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FATE OF THE LAMPRICIDE
3-TRIFUOROMETHYL-4-NITROPHENOL (TFM)
IN THE ENVIRONMENT

presented by

MAQBOOL HUSSAIN

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Major professor

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By

MAQBOOL HUSSAIN

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ABSTRACT

FATE OF THE LAMPRICIDE 3-TRIFUOROMETHYL-4-NITROPHENOL (TFM) IN THE ENVIRONMENT

By

MAQBOOL HUSSAIN

The fate of 3-trifluoromethyl-4-nitrophenol (TFM), a lampricide used in Great Lakes basin, has been modeled based on its sorption, degradation and volatilization characteristics. This study consisted of three parts: sorption isotherm studies (Freundlich model), determination of biodegradation rate constants (microcosms studies), and estimation of distribution and persistence of TFM in the environment using fugacity modeling. Sorption behavior of all soils and sediments was slightly non-linear. K_d values range from 0.05 to 11.42. Soil/sediment-water partitioning of TFM was found to be dependent upon pH and organic content of soil (OC). K_d increased with increases in OC and decreased with rise of pH. Cation exchange capacity did not appear to play significant role in TFM distribution among soil, sediments and water. Consistent K_{oc} values (calculated using K_d) indicate that hydrophobic properties of TFM cause its partitioning between two phases. TFM was biotransformed only under anaerobic conditions with rate constant 0.00091 h^{-1}. More than 90 % of TFM remains in water. Its persistence in sediment-water system is 13-14 days.

DEDICATED TO

My father (a poor farmer) who did his best to make his issues educated, my mother (an ill-literate woman) who sacrificed her sweet sleep to keep me up to school routine, my brothers and sisters who always prayed for my success, my son Tabish who is away from me since his birth because of my studies, and my sincere friends who were friends in need.

ACKNOWLEDGEMENTS

The word "Thanks" is just a token to acknowledge the sacrifice of the poor people of Pakistan. I salute their greatness, which they showed by supporting me financially to complete a MS degree. This research work was carried out towards partial fulfillment of the requirements for the same.

Dr. Thomas C. Voice took a keen interest in my research work. I owe special thanks to him for his invaluable guidance and timely advice throughout this study.

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Chapter 1

INTRODUCTION

Sea lamprey are native to the Atlantic Ocean, not the Great Lakes. They moved into the Great Lakes from Lake Ontario through the Welland Canal in 1829 and the Trent Waterway in 1918. Lamprey predation had a great impact on the commercial and sports fisheries in Great Lakes waters. They were a major cause of the collapse of lake trout, whitefish, and chub populations during 1940s and 1950s (19).

Mechanical and electrical methods employed to control sea Lamprey proved to be uneconomical and inefficient. Research was conducted to find a direct and rapid method for control of this nuisance species. It was decided to develop chemicals acutely toxic to larval lamprey at extremely low concentration and non-toxic, at the same concentration, to other fish species. During the 1950s, under the direction of the U.S. Fish and Wildlife Service, scientists tested almost 6,000 compounds to identify one to which sea lamprey were especially sensitive. In 1958, it was discovered that TFM (3-trifluoromethyl-4-nitrophenol) was remarkably effective in controlling sea lamprey without significantly impacting other species (28). In the same year, TFM was selected for lamprey control on the basis of its physical-chemical properties, ease of handling in the field, effectiveness at low concentrations, and cost.

Since its discovery as an effective sea lamprey control tool, the Great Lakes Fishery Commission has sanctioned the use of TFM to suppress sea lamprey populations in the Great Lakes; it is now the primary means by which sea lamprey are controlled. About 250 Great Lakes tributaries are treated at regular interval with the lampricide. The concentration of TFM applied to each stream is determined from bioassays to maximize mortality of larval lamprey and minimize mortality of non-target organisms. Prior to lampricide treatment, extensive research is done to understand the chemical and physical condition of the stream. The stream's rate of flow, temperature, pH, and alkalinity, for instance, all influence the effectiveness of TFM. Typical treatment takes 48 to 72 hours to complete, but could take as long as a week, depending on the size of river (19).

Exhaustive laboratory tests over more than 40 years show that at the dose needed to eliminate sea lamprey, TFM is nontoxic or has minimal effects on aquatic plants, other fish, and wildlife. The impact on non-target species can be reduced by closely controlling the concentration of TFM applied.

This compound is registered as a lampricide by the U.S. Environmental Protection Agency and Agriculture Canada and has met or surpassed all criteria for application in Great Lakes streams. Although TFM has proven to be an effective control measure, there are several reasons including high cost, lack of effectiveness in large rivers and open water, and concern with the use of chemical pesticides, to search for alternatives. Average annual use of TFM during 1980-89 was 52,000 Kg and for 1990-95 were 42,000. One of the GLFC's stated goals is to reduce the amount of TFM used by 50%, and it is currently funding research on non-chemical control measures (28).

The contamination of natural waters by anthropogenic chemicals has become a major issue in environmental protection. An organic chemical that is introduced into a body of water is subjected to various transport, mixing, mass-transfer, and reaction processes. These processes will result in chemical moving to locations and phases within an ecosystem other than those associated with its release, and being transformed to other chemical species. Only by completely understanding and quantifying those processes, we can assess the environmental impacts of chemical use and release.

TFM is of environmental concern because it is used in large quantities yearly. Transport and transformation mechanisms of TFM determine its long-term effects on the environment and life. It is of sufficient value to society that its continued use is justified, but only under the conditions in which we fully understand its fate and effects.

Chapter 2

BACKGROUND

2.1 Chemical and Physical Properties

TFM is yellow crystalline solid at room temperature. It has melting point of 76-79°C, molecular weight of 207, and ionization constant of 4.4×10^{-7}. Its solubility in water is 0.498 gm/100 gm H_2O at 24.5°C. Aqueous solutions of TFM are acidic ($pK_a = 6.07 \pm 0.03$) and form phenolate salts in the presence of alkalis. Phenolates of the alkali metals are weak bases, the free phenol is colorless/light yellow in acid solution but deep yellow in base solution. (24). It is almost completely ionized at pH range of natural waters (2).

2.2 Environmental Transport and Transformation Processes

The major differences between the behavior profiles of different organic chemicals in the environment are attributed to physical-chemical properties such as solubility, volatility, partition coefficient, dissociation constant and susceptibility to degradation or transformation reactions. The mechanisms that may breakdown TFM include photolysis, biodegradation, hydrolysis, and dissociation. Transport processes include sorption, bioaccumulation, and volatilization. Many researchers have attempted to explore the fate of TFM in the aquatic environment. A critical review of their work is being presented here.

2.2.1 Biotransformation

Biodegradation, cometabolic transformations, conjugation, microbial accumulation and nonenzymatic transformations are the basic processes that are involved in the microbially mediated transformation of organic molecules. While the rate and extent of biotransformation can be studied in the laboratory. Considerable work needs to be done to relate the results of the laboratory tests to the behavior of chemical under various environmental conditions. This requires coordinated laboratory and field studies conducted so as to determine the factors influencing biotransformation in environmental systems (27).

Dissolved TFM is reported to be very stable, no degradation products are found in aqueous phase. TFM slowly reduces to 3-trifluoromethyl-4-aminophenol (RTFM) and other unidentified products in sediment (3,7). TFM can be rapidly converted to RTFM by sediment bacteria in a cyclone fermentor system under anaerobic conditions but the reaction does not proceed aerobically (2,3,9). While the major anaerobic TFM degradation product is RTFM (2), another transformation product, 4,4/-dinitro-2, 2/-bistrifluoromethylazobenzene has been identified and confirmed (2). Azobenzene may also be produced by microbial activities in the anaerobic zone of periphytic communities (6).

2.2.2 Photolysis

Photodegradation is a significant route of TFM degradation in the aquatic environment under conditions that might be encountered during an actual stream treatment. Different workers have observed photonucleophilic substitution, photoreduction, photohydroxylation, photochemical radical production and photodecomposition of TFM. Photodegradation of TFM exhibits first-order kinetics in streams exposed to sunlight (2). Its rate of photodecomosition is slow at low pH and reaction goes to completion at high pH. TFM is photodecomposed to give seven products in stream water (2) which are themselves subject to further degradation (6), none of them is likely to be stable end product. The specific rate constant values are reported to be approx. 0.060 d^{-1} and 0.078 d^{-1} for commercial and pure grade TFM respectively. Methyl-2,5-hydroxybenzoate, and trifluoromethylquinone are two of the identified photoproducts (2). The expected half-life for direct photolysis is 3.5 days in spring and 3.0 days in summer, for noonday sunlight.

Nitrite analysis revealed that 50-60% of the reacted TFM appears to have lost nitrite. Fluoride present after irradiation could account for 15% TFM degraded. Thingvold and Lee (7) used ring labeled [^{14}C] TFM for experimentation and could not detect any F- released, indicating that C-F bond was not broken.

The major route of TFM photodegradation appears to be a pathway (Figure 1) that eventually leads to humic like polymers.

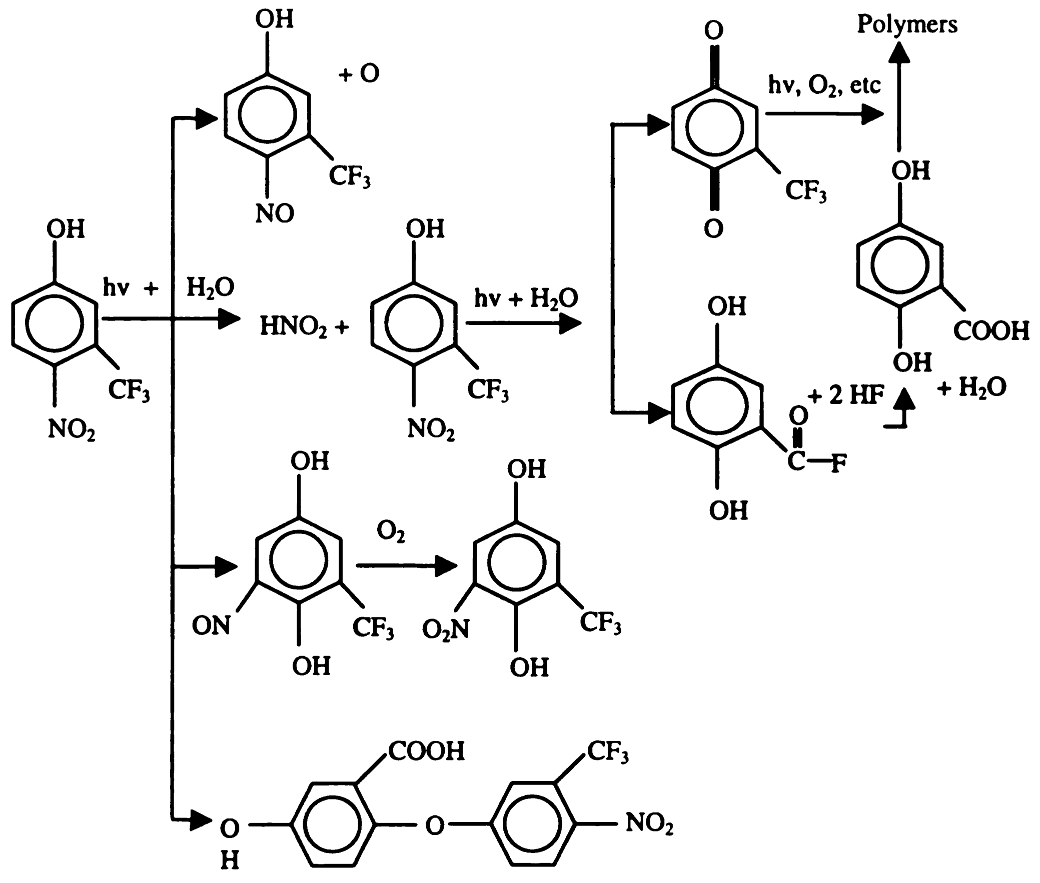

Figure 1. Pathway of TFM photodegradation (Carey and Fox 1988)

In distilled water, the order of reaction becomes pH dependent and the presence or absence of oxygen has no effect on photolysis rate. Nitrates and fluoride concentrations were high after photolysis. A specific examination for RTFM revealed that this species is not a photoproduct (6).

2.2.3 Hydrolysis and Volatility

Previous work has clearly shown that TFM is not readily lost from aqueous system by volatilization or hydrolysis, (3,5,7).

2.2.4 Sorption

Partitioning of a solute between the aqueous phase, and inorganic and organic particles will largely determine where the chemical will reside in an aquatic system and what reaction process will affect it.

The capacity of soil and sediment to adsorb and retain contaminants varies with their composition. Retention by soil and sediment is related to organic matter content, clay mineral content, and carbonate content (as a buffer against pH changes). Sorption of ionizable species is highly pH dependent (17). Soil constituents with high specific surface and net charge, i.e. organic matter, clay minerals, metal oxides and hydroxides, largely determine adsorption.

The relevant boundary conditions are concentration and dissociation or polarity of chemical on one hand, soils, moisture, temperature, pH, and oxidation and reduction potentials on the other hand. These inherent filtering and buffering capacities enable soils to reduce the impact of potentially toxic substances on the biosphere, making them an important temporary sink for environmental chemicals.

Strong adsorption can often increase the persistence of chemicals and results in accumulation effects. Swelling clay in the sediment may also affect distribution ratios of nonionic organic compounds (13).

Organic matter in the soils has a significant role in regulating the behavior of soil pollutants. It provides high storage capacity for organic micropollutants (16). Sorption of hydrophobic dissolved organic matter is strongly favored over binding of the hydrophilic fractions on soil (22).

The hydrophilic-hydrophobic balance of surface properties may be especially influenced by organic coating materials, such as humic substances. The significance of organic coatings for aquatic systems is based on their ability to increase the adsorption capacities, as well as their properties to influence the aggregation and disaggregation processes.

The type of mineral surface is also important in the sorption of non-ionic, hydrophobic organic chemicals. Sorption of hydrophobic compounds controls their concentration and rate of transport in the aquifer. It can also control reaction that degrades the organic chemical (15). It may be possible that K_d could be sum of the mineral and organic matter contributions.

Sorption of TFM by sediment has been studied to a limited extent and appears to vary with the sediment source (3). It is reported that the lampricide was adsorbed by silty sediment that were high in organic matter. At basic pH, TFM exists in its anion form and exhibits a reduced tendency for adsorption relative to the behavior at acidic pH with organic sediment.

The reported K_d values for TFM range from 0-10 (4) which show adsorption tendency of TFM on sediment will not greatly affect its transport through water. The binding is reported to be readily reversible and is very pH dependent (7). TFM can be removed from water applying 30-50 mg/L of activated carbon and this process is more efficient at high pH (14).

Run off and tributaries carry different types of soil into the Great Lakes. Sorption may be important in controlling TFM fate, even though binding is not strong, because it is the only likely mass-transfer process that will remove it from the water phase. Moreover, incubation of sea lamprey in bottom stream sediment also adds to the need for comprehensive investigation of TFM partitioning to confidently determine the role of sorption in the fate of TFM in the Great Lakes.

2.3 Information Summary of Deficiencies

Researchers generally agree that TFM is biotransformed to RTFM, and azobenzene under anareobic conditions and RTFM is not a photolysis product. There is conflict over photolytic cleavage of C-F bond (1,7) and further studies are necessary to address this. The kinetics of photodecomposition of TFM has been studied but biotransformation rates are not reported in the literature.

Although TFM is reportedly non-volatile but there is no data in the recent reference material in favor of this claim. In the absence of such data this may be assumed that loss of TFM from water to gas phase by volatilization is minimum.

Limited attention has been paid to TFM and RTFM interaction with suspended solids and sediment in the water. Some studies have shown that TFM irreversibly sorbs to sediment and that sorption rate is low. The number of soil types used for these studies is limited and the effect of pH have not been fully studied.

2.4 Study Objectives

Studies of the influence of soil/sediment characteristics on TFM sorption are insufficient to predict partitioning in the environment. In addition, biotransformation rate constants for systems with soil present have not been reported. Previous research has not integrated the effects of individual processes to produce a complete picture of TFM fate in the environment.

The present study was designed to address these shortcomings and conduct additional experimentation on sorption and biodegradation to model the disappearance of TFM in a model aquatic system.

Three tools were utilized to achieve these objectives. First, isotherm experiments were performed to study TFM sorption on different soils and sediment as a function of pH. Second, microcosm studies were carried out to determine a biotransformation rate constant with sediment present in the system. Third, fugacity calculations were performed to determine percentage of TFM in different compartments of a model environmental system and to estimate TFM persistence in the environment.

Chapter 3

MATERIALS AND METHOD

3.1 Materials

The materials used in this study were, 3-trifluoromethyl-4-nitrophenol (99%, Laboratory grade, Aldrich Chemical Co); monobasic sodium phosphate (AR grade, Malinckrodt); 1N Sodium Hydroxide solution (Columbus Chemical Industries); Acetonitrile (HPLC grade, 99.8%, EM Science); Acetic Acid GR (Glacial, EM Science); Sodium Acetate Anhydrous (Baker Analyzed ACS reagent, J.T. Baker); TCLP Glass Fiber Filter (47mm, 0.7 micrometer Nominal, Gelman Science).

Keeping in view their organic content and cation exchange capacity, the following previously collected soils were used for adsorption studies: muck, clay loam, sandy loam, fine sand, and sand. A freshly collected sediment was also used for both adsorption isotherm and biodegradation studies. 5 Kg of sediment was collected by scrapping almost 1.5 inches of sediment from the bottom of the Red Cedar River, 3 meters away from the shore, opposite to the MSU Main Library. The sediment was incubated at 4°C for one week.

3.2 Analytical Method Development

A new method was developed for TFM analysis using high pressure liquid chromatography (HPLC) with ultra-violet detection. The mobile phase chosen for TFM analysis was a mixture of acetonitrile and acetate buffer (pH-5) at a ratio of 65:35 respectively.

It was observed that TFM shows maximum absorbance at 220 and 300 nm. Calibration curves constructed by running standard solutions of concentrations 0,1,3,6,9,12 were highly linear with good correlation coefficients for both wavelengths and detection limits of 0.444, and 0.973 ppm were found at 300 and 220 nm respectively. For the superior sensitivity, 300 nm was selected for TFM detection. The detection limits were calculated using procedure described by Michael et al. (10). The retention time of TFM was found to be 5 minutes for soil extract (using de-ionized water) and 10 minutes for sediment extract (using river water)

3.3 Time-Concentration Curve

A sorption rate experiment was performed using the muck soil as the sorbent most likely to produce kinetic limitations. The initial concentration of TFM was 100 PPM, and the quantity of muck soil used was 150 gm in 240 ml buffer. Samples were collected at regular intervals, centrifuged at 7000 rpm, filtered using a 0.7 µm glass-fiber filter and analyzed by HPLC. Sorption was essentially complete after 2 days, but 4 days was selected as the equilibration time for the isotherm studies to ensure establishment of equilibrium conditions.

3.4 Sorption Isotherm Studies

Five soils, fine sand (0.04% OC), sandy loam (0.05 % OC), clay loam (0.69 % OC), sand (1.15% OC), and sediment (2.65% OC) were chosen for TFM adsorption studies in the laboratory. The selection of soils was made taking in to account their organic content and cation exchange capacity (Table-1). Partitioning of TFM was also investigated between sediment and water because of potential importance of sediment in the aqueous environment.

Sorption istherms were performed in the laboratory by using a shake flask technique. Initial TFM concentrations at different pH levels were selected based on K_d values for muck soil obtained from time-concentration plot and the reported optimum concentration of TFM (17 mg/L) to kill sea lamprey.

The soil was oven-dried 103 °C, and 8 gm of soil was transferred into a vial. Some of the buffer was introduced into the vial to soak the soil, vial was put on a shaker for one day to check for any pH change greater than ± 0.05 pH units. The vial was then closed with a rubber seal and crimped. It was autoclaved and stock TFM solution was injected into it to produce a total volume of 13 ml.

Soil/water/TFM systems were prepared at pH levels of 5, 7, and 9. All vials were put on a rotary shaker at 6 rpm.

Vials were taken off the shaker after four days and samples were collected from them.

3.5 Microcosms studies

Microcosm experiments are designed to simulate the processes actually taking place in the environment. In order to simply represent a common set of environmental conditions, the following incubation procedure was adopted.

Sediment taken from the Red Cedar River were kept in cold storage (4 °C) for a week. 50 g (approx. dry weight) of wet sediment, 65 ml of river water (pH-7.8), and 20 ml TFM solution (3000 PPM prepared in autoclaved river water) were added to each vial (160 ml). The TFM concentration in each vial was approximately 600 mg/l. Control, aerobic and anaerobic microcosms were prepared in triplicate.

The microcosms used as controls were autoclaved prior to TFM addition to vials. The anaerobic microcosms were flushed with N_2 for three hours. These microcosms were inoculated with 1 ml anaerobic seed obtained from the anaerobic digester at the Mason (MI) waste water treatment plant; and the aerobic microcosms were inoculated with 1 ml seed obtained from the activated sludge tank at the East Lansing (MI) waste water treatment plant. All vials were stored for 48 hours in stagnant conditions at room temperature (~20°C). Then the vials were transferred to rotary shaker (6 rpm) and shaken for 689 hours. Samples were taken from the vials at regular time intervals. Samples were first centrifuged at 7000 rpm and then filtered through 0.7 μm glass fiber filter. The filtrate was analyzed by HPLC.

3.6 Mackay's Hypothetical Model World

The model world consists of a 1-km square with a 10-km high atmosphere; 30% of the area is covered by soil whose depth is 3 cm; and 70% is water covering an average depth of 10 m, with 3 cm of sediment, 5 PPM by volume of suspended solids, and 0.5 PPM of biota. The densities are 1000 kg/m^3 for water and biota, 2400 kg/m^3 for soil and sediment, and 1.19 kg/m^3 for air. The volumes of air, soil, water, biota and sediment turn out to be 10^{11}, $9*10^3$, $7*10^6$, 3.5, $2.1*10^4$ m^3 respectively (11,13).

Chapter 4

RESULTS AND DISCUSSION

4.1 Time-Concentration Curve

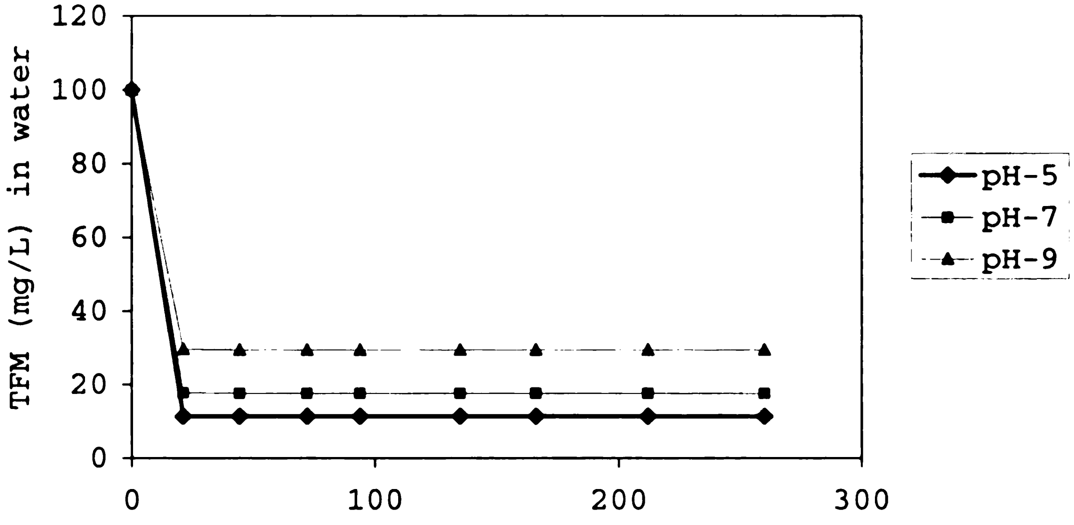

Figure 2: Time-Concentration curve for TFM sorption on loam (Muck RDC) with 3.01% OC

Figure-2 is time-concentration data for the kinetic studies. It was constructed to estimate K_d values, which were required to determine the range of TFM concentrations for isotherm studies.

It is evident from the curve that equilibrium reached within a day, which agrees with the previously reported (4) equilibrium time of 16 hrs. This is also in the range (4-24 hrs) of equilibrium times generally estimated for chemicals (4). It can be seen that the tendency of TFM to adsorb to soil increases as pH of the solution decreases. At a low pH, the TFM in un-ionized form tends to adsorb more to soil due to its hydrophobic nature. At high pH, it is almost all in the ionized form, and becomes comparatively hydrophilic and adsorbs less to the soil.

4.2 Isotherm

Simple isotherm are slightly non-linear (Figure-3) and the data obtained from these studies reasonably fit the Freundlich isotherm model (Figure-4). K_F and n values are presented in Table-1.

Table-1 Soil Characteristics and Freundlich Constants

Soil	pH	OC %	CEC meq/100g	n			K_F		
				PH-9	PH-7	PH-5	PH-9	PH-7	PH-5
Fine Sand	5.9	0.0	0.4	1.1	1.1	1.1	0.1	0.2	0.2
Sandy Loam	5.2	0.1	11.3	1.0	1.1	1.2	0.1	0.1	0.4
Clay Loam	4.2	0.7	12.8	1.2	1.2	1.1	1.6	3.2	3.9
Sand	5.1	1.2	6.4	1.2	1.1	1.1	2.4	4.1	5.9
Sediment	7.8	2.7	4.4	1.1	1.1	1.0	3.9	7.6	11.7

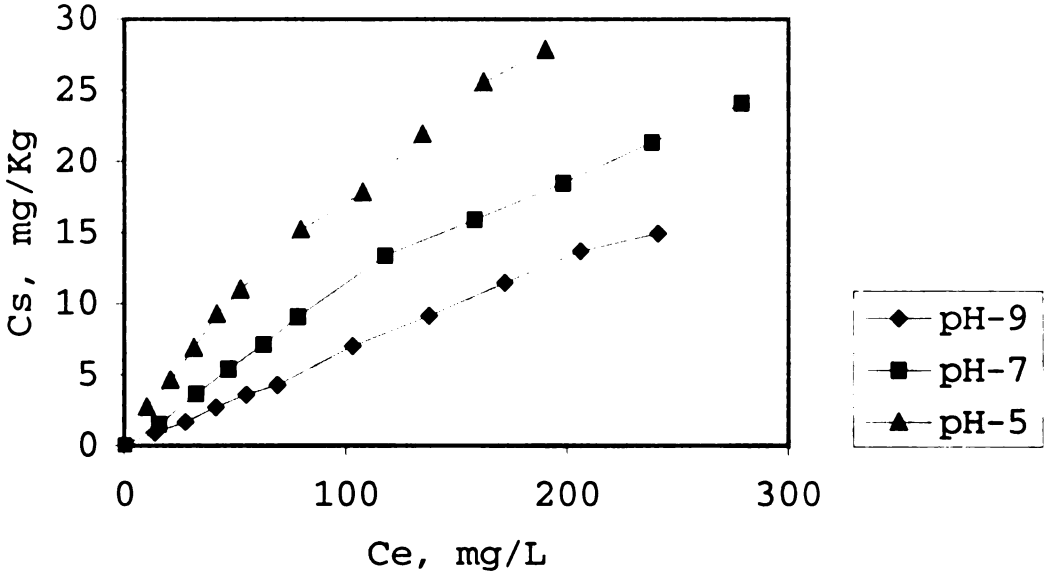

Figure-3: Simple isotherm for TFM sorption on sandy loam

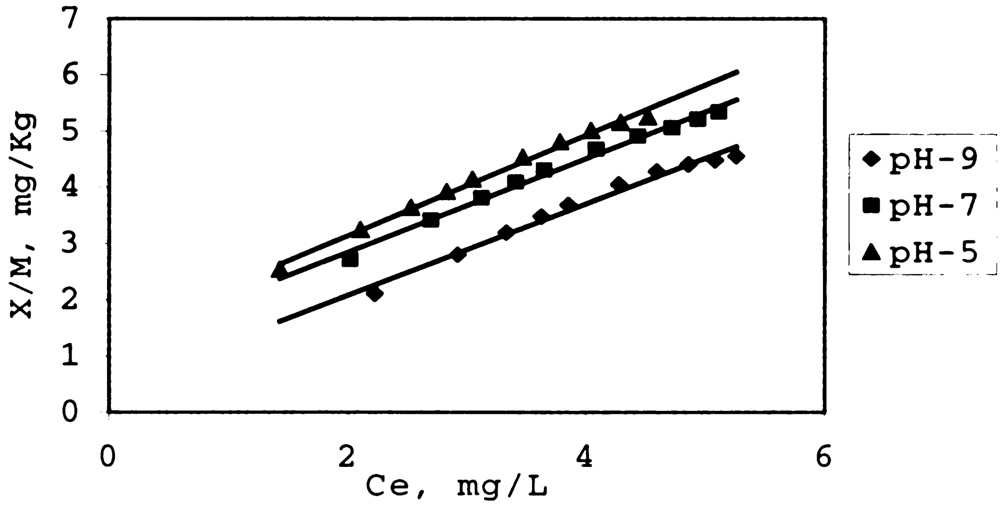

Figure-4 Freundlick Isotherms for TFM adsorption on Clay Loam

Although n values are greater than 1 but they are close enough to allow comparison between K_F values and linear partition coefficients (K_p). Our K_F values are comparable to previous studies. The n values reported for partitioning of chemicals from water to soil are mostly less than 1 (4). K_d for each soil was also calculated using straight portion of the simple isotherm. Figure-5 elaborates K_d dependence on organic content of soil. K_d and K_F are increasing with organic content of soil. pH has also played significant role in the partitioning of TFM between water and soil (Figure 2, 3, 4). K_d is decreasing as pH of the system moves from acidic to basic.

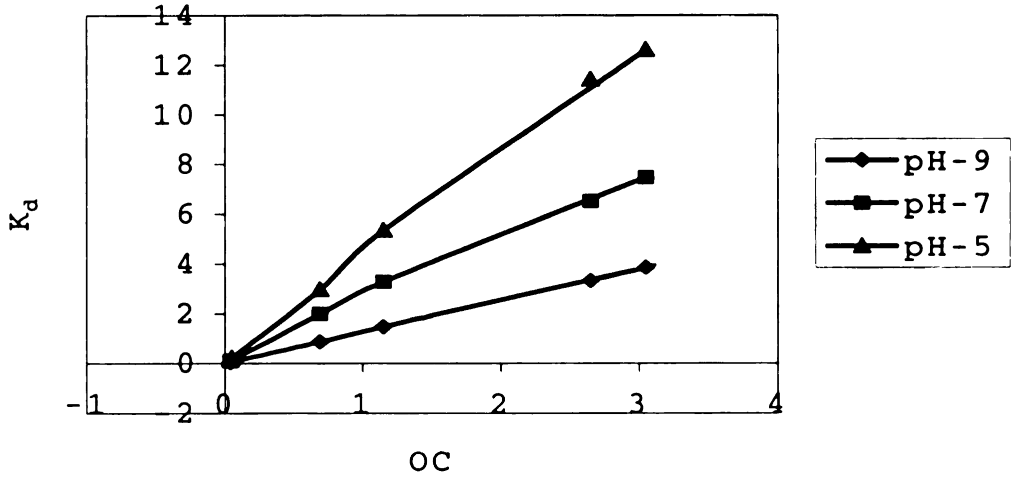

Figure-5 Kd Dependence on Organic Content

K_d values were used to calculate normalized organic carbon coefficient (K_{oc}), octanol-water partition coefficient (K_{ow}) (Table-2), bioconcentration factors (BCF, Kb) and solubility (SW) (Table-3) of TFM in the system at different pH.

It has already been established that solution and soil composition affect sorption of ionizable compounds, and that sorption of ionizable species increases with decreasing pH (25). TFM showed similar behavior because of the increased fraction of the molecular form under acidic conditions which can be sorbed by organic matter. Distribution coefficient values are generally in agreement with the values (0-10) determined in past.

Table-2 Koc, Kow, WS of TFM

Soil	K_{oc}			K_{ow}			SW		
	PH-9	PH-7	PH-5	PH-9	PH-7	PH-5	PH-9	PH-7	PH-5
Fine Sand	125	250	400	60	154	291	255	105	57
Sandy Loam	130	240	440	63	145	331	242	110	51
Clay Loam	125	290	430	60	188	321	256	87	52
Sand	130	285	465	63	184	357	243	89	47
Loam(muck)	127	245	414	61	150	304	251	107	55
Sediment	126	246	431	60	151	322	253	107	52

Table-3 Bioconcentration Factors for TFM

	BCF(t)			BCF(f)			Kb		
Soil	PH-9	PH-7	PH-5	PH-9	PH-7	PH-5	PH-9	PH-7	PH-5
Fine Sand	4	8	15	6	13	22	6	14	25
Sandy Loam	4	8	16	6	12	24	7	14	28
Clay Loam	3	10	16	6	15	23	6	17	27
Sand(C.W)	4	10	18	6	15	25	7	17	29
Loam(muck)	4	8	15	6	12	22	7	14	26
Sediment	4	8	16	6	13	23	7	14	27

4.3 Biodegradation

In the microcosm studies we found biodegradation in the anaerobic systems but not in the aerobic ones (Figure-6), consistent with previous research (3,9). We did not analyze samples for transformation products, but these products have already been reported in past, i.e. RTFM.

The rate of TFM biotransformation was determined applying a mass-balance approach. The following relationship was established and used for this purpose.

$$\ln\ [TFM]_{aq} = -\ (V_{aq}\ /\ (V_{aq} + M_s\ K_p))\ k\ t$$

Where

$[TFM]_{aq}$ = Concentration of TFM in aqueous phase at time, t

V_{aq} = Volume of aqueous phase

M_s = Mass of sediment used

K_p = Linear partition coefficient

k = rate constant

Figure-7 is a plot of ln $[TFM]_{aq}$ against time. It represents the first order kinetics of anaerobic biodegradation of TFM with rate constant value 0.00091 h^{-1}. This value was used to calculate a persistence of TFM in a model world.

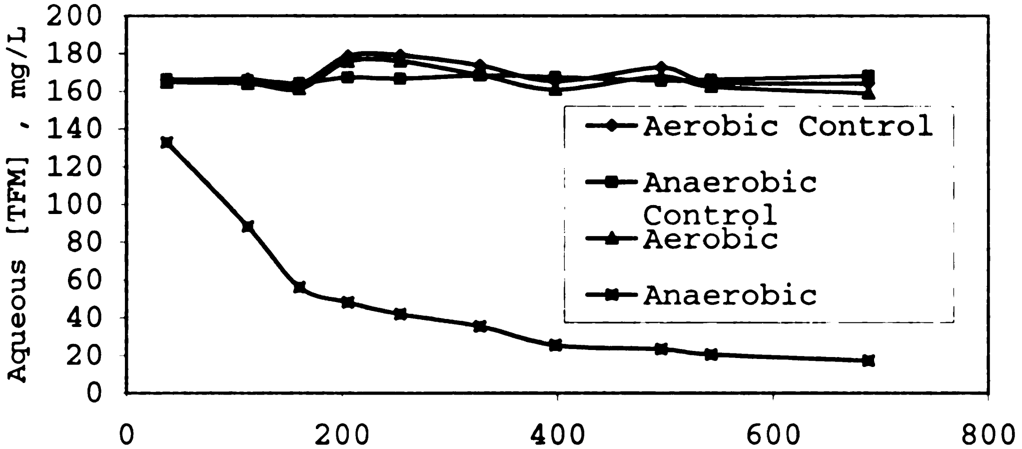

Figure-6 TFM biotransformation in water-sediment system

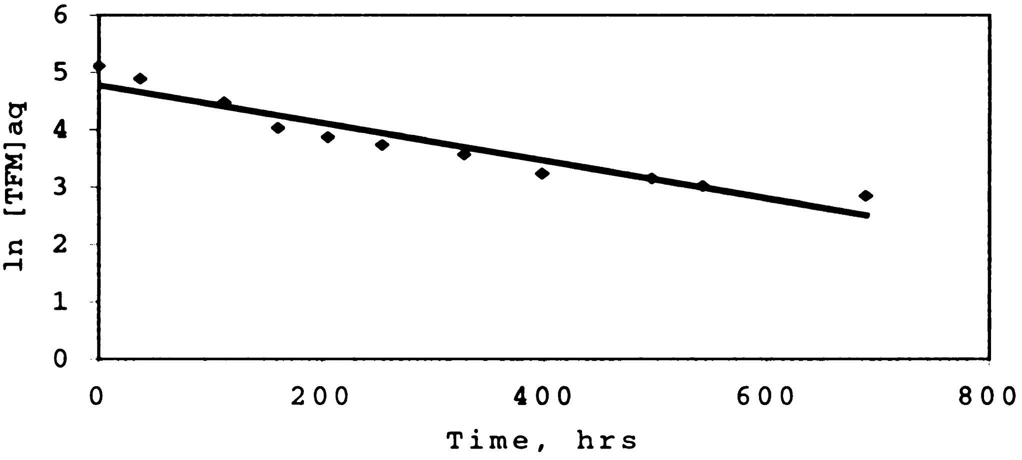

Figure-7 First order rate constant determination of anaerobic biotransformation

4.4 Distribution and Persistence

4.4.1 Mackay's Hypothetical World

We used sorption and degradation rate data to determine TFM distribution and persistence in different compartments of Mackay's "Hypothetical World" (20,29). Level I and II fugacity calculations were performed to model TFM fate in this system. The level I calculations describe how a given amount of chemical partitions at equilibrium between six media: air, water, bottom sediment, suspended solids and fish. No account is taken of reactivity. The level II calculations simulate a situation in which a chemical is continuously discharged into the multimedia environment and achieves a steady-state equilibrium condition at which input and output rates are equal. The task is to deduce the rates of loss by reaction.

Based on the K_d values, distribution of TFM between water and suspended solids (10-100 mg/L) in the river was calculated. Figure-8 illustrates that TFM adsorption to suspended solids is not significant, therefore we excluded the suspended solids compartment from the calculations.

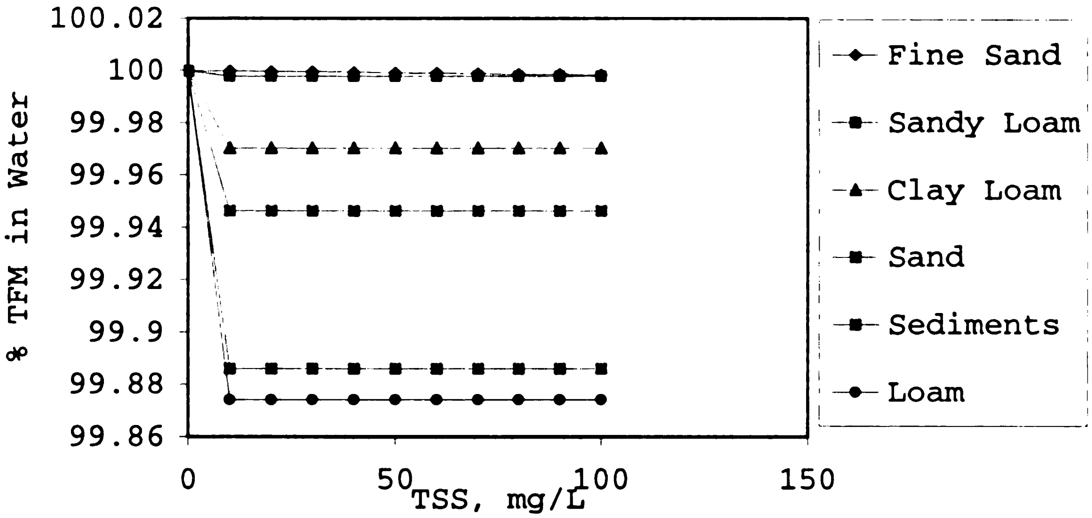

Figure-8 TFM distribution as a function of TSS Conc at pH-5

It was assumed that the only mechanism of TFM disappearance in water compartment is photolysis, while biodegradation occurs in sediment where conditions are anaerobic. A photolysis rate constant of $0.078d^{-1}$ was taken from previous work (2) and biodegradation rate constant was obtained from the present study. It was also assumed that there is no hydrolysis of TFM in the environment, as reported previously.

Vapor pressure of TFM was not available any where in the literature, it was therefore calculated using the boiling point (at 10^{-5} bar pressure) as described by Lyman and Warren (23). This estimation procedure resulted in a value of $1.8 * 10^{-5}$ Pa, low enough to assume transfer to the atmosphere is insignificant.

In the level-1 fugacity calculations, we found that 89-98 percent of TFM remains in water depending on pH of the system and OC in the soil. The overall distribution of TFM is in the order of water (Figure-9) > sediment (Figure-10) > soil (Figure-11). The amount of TFM in biota and air are insignificant.

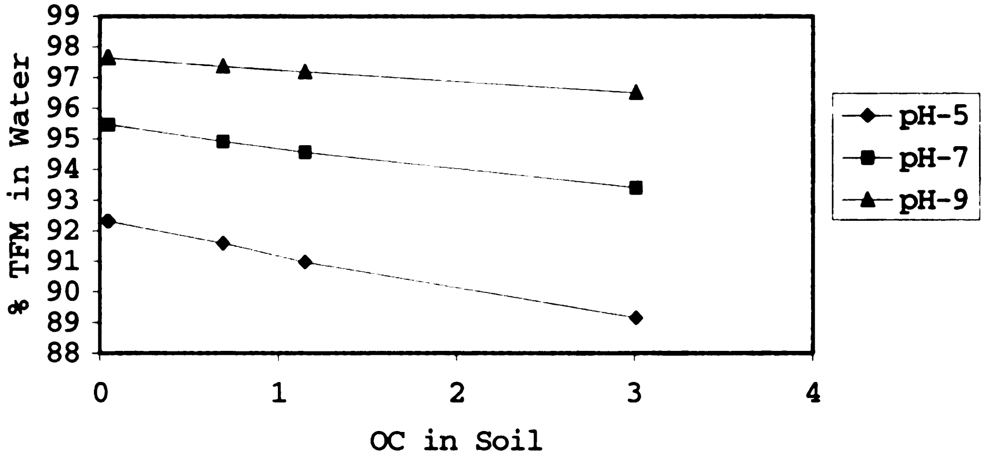

Figure-9: % TFM in Water (Mackay's World) as a Function of OC in Soil

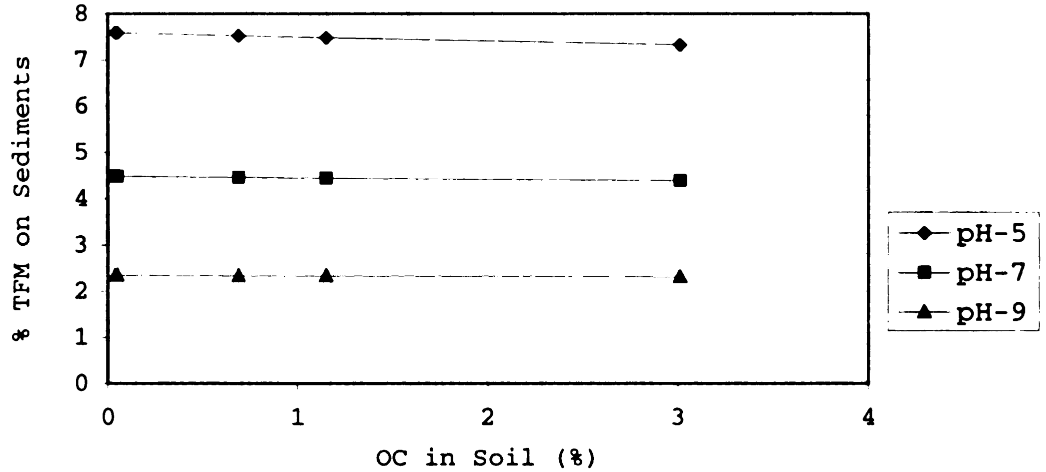

Figure-10 % TFM Sorbed on Sediments (Mackay's World)as a Function of OC in Soil

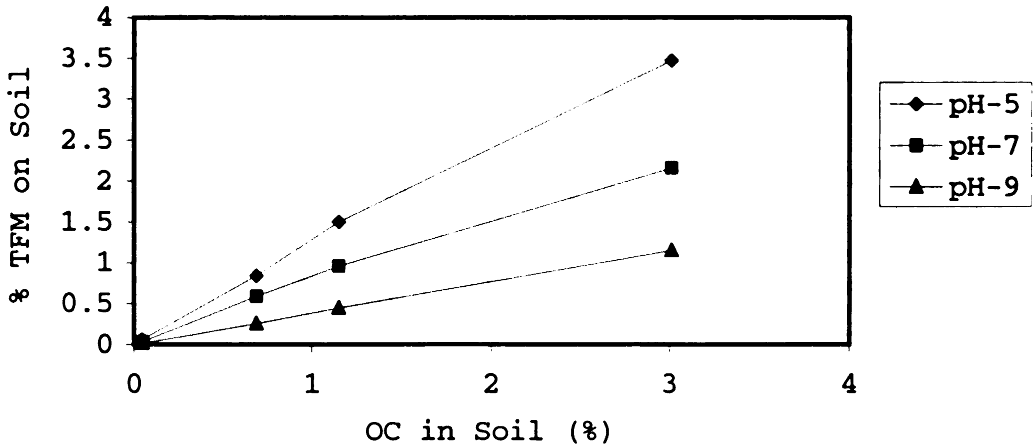

Figure-11 % TFM Sorbed on Soil (Mackay's World) as a Function of OC in Soil

In the level-II calculations, we determined a persistence time of TFM in that world: 315-342 hrs. Figure-12 illustrates how average residence time of the TFM in the world varies with OC in soil and pH of the system. The persistence time increases with increase in OC and pH. Moreover TFM persistence time in the environment is dependent upon its emission rate.

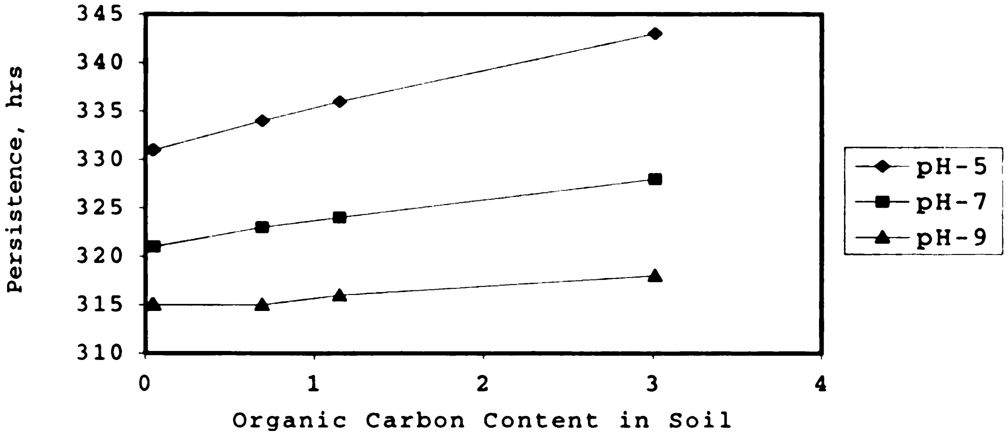

Figure-12: TFM persistence dependence on OC in Soil

4.4.2 Sediment-Water System

It is assumed in Mackay's world that the system is well mixed but real systems often exhibit poor mixing. To simulate the real environment, the world was made more simplified. It was conceived as a river/lake with water and sediment only by excluding the soil compartment. It was found that average residence time of TFM in the water-sediment system was 13-14 days similar to that found for the more complex system. Distribution of TFM between water and sediment compartments in the simple system is given in Table-4.

Table-4. TFM Distribution and Persistence in Water-Sediment system

pH	mol (%)		Persistence	
	Water	Sediment	hrs	Days
5	92	8	326	13.6
7	96	4	318	13.3
9	98	2	313	13.0

TFM persistence may be influenced by the mixing characteristics of the system, distance of the lake from the treatment point, flow of the stream, and depth of water body to which light penetrates.

Chapter 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Summary of Findings

The slightly non-linear partitioning behavior of TFM is well-fit by Freundlich isotherm model. TFM shows more affinity for soils at low (acidic) pH and tends to sorb more on to solids with higher organic carbon content. Our investigation agrees with the theoretical concepts and previous work (12,13). TFM Patitioning coefficient values are almost in agreement to the values (0-10) determined in past.

K_{ow} and K_{oc} values indicate that TFM has negligible adsorption, accumulation, bioaccumulation, food contamination, and persistence potential. It may be highly mobile and dissipated, and biodegraded.

In the model system, very little TFM associates itself with biota. TFM volatilization from water to air is also insignificant. At natural stream conditions, more than 90% TFM remains in water compartment.

TFM is not biodegraded when conditions are aerobic, it is transformed by microbial activities in sediment under anaerobic conditions. Photolysis rate constant is 4 times higher than that of biotransformation. TFM is not long-lived in the environment. Its persistence time in the environment is approximately 13-15 days depending upon pH and rate of degradation, and emission rate of TFM.

TFM persistence may be influenced by the mixing characteristics of the system, distance of the lake from the treatment point, flow of the stream, and depth of water body to which light penetrates.

5.2 Implications and Future Research

- Fate and analytical measurement of TFM photodecomposition and biotransformation products in a real system needs to be studied.
- Further investigation is warranted on fluoride ion release from TFM in the aqueous environment.
- Attention may be paid to possibility of flouroacid formation due to fluoromethyl group breakage from TFM.

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