occurred; the exception is the Lehman surface soil in which volatilization flux had already significantly declined from the peak when leaching occurred. In the Columbia soil volatilization flux did not decrease to as low a level as in the other soils after the first leaching event, and a slight rebound in volatilization flux was measured between the first and second leaching events.

Total volatilization losses for each soil type were calculated as the sum of daily volatilization losses over the duration of the experiment (Table 4.4). Soil type had a significant effect on total volatilization losses (Table 4.5). Volatilization losses were highest from the Monroe soil, but were only approximately 3% of applied MITC, lower from the Columbia soil, and lowest from the two Lehman soils which did not have significantly different total volatilization losses (Table 4.4).
Table 4.4. Total MITC loss by volatilization and leaching, MITC extracted from soil after completion of the experiment, and MITC degradation with varying soil type under identical leaching regimes of 83 day total duration (% of MITC applied ± 1 SE, n=2)z.

<table>
<thead>
<tr>
<th>Soil</th>
<th>Volatilization Lossy</th>
<th>Leaching Loss</th>
<th>Total Lossx</th>
<th>Extracted from Soilw</th>
<th>Degradationu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monroe</td>
<td>3.1 ± 0.2a</td>
<td>0.072 ± 0.071b</td>
<td>3.2 ± 0.1b</td>
<td>ND</td>
<td>96.8 ± 0.1b</td>
</tr>
<tr>
<td>Columbia</td>
<td>1.32 ± 0.01b</td>
<td>7.22 ± 0.03a</td>
<td>8.5 ± 0.3a</td>
<td>0.27 ± 0.03</td>
<td>91.2 ± 0.3c</td>
</tr>
<tr>
<td>Lehman Surface</td>
<td>0.72 ± 0.11c</td>
<td>0.0006 ± 0.0001b</td>
<td>0.72 ± 0.11c</td>
<td>ND</td>
<td>99.3 ± 0.1a</td>
</tr>
<tr>
<td>Lehman Subsurface</td>
<td>0.54 ± 0.10c</td>
<td>0.10 ± 0.04b</td>
<td>0.65 ± 0.14c</td>
<td>ND</td>
<td>99.4 ± 0.1a</td>
</tr>
</tbody>
</table>

z Means within a column without the same letter are significantly different (P < 0.05) as determined by LSD test.
y Results corrected for 71% recovery efficiency from charcoal traps.
x Total loss = sum of leaching and volatilization losses.
w Results corrected for recovery efficiencies for each soil type.
u Degradation values calculated by mass balance.
ND = not detectable; detection limit was 0.10% of applied MITC.
Table 4.5. Analysis of variance for results presented in Table 4.4 (values are mean squares).

<table>
<thead>
<tr>
<th>Source</th>
<th>df</th>
<th>Volatilization Loss</th>
<th>Leaching Loss</th>
<th>Total Loss</th>
<th>Degradation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil Type</td>
<td>3</td>
<td>2.815**</td>
<td>25.659**</td>
<td>27.433**</td>
<td>29.370**</td>
</tr>
<tr>
<td>Error</td>
<td>4</td>
<td>0.031</td>
<td>0.050</td>
<td>0.073</td>
<td>0.059</td>
</tr>
<tr>
<td>Total</td>
<td>7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

** P < 0.01.

For the four soils used in the soil properties experiment, a inverse relationship between percent clay content (Table 3.11) and both total volatilization loss (Table 4.4) and peak volatilization flux (Fig. 4.5) was observed (Fig. 4.6). Peak volatilization flux also increased curvilinearly with increasing air filled pore space above the plane of MITC injection (Fig. 4.7). Data for individual columns were used because of high variability in air filled porosity among duplicate columns of the same soil type. Air filled porosity to the 10 cm depth was used because the MITC was injected at this depth. Neither peak volatilization flux nor total volatilization losses showed any correlation with soil organic carbon content or with soil bulk density above the plane of MITC injection.

Large differences in MITC volatilization flux from the Monroe soil were seen between the soil water regime experiment and the soil property experiment. Because of the effects of differing leaching regimes on volatilization, volatilization fluxes can only be compared between the initial stages of both the LILR and of the Monroe soil type treatment, when no leaching occurred (Fig. 4.8). The peak volatilization flux in the LILR was over four times as high as for the Monroe. Furthermore, volatilization flux was first detected sooner, and the volatilization flux increased at a greater rate, and peaked sooner for the LILR treatment than in the Monroe.
Figure 4.6. Relation of total MITC volatilization loss and peak MITC volatilization flux to % clay content for four soils. Values are means for duplicate soil columns.

Figure 4.7. Relationship between peak MITC volatilization flux and average air filled porosity from the soil surface to the 10 cm MITC injection depth for eight soil columns including four soil types.
Figure 4.8. Comparison of volatilization fluxes during the time period prior to the first leaching event from Monroe soils used in the Low Intensity leaching regime treatment and in the Monroe soil type treatment. Values are means for duplicate soil columns, bars represent one standard error.

There was little difference in bulk density or air-filled porosity above the 10 cm injection plane among the Monroe soil columns from the LILR treatment and from the Monroe soil type treatment (Table 3.12). However, it was observed that the 200 mL of water applied with each leaching event over a four hour period infiltrated without ponding on the soil surface for the LILR columns. In comparison, ponding occurred after about one-half hour in the Monroe soil type columns and all the water did not infiltrate until seven or eight hours after the start of leaching. This would suggest that the columns used for the LILR treatment had a higher hydraulic conductivity.

4.2.2. MITC Leaching Losses

MITC was first detected in the leachate from the second leaching event for the Columbia soil (Table 4.6). The peak mass leached for the Columbia soil was an average of
1630 μg and occurred from the sixth leaching event for both soil columns. Relatively high leaching losses were maintained for the remainder of the leaching events. The duplicate Columbia soil columns had very similar masses leached for all leaching events, generally within 5%.

In the Lehman Subsurface soil, MITC was first detected in leachate from the second leaching event (Table 4.6). The peak masses leached, of approximately 38 and 79 μg, were measured from the fifth and sixth leaching events for the duplicate soil columns, respectively. Leaching losses from the duplicate Lehman subsurface soil columns decreased quite rapidly after this peak to non-detectable levels by the tenth and twelfth leaching events, respectively.

With the Lehman Surface soil, MITC was detected in the leachate only from the fourth and fifth leaching events in one soil column, and only from the fifth leaching event in the second soil column (Table 4.6). In both columns the magnitudes of the peak losses were small, less than 0.71 μg.

Leaching losses were quite different between the two Monroe soil columns (Table 4.6). One column had small leaching losses, with detectable MITC in leachate from only the third and fourth leaching events. The other column had detection of MITC in leachate from the first leaching event, and the peak leaching loss from the third leaching event. In this column, small amounts of MITC were present in the leachate up to the thirteenth leaching event, after which MITC levels were not detectable. Between the two Monroe soil columns there was approximately a two order of magnitude difference in both the peak mass leached and the total leaching loss.

The Columbia and Lehman Subsurface soils both had the first detection of MITC in leachate from the second leaching event, the same as for both the MILR and HILR in the soil water regime experiment. The Columbia soil had the highest peak mass leached for the four soil types, which was approximately two orders of magnitude higher than for the Lehman Subsurface soil, and four orders of magnitude higher than for the Lehman surface
Table 4.6. Mass of MITC leached (μg column\(^{-1}\)) from duplicate columns of the four soil types with each leaching event.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (14(^2))</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>1.66</td>
</tr>
<tr>
<td>2 (18)</td>
<td>5.51</td>
<td>0.28</td>
<td>ND</td>
<td>ND</td>
<td>0.82</td>
<td>1.00</td>
<td>ND</td>
<td>58.83</td>
</tr>
<tr>
<td>3 (22)</td>
<td>170.03</td>
<td>20.61</td>
<td>ND</td>
<td>ND</td>
<td>14.27</td>
<td>15.02</td>
<td>1.07</td>
<td>136.70</td>
</tr>
<tr>
<td>4 (26)</td>
<td>414.55</td>
<td>203.57</td>
<td>ND</td>
<td>0.36</td>
<td>32.03</td>
<td>41.86</td>
<td>0.44</td>
<td>3.07</td>
</tr>
<tr>
<td>5 (30)</td>
<td>710.27</td>
<td>445.44</td>
<td>0.71</td>
<td>0.65</td>
<td>38.09</td>
<td>67.98</td>
<td>ND</td>
<td>1.41</td>
</tr>
<tr>
<td>6 (34)</td>
<td>1335.54</td>
<td>1923.37</td>
<td>ND</td>
<td>ND</td>
<td>4.46</td>
<td>78.70</td>
<td>ND</td>
<td>1.28</td>
</tr>
<tr>
<td>7 (38)</td>
<td>1185.67</td>
<td>1283.67</td>
<td>ND</td>
<td>ND</td>
<td>0.36</td>
<td>0.41</td>
<td>ND</td>
<td>0.60</td>
</tr>
<tr>
<td>8 (42)</td>
<td>1122.79</td>
<td>1373.31</td>
<td>ND</td>
<td>ND</td>
<td>0.15</td>
<td>0.23</td>
<td>ND</td>
<td>0.39</td>
</tr>
<tr>
<td>9 (46)</td>
<td>1134.03</td>
<td>1318.05</td>
<td>ND</td>
<td>ND</td>
<td>0.11</td>
<td>0.14</td>
<td>ND</td>
<td>0.19</td>
</tr>
<tr>
<td>10 (50)</td>
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<td>970.52</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>0.07</td>
<td>ND</td>
<td>0.19</td>
</tr>
<tr>
<td>11 (54)</td>
<td>829.50</td>
<td>945.80</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>0.13</td>
<td>ND</td>
<td>0.31</td>
</tr>
<tr>
<td>12 (58)</td>
<td>559.33</td>
<td>519.60</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>0.12</td>
</tr>
<tr>
<td>13 (62)</td>
<td>394.62</td>
<td>348.88</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>0.10</td>
</tr>
<tr>
<td>14 (66)</td>
<td>453.20</td>
<td>441.38</td>
<td>ND</td>
<td>ND</td>
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<td>ND</td>
</tr>
<tr>
<td>15 (70)</td>
<td>305.96</td>
<td>299.17</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>16 (74)</td>
<td>264.79</td>
<td>392.12</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
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<td>ND</td>
</tr>
<tr>
<td>17 (78)</td>
<td>143.17</td>
<td>224.76</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>18 (82)</td>
<td>62.19</td>
<td>127.27</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Total</td>
<td>9961.14</td>
<td>10837.80</td>
<td>0.71</td>
<td>1.01</td>
<td>90.28</td>
<td>205.53</td>
<td>1.51</td>
<td>204.87</td>
</tr>
</tbody>
</table>

\(^2\) Days after MITC injection.
ND= not detectable. Detection limit approximately 0.02 μg leaching event\(^{-1}\).
soil (Table 4.6). For the Monroe soil, one column had a peak similar in magnitude to the Lehman surface soil, while the other column had a peak similar to the Lehman Subsurface soil. In addition, the Columbia soil was the only soil to have detectable leaching losses for the duration of the experiment. The peak mass leached for the Columbia soil was, however, much smaller than the peak mass leached from any of the treatments in the soil water regime experiment.

The MITC breakthrough curves for the four soils were all distributed fairly closely around one pore volume of leachate, with peaks at 0.84, 1.13, 1.15, and 1.20 pore volumes for the Monroe, Lehman Subsurface, Lehman Surface, and Columbia soils, respectively (Fig. 4.9). Both the Monroe and Lehman Surface soils had sharp, narrow peaks (Fig. 4.9) resulting from the majority of MITC leaching loss occurring over a small number of leaching events (Table 4.6). The peak for the Lehman Subsurface soil is only approximately half as high, is slightly broader, and appears skewed slightly to the right, as compared to the Monroe and Lehman Surface soils. The Columbia soil has the smallest peak; it is less than half as high as the Lehman subsurface peak and is the most broad and diffuse, with a prominent slowly declining tail after the peak.

Soil type significantly influenced the magnitude of total leaching losses (Table 4.5). The total mass of MITC leached over the duration of the experiment was significantly higher for the Columbia soil compared to the other soil types (Table 4.4). Leaching losses in the Monroe, Lehman Surface, and Lehman Subsurface soils were all extremely low by comparison, and not significantly different from each other. The Lehman surface soil had a mean leaching loss approximately two orders of magnitude smaller than the means for both the Monroe and Lehman subsurface soils, but due to variability in these means the difference was not statistically significant.

The magnitudes of leaching losses for the four soil types did not appear to be related to soil clay or organic carbon content, or bulk density of the packed soil columns (Tables 3.11, 3.12).
Figure 4.9 MITC breakthrough curves for four soils under identical leaching regimes. Values are means for duplicate soil columns. Pore volumes calculated from the MITC injection plane (10 cm depth) downward.
The leaching loss for the Monroe soil in this experiment was much less than the leaching losses from the Monroe soil in the soil water regime experiment. All three leaching regimes in the soil water regime experiment had leaching losses two orders of magnitude higher than the Monroe soil treatment in the soil property experiment.

The sum of leaching and volatilization loss over the duration of the experiment, reported as total loss, was significantly affected by soil type (Table 4.5). The Columbia soil had the highest total loss followed by the Monroe soil; the two Lehman soils had the lowest total losses, and were not significantly different from each other (Table 4.4). For all soils, however, the total loss was relatively small. Most of the total loss in the Columbia soil was due to leaching loss, whereas in the Monroe soil most was due to volatilization loss.

4.2.3. MITC Extracted from Soil and MITC Degradation in Soil

Only the Columbia soil columns had detectable levels of MITC extracted from soil (Table 4.7). MITC was detected in the lower two sections of these columns, but concentrations were high enough for quantification only in the lowest (21.5 to 30 cm) depth.

Soil type had a significant effect on the proportion of MITC degraded over the duration of the experiment (Table 4.5). Degradation was not significantly different between the two Lehman soils, but both had significantly more degradation than the Columbia or Monroe soils (Table 4.4). The Monroe soil, in turn, had significantly higher degradation than the Columbia soil. The proportion of degradation was over 90% of applied MITC in all four soils examined, indicating degradation was the dominant process affecting the fate of MITC for all soils in this experiment. The proportion of degradation in the four soils did not follow any trends with soil clay content, soil organic carbon content, or soil pH (Table 3.11).
Table 4.7. MITC extracted from soil (μg g⁻¹ ± 1 SE, n=4) with depth in the soil column for the four soil types at the end of the soil type experiment. Results are presented on an oven dry soil weight basis and are not corrected for MITC recovery efficiency from soil.

<table>
<thead>
<tr>
<th>Soil Type</th>
<th>Depth from Soil Surface (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 -7</td>
</tr>
<tr>
<td>Monroe</td>
<td>ND</td>
</tr>
<tr>
<td>Columbia</td>
<td>ND</td>
</tr>
<tr>
<td>Lehman Surface</td>
<td>ND</td>
</tr>
<tr>
<td>Lehman Subsurface</td>
<td>ND</td>
</tr>
</tbody>
</table>

ND = not detectable. Quantification limit = 0.16 μg g⁻¹; concentrations < 0.16 μg g⁻¹ which were confirmed by retention time were reported as trace.

A large difference in MITC degradation losses within the Monroe soil was evident in comparing the Monroe soil in the soil type experiment (Table 4.4) with the soil water regime experiment (Table 4.1), which used Monroe soil for all regimes. The total degradation loss in the Monroe soil type treatment was approximately 1.5 to 3 times larger than losses for the soil water regime treatments.

4.3. BROMIDE TRACER EXPERIMENT

4.3.1. Bromide Recovery in Leachate

For the Columbia soil, bromide was detected in the leachate from the first leaching event for both soil columns (Table 4.8). The peak mass leached from the Columbia soil was an average of 12.3 mg and occurred from the fifth leaching event for both soil columns. The mass leached declined to below the detection limit of 0.02 mg bromide per leaching event from the fourteenth or fifteenth leaching events, respectively, for the
Table 4.8. Mass of bromide leached (mg column\(^{-1}\)) from duplicate columns of the four soil types with each leaching event.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (14(^2))</td>
<td>0.2</td>
<td>0.3</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>2.8</td>
<td>ND</td>
</tr>
<tr>
<td>2 (18)</td>
<td>3.5</td>
<td>4.5</td>
<td>2.1</td>
<td>2.9</td>
<td>1.6</td>
<td>2.0</td>
<td>12.0</td>
<td>6.0</td>
</tr>
<tr>
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<td>18.6</td>
<td>12.8</td>
<td>13.3</td>
<td>12.8</td>
<td>20.8</td>
</tr>
<tr>
<td>4 (26)</td>
<td>11.5</td>
<td>7.8</td>
<td>28.3</td>
<td>27.1</td>
<td>23.1</td>
<td>24.4</td>
<td>11.2</td>
<td>24.0</td>
</tr>
<tr>
<td>5 (30)</td>
<td>11.5</td>
<td>13.1</td>
<td>15.2</td>
<td>11.5</td>
<td>16.4</td>
<td>16.4</td>
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<td>3.5</td>
<td>4.2</td>
<td>6.6</td>
<td>8.4</td>
<td>10.4</td>
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<tr>
<td>7 (38)</td>
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<td>0.7</td>
<td>0.7</td>
<td>1.9</td>
<td>2.6</td>
<td>5.2</td>
<td>ND</td>
</tr>
<tr>
<td>8 (42)</td>
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<td>4.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.4</td>
<td>0.6</td>
<td>2.2</td>
<td>ND</td>
</tr>
<tr>
<td>9 (46)</td>
<td>2.7</td>
<td>2.4</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.9</td>
<td>ND</td>
</tr>
<tr>
<td>10 (50)</td>
<td>1.2</td>
<td>1.1</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>0.2</td>
<td>ND</td>
</tr>
<tr>
<td>11 (54)</td>
<td>0.6</td>
<td>0.5</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>12 (58)</td>
<td>0.3</td>
<td>0.2</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>13 (62)</td>
<td>0.1</td>
<td>0.1</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>14 (66)</td>
<td>0.1</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>15 (70)</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>16 (74)</td>
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<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>17 (78)</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>18 (82)</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Total</td>
<td>62.1</td>
<td>57.5</td>
<td>67.9</td>
<td>65.4</td>
<td>62.8</td>
<td>67.9</td>
<td>71.8</td>
<td>55.4</td>
</tr>
<tr>
<td>% of Br(^{-}) Applied</td>
<td>79.0</td>
<td>73.1</td>
<td>86.4</td>
<td>83.2</td>
<td>80.0</td>
<td>86.4</td>
<td>91.3</td>
<td>70.5</td>
</tr>
</tbody>
</table>

\(^2\) Days after MITC injection.
ND= not detectable. Detection limit approximately 0.02 mg leaching-event\(^{-1}\).
duplicate soil columns. The mean total recovery of bromide for the Columbia soil was 76.1% of applied bromide.

Bromide was first detected in the leachate from the second leaching event in both Lehman Surface soil columns (Table 4.8). The mass of bromide leached peaked at an average of 27.7 mg from the fourth leaching event, then decreased to below the detection limit by the tenth leaching event for both soil columns. For the Lehman Surface soil, the mean total bromide recovery was 84.8% of applied bromide.

For the Lehman Subsurface soil, bromide was first detected in leachate from the second leaching event, peaked at an average of 23.8 mg on the fourth leaching event, then dropped to below the detection limit by the tenth leaching event for both soil columns (Table 4.8). The mean total bromide recovery was 83.1% of applied bromide for the Lehman Subsurface soil.

Bromide leaching losses were quite different among the two Monroe soil columns (Table 4.8). In one column, bromide was detected in leachate from the first leaching event, peaked at 12.8 mg from the third leaching event, then declined to below the detection limit on the eleventh leaching event. A total of 91.3% of applied bromide was recovered from this column. In the second soil column, bromide was not detected in leachate until the second leaching event, peaked at the fourth leaching event at 24.0 mg, then declined to below the detection limit after only seven leaching events. In this column, a total of only 70.5% of applied bromide was recovered.

Within the four soil types, the Columbia soil had the first detection of bromide in the leachate, and maintained detectable leaching losses for the greatest number of leaching events. The Lehman Surface and Subsurface soils had very similar bromide leaching behavior, with the first detection, peak, and last detection of bromide leaching on the same leaching events. The magnitude of the peak mass of bromide leached was similar for the Lehman soils, and was approximately twice as high as for the Columbia soil. One Monroe soil column had a peak mass leached similar in magnitude to the Columbia soil, while the
other Monroe column was similar to the Lehman soils. The total bromide recovery for all soils was fairly similar, around 80% of applied bromide.

The bromide breakthrough curves for the four soils all peaked slightly before one pore volume of leachate, with peaks at 0.74, 0.83, 0.87, and 0.98 pore volumes for the Columbia, Lehman Subsurface, Lehman Surface, and Monroe soils, respectively (Fig. 4.10). The breakthrough curve for the Columbia soil was the most broad and diffuse, with the lowest peak, and a prominent slowly declining tail after the peak. The Monroe soil breakthrough curve was less broad and diffuse and had a higher peak than the Columbia soil curve, but also had a prominent tail after the peak. The breakthrough curves for the Lehman soils had very similar shapes and peak heights, and the peaks were sharper and narrower than for the other soils. The pore volume of leachate at which the bromide breakthrough curve peak occurred decreased with increasing soil organic carbon content for the four soils (Fig. 4.11a)

4.3.2. Comparison of Bromide and MITC Breakthrough Curves

The pore volumes of leachate at which the peaks of the MITC breakthrough curves occurred for the four soils increased with increasing soil organic carbon content (Fig. 4.11b). This is in contrast with the bromide breakthrough curves for these soils, where the pore volumes of leachate at the peaks decreased with increasing soil organic carbon content (Fig. 4.11a).

For the Monroe soil, the MITC breakthrough curve has a much sharper and narrower peak, and a larger peak height compared to the bromide breakthrough curve (Fig. 4.12). The MITC breakthrough curve peaks at 0.84 pore volumes compared to 0.98 for the bromide.
Figure 4.10. Bromide breakthrough curves for four soils under identical leaching regimes. Values are means for duplicate soil columns. Pore volumes calculated from the bromide injection plane (10 cm depth) downward.
Figure 4.11. Relationship of soil organic carbon content for four soils to A) pore volumes of leachate at the peak of the bromide breakthrough curves, B) pore volumes of leachate at the peak of the MITC breakthrough curves, and C) retention of MITC breakthrough curve peaks compared to bromide breakthrough curve peaks.
Figure 4.12. Comparison of bromide and MITC breakthrough curves for four soils. Values are means for duplicate soil columns. Pore volumes are calculated from the bromide and MITC injection planes (10 cm depth) downward.
The MITC and bromide breakthrough curves were quite similar in shape for the Columbia soil (Fig. 4.12). However, the MITC curve has a slightly lower peak height and a slightly more pronounced tail after the peak compared to the bromide curve. In addition, the bromide curve peaked at 0.74 pore volumes, versus 1.20 pore volumes for the MITC curve.

For the Lehman Surface soil, the MITC breakthrough curve had a much sharper and narrower peak, and a larger peak height compared to the bromide curve (Fig. 4.12). The MITC breakthrough curve peaked slightly after the bromide, at 1.15 versus 0.87 pore volumes, respectively.

The MITC and bromide breakthrough curves for the Lehman Subsurface soil were very similar in shape and peak height (Fig. 4.12). However, the MITC breakthrough curve peaked slightly after the bromide, at 1.13 pore volumes compared to 0.83 pore volumes for the bromide.

The differences among pore volumes of leachate at the peaks of the MITC and bromide breakthrough curves is correlated with the organic carbon content of the soils (Fig. 4.11c). In the Monroe soil, with the lowest organic carbon content, the MITC breakthrough curve peaked slightly before the bromide curve. In the Lehman soils, which have similar organic carbon contents, the MITC breakthrough curve peaks occurred at similar pore volumes, slightly after the bromide peak. In the Columbia soil, with the highest organic carbon content, the MITC breakthrough curve peak was delayed the most compared to the bromide peak.
5. DISCUSSION

5.1. DEGRADATION

MITC degradation was calculated by mass balance. MITC leaching and volatilization losses over the duration of each treatment and MITC extractable from soil at the end of each treatment were subtracted from the total MITC applied, and the difference assumed to be degradation.

This estimate of degradation was quite accurate because all other losses of MITC from and within the soil column system should have been negligible. Photodegradation of MITC in the volatilization chamber should have been negligible because the air in the chamber was exchanged at a sufficient rate so that MITC would be exposed to light for only about 5 minutes before being drawn into the charcoal traps. Furthermore, the soil column system was not exposed to direct sunlight. Adsorption of MITC to the soil column system materials should have also been negligible, considering the negligible adsorption of MITC to these materials from aqueous solution (Section 3.2.1). Some MITC may have been unextractable from soil with the procedure used. However, the MITC recovery efficiency from soil did not decrease from one to 24 hour equilibration times (Section 3.5.3), indicating unextractable MITC did not increase over this time period. Thus, the recovery efficiency should have corrected for the majority of MITC unextractable from soil.

MITC degradation was rapid under all conditions examined. All four soils examined in the soil property experiment had > 90% of applied MITC lost by degradation over the 83 day duration of the experiment. In the leaching regime experiment, approximately 55 to 60% of applied MITC was lost by degradation over the 53 to 70 day durations for the MILR and LILR treatments.

Exact degradation rates or half-lives cannot be calculated from these experiments because the kinetics of the degradation process is unknown. The proportion of MITC
degraded by the end of each experiment was calculated, but the actual time period over which this degradation took place is unknown. In addition, MITC lost by volatilization and leaching processes during the experiment would have decreased the MITC concentration in the soil column, thereby affecting concentration dependent degradation rates.

Degradation rates can, however, be approximated by using several simplifying assumptions. First, it was assumed that MITC degradation was essentially complete when MITC concentration in the leachate fell below detectable levels. This assumption is consistent with the finding that MITC was not detected in the soil at the end of the experiments, except where MITC was still present in the leachate from the final leaching event. In these exceptions, degradation was assumed to have taken place over the total duration of the experiment.

Second, because the actual degradation kinetics are not known, first-order degradation kinetics were assumed. Nearly all studies examining MITC degradation have found that it follows first-order kinetics (e.g., Smelt and Leistra 1974; Gerstl et al. 1977; Smelt et al. 1989; Boesten et al. 1991).

Third, it was assumed that MITC leaching and volatilization losses occurred after the time period used for calculating the degradation rate and thus had no effect on the degradation rate. That is, the MITC concentration was decreased from the initial concentration only by degradation losses over this time period.

MITC degradation half-life was then estimated using the first-order rate equation \( \ln \left( \frac{C}{C_0} \right) = -kt \), where \( t \) is the time in days, \( C_0 \) is the concentration of MITC at time zero, \( C \) is the concentration of MITC at time \( t \), and \( k \) is the degradation rate constant. The ratio \( C/C_0 \) was assumed to be proportional to the ratio of the mass of MITC remaining in the soil column at time \( t \) to the mass of MITC present at time zero, or \( M/M_0 \), because the mass and volume of soil in the columns was constant.

The time \( t \) was the number of days after the start of the experiment when it was assumed no MITC remained in the soil column, as stated in the first assumption above.
The percentage of applied MITC that was degraded over the time t was calculated as the percentage of applied MITC that had not been recovered as leaching loss, volatilization loss, or MITC extracted from soil. It was then assumed that the percentage of applied MITC that had not been degraded was still present in the soil column at time t, as stated in the third assumption above. Therefore, the ratio M/M₀ at time t was taken as the proportion of applied MITC that had not been degraded.

The degradation rate constant k was calculated for each treatment using the first-order rate equation, using the single value of M/M₀ at time t. The rate constant k was then converted to a degradation half-life.

For example, for one replicate of the MILR treatment in the soil water regime experiment the time t, when MITC leaching losses were no longer detected, was 65 days. The percentage of applied MITC that was degraded over this time period was 52.0%. Therefore, it was assumed 48.0% of applied MITC was not degraded, and therefore the ratio M/M₀ was 0.480. In this example k was calculated to be 0.01131, which is equivalent to a half-life of 61.3 days.

For the soil property experiment, estimated MITC half-lives were 23 ± 0, 7 ± 1, 5 ± 0, and 10 ± 3 days (mean ± 1 SE, n=2) for the Columbia, Lehman Subsurface, Lehman Surface, and Monroe soils, respectively. Estimated half-lives from the Monroe soil used in the soil water regime experiment were 54 ± 8 and 47 ± 1 days (mean ± 1 SE, n=2) for the MILR and LILR treatments, respectively.

These estimated half-lives fall generally within the range of MITC half-lives of 0.5 to 50 days reported by Smelt et al. (1989). However, Smelt et al. measured these half-lives at 15 °C compared to approximately 20 °C for this study.

MITC degradation rates have been reported to increase with increasing soil clay content (Smelt and Leistra 1974), soil organic matter content (Gerstl et al. 1977) and soil pH (Ashley et al. 1963). However, the proportion of MITC lost by degradation for the
four soils in the soil property experiment did not appear to follow any trends with respect to soil clay content, soil organic matter content, or soil pH.

The differences among estimated degradation rates for the four soils of the soil property experiment may be due to factors affecting microbial activity. The lower MITC half-life in the Lehman Surface soil compared to the Lehman Subsurface soil may be due to higher levels of microbial activity that would be expected in a surface soil. The management history of these soils, such as manure applications, cropping rotations, and pesticide applications is unknown, but probably had an important influence on their microbial status, and thus MITC degradation kinetics. Smelt et al. (1989) found soils frequently treated with metam-sodium had higher MITC degradation rates than never-treated soils, which they attributed to adaptation of the microbial population.

The generally higher MITC degradation rates for all soils in the soil property experiment compared to the soil water regime experiment may be due to the effects of differing storage times of the soils in an air dried state on microbial activity. All the soils used in the soil property experiment were stored air dry for approximately two weeks, whereas the soil used in the MILR and LILR treatments of the soil water regime experiment was stored air dry for approximately six months. Anderson (1987) showed that survival of microbial biomass in soil samples stored at 2.4% water content decreased with increasing storage time from 0 to 70 days.

The lower estimated MITC degradation half-lives for the Monroe soil in the soil property experiment than in the soil water regime experiment may also be due to the fact that the former had received a liquid manure application in the field before sampling. It is possible that the manure application to the Monroe soil used in the soil property experiment resulted in enhanced microbial activity compared to the non-manured Monroe soil used in the soil water regime experiment, thus increasing the MITC degradation rate in the former. This is plausible since Ashley et al. (1963) and Smelt et al. (1989) found microbial degradation was the dominant process in MITC breakdown in soil.
MITC degradation rates could differ significantly under field conditions compared to the soil columns because of differences in soil temperature and aeration. The laboratory air temperature, and therefore the temperature in the soil columns, was held at approximately 20 °C for all experiments. When metam-sodium is applied to raspberry fields in late August or early September in the Abbotsford Aquifer area temperatures should be similar to this, but will decrease significantly starting around late September. The long term monthly normal soil temperatures at Abbotsford for the 10 cm soil depth, estimated from climate information, are 17.9, 15.6, 11.9, and 7.3 °C for August, September, October, and November, respectively (Oulette et al. 1975). Rates of chemical and biological degradation of MITC would be expected to significantly decrease with decreasing soil temperature.

Soil aeration would likely be higher in the field than it was in the soil columns due to generally high moisture contents in the columns. The regular leaching of the columns and the very low evaporation rates from the soil column surfaces resulted in very high soil moisture contents and average air filled porosities of approximately 5 to 15%. This relatively poor aeration may have resulted in decreased aerobic microbial activity and decreased the extent of chemical oxidation reactions, possibly reducing MITC degradation rates as compared to a well aerated field soil.

The air drying of the soils used in the soil columns may have had some impact on the soil microbial status. Even short term drying of soil causes a significant reduction active microbial biomass (Anderson 1987); however, upon re-wetting a large increase in microbial metabolic activity and population is typically seen (Stevenson 1956). Stevenson (1956) reported that for most soils, this flush of microbial activity would decrease to a fairly constant level, similar to that before drying, within one to two weeks. In all experiments in this study, the soil columns were re-wet approximately one week before MITC injection. During this period microbial activity and population would have had a chance to recover to some extent from changes caused by air-drying.
The MITC degradation rates found in this study and those reported in the literature are fast relative to other pesticides, including other soil fumigants. The compound 1,2-dichloropropane (1,2-DCP) is much more persistent than MITC, with a hydrolytic half-life of 6 months to several years (Cohen et al. 1984), whereas the soil half-life of 1,3-DCP of 25 d at 15 °C (Siebering and Leistra 1979) is similar to the upper range of reported half-lives for MITC.

The rapid MITC degradation rates seen in the present study and other studies is not expected to substantially decrease the efficacy of soil fumigation with metam-sodium. Gerstl et al. (1977) concluded that their measured degradation half-lives of three to ten days were slow enough that the minimum effective MITC solution concentration would be maintained long enough for acceptable control of the target organisms. The authors reasoned that in the higher organic matter level soils, the higher degradation rates observed would be balanced by higher recommended metam-sodium application rates, thus maintaining sufficient control. When degradation rates are fast, efficacy will also be improved by reducing the time needed for uniform spreading of the MITC throughout the arable layer (Smelt et al. 1989). Uniform spreading will occur quickly with the rotovation method of metam-sodium application, and in friable soils with low moisture contents (Smelt et al. 1989).

5.2. ADSORPTION AND RETENTION

The quantity of MITC extracted from soil was negligible in all soils examined. Non-detectable or very small amounts of MITC were measured in the soil columns upon completion of both the soil water regime and soil property experiments. The only MITC soil concentrations above the quantification limit were found in the 21.5 to 30 cm depth, in soil columns from the LILR and Columbia soil type treatments. These were also the only
treatments that had detectable MITC leaching losses with the final leaching event of the

treatment.

The mass of MITC extracted from each of these soil column sections was converted
to an equivalent concentration of MITC in the pore water present in that soil column
section, and compared to the MITC concentration in the leachate of the final leaching event.
For the LILR soil columns, the calculated pore water MITC concentration was 707 ± 67 µg
L⁻¹ (mean ± 1 SE, n=2), very similar to the actual leachate concentration of 660 ± 142 µg
L⁻¹ (mean ± 1 SE, n=2). This suggests that a large proportion of the MITC extracted from
the LILR soil columns was not adsorbed to soil solids, but present in the soil solution. For
the Columbia soil columns the calculated MITC pore water concentration was 1053 ± 205
µg L⁻¹ (mean ± 1 SE, n=2), higher than the actual leachate concentration of 493 ± 182 µg
L⁻¹ (mean ± 1 SE, n=2) suggesting that a large proportion of the MITC extracted from
these columns may have been adsorbed to soil solids.

Although negligible amounts of MITC were extracted from the soil at the end of the
experiments, some MITC retention appeared to occur in several soils during the
experiments. Retention of MITC was apparent from the shifting of MITC breakthrough
curves to the right of the bromide breakthrough curves. The extent of MITC retention, as
indicated by the magnitude of the shift of the breakthrough curve peaks, was directly
correlated with the organic carbon content of the soils.

It is hypothesized that this retention of MITC compared to bromide was due to
reversible adsorption of MITC on soil colloid surfaces. The increasing extent of MITC
retention with increasing soil organic carbon content suggests that soil organic carbon may
be primarily responsible for this adsorption. In addition, increasing MITC adsorption with
increasing soil organic carbon content is consistent with the comparison of calculated MITC
pore water concentrations with actual column leachate MITC concentrations, described
above.
It is unlikely that the observed shifting of the MITC breakthrough curves to the right of the bromide breakthrough curves resulted from gas phase diffusion of MITC up the soil columns. First, the vertical movement of MITC by gas phase diffusion needed to cause this effect should have also resulted in significant spreading of the MITC breakthrough curves and more pronounced tails after the peaks compared to the bromide breakthrough curves. Second, the shift of the MITC breakthrough curves should have occurred in all four soils and increased with the magnitude of volatilization losses for the four soils. However, the Monroe soil, which had the highest volatilization losses, had no shift of its MITC breakthrough curve.

Negligible MITC retention in the Monroe soil was also seen in the soil water regime experiments. The MITC breakthrough curves for all three treatments peaked at approximately one pore volume, similar to the bromide breakthrough curve peak for the Monroe soil.

The extent of MITC retention seen in the soils examined was relatively small. Even with the greatest retention observed, the peak of the MITC breakthrough curve was eluted at approximately 0.45 pore volumes after the bromide peak.

Very low MITC adsorption in soil and MITC adsorption that is strongly related to soil organic carbon content has been reported in the literature. Smelt and Leistra (1974) and Gerstl et al. (1977) reported low MITC adsorption coefficients (K_{s/w}) for a wide range of soil types, with a maximum K_{s/w} of 0.57 mL g^{-1} for a soil with 65 % clay and 4 % organic carbon content. Gerstl et al. (1977) also reported K_{s/w} values increased with increasing soil organic carbon content from 0.012 mL g^{-1} for a soil with 0.45 % organic carbon to 1.8 mL g^{-1} for peat.

Gerstl et al. (1977) also noted increased MITC adsorption with increasing clay content in soils ranging from 3 to 75 % clay. In the present study no relationship between MITC retention and soil clay content was observed. However, the range of clay contents examined in this study is much narrower than the range examined by Gerstl et al. (1977).
MITC adsorption and retention behavior could be significantly different under field conditions compared to the soil columns used in this study because of differences in the rate of water infiltration and in soil structure. Differences in the rate of water infiltration could affect the extent of MITC adsorption equilibrium. For example, precipitation and therefore water infiltration rates in the field would likely be lower than used in the soil columns. Lower water flow rates could increase the extent of MITC retention by increasing contact time between soil solution and solids. However, this effect would depend on the rate at which MITC could achieve adsorption equilibrium in a given soil, which is unknown. Gerstl et al. (1977) found that the MITC soil adsorption coefficient for a particular soil, measured by retention in soil columns, decreased with increasing rate of water movement in the column.

An undisturbed field soil would likely have more macro-aggregation than the sieved soil samples used in the soil columns. With high rates of water infiltration, more preferential flow of water down macropores, cracks and channels would therefore be expected in the field soil. As a result, much of the soil surface area may be bypassed by the flowing water, reducing the possibility for MITC adsorption.

The degree of MITC retention seen in the present study would be expected to have minimal impact on MITC leaching behavior. Retention would decrease MITC leaching potential if it delayed MITC movement through the root zone sufficiently to significantly increase degradation. However, the extent of retention seen here, even for the highest organic carbon content soil, would not have a significant impact on MITC movement if there was sufficient water movement through the soil profile. In soils with organic carbon contents much higher than those used in these experiments, such as an organic soil, retention may have a significant impact on MITC leaching behavior.

The other soil fumigants detected in the Abbotsford Aquifer, 1,2-DCP and 1,3-DCP have lower reported adsorption coefficients than MITC. $K_{om}$ values of 14 to 15 mL g$^{-1}$ and 27 mL g$^{-1}$ have been reported for 1,3-DCP (Leistra 1970) and 1,2-DCP (Cohen et
al. 1984), respectively, compared to 2.7 mL g\(^{-1}\) for MITC (Smelt and Leistra 1974). This suggests that MITC has sufficient mobility in soil to be transported to groundwater in the Abbotsford Aquifer. However, other factors, especially persistence, will have a significant influence on the actual potential for MITC to contaminate groundwater in the aquifer.

The low retention of MITC seen in the present and in other studies will have a positive effect on the efficacy of soil fumigation with metam-sodium. Gerstl et al. (1977) noted that the low adsorption of MITC means a greater proportion of MITC will remain in the soil liquid and gas phases, where it is effective against the target organisms. In addition, MITC in the liquid and gas phases will quickly spread throughout the treated soil layer, resulting in better control. However, low adsorption also means rainfall shortly after application can leach much of the MITC to lower layers, reducing its effectiveness near the soil surface (van Berkum and Hoestra 1979).

5.3. VOLATILIZATION

5.3.1. Processes and Controlling Factors

The results of this study indicate that MITC volatilization losses from the soil surface are primarily controlled by the rate of gas phase diffusion of MITC from the injection plane to the soil surface. Volatilization losses were therefore strongly dependent on the factors that affect gas phase diffusion of MITC through the soil, namely the MITC concentration gradient, and the abundance and nature of air-filled soil pores. The effects of these factors are evident in the inhibition of volatilization losses by leaching seen in both the soil water regime and soil property experiments, and in the differences in volatilization losses among soil types in the soil property experiment.

In the soil water regime experiment, leaching of the soil columns inhibited volatilization loss of MITC. The treatments with frequent leaching, the HILR and MILR,
had significantly lower total volatilization fluxes than the LILR, which was not leached for the first 35 days after MITC injection. In addition, the maximum daily volatilization flux was approximately two orders of magnitude higher under the LILR than the other two leaching regimes.

Inhibition of volatilization loss by a single leaching event was seen in both the soil water regime and the soil property experiments. Daily volatilization flux decreased immediately following the first leaching event in the LILR and in all four soil types in the soil property experiment. In addition, step-wise decreases in volatilization flux were observed with the first four leaching events in the MILR.

There are several mechanisms by which leaching can inhibit volatilization loss of MITC from the surface of the soil columns. First, the addition of water can create a saturated layer at the soil surface, filling most air filled pores with water. MITC would thus be unable to move through this layer by gas phase diffusion. Second, water infiltrating into the soil column would displace soil water containing dissolved MITC further down into the soil column, and away from the soil surface. Third, because the infiltrating water would be free of MITC, it would pick up MITC adsorbed on soil colloids or MITC present as vapor in air filled pores by partitioning, and subsequently transport this MITC away from the surface.

These mechanisms can offer a possible explanation for the observed "rebound" in volatilization fluxes in the four day period between the second and third leaching events in the MILR, and between the first and second leaching events in the Columbia soil. Following the water application, the saturated soil layer at the surface drained, opening some air filled pores and again allowing gas phase MITC diffusion. Over the four day period between leaching events, MITC would again begin to diffuse away from the high-concentration injection plane area, toward the soil surface. Also, it is possible that during this period MITC trapped in pockets of immobile water near the soil surface could diffuse out of these areas, vaporize into air filled pores, and diffuse to the soil surface.
Nevertheless, after a number of leaching events, the water infiltration was sufficient to remove most MITC from near the soil surface to lower regions of the soil column, reducing volatilization to non-detectable levels. This occurred after four leaching events in both the HILR and MILR treatments of the soil water regime experiment, and after two or three leaching events for all four soils examined in the soil property experiment.

In the LILR, volatilization flux did not decrease to below detection limits even after all 18 leaching events of the treatment, although it was only slightly above the detection limit for the last several days. Over the first 35 days of this treatment, when no leaching occurred, the LILR had the highest daily volatilization loss measured in any of the experiments. The high volatilization flux indicates significant MITC diffusion toward the soil surface had occurred, and relatively high MITC concentrations were present near the soil surface in all soil phases. It is hypothesized that the infiltrating water did not completely remove MITC from near the soil surface in the LILR, as occurred in the other treatments, because the MITC concentrations were much higher compared to these other treatments. For example, MITC could have been present at high concentrations in pockets of immobile water near the soil surface. Over the duration of the leaching events this MITC would slowly diffuse out, supplying MITC for volatilization losses.

In the soil property experiment, the decrease in volatilization loss from the Columbia soil following the first leaching event was not as large as that for the other three soil types. It is hypothesized that this was a result of retention of MITC on the soil solid surfaces or in pockets of immobile water in the Columbia soil. The Columbia soil had the strongest retention of MITC compared to the bromide tracer for all the soils examined, and may have had a significant amount of immobile water, as suggested by the large tail after the peak of the bromide breakthrough curve. Retention of MITC on the soil solids or in immobile water near the surface of the soil column would have prevented its movement downward with the infiltrating water, keeping it at the soil surface where it could volatilize thereafter.
Differences in volatilization losses from the four soils examined in the soil property experiment can also be related to differences in factors affecting gas phase transport of MITC, in particular, the abundance and size of air filled pores.

The peak daily volatilization flux for the four soil types was highly correlated to the percent volume of air filled pores between the MITC injection plane and the soil column surface, indicating the importance of the total amount of air filled pores. In addition, the volatilization loss appeared to increase with increasing size of the air filled pores, as indicated by the inverse relationships of both peak volatilization flux and total volatilization loss with percent clay content. With increasing clay content in a repacked soil column, the dominant size of air filled pores would be expected to decrease.

Transport of MITC by gas phase diffusion occurs through continuous air filled pore spaces. The greater the number and the larger the size of air filled pores, the larger the cross sectional area available for diffusion. Larger pores will also be more likely to be interconnected, creating extended pathways for MITC diffusion.

The large variability in volatilization fluxes between the duplicate MILR soil columns can be explained by differences in air filled porosity as well. The soil columns with the higher and lower volatilization fluxes had calculated air filled porosities from the 0 to 10 cm depth of 12.1 % and 9.1 %, respectively.

The large differences in volatilization flux seen within the Monroe soil between the initial, no leaching stages of both the LILR and the Monroe soil in the soil property experiment, however, cannot be explained by differences in total air filled porosity. The LILR had peak volatilization fluxes over four times as high as for the Monroe soil type, despite the LILR actually having slightly higher measured bulk density and slightly lower air filled porosity from the 0 to 10 cm depth compared to the Monroe soil type. Although the degradation rate was much higher in the Monroe soil type columns, large differences in volatilization were seen only several days after injection, when differences in degradation rates would have not yet had a significant effect.
However, there was one notable difference between the soil columns of the LILR and Monroe soil type treatments. The hydraulic conductivity at the surface of the Monroe soil type columns was much lower than for the LILR columns, as indicated by the much slower water infiltration rate visually observed in the Monroe soil type columns. The packing of the soil columns in small increments near the soil surface could have created a more highly compacted layer or layers near the surface of the Monroe soil type columns. Such a compacted layer would have less porosity and smaller pore sizes, which would lower hydraulic conductivity and thus impede water infiltration. The air filled porosity in such a layer would also be very low, impeding the gas phase transport of MITC.

The dependence of volatilization losses of soil incorporated pesticides, including soil fumigants, on transport to the soil surface by gas phase diffusion has been well documented. Taylor and Spencer (1990) stated that the "effective diffusion coefficient" of a particular pesticide through a particular soil is sensitive to changes in soil bulk density and water content, both of which would affect air filled porosity. Farmer et al. (1973) found decreasing volatilization losses of the pesticide dieldrin with increasing soil bulk density, which they attributed to decreasing air filled porosity. In a model describing volatilization of soil applied pesticides, Jury et al. (1983) calculate vapor phase diffusion as a function of a soil-gas diffusion coefficient that depends on a soil tortuosity factor determined by soil volumetric air content and total porosity.

The sensitivity of MITC volatilization and gas phase transport to soil bulk density and water content has important implications for the efficacy of soil fumigation with metam-sodium. Good efficacy will require a uniform distribution of MITC throughout the treated soil volume. With the shank injection method of application, uniform distribution will occur only where the soil water content is low enough to allow sufficient gas phase diffusion of MITC. Distribution by gas phase diffusion will be less crucial when the irrigation or rotovation application methods are used. Losses of MITC to the atmosphere by volatilization will also reduce efficacy, regardless of the application method, by reducing
the MITC concentration in the soil. Thus, the treatment of the soil surface after metam-
sodium injection by compaction or irrigation will be crucial for minimizing volatilization
losses. Surface treatment will be especially important in coarse textured and well
aggregated soils where there is an enhanced potential for volatilization losses.

5.3.2. Magnitudes of Volatilization Losses

A wide range of magnitudes of total volatilization losses were found in this study.
Under conditions most favorable for MITC gas phase diffusion to the soil surface, such as
in the LILR where the soil was coarse textured and there was no leaching, a substantial
proportion (30%) of applied MITC was lost by volatilization. Under conditions with more
frequent leaching or under finer textured soils with lower air filled porosity, total
volatilization losses were much smaller, ranging from 3 to 0.03% of applied MITC. The
peak daily volatilization fluxes measured in this study vary in a manner similar to the total
volatilization losses, with the highest daily volatilization flux measured in the LILR.

There have been no reports of actual measurements of total MITC volatilization
losses from soils, but there have been several predictions generated by simulation models.
Van den Berg (1993) predicted a 10% total volatilization loss of MITC in three weeks from
a field treated with metam-sodium, while Leistra and Crum (1990) computed MITC losses
of 50 to 64% from a greenhouse soil over two weeks following application of metam-
sodium. However, it is difficult to directly compare any measurements of MITC
volatilization loss because of the influence of mostly unknown factors such as soil bulk
density and water content, and MITC degradation rates. The sensitivity of volatilization
losses to these factors is illustrated by the wide range of volatilization losses measured
within this study.

Several studies have measured or computed MITC concentrations in air above
treated fields after fumigation with metam-sodium. However, it is difficult to compare
MITC volatilization flux values from this study to reported MITC air concentrations. This is because it is not possible to convert the flux values from the present study to equivalent air concentrations above a hypothetical treated field. In order to do this the rate of MITC dispersion into the air above the treated field would be required, and this dispersion rate would depend on meteorological factors such as wind speed.

Van den Berg (1993), however, used a model to compute peak volatilization fluxes per m$^2$ surface area from two fields treated with metam-sodium. MITC fluxes were 1.37 $\mu$g m$^{-2}$ s$^{-1}$ at 3.4 days after treatment and 0.96 $\mu$g m$^{-2}$ s$^{-1}$ at 5.8 days after treatment for soils with 14 and 6 % organic matter content, respectively; the soils had similar clay contents of approximately 2.5 %. The largest daily volatilization flux in this study was 2563 $\mu$g day$^{-1}$ six days after injection under the LILR; for the area of the 10 cm diameter soil column, this corresponds to 3.78 $\mu$g m$^{-2}$ s$^{-1}$ averaged over that day. The peak daily volatilization fluxes calculated similarly for the Monroe, Columbia, Lehman Surface, and Lehman Subsurface soils are 0.81, 0.47, 0.25, and 0.22 $\mu$g m$^{-2}$ s$^{-1}$, respectively. The Monroe soil, which was the closest in texture to the soils examined by Van den Berg (1993) also had the most similar volatilization fluxes, considering both the LILR and Monroe soil type results. Overall, maximum volatilization fluxes measured in this study correspond fairly well to those predicted by Van den Berg (1993) considering differences in experimental conditions.

Van den Berg (1993) also predicted MITC air concentrations around these treated fields given the calculated volatilization fluxes. MITC air concentrations peaked in both fields five days after treatment at 14.0 and 3.9 $\mu$g m$^{-3}$. Given the similarity between peak MITC flux ($\mu$g m$^{-2}$ s$^{-1}$) values used by Van den Berg in the model and those found in this study, it would be expected that similar air concentrations would be computed for the volatilization fluxes found in this study, holding all other model input parameters constant.

These air concentrations can be compared to emergency action levels for MITC concentrations in air developed by the California Environmental Protection Agency.
(Alexeeff et al. 1994; Jackson and Book 1992). They defined three critical MITC air concentration levels for one hour exposure above which certain adverse acute human health effects would be expected. Symptoms producing discomfort are possible at concentrations above 1.5 \( \mu g \ m^{-3} \), those producing disability at concentrations above 120 \( \mu g \ m^{-3} \), and those producing death or life threatening effects at concentrations above 450 \( \mu g \ m^{-3} \). Thus, the MITC air concentrations above fields treated with metam-sodium predicted by Van den Berg (1993) are high enough to cause possible discomfort with greater than one hour exposure. The primary symptom at this exposure level would be eye irritation or tearing (Jackson and Book 1992).

MITC volatilization behavior could differ significantly under field application of metam-sodium by injection compared to the soil columns because of several factors. First, the depth of MITC injection in the field may be 5 to 10 cm deeper than the 10 cm depth used in the soil columns.

Second, the incremental packing of the soil columns with a plunger may have created thin compacted soil layers between the MITC injection plane and the soil surface. These layers may have interfered with MITC gas phase diffusion. A field soil would not have these compacted layers throughout, but the soil surface would be compacted after application to inhibit volatilization losses.

Third, significantly more drying of the soil surface by evaporation would be expected in the field than in the columns. The air flow rate through the volatilization chambers was not fast enough to cause significant evaporation losses. In the field, water flowing upward in response to evaporation at the soil surface could transport MITC along with it to the surface, thus increasing volatilization losses (Spencer et al. 1973). Drying of the soil surface would also increase the air filled pore space, facilitating MITC diffusion through that soil layer. On the other hand, adsorption of MITC may be greatly enhanced on the dry soil at the surface, inhibiting volatilization loss. Adsorption of volatile organic compounds on soils has been shown to increase by several orders of magnitude at water
contents equivalent to less than one to four molecular layers of water on adsorption surfaces (Spencer et al. 1973; Taylor and Spencer 1990; Petersen et al. 1994); this is attributed to reduced competition with water molecules for adsorption sites.

The wind speed over the soil surface would likely be much higher in the field than for the soil columns, considering the low rate of air flow through the volatilization chambers. However, these differences in air flow rate over the soil surface may not have had a large impact on volatilization fluxes. Jury et al. (1984) found that for very volatile soil incorporated pesticides, such as soil fumigants, the volatilization flux would be limited only by transport from within the soil to the soil surface, and would not be limited by diffusion through the boundary layer above the soil surface. Furthermore, after reviewing a number of field experiments measuring volatilization loss of soil incorporated pesticides, Taylor and Spencer (1990) concluded that soil conditions were the dominant control on volatilization rates and that meteorological variables such as wind speed are of secondary importance.

Under field application of metam-sodium by methods other than injection, such as rotovation or irrigation, the magnitudes, temporal patterns, and factors controlling volatilization fluxes would be expected to be much different than seen in this study.

The potential for MITC to be lost by volatilization from the soil surface after application is generally considered less than that for the soil fumigants 1,2-DCP and 1,3-DCP (e.g., Smelt and Leistra 1974). This assumption is made primarily on the basis of MITC's lower vapor pressure and higher water solubility, although there have been no experimental comparisons.

The potential for MITC to contaminate groundwater supplies will decrease with increasing volatilization losses. MITC released from the soil into the atmosphere is no longer available for leaching to groundwater. Extremely high volatilization losses, however, may reduce the efficacy of the soil fumigation, and the resulting high concentrations of MITC in air may pose a health concern. Ideally, MITC volatilization
losses should be minimized immediately after treatment to improve efficacy and protect the applicator's safety, but then enhanced at a later time to remove MITC residues from the soil. Removal of MITC residues from the soil several weeks after treatment by enhancing volatilization with repeated cultivation is often done to reduce the potential for phytotoxic effects on the next crop (van Berkum and Hoestra 1979), and will also reduce leaching potential. However, the human health and environmental effects of releasing MITC into the atmosphere also need to be considered.

5.4. LEACHING

5.4.1. Factors Affecting Shape of MITC Breakthrough Curves

The shape of the MITC breakthrough curves were determined primarily by the soil physical properties affecting water movement through the soil columns. Soil texture and structure had important effects on the amount of dispersion of infiltrating water and the amount of "immobile" water in the soil columns. In some cases, diffusion of MITC in gas and liquid phases also affected the shape of the breakthrough curves.

The HILR breakthrough curve peaked at one pore volume of leachate, indicating MITC was transported along with infiltrating water without significant retention. The slight tail after the peak was most likely due to MITC in water in smaller soil pores moving at a slower rate than the majority of the infiltrating water, i.e., dispersion, or MITC in small pockets of "immobile" water that were not displaced by infiltrating water. As MITC in surrounding "mobile" water was leached away, the MITC in these pockets would slowly diffuse back out into the mobile water, contributing to the tail seen in the breakthrough curve. A similar tail was seen in the bromide breakthrough curve for the Monroe soil type, indicating the tail was indeed caused by dispersion and/or immobile water and not by MITC retention on soil colloids.
The MILR breakthrough curve differed from the HILR in having a peak that was slightly more broad and diffuse, and in having a tail after the peak that was slightly larger. It is hypothesized that the more diffuse peak resulted from increased vertical spreading of MITC by gas and/or liquid phase diffusion over the much longer duration of the MILR treatment compared to the HILR treatment. The longer duration of the MILR treatment also provided more opportunity for MITC diffusion into pockets of immobile water.

The bromide breakthrough curve for the Monroe soil type was very similar in shape to the MILR breakthrough curve. The leaching events for both of these treatments took place over an identical time period, with one leaching event every fourth day. This indicates the bromide and MITC underwent the processes of vertical spreading by diffusion and of diffusion into pockets of immobile water to the same extent. The vertical spreading of MITC must have been primarily liquid phase diffusion since the bromide was spread to a similar extent, and no gas phase transport of bromide can occur. The similar MITC and bromide breakthrough curves also support the hypothesis that the tails after the peaks of the MITC breakthrough curves in these treatments were not due to retention of MITC on soil colloids.

The LILR breakthrough curve was in turn more broad and diffuse and had a larger tail after the peak than the MILR breakthrough curve. The peak was spread sufficiently that a significant amount of MITC was leached during the first leaching event of the LILR, compared to the HILR and MILR where leaching loss was delayed until the second leaching event, and then occurred in much smaller amounts. Because the duration of the LILR treatment was shorter than for the MILR, the increased breadth of the peak cannot be attributed to greater vertical spreading of MITC by liquid phase diffusion over a longer time period. It is hypothesized that the broad MITC breakthrough curve was the result of significant vertical spreading of MITC by gas phase diffusion over the 34 day period before the first leaching event. This is supported by the very high MITC volatilization fluxes seen in this treatment; high volatilization fluxes indicate rapid transport of MITC by gas phase
diffusion from the injection plane within the soil column to the soil surface. This rapid diffusion of MITC would have occurred both upward and downward from the injection plane, vertically spreading the MITC and resulting in the broad breakthrough curve.

The extended tail after the peak on the LILR breakthrough curve can also be attributed to redistribution of MITC by gas diffusion. Significant quantities of MITC diffused above the injection plane before the first leaching event. Thus, larger volumes of infiltrating water were required to transport this MITC to the bottom of the soil column, resulting in a larger right hand tail on the breakthrough curve than due to the effects of dispersion and immobile water alone.

The organic carbon contents of the soils in the soil property experiment had an important influence on the timing of the peaks of the bromide and MITC breakthrough curves. The decreasing pore volumes of leachate at the bromide breakthrough curve peaks with increasing soil organic carbon content can be attributed to the effects of soil organic carbon on soil structure. Increasing soil organic carbon content would be expected to increase the extent of soil aggregation, also increasing the relative proportion of larger pores within each soil. Water would have flowed preferentially down the larger pores, resulting in the bromide breakthrough curve peaks at less than one pore volume of leachate. Thus, increasing soil organic carbon content lead indirectly to increasing preferential water flow, and therefore bromide breakthrough curve peaks at decreasing pore volumes.

With the MITC breakthrough curves, however, peaks occurred at increasing pore volumes of leachate with increasing soil organic carbon content. This was a result of the increasing retention of MITC breakthrough curve peaks compared to bromide peaks, with increasing soil organic carbon content.

The MITC breakthrough curve for the Columbia soil was the most broad and diffuse and had the largest tail after the peak for the four soil types. The bromide breakthrough curve for the Columbia soil has a similar broad shape and large tail after the peak, indicating the shape of both the MITC and the bromide peaks were due to the effects
of soil structure on dispersion and immobile water. The broad shape of the Columbia breakthrough curves compared to the other soil types suggests the Columbia soil had the widest range of pore sizes, likely due to aggregation associated with the high soil organic carbon content. The peak of the bromide breakthrough curve before one pore volume of leachate and the early detection of bromide in leachate seen for the Columbia soil indicates bromide transport by preferential flow, which is also consistent with a wide pore size distribution. Furthermore, the large tail after the peak suggests a large proportion of the solute was retained in small pores or immobile water. However, the tail on the MITC breakthrough curve was slightly more pronounced than for the bromide. It is hypothesized that this was due to the slight retention of MITC on the Columbia soil, which would have retarded MITC movement with infiltrating water, causing it to be eluted from the column after more pore volumes of leachate. Retention of MITC on the Columbia soil was illustrated by the shifting of the entire MITC breakthrough curve to the right compared to the bromide breakthrough curve.

The Monroe and Lehman Surface soil MITC breakthrough curves were both very sharp and narrow. This resulted from the majority of MITC leaching loss from each soil occurring over only two to three leaching events. In the Monroe soil, the MITC breakthrough curve peak occurred at a similar pore volume as the bromide breakthrough curve peak, indicating no retention of MITC compared to bromide, whereas in the Lehman Surface soil, the MITC peak was approximately 0.3 pore volumes after the bromide peak, indicating some retention of MITC compared to bromide.

For the Lehman Subsurface soil, the MITC breakthrough curve was very similar in shape to the bromide breakthrough curve. This indicates the movement of both compounds was controlled by the same processes of mass flow and dispersion of infiltrating water. The MITC breakthrough curve peak was shifted slightly to the right of the bromide peak, indicating some retardation of MITC movement by retention to soil solids.
The bromide breakthrough curves for the Lehman Surface and Subsurface soils were very similar in shape, indicating similar soil structure and pore size distribution in these soils. For these two soils the MITC breakthrough curves also peaked at a similar pore volume, slightly after the bromide peaks, indicating a similar extent of MITC retention. The shape of the MITC breakthrough curves differed, however, in that the Lehman Subsurface peak was much more broad than the Lehman Surface peak. This difference is due to MITC leaching losses that occurred over a much larger number of leaching events in the Subsurface soil, as a result of its slightly lower MITC degradation rate compared to the Surface soil.

Overall, MITC leaching behavior was determined primarily by the characteristics of water movement through the soil. The shape of the MITC breakthrough curves appeared to be most affected by the processes of MITC mass flow, dispersion, and partitioning into pockets of immobile soil water, which were dependent on soil structure and the intensity of leaching. Retardation of MITC movement by retention on soil solids was seen to have little or no effect on MITC transport.

It was also seen that MITC gas phase transport down the soil columns could result in MITC leaching losses with relatively small amounts of water infiltration. Under soil conditions favorable for gas phase diffusion of MITC, significant downward movement of MITC was observed over a time period of several weeks. Thus, under such conditions in the field, MITC could potentially be leached out of the soil root zone with much smaller amounts of water infiltration than would be required for leaching from the soil surface.

5.4.2. Magnitudes of Leaching Losses

The magnitude of MITC leaching losses in all experiments was primarily determined by an interaction between the rate of water movement through the soil columns, which was controlled by the intensity of leaching, and the rate at which MITC was
removed from the soil columns by volatilization and degradation processes. For example, with a given rate of MITC removal by volatilization and degradation, increased intensity of leaching would increase leaching losses because MITC would be leached out of the soil column at a greater rate, thereby leaving less MITC available for removal by volatilization and degradation processes. In contrast, lower intensity of leaching would decrease leaching losses by allowing more time for MITC to be removed by volatilization and degradation processes, thus decreasing the amount of MITC available for leaching.

The three treatments of the soil water regime experiment illustrate these effects. Under the HILR, large leaching losses occurred because of the intense leaching regime. The majority of the applied MITC was leached out of the soil columns before it had time to degrade. The frequent leaching events also inhibited volatilization losses of MITC, leaving more MITC available for leaching.

Under the MILR the intensity of leaching was much lower than in the HILR. The less frequent leaching events afforded the MITC more time for degradation before reaching the bottom on the soil columns, decreasing the total leaching losses. Leaching events were sufficiently frequent, however, to suppress volatilization losses to a large extent.

For the LILR, the 34 days before the first leaching event allowed much of the applied MITC to be removed by volatilization and degradation processes. Although the leaching was intense when it commenced, much of the MITC had already been removed from the columns, resulting in the lowest total leaching losses for the three leaching regimes.

In the soil property experiment, total leaching losses were low for all four soils examined. Over the first 14 days of the experiment, when no leaching occurred, the volatilization losses of MITC were low, 3% or less of MITC applied for all soil types. Only relatively small leaching losses were seen when leaching commenced, indicating a large proportion of applied MITC had already been degraded. The MITC could have been degraded over the 14 days before the start of leaching or over the time required to transport
it to the bottom of the soil column. Thus, degradation was the dominant process controlling MITC leaching behavior in all four soils examined in this experiment.

The total leaching loss was significantly larger in the Columbia soil compared to the other three soils. More MITC was available for leaching in the Columbia soil than in the other soil types, indicating a lower degradation rate.

Leaching losses were much lower from the Monroe soil in the soil property experiment than from the Monroe soil in the soil water regime experiments, even when differences in leaching regime are taken into consideration. For example, in the LILR, 15 % of applied MITC was lost by leaching which started on day 35, even though 30 % of applied MITC had already been lost by volatilization over the first 34 days of the experiment. In the Monroe soil type treatment, even though there was only a 3 % volatilization loss of MITC over the first 14 days of the experiment, the subsequent leaching produced an average total leaching loss of only 0.072 % of applied MITC. This indicates much higher MITC degradation rates in the Monroe soil used in the soil property experiment.

The results from the soil property experiment showed that the magnitudes of MITC leaching losses were not related to soil clay or organic carbon contents. An inverse relationship between pesticide leaching potential and soil clay and organic carbon content is often expected (e.g., Nicholls 1988), because of increased pesticide retention in the soil root zone with increases in clay and organic carbon content. However, this effect was not observed here because MITC exhibited insignificant retention on all soils examined.

Overall, from the results presented in this study it is apparent that the potential for MITC to leach from the soil root zone will depend on the rates of losses of MITC by volatilization and degradation processes, and the frequency and timing of leaching relative to application. These effects were also demonstrated by Oki and Giambelluca (1989) for the soil fumigants DBCP and EDB. They found groundwater recharge events during or shortly after fumigant application greatly increased the amount of fumigant leached from the
surface layer of soil and thus increased the potential for groundwater contamination. The timing of recharge was important because it affected the length of time the fumigants remained near the soil surface, where they could undergo degradation, volatilization, and adsorption processes.

There will be significant differences in total MITC leaching loss and the shape of MITC breakthrough curves under field conditions compared to the soil columns. Total leaching losses will be affected by possible differences in degradation, adsorption, and volatilization between the field and the columns that have been discussed in previous sections.

The shape of the MITC breakthrough curves will be affected by differences in soil structure and rates of water infiltration between the soil columns and a field situation. Wild and Mazaheri (1980) compared chloride movement in repacked soil columns and undisturbed field soils; their results can be applied to the present comparison. They found the wider pore size distribution in the field soil resulted in greater spread of the breakthrough curves compared to the disturbed cores. Under higher rates of water flow such as intense rainfall, water would preferentially flow down the larger channels of the field soil, shifting the breakthrough curve peak to the left compared to the disturbed soil. However, under slow rates of water flow such as light or intermittent rainfall, the breakthrough curve peak was shifted further right for the field soil. The authors attributed this shift to increased diffusion of chloride into immobile water which was then bypassed by subsequent rainfall.

Knowledge of the factors affecting MITC leaching losses can be used to predict the relative potential for groundwater contamination with MITC under various weather and soil conditions. Generally, the earlier in the fall the fumigation is done, the lower will be the groundwater contamination risk. Higher soil temperatures earlier in the fall should result in higher MITC degradation rates. Earlier application will also allow a longer time period for
degradation and volatilization losses to occur before the high rainfall season that typically starts in October or November.

A rainfall event shortly after fumigation will increase the potential for groundwater contamination with MITC. The rainfall will inhibit volatilization losses of MITC, leaving more MITC within the soil available for leaching. MITC will also be transported with the infiltrating rainfall down the soil profile where MITC degradation rates will presumably be lower than near the surface because of lower temperature and microbial activity. A small rainfall event that just wets the soil surface will have a minimal impact on leaching potential because it will only temporarily decrease MITC volatilization fluxes and it will not transport MITC down the soil profile. However, a more substantial rainfall event that results in a large amount of water infiltration will significantly increase the potential for MITC to migrate below the root zone.

In the field, soil texture and structure would affect the rate of water movement through the soil profile, which would affect the rate of MITC transport. Coarse textured soils would therefore have a higher MITC leaching potential than finer textured soils. However, higher volatilization losses could also be expected from coarse textured soils, which could decrease the leaching potential despite the effects of more rapid water movement.

MITC degradation rates are probably the most important process influencing its leaching potential. Quite a wide range of degradation rates were observed in this study, but the factors determining the rates are unclear. It appears that factors affecting soil microbial activity, such as soil management history, may be important.

Further research is needed to measure the rates of, and to determine factors controlling, the degradation of MITC in the soils above the Abbotsford Aquifer. This information would greatly improve the ability to predict the risk of MITC contamination to the Abbotsford Aquifer from soil fumigation with metam-sodium.
6. REFERENCES


Kleindienst, H. Fumigant Applicator. Coast Agri Ltd., Abbotsford, BC.


Szeto, S.Y. Research Scientist, Pesticide Chemistry, Pacific Agriculture Research Center, Agriculture and Agri-Food Canada, Vancouver, BC.


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