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Biogeochemical cycling of methyl bromide in soils

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BIOGEOCHEMICAL CYCLING OF METHYL BROMIDE IN SOILS

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DISSERTATION

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ABSTRACT

BIOGEOCHEMICAL CYCLING OF METHYL BROMIDE IN SOILS

by

Ruth K. Varner

University of New Hampshire, May, 2000

Tropospheric methyl bromide (CH_3Br) is a significant source of ozone (O_3) destroying bromine to the stratosphere. Due to this threat, the cessation of the production and use of fumigant CH_3Br has been slated for 2005 by the Montreal Protocol nations. This decision was based on CH_3Br's relatively long atmospheric lifetime which is estimated from the current understanding of its natural and anthropogenic sources and sinks. The research presented in this dissertation has focused on determining the magnitude and characteristics of the biogeochemical exchange of atmospheric CH_3Br with upland and wetland soils to attain a better understanding of these portions of the tropospheric budget of CH_3Br.

An accurate and precise method to determine ambient mixing ratios of CH_3Br was developed and implemented. Samples were analyzed for CH_3Br by preconcentrating a large volume of air (200 to 700 mL) on a packed sample loop held at -70°C. The sample loop was then heated to 120° and flushed into a gas chromatograph equipped with an oxygen doped electron capture detector (GC-ECD).

Laboratory incubations of soils collected from around the world were completed to determine if the upland soil sink was universal. Manipulation of soil

samples were completed to determine the characteristics of uptake. Field flux measurements over a growing season were completed at two upland sites in the Northeastern United States using a chamber method. Laboratory incubations and field measurements revealed that upland soils are net sinks of atmospheric CH_3Br. The process of uptake appears to be bacterial. There was also some indication from field measurements that there are mechanisms for production of CH_3Br in these upland systems.

Exchange of CH_3Br at two temperate wetlands was studied over an entire growing season revealing an estimate of net emissions of CH_3Br to the atmosphere of approximately 2.2 Gg yr^{-1} from global wetlands. This is approximately 4% of the missing source term in the tropospheric budget of CH_3Br. This result reveals a significant terrestrial source of atmospheric CH_3Br. This research also implies that the exchange of CH_3Br in terrestrial systems is a complex interaction of in situ production and consumption.

CHAPTER 1

BIOGEOCHEMICAL CYCLING OF ATMOSPHERIC METHYL BROMIDE

1.1. Introduction

Methyl bromide (CH_3Br) is a fumigant that is relied on heavily in strawberry agriculture, fruit and vegetable importation and the termite extermination industry. During fumigation of soil, structures and durables, CH_3Br has the potential to escape to the troposphere and enter the stratosphere. In 1992, it was classified by the Montreal Protocol signatory nations as a potential stratospheric ozone destroyer and its industrial production was frozen at 1991 levels [*UNEP*, 1992]. It is theorized that CH_3Br that is allowed to volatilize during fumigation will be transported to the stratosphere at mixing zones (e.g. above the Inter-Tropical Convergence Zone (ITCZ) and along the boundary of the stratosphere and troposphere). In the stratosphere, CH_3Br is broken down by uv radiation which releases Br that is available for reaction with ozone [*Solomon et al.*, 1992 ; *Mellouki et al.*, 1992]. Br is 20 to 100 times more effective at destroying ozone than Cl with CH_3Br being the largest source of bromine to the stratosphere [*Wofsy et al.*, 1975; *Yung et al.*, 1980; *McElroy et al.*, 1986; *Solomon et al.*, 1992; *Kurylo et al.*, 1999]. Due to this potential threat to the environment, in 1995 strict limitations were put on the production and use of CH_3Br with phasing out in industrialized countries of manufacturing and application by the year 2010 [*UNEP*, 1995]. In 1997, the Montreal Protocol accelerated these controls on production and use of CH_3Br to a final phasing out

in 2005 for industrialized nations and 2015 for developing countries [*UNEP*, 1997]

The actual threat of CH_3Br to the ozone layer is calculated as its ozone depletion potential (ODP). This potential is dependent on the removal processes in the atmosphere and the chemistry of CH_3Br with respect to that of Cl in the stratosphere [*Kurylo et al.*, 1999]. The removal of CH_3Br from the atmosphere is represented by the following calculation of the lifetime (τ_{TOTAL}) of CH_3Br in the atmosphere:

$$\frac{1}{\tau_{TOTAL}} = \frac{1}{\tau_{ATMOS}} + \frac{1}{\tau_{OCEAN}} + \frac{1}{\tau_{SOIL}}$$

where τ_{ATMOS}, τ_{SOIL} and τ_{OCEAN}, are the lifetimes of CH_3Br due to removal by interaction with the atmosphere, soil and ocean, respectively. Based on the most recent calculation of the lifetime of CH_3Br in the atmosphere of 0.7 years, its ODP is estimated to be 0.4 [*Kurylo et al.*, 1999]. This estimate is considerably less than the original 1.4 calculated when the Montreal Protocol first recognized the potential for ozone destruction of CH_3Br [*UNEP*, 1992]. The reason for this decrease in ODP is due to our better understanding of the tropospheric sinks and sources of CH_3Br.

1.2. Tropospheric Methyl Bromide Budget

CH_3Br in the atmosphere has natural as well as anthropogenic origins. It occurs in the atmosphere at an average mixing ratio between 9 and 10 pptv (parts per trillion by volume) with a total atmospheric burden of 146 Gg (Gg = 10^9 g) [*Kurylo et al.*, 1999 *and references therein*]. The NH/SH interhemispheric gradient has been measured to be 1.3 ± 0.1 [*Lobert et al.*, 1995, 1996; *Grozko and Moore*, 1998; *Schauffler et al.*, 1998] and 1.2

± 0.03 when seasonal variability is taken into account [*Wingenter et al.*, 1998].

As a result of the decisions by the Montreal Protocol, scientists around the globe increased their research efforts to define the tropospheric budget of CH_3Br. Table 1.1 is a compilation of the current understanding of the CH_3Br tropospheric budget. At first glance it is quite noticeable that the budget is severely out of balance and has very large error bars associated with all of its elements. As a matter of fact, soils were not even considered a sink of CH_3Br until we published our results from laboratory and field uptake experiments in 1995 [*Shorter et al.*, 1995]. With the addition of soils as a significant sink of CH_3Br, the estimated lifetime of CH_3Br in the atmosphere decreased from 1.0 to 0.7 years [*Shorter et al.*, 1995].

The tropospheric CH_3Br budget reveals an imbalance in the budget of 59 Gg yr^{-1} [*Yvon-Lewis*, 2000]. Natural sources of CH_3Br include biological production and subsequent release from the supersaturation of ocean surface water [*Butler*, 1994; *Lobert et al.*, 1995; *Grozko and Moore*, 1998], release from freshwater wetlands [*Varner et al.*, 1999b; *Dimmer et al.*, 1999], emissions from salt marshes [*Rhew et al.*, 2000], emissions from rice fields [*Redecker et al.*, 1999], production from wood rot fungi [*Harper*, 1985; *Lee-Taylor and Holland*, 1999], and release by rapeseed plants [*Gan et al.*, 1998]. Anthropogenic sources include emissions from fumigation [*Kurylo et al.*, 1999 *and references therein*], combustion of leaded gasoline [*Hao*, 1986; *Baker et al.*, 1998; *Chen et al.*, 1998] and biomass burning [*Andreae et al.*, 1996; *N.J.Blake et al.*, 1996]. From these estimates the natural sources outnumber the anthropogenic source estimates, 84.4 to 65.8 Gg yr^{-1} respectively.

Table 1.1. Tropospheric CH_3Br budget.

Sources	Exchange (Gg yr^{-1})	Range	Sinks	Exchange (Gg yr^{-1})	Range
Oceans[†][l]	56	(5-130)	Oceans[†][l]	-77	(37-133)
Fumigation (soils, structures , durables, and perishables)[l]	40.8	(28.2-64.4)	Soils[§]	-46.8	(32-154)
Gasoline, leaded[©]	5	(0-10)	OH and hv[*]	-86	(65-107)
Biomass Burning[‡]	20	(10-40)			
Wetlands[ł]	4.6	?	Green Plants[ś]	-?	!!!
Plants - rapeseed[ś]	6.6	(4.8-8.4)			
Rice fields[ś]	1.5	(0.5-2.5)			
Fungus[*]	1.7	(0.5-5.2)			
Salt marshes[ń]	14	(7-29)			
Total	**151**	(56-290)	Total	**-210**	(134-394)

[†]*Yvon-Lewis and Butler*, 1997; [l]*Kurylo et al.*, 1999; [©]*Chen et al.*, 1998; *Baker et al.*, 1998; *Hao*, 1986; [‡]*Andreae et al.*, 1996; *N.J.Blake et al.*, 1996; [ł]*Varner et al.*, 1999b; [ś]*Gan et al.*, 1998; [ś]*Redecker et al.*, 1999; [*]*Lee-Taylor and Holland*, 2000; [ń]*Rhew et al.*, 2000; [*]*Penkett et al.*, 1995; *Prinn et al.*, 1995; [§]*Shorter et al.*, 1995; *Varner et al.*, 1999a; [ź]*Jeffers and Wolfe*, 1997; *Jeffers et al.*, 1998

Sinks of atmospheric CH_3Br include destruction by hydroxyl radicals and photolysis [*Penkett et al.*, 1994; *Prinn et al.*, 1995], loss to the ocean [*Butler*, 1994; *Lobert et al.*, 1995; *Yvon-Lewis and Butler*, 1997] and uptake by upland soils [*Shorter et al.*, 1995; *Serça et al.*, 1998; *Varner et al.*, 1999a]. Green plants also consume CH_3Br but global estimates of this consumption have not been made [*Jeffers and Wolfe*, 1997; *Jeffers et al.*, 1998].

The imbalance of the tropospheric budget can either be explained by an overestimate of the sinks of atmospheric CH_3Br or a significant missing source. We

discovered the soil sink of CH_3Br and reported our first findings in *Shorter et al.*, 1995 with more detailed results in *Hines et al.*, 1998. I have published a more extensive examination of the cultivated soil uptake of ambient CH_3Br in *Varner et al.*, 1999a. Results from all our soil research are presented in Chapter 3 including laboratory as well as field measurements of CH_3Br exchange with upland soils.

Some have theorized that the missing source(s) is terrestrial in origin due to the seasonal signature of atmospheric CH_3Br [*Singh and Kanakidou*, 1993]. Recently, many researchers have found previously unidentified terrestrial sources of CH_3Br (Table 1.1). I published our original findings on the freshwater wetland source of CH_3Br in early 1999 [*Varner et al.*, 1999b], Chapter 4 of this dissertation is devoted to this terrestrial source of CH_3Br and its seasonal signature.

1.3. Biogeochemistry of CH_3Br in Soils

The focus of much of my research has been on the consumption of ambient CH_3Br in soils and the production of CH_3Br in wetland ecosystems. In 1995, we released the first estimate of the soil sink of atmospheric CH_3Br [*Shorter et al.*, 1995]. The research we completed revealed that the uptake by soils was an aerobic microbial consumption that appeared to be common in many types of soils and environments [*Hines et al.*, 1998]. The pathway of destruction could be explained either by anaerobic dehalogenation and/or oxidation processes. Recently, we published the first numbers for production of CH_3Br by wetland ecosystems in the Northeast United States [*Varner et al.*, 1999b]. The methylation of compounds in wetland environments is a common anaerobic process that has been studied in detail.

1.3.1. Dehalogentation in Soils

Pesticides like CH_3Br and other man-made toxic contaminants have been produced and utilized with the express purpose of creating the best crop, bountiful and cheap energy, and more consumer comforts. The introduction of these compounds into the natural environment, namely soil, has created an entire field of science with one objective: the determination of the environmental fate of these contaminants. Much research has been completed to determine whether the contaminants leave the soil reservoir, being released for further chemical reaction or escape into soil solution, leached through the soil, or volatilized to the atmosphere [*Breth*, 1966]. Soil appears to be a major component of biogeochemical cycling of these contaminants. The fate of these pesticides and industrial contaminants in the soil is determined by the following processes: adsorption, chemical and/or microbial degradation, volatilization, or leaching.

Many pesticides and industrial contaminants found in soil contain halogens. Halogenated compounds are produced both through natural and anthropogenic processes. Synthetic halogenated compounds include a variety of pesticides, cleaning agents and solvents for industrial and commercial use as well as industrial manufacturing waste products. Many of these compounds are persistent in the environment and can be toxic at very low concentrations [*Cheng*, 1990]. They often contain chlorine (Cl), fluorine (F), bromine (Br), and/or iodine (I) which contribute most significantly to their toxicity. Naturally occurring halogenated compounds include methyl bromide (CH_3Br), methyl iodide (CH_3I), and methyl chloride (CH_3Cl). These compounds are produced mainly in the ocean and by marine biota but may also be byproducts of biomass burning as well as

decompostion of organic matter [*Harper*, 1985; *Öberg et al.*, 1997]. They occur at relatively low concentrations (parts per trillion range) in the atmosphere and therefore are generally not considered toxic.

The major pathway of destruction of these sometimes toxic compounds when they reach the soil environment is by removal of the halide(s) portion of the compound, i.e. dehalogenation. Dehalogenation is an important process in making these halogenated compounds less toxic and more readily biodegradable [*Mohn and Tiedje*, 1992].

Dehalogenation can occur via several pathways (e.g. hydrolysis and vicinal reduction) but occurs almost always in the presence of an enzymatic micro-environment (Grover, 1988). Halogenated compounds can be reduced by the removal of one or two halides thereby decreasing the toxicity of the compound and making it more susceptible to further degradation. Reductive dehalogenation involves the removal of the halogen component of a molecule while adding electrons to the molecule [*Mohn and Tiedje*, 1992]. Reductive dehalogenation must occur in a reducing environment and is therefore often completed by anaerobic microorganisms [*Mohn and Tiedje*, 1992].

Two processes of reductive dehalogenation have been identified: hydrolysis and vicinal reduction [*Mohn and Tiedje*, 1992]. Hydrolysis occurs when the halogen is replaced with a hydroxyl group. A hydrogen atom forms a complex with the halogen and is released to the soil solution:

$$RCl + H_2O \rightarrow HCl + ROH$$

where R is an organic substance with a chlorine atom attached.

Vicinal reduction is the removal of two halogen substituents from adjacent carbon

atoms with the formation of an additional bond between the carbon atoms. Generally the halogen atoms are released as halide atoms:

$$RCl_2 + 2e^- \rightarrow 2Cl^- + R$$

Dehalogenation in soils is important for the determination of the persistence of a particular compound in the soil environment. As a compound is decomposed, it becomes less toxic for its surrounding environment and therefore less toxic when it is finally released from the soil environment through leaching, volatilization, or other processes. This is particularly of great importance in agricultural soils where pesticides are applied on a yearly basis and therefore a buildup of the particular pesticide can prove to be a contaminant in the local groundwater supply as well as in runoff to the local reservoir.

Factors controlling the breakdown of pesticides and toxic contaminants include the following: soil type, soil structure, type and concentration of the chemical, and climatic conditions of the site [*Chichester*, 1965; *Breth*, 1966]. Soil type controls the dehalogenation process because the percentage of clay, sand, and silt and percentage of organic matter can determine whether certain compounds are adsorbed by the soil. The soil structure affects the destruction of toxic compounds due to the characteristics of the soil: bulk density, surface area, and heterogeneity of the soil structure. The type and concentration of the chemical in question also has a great effect on the rate and process that breaks down the constituent. The climatic conditions of a site also determine in part the rate and processes that help to break down the chemical. The precipitation and temperature at the site can have a great effect on the rate of break down.

Depending on whether the compound is adsorbed, broken down through chemical

or microbial processes, or volatilized, the aforementioned factors will have different effects. Considering only chemical and microbial breakdown of the compound the amount of sand, silt and clay will not be as important as the amount of organic matter. Compounds found in organic matter actually act as solvents for pesticides [*Breth*, 1966]. Humic and fulvic acids act on the compounds and break them down. Chemical bonding also occurs directly with the organic matter thereby effectively isolating the contaminant from further transport [*Breth*, 1966]. This then allows the microbial population the time to degrade the contaminant to a progressively smaller molecule with less toxic effects on the soil environment [*Grover*, 1988].

Chemical dehalogenation through hydrolytic processes can be affected by the moisture content, pH, and temperature of the soil environment. All three of these affect the kinetics of hydrolysis reactions [*Grover*, 1988]. The amount of moisture in the soil is obviously an important factor in determining whether there will be hydrolysis occurring; more water, more potential for hydrolysis. Drier conditions will result in more adsorption occurring than hydrolytic dehalogenation [*Breth*, 1966]. There is a direct relationship between temperature and hydrolysis; as temperature increases the hydrolysis rates increase [*Sparks*, 1995]. pH has been shown to decrease with the degradation of many contaminants mainly due to the formation of acids during the hydrolysis process [*Hance*, 1980].

Since most dehalogenation is either microbially mediated or occurs in the presence of microbial enzymes, temperature and moisture content of the soil have a significant effect on the rates of decomposition. *Madigan et al.*, 1997 show that the

microbial enzymatic relationship between temperature and reaction rate has a maximum value of temperature where the enzyme system works. Above this temperature, the enzyme system breaks down.

1.3.2. Oxidation of Methyl Bromide

Aerobic microbial degradation of fumigant CH_3Br is cited in many works but is hard to quantify since hydrolysis and reaction with soil organic matter are also breaking down the CH_3Br. Methane-oxidizing bacteria can oxidize CH_3Br but do not support growth of these microbes [*Oremland et al.*, 1994]. In the presence of methane (CH_4), cell suspensions of CH_3Br-consuming bacteria were inhibited suggesting a competitive relationship [*Oremland et al.*, 1994]. Addition of methyl fluoride, an inhibitor of CH_4 uptake, did not stop all consumption of CH_3Br, therefore, another microbe or chemical processes in culture must have been responsible for some of the consumption [*Oremland et al.*, 1994]. Ammonia-oxidizing nitrifiers showed increased uptake of fumigant CH_3Br after addition of ammonia fertilizer [*Ou et al.*, 1997]. An increase in abundance of the small bacterial colony forming units was measured after exposure to CH_3Br but this was not attributed to an increase in the ammonia-oxidizing nitrifier populations [*Ou et al.*, 1997].

Connell Hancock et al., 1998 isolated Strain IMB-1, a facultative methylotroph from previously fumigated soils. *Miller et al.*, 1997 report that this microorganism oxidizes and grows on CH_3Br. They suggest that Strain IMB-1 uses CH_3Br during its metabolic processes in the following way:

$$CH_3Br + 1.5O_2 \rightarrow HCO_3^- + 2H^+ + Br^-$$

Miller et al., 1997 determined that the consumption of a fumigant application of CH_3Br is partitioned as follows: 50% to volatilization of CH_3Br directly to the atmosphere, 20% to adsorption of Br to soil organic matter, 25% to microbial consumption, and the remaining 5% to hydrolytic breakdown in pore water. As the concentration of the applied fumigant increased, adsorption and volatilization became the major measurable processes.

The rates of the soil uptake processes are also influenced by environmental factors such as temperature, moisture content, and organic matter content [*Gan et al.* 1994; *Rice et al.* 1996; *Yates et al.*, 1996; *Gan et al.* 1996; *Anderson et al.*, 1997; *Gan et al.* 1997; *Wang et al.*, 1997; *Dimitriou and Tsoukali*, 1998] as well as by the presence and abundance of microorganisms that are responsible for the destruction [*Oremland et al.* 1994; *Ou et al.*, 1997; *Connell Hancock et al.*, 1998; *Miller et al.* 1997].

1.3.3. Production of Methyl Halides in Soils.

Aerobic Production. Production of methyl halides in soils may occur via aerobic methylation of Br by fungi during the decomposition of organic matter [*Harper*, 1985]. Production of methyl halides by fungi was first detected by Hutchinson in 1971 but was not quantified until Harper and coworkers measured the accumulation of CH_3Cl, CH_3Br and CH_3I in the headspace of flasks of growing white-rot fungi [*Harper*, 1985; *Harper and Kennedy*, 1986]. CH_3Cl produced by fungi was originally hypothesized to be a secondary metabolite [*Harper*, 1985], but it was later found that the production of CH_3Cl was related to the ability of fungi to provide a methyl group during the biosynthesis of methyl ester [*Watling and Harper*, 1998]. CH_3Cl escapes from this cycle as the system enters a later growth phase and becomes leaky [*Watling and Harper*, 1998].

Significant quantities of CH_3Cl can be produced by fungi even when they are in a low Cl^- environment similar to what occurs in decaying litter because of the high affinity of the fungal methylating system for halides [*Watling and Harper*, 1998]. Bromides are more readily retained by soils than chlorides and are concentrated in humic substances [*Ermolenko*, 1972]. Br in costal upland soil litter has been measured as high as 35 ppm decreasing to 3 ppm 440 km inland [*McKenzie et al.*, 1996]. Br in peat has been reported as high as 60 ppm [*Ermolenko*, 1972]. The potential CH_3Br production from the decomposition of litter has been globally extrapolated to a yearly production rate of 1.7 Gg [*Lee-Taylor and Holland*, 2000].

Anaerobic Production. Production of methyl halides in soils may occur via methylation of Br by anaerobes during the decomposition of peat in saturated soils. Anoxic conditions in soils results in a reduction/oxidation zonation where each zone is characterized by a dominant electron acceptor. Methanogens consume CO_2 to produce CH_4 in these flooded soils. Methylation occurs as an end product of microbial metabolism. Production of dimethyl sulfide (DMS) has been measured in fresh water wetlands [*de Mello et al.*, 1994]. Acidic (pH , 4.6) and cool (<15°C) wetland environments exhibit high rates of production of methylated sulfur compounds [*Kiene and Hines*, 1995]. In these environments studied, methanogens, potential consumers of methylated compounds, were not capable of consuming DMS or other methylated compounds, therefore flux out of the peat surface approximated actual production rates [*Hines*, personal communication]. *Dimmer et al.*, 1999 measured emissions of CH_3I, CH_3Cl and CH_3Br from peatland ecosystems in Ireland. They suggest that plant species

are responsible for much of the variability seen between flux measurements because they may have different leaf methyl transferase enzyme activity which has been found to be responsible for methyl halide production [*Wuosmaa and Hager*, 1990; *Saini et al.*, 1995].

CH_3I has been measured as a byproduct of either root or microorganism activity in rice plant pots in a greenhouse [*Muramatsu and Yoshida*, 1995]. Recently, CH_3I, CH_3Cl and CH_3Br production have been measured in rice fields [*Redecker et al.*, 1998]. Salt marshes have also been characterized as a source of CH_3Br and CH_3Cl to the atmosphere with the following suggested conditions for production: readily available high chloride and bromide ion concentrations, interaction between plant and associated microflora, and the influence of the whole plant on emissions [*Rhew et al.*, 2000].

Recently, *Keppler et al.*, [2000] measured abiotic production of CH_3Br from suspended organic matter from peat water. These measurements were made under controlled laboratory conditions and resulted in the production of CH_3Br during the oxidation of organic matter. The production increased when more Br^- and Fe(III) were present.

1.4. Objectives

The objectives of this research were

1) To determine the sink strength of different soil types from different climatic regimes,

2) to determine the seasonality of the soil sink at two temperate sampling locations,

3) to globally extrapolate the soil sink and

4) to determine if wetlands are a source of CH_3Br and if so, to study the seasonality of this source.

This dissertation represents the summary of my research on the upland and wetland exchange of atmospheric CH_3Br. A third of my research effort was spent on optimization of our analytical system to measure ambient levels of CH_3Br, the details of which are presented in Chapter 2. Chapter 3 contains all the data collected on the upland soil exchange of atmospheric CH_3Br including laboratory and field measurements. Chapter 4 is the summary of our discovery of the wetland source of CH_3Br and a seasonal study of it at two temperate sites. Finally, I address the significance of these findings in Chapter 5 along with recommendations for further research endeavors.

CHAPTER 2

COLLECTION AND ANALYSIS OF SAMPLES FOR CH_3Br

2.1. Introduction

The methodology for the measurement of atmospheric CH_3Br by cryotrapping/gas chromatography is described in the following chapter. Throughout the years of this study, the system has changed as understanding of the analysis has improved. The system has been used to analyze laboratory as well as field samples in a variety of configurations. I will describe the original system as it was used for much of the data acquisition and will highlight changes that were made when appropriate.

Measuring at and near ambient mixing ratios of CH_3Br (~10 parts per trillion by volume (pptv)) has presented quite a challenge to the research community. Other research groups have developed methodologies to detect CH_3Br with high sensitivity that are similar to ours. Gas chromatographic techniques in combination with electron capture [*Singh et al.*, 1983; *Woodrow et al.*, 1988; *Rhoderick*, 1995], mass spectroscopic [*Cicerone et al.*, 1988; *Manö, and Andreae*, 1994; *Lobert et al.*, 1995; *Rhoderick*, 1995] and photoionization [*Dumas and Bond*, 1985] detection have been applied to the detection of methyl bromide at low mixing ratios. The detection limits achieved by these groups ranged from 3.0 to 0.1 pmoles. We chose our detection system because it is designed to be applied to a wide range in concentrations in field and laboratory experimentation. This system is also relatively inexpensive and our detection limit, 0.23

pmoles, lies at the low end of the cited range. With the recent changes made to our system, our detection limit has dropped to 0.02 pmoles.

2.2. Apparatus

Gas samples were analyzed using a Shimadzu GC-8A gas chromatograph equipped with an electron capture detector (ECD). To separate CH_3Br chromatographically, two 3.18 mm o.d. stainless steel columns, a 1 m precolumn packed with PoropakQ 100/120 mesh and a 2 m analytical column packed with 80/100 mesh HayeSepQ (Alltech), were connected in series. Column and injector/detector temperatures were 140°C and 290°C, respectively. We used an Oxygen (O_2) doped carrier gas of Ultra High Purity (UHP) Nitrogen (N_2) at a flow rate of 30 ml/min. The O_2 dopant was diffused into the N_2 carrier flow through a 4.0 cm sealed 6.35 mm o.d. Teflon tube. The Teflon tube was placed inside a bored out stainless steel tee and sealed with compression fittings. O_2 diffused across the Teflon tube via the third side of the tee. The Teflon diffusion device was attached to the O_2 and N_2 cylinders 5 m upstream of the GC-ECD to ensure proper mixing of the two gases. We are uncertain of the final concentration of the O_2 in the UHP N_2. It was operationally determined by varying the delivery pressure of O_2 to the diffusion device. Too much O_2 in the carrier gas resulted in an unacceptably noisy baseline. Conversely, too little O_2 resulted in reduced sensitivity of the detector to CH_3Br. The GC-ECD was equipped with a 10 port, two position electrically actuated valve (Valco Instruments Company, Inc.) (Figure 2.1a). The valve controlled sample injection to the detector as well as backflush through the precolumn. The system was designed to backflush all unwanted compounds that eluted from the

precolumn later than CH_3Br. The total retention time for CH_3Br for both columns was 6.0 minutes. The entire GC-ECD system was controlled by a Hewlett Packard Vectra 486/33VL computer equipped with HPChemstation software.

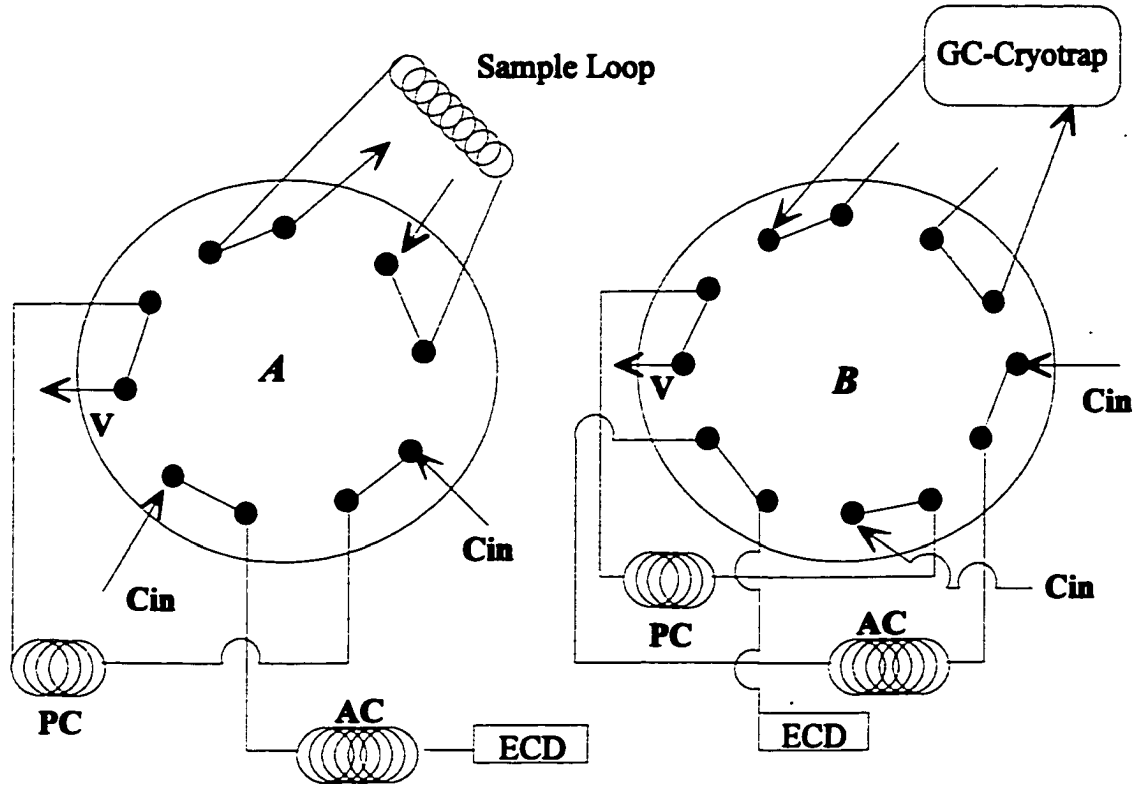

Figure 2.1 a and b. Valve diagram showing (A) the 10-port backflush system and (B) the 12-port "heart cutting" setup both in the LOAD position. AC = analytical column; PC = pre-column, V = vent; Cin = Carrier gas inflow.

Gas samples were cryotrapped in a loop consisting of an inert valve (Hamilton, Co.), flangeless Delrin bushings, Tefzel ferrules, 0.4 m of 3.18 mm o.d. Teflon tubing (Alltech Associates, Inc.), and a 2 cm plug of quartz wool/PoropakQ. Samples were trapped in a bath of isopropanol and dry ice. A vacuum pump was used to pull a sample through the sample loop (immersed in the cryotrap) then through a totalizer/mass flow meter (MFM) (Brooks Instruments). The total volume of the air sampled was recorded

and the sample loop was connected to the GC-ECD. After carrier gas flushed the dead volume, the sample loop valve was opened and the loop was immersed in boiling water to revolatilize the CH_3Br. Once CH_3Br had reached the analytical column, the computer activated the electric actuator to backflush the precolumn. The time of backflush was determined by running a series of CH_3Br standards through the GC-ECD with different backflush times and comparing peak areas. In this configuration, the backflush time was 3.9 minutes after injection of sample and the CH_3Br peak eluted at about 6.0 minutes.

Major changes in the analytical system were implemented during the summer of 1998. The removable, Teflon sample loop was replaced with a 30.5 cm sample loop made of 1.6 mm o.d. stainless steel tubing. It was packed with PoropakQ 80/100 mesh packing and sealed at both ends with a quartz wool plug. This loop was permanently connected to a 6-port , two position electrically actuated valve (Valco Instruments Company, Inc.) attached to the outside of the GC-ECD. At the same time, a 12-port, two position electrically actuated valve (Valco Instruments Company, Inc.) replaced the 10-port valve previously used (Figure 2.1b). The extra ports on this valve allowed us to "heart cut" the CH_3Br peak. "Heart cutting" refers to the venting off of sample before and after the desired fraction to reduce interference by other detectable materials at the detector. The chromatographic columns in the GC-ECD were replaced with two stainless steel, 1.6 mm o.d., 1 and 2 m columns (pre-column and analytical column, respectively) packed with PoropakQ 80/100 mesh. The backflush and elution times for CH_3Br are 12.1 and 23.3 minutes, respectively.

In April of 1999, the cryotrapping portion of the system was also upgraded. A GC

Cryotrap (Model 951, Scientific Instrument Services, Inc.) replaced the manual cooling and heating previously completed with a dry ice/isopropanol bath and boiling water. A new 12 cm sample loop, with a small plug of quartz wool and PoropakQ 80/100 mesh packing, was inserted in the GC-Cryotrap and could now be cooled and heated automatically. The entire system could be controlled through the computer. Standards and field samples in stainless steel cylinders could be set up to run automatically overnight. These changes to the system also yielded more precise and accurate measurement of ambient CH_3Br samples.

2.3. Calibration

Calibration of samples was completed in one of three ways. The static laboratory soil incubations as well as the field samples required the use of a purchased standard (Scott Specialty Gas, Inc.) equal to 270.1 ± 7.8 ppbv. A measured volume of standard was cryotrapped on the sample loop by addition through a stainless steel tee attached to the N_2 sweep line. The standards were analyzed on the GC-ECD as previously described. The daily standard curves included replicates of the following 5 volumes of standard: 1.0, 0.5, 0.25, 0.1 and 0.05 ml of 270 ppbv CH_3Br. The average r^2 of the linear regression fit of peak area versus nmoles of CH_3Br for a 6 month period of sampling was 0.9998.

Dynamic soil incubations required the calibration standards to be prepared in a slightly different way through the use of a 3-stage dynamic dilution system modified from the designs of *Goldan et al.* [1986] and *Fried et al.* [1990] developed and constructed in our laboratory (Figure 2.2). Briefly, zero air (Aadco Instruments, Inc.) flowed through a permeation oven held at 30°C ± 0.1°C (VICI Metronics) where it mixed with CH_3Br

emitted from a permeation tube (KIN-TEK) calibrated gravimetrically (Mettler AE1, 5 decimal place balance). The air then flowed through the 3-stage dilution box where it was subsequently diluted with zero air and/or bled from the system using mass flow controllers (Brooks Instruments, Inc.). The mass flow controllers were manually manipulated to produce the desired mixing ratio. Equilibration of the dilution system to a new mixing ratio when the mass flow controllers were changed is a function of the flow rate through the system and the volume of the dilution system that needs to be flushed. Goldan et al.,1986 and Fried et al.,1990 showed that equilibrium could take up to 1 hour. Our system required between fifteen minutes and an hour for equilibrium to be established. The zero air had no detectable amounts of CH_3Br.

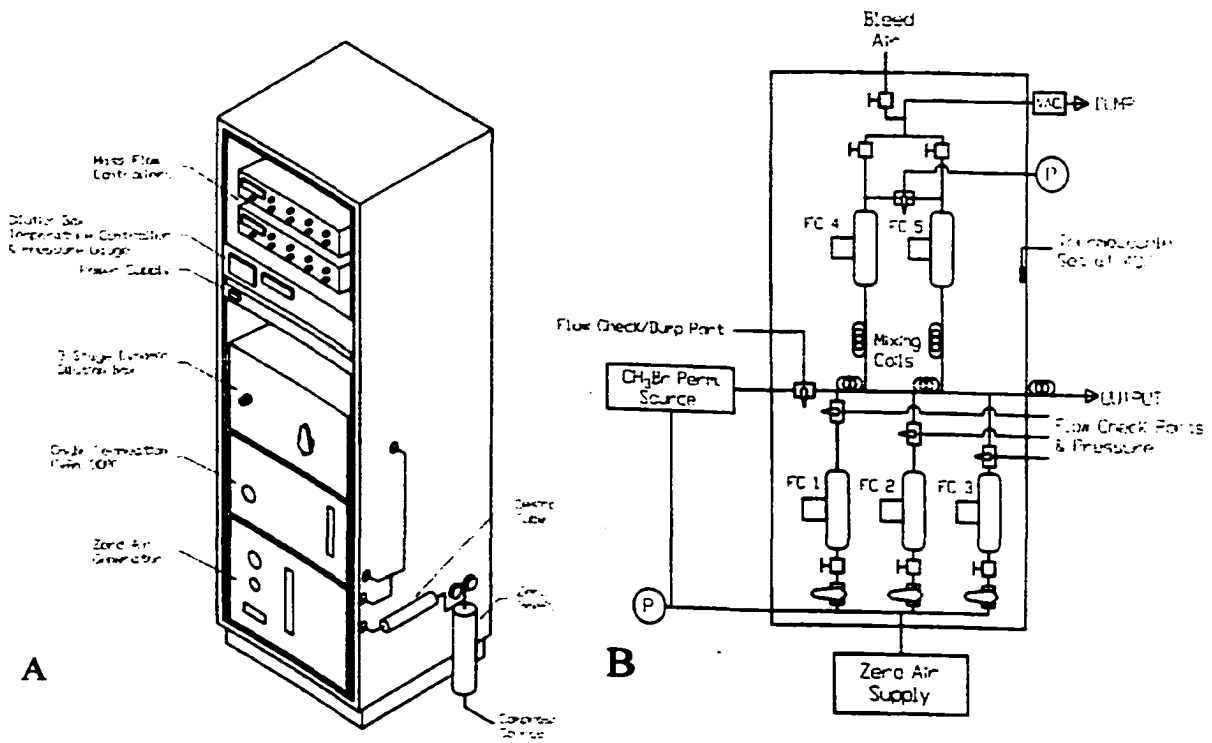

Figure 2.2a and b. Diagram of the 3-Stage Dynamic Dilution System. a. 3-stage dynamic dilution rack. b. 3-stage dynamic dilution box interior.

The dilution system continuously produced calibrated mixing ratios of CH_3Br ranging from 70 to 1000 pptv. Lower mixing ratios (4-70 pptv) were obtained by completing an additional external dilution. The external dilution involved mixing the dilution system air with compressed air in a mixing volume, a 1 liter mason jar, until the desired mixing ratio was achieved.

The permeation tube was weighed approximately every 5 days to 2 weeks for the first 5 months and then once every six weeks after that for a total length of 10 months (Figure 2.3a). The permeation rate quantified over this period, 271 ± 0.6 ng min^{-1}, was exceptionally linear. Short term variations in the permeation rate were minimized by keeping the permeation oven and the 3-stage dilution box at a constant temperature, pressure and flow rate.

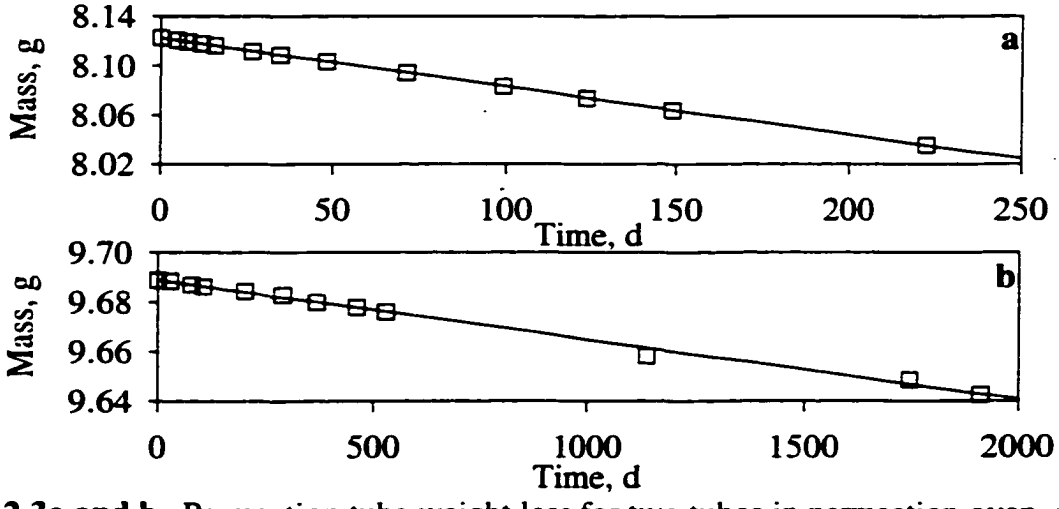

Figure 2.3a and b. Permeation tube weight loss for two tubes in permeation oven. a) permeation tube #1, data (□) and linear regression, b) permeation tube #2, data (□) and linear regression.

A second permeation tube was purchased and placed in the permeation oven on September 14, 1995. It was weighed periodically over the following 5 years and was

determined to produce approximately 16.8 ± 0.4 ng/min (Figure 2.3b). This permeation rate in the dilution system produced calibrated mixing ratios of CH_3Br ranging from 6.4 to 2000 pptv. This lower permeation rate eliminated the need for an additional, external dilution to achieve ambient concentrations.

Before dynamic soil incubations were conducted, calibration standards were analyzed using a procedure identical to that used for sample analysis to ensure direct comparability. The dilution system produced the desired mixing ratio of CH_3Br by manual manipulation of the fractional flows of the five flow meters. An empty serum vial (150 ml) was flushed thoroughly with flow from the dilution system. The flow out was sampled as previously described in the calibration section. A progression of sample volumes, therefore different masses of CH_3Br, from the outflow were analyzed to generate a standard curve. Figure 2.4 is an example of the standard curve generated on March 16, 1995. In general, the standard curves generated on a particular day would bracket the mixing ratios that were going to be used in the soil incubation studies that day.

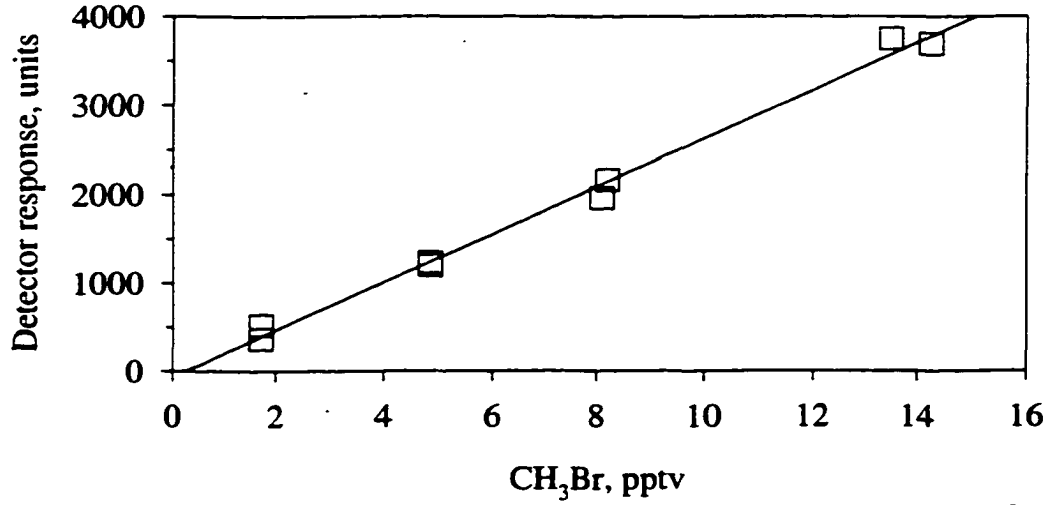

Figure 2.4. Standards analyzed on March 16, 1995 for dynamic soil incubations. Linear regression fit : $y = 270.1x - 72.3$, $r^2 = 0.993$.

Standards for field sampling with syringe samples were run in a similar fashion as static soil incubations. When field samples were taken with sample canisters the following method was used. Canisters were cleaned by a process of evacuation with a vacuum pump and pressurization with UHP N_2 repeated 4 times. This progression ended in an evacuated cylinder. The standards were prepared by adding a measured volume of CH_3Br with a gas tight syringe to the evacuated cylinder then filling the cylinder to 60 psig with UHP N_2. Six canisters were filled for standard analysis: 1 blank, 5 standard mixtures with concentrations ranging between 5 to 30 pptv; exact concentrations depending on expected range of sample concentrations. An example of a one day standard run is shown in Figure 2.5. Blanks of UHP N_2 were run everyday.

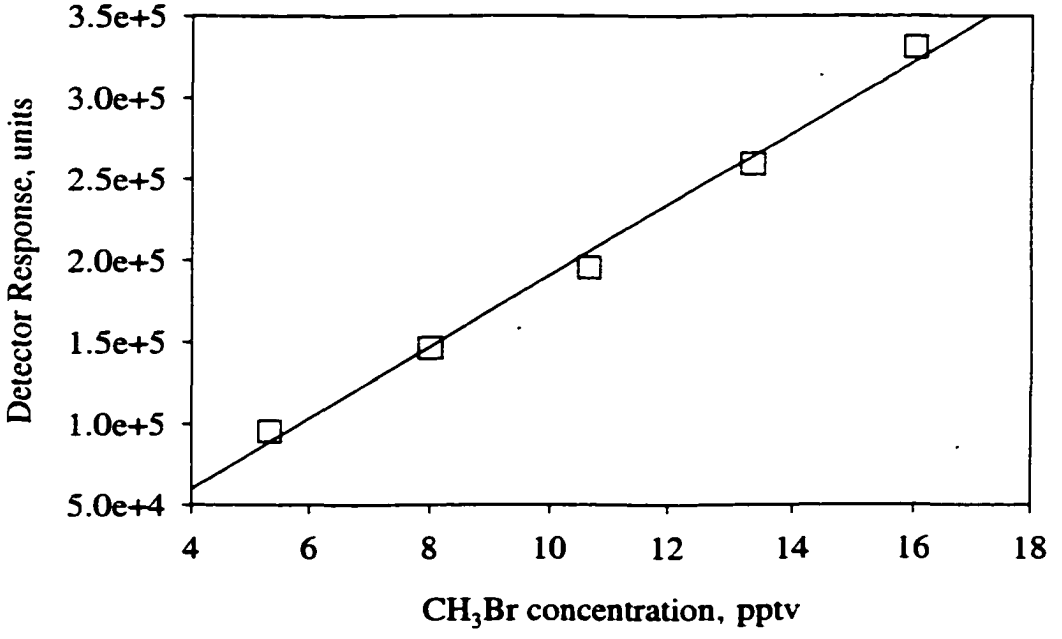

Figure 2.5. Standards from December 2, 1999. □ are data. Linear regression equation: y = 2.4E-09x + 9.9E-06, r^2 = 0.9999.

2.4. Data Collection

2.4.1. Laboratory Soil Incubations

CH_3Br soil uptake kinetics were determined using two methods: dynamic and static. Soil kinetics measurements using the dynamic method began with dynamic dilution system air being metered off from the dilution system (or the external dilution depending on the desired mixing ratio) to regulate the flow rate. This flow rate was measured by using a soap-bubble flow meter (Teledyne Hastings-Raydist). To determine the loss of CH_3Br to soil surfaces, the dilution system air was sampled before and after it flowed over the soil. The air was sampled 6-10 times before soil was added to the vial. 5 to 10 grams of soil was placed in the vial and the dilution system air was allowed to flow through the vial for 10-15 minutes before sampling (10 volume changes). Air samples were collected after the soil/air system had equilibrated. The vacuum pump pulled a sample (500 ml to 1 L) from the vial outflow, through the sample loop, and through the totalizer/MFM. The sample loop was then connected to the GC-ECD and the CH_3Br analyzed. The uptake rate of CH_3Br (pmoles/min) was determined as the difference between the concentration of CH_3Br in the inlet and outlet flows multiplied by the flow rate of the dilution system air through the vial.

Static soil incubations entailed placing 5 to 20 grams of soil into twelve, 200 ml glass vials which were sealed and suspended in a 25°C water bath. The vials were injected with 3 ml of 270 ppbv CH_3Br to obtain an initial head space mixing ratio of approximately 4 ppbv. The vial head space was evacuated at specified time intervals with UHP N_2 onto a Teflon sample loop immersed in a dry ice/isopropanol bath (Figure 2.6).

Samples were then run on the GC-ECD as stated previously.

The resulting peak areas were compared to daily standard curves and concentrations calculated. Replicate head space samples for each of the six time segments were completed. A reaction rate constant, k, was determined as the slope of the regression fit of the natural log of nmoles of CH_3Br versus time. This k, in min^{-1}, was then divided by the grams of dry soil (ds) in the vial resulting in a measured reaction rate constant with the units of $min^{-1}g^{-1}_{ds}$.

To quantify the error of the totalizer/MFM, we simulated sample trapping conditions using flow from a cylinder of compressed air. The flow out of the totalizer/MFM was measured using a soap-bubble flow meter. The estimated error in the MFM was found by bubble flow meter calibration to be ± 0.32%.

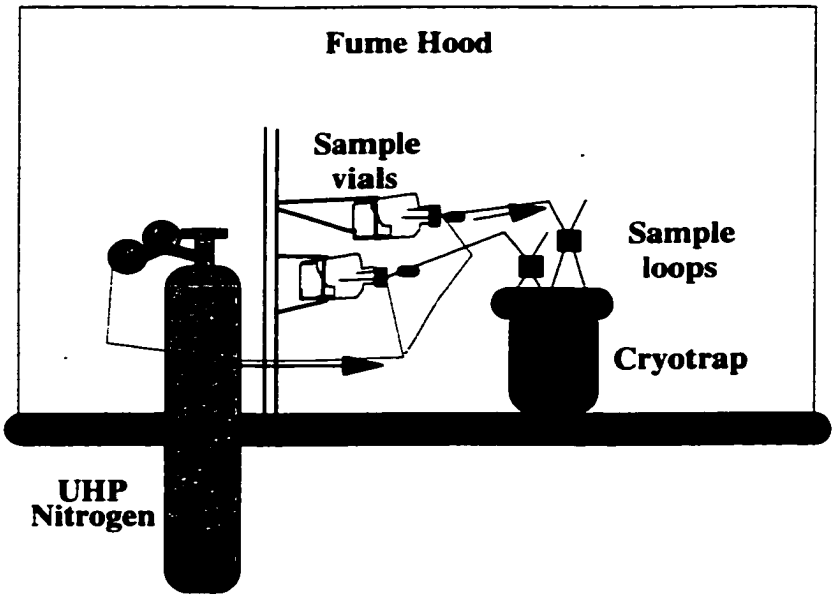

Figure 2.6. Schematic of static soil incubation sampling.

2.4.2. Field Sampling.

Briefly, field sampling entailed placing either a clear chamber made of Teflon film and Lexan or a dark chamber made of aluminum on an aluminum collar cut into the soil/peat surface. All materials were tested and proven non-reactive with CH_3Br. Samples of the enclosed headspace were taken at specified time intervals. Field samples collected in 1994 were taken with 60 mL polypropylene syringes (Becton Dickinson). The syringes were loaded on the sample loop immersed in the cryobath similarly to standard loading and analyzed by GC-ECD as described previously.

Field samples taken after August, 1998 were taken with stainless steel 500 mL sample canisters. Approximately 533 mL of sample were passed through the sample loop held at -70°C in the GC Cryotrap. Automated analysis of up to 15 sample cans could occur after the addition of a 16-port sampling valve and a mass flow controller (MKS Instruments, Model #1179A) and totalizer (KEP,Co. Model INT69) unit (Figure 2.7). The computer signaled the GC cryotrap to cool the sample loop to -70°C and waited 3 minutes to ensure temperature equilibration. The computer then switched the 16-port valve to switch to the desired sample canister and then switched the 6-port valve to load the sample to the sample loop. The flow rate through the system was set at 59.3 mL/min and samples were loaded for 9 minutes resulting in the loading of approximately 533 mL of sample. Once the sample was loaded, the computer signaled a simultaneous valve switch of the 6 and 12-port valves and the heating of the sample loop to 120°C. This allowed the sample to be revolatilized and swept into the GC-ECD for analysis as previously described.

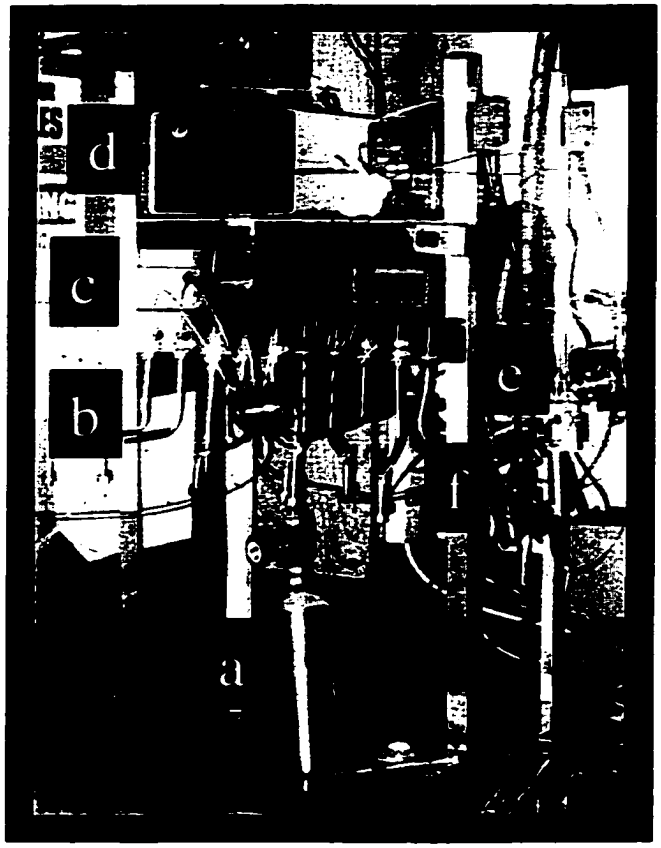

Figure 2.7. Photograph of automated analysis system. **a** - sample canister, **b** - 16-port sampling valve, **c** - MFC/Totalizer, **d** - GC Cryotrap control box, **e** - 6-port sample loop valve, **f**- GC-Cryotrap with sample loop.

2.5. Results and Discussion

2.5.1. GC-ECD Efficiency

The effect of the configuration of the system components on the sensitivity of the GC-ECD system to methyl bromide detection was examined. A cylinder of 270 ppbv CH_3Br (Scott Specialty Gases) was used to determine the effect of changing O_2-dopant and N_2 carrier gas pressures, at the second stage of the regulator, on the sensitivity of the system. The increase of the O_2 pressure from 4 to 50 psi and the N_2 pressure from 40 to 50 psi resulted in a considerable increase in the sensitivity of the GC-ECD. The peak

areas of the standard increased an average of 6.61% and the error of ten standard samples decreased from 1.04% to 0.41%. The remaining experiments were run with O_2 and N_2 pressures at 50 psi. No significant increase in noise of the baseline was observed with the increase in O_2 pressure.

The magnitude of the baseline noise appeared to increase throughout the sampling day. This may have been caused by the Teflon O_2 diffusion device becoming more permeable as the temperature in the room changed. Slow contamination of the GC-ECD column with continual injections of samples over the course of a day could be another source of noise. The column temperature was increased from 140°C to 180°C every night to bake out any contamination and reduce baseline noise. This baking did not have any negative effect on the overall sensitivity of the instrument. The signal (voltage response of the detector to the sample) to noise (voltage width of random baseline variability without sample) ratio for samples from a 270 ppbv cylinder of CH_3Br varied between 618 and 793 over a period of three months. The signal to noise ratio for a 30 pptv standard from the dynamic dilution system varied between 30 and 43 over a period of two months.

The detection limit of our GC-ECD system was defined using a signal to noise ratio of 3 [*Long and Winefordner*, 1983]. Initially this was 0.23 pmoles, which represents the amount of CH_3Br contained in about 500 ml of air at the average global mixing ratio. After major changes were made to the system, the detection limit as defined above is equal to 0.02 pmoles. This is a dramatic improvement to our analysis capability that allows us to measure at and below ambient levels of CH_3Br in smaller sample volumes.

Figure 2.8 shows the change in detector response of the detector over the years of analysis.

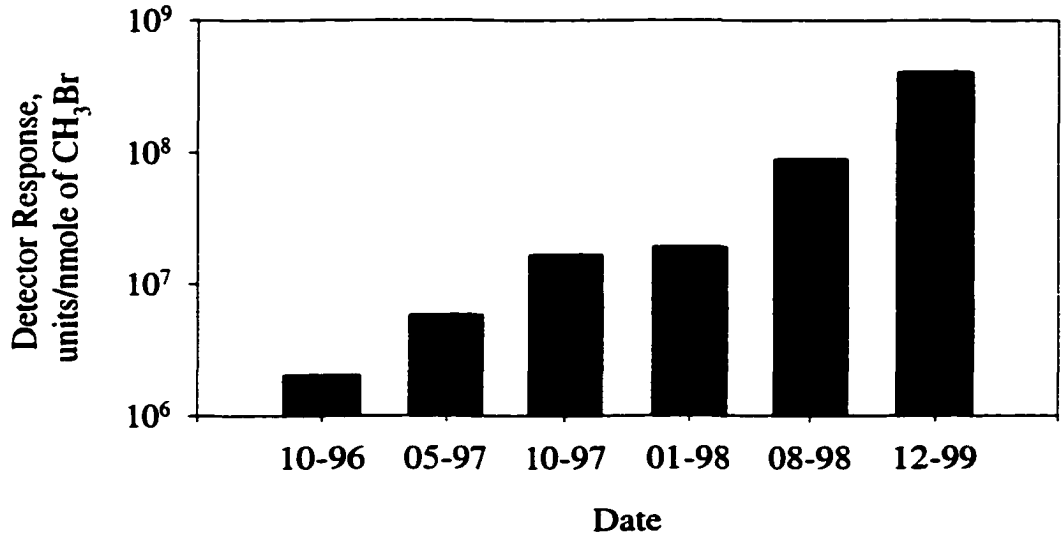

Figure 2.8. Change in response of analytical system as response of detector in area per nmole of CH_3Br versus date of analysis.

2.5.2. Dynamic Dilution System Efficiency

The dynamic dilution system output of CH_3Br was dependent on the measurement of the permeation tube weight loss. Figure 2.4a. and 2.4b. reveals that the weight loss over the measurement period was linear. In figure 2.4a. the r^2 of the linear regression is 0.9999 and the standard error ± 0.29%. Figure 2.4b. reveals an r^2 of the linear regression of 0.991 and the standard error ± 3.2%. The standard curves from the dilution system reveal standard error estimates of ± 2.0 - 3.5%. There appeared to be no correlation between relative error and mixing ratio of the standard gas.

The dilution system can consistently and precisely produce a range of mixing ratios of CH_3Br. Figure 2.9 is an example of the within day variability of the dilution

system response using standard samples from the dilution system processed over a nine hour period. The within day variability is between 2.0 and 3.5%. The equation of the weighted regression is: $y = 3552.3x - 159.6$ with an r^2 of 0.998. Figure 2.10 reveals the between day variability of the dilution system response. This plot shows data for dilution system standards analyzed on 14 different days spanning a two month period. The variability is small as shown by the linear regression relationship: $y = 5611.9x - 154.6$, $r^2 = 0.972$. The variability in response can be attributed to changes in the temperature of the laboratory, slight changes in flow rate through the GC-ECD, or slight changes in pressure and temperature of the O_2 doping device. Our permeation system standard was also intercalibrated with the Rowland and Blake laboratory at UC-Irvine.

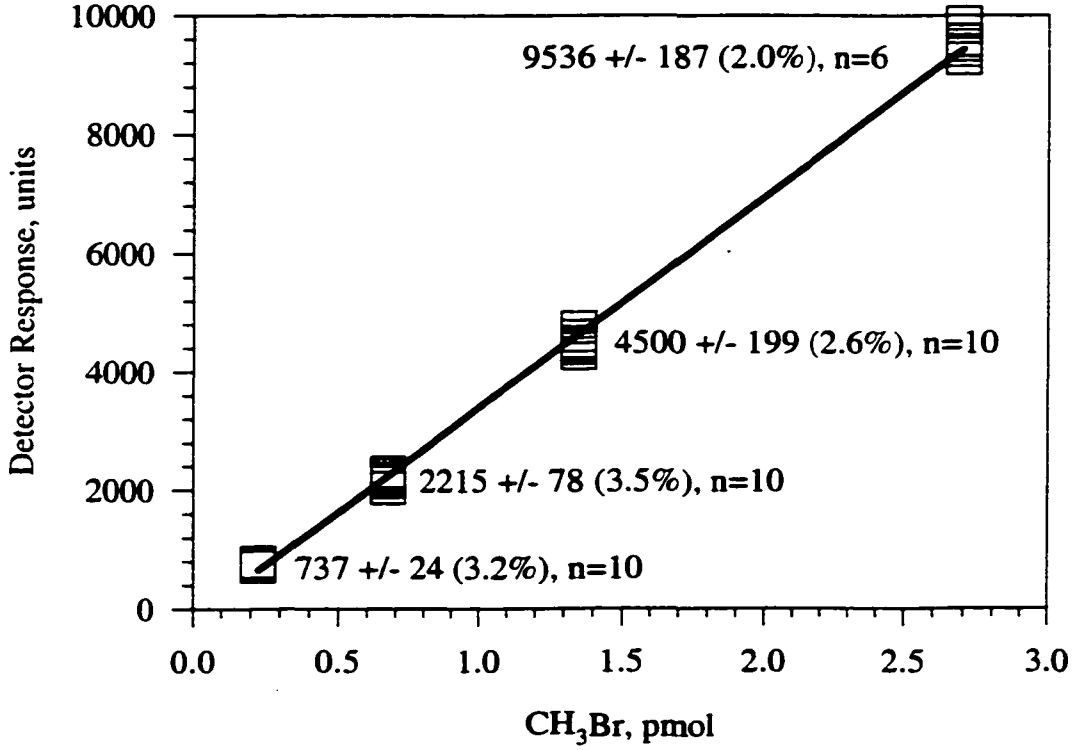

Figure 2.9. Weighted linear regression of 3-Stage Dynamic Dilution System standards for May 24, 1995, detector response vs. pmoles of CH_3Br. With our sampling and analysis technique, the mixing ratio that this would represent is 5 to 60 pptv. Equation for weighted linear regression: $y = 3552.3x - 159.6$, $r^2 = 0.998$.

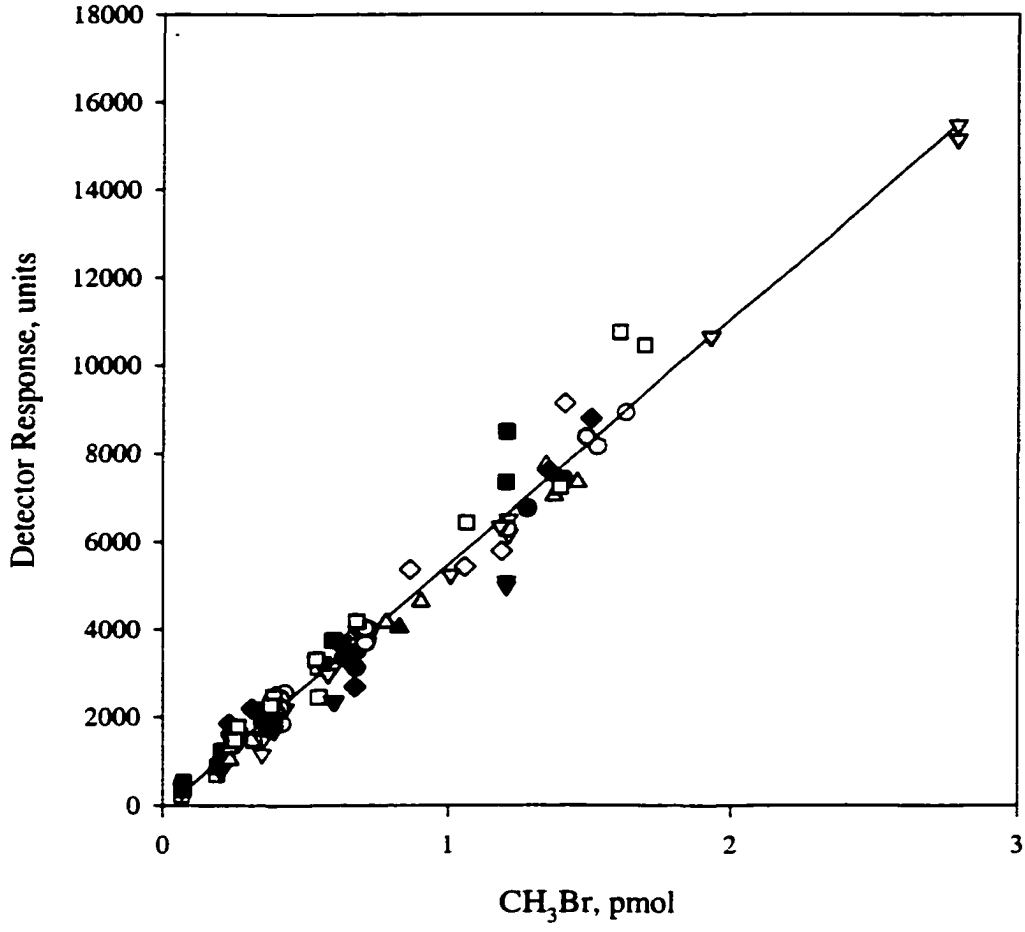

Figure 2.10. Linear regression of 3-Stage Dynamic Dilution System standards for 14 days over a two month period, detector response vs. pmoles of CH_3Br. With our sampling and analysis technique, the mixing ratio that this would represent is 2 to 60 pptv. Equation for the linear regression: $y = 5611.9x - 154.6$, $r^2 = 0.972$. The symbols represent the following sampling days: ■, 3/16/95; □, 3/21/95; ▼, 3/22/95; ▽, 3/23/95; ●, 3/28/95; ○, 3/29/95; ▲, 3/31/95; △, 4/4/95; ◇, 4/6/95; ◆, 4/7/95; ●, 4/11/95; ▲, 4/12/95; ▼, 4/14/95; ■, 4/28/95.

The comparison of our dilution system air with a standard from a commercial supplier revealed that the commercial standard was approximately 50% less than the supplier's original calibration. The commercial standard had been prepared more than 2 years before our analysis and the cylinder was apparently untreated. Roderick, 1995

showed that cylinders not treated to retain stability show a dramatic decrease in some compounds including CH_3Br. Due to the difficulty in obtaining dependable gas standards with known mixing ratios from commercial suppliers, a stable permeation/dynamic dilution system is extremely important for calibration of air samples which are near ambient levels.

The dynamic soil incubations produced uptake rates that increased with increasing CH_3Br mixing ratios [*Shorter et al.*, 1995; *Hines et al.*, 1998]. The uptake rates ranged from 7.9×10^{-3} pmoles min^{-1} g_{ds}^{-1} to 1.2×10^{-1} pmoles min^{-1} g_{ds}^{-1} for mixing ratios of 4.1 to 97.9 pptv. Changing the flow rates of the dilution system air through the vials had no effect on the relationship between the mixing ratios and uptake rates. This observation was confined to the dynamic experiments that we completed with flow rates ranging from 98 to 155 ml/min and CH_3Br mixing ratios ranging between 4.1 and 97.9 pptv.

Table 2.1 shows an example of the results from soil incubations. The volume weighted response refers to the response in units of the GC-ECD divided by the total volume of the sample taken. These units were chosen to normalize response since all samples taken were of different volumes. Zero air from the dilution system was run to determine if there was any CH_3Br response. The CH_3Br in the zero air was below the detection limit. As the table illustrates, when blank vials were run there was no difference between the initial 11 pptv CH_3Br air "before" and "after" the vial thus determining the inertness of the sample vial. The table also shows that the difference between the "before" and "after" values for vials with soil were between 25 to 50%. The values for the "before" and "after" samples varied less than 6%. Calculated fluxes for the

given soils are also shown in Table 2.1.

Sample Type	Volume Weighted Response (units/ml)	Nominal Concentration (pptv)	Volume Weighted Response (units/ml)	Nominal Concentration (pptv)	Uptake Rate (pmoles $min^{-1}g^{-1}_{dw}$)
"before" = air in "after" = air out	"before"	"before"	"after"	"after"	
Blank Zero Air	b.d.	b.d.	b.d.	b.d.	n.a.
Blank No Soil	2.9 ± 0.16 n = 10	11	2.9 ± 0.16 n = 10	11	0.0
0-3 cm Temperate Forest Soil	2.9 ± 0.16 n = 10	11	1.4 ± 0.02 n = 6	5.6	2.1×10^{-2} $\pm 3.7 \times 10^{-4}$
3-7 cm Temperate Forest Soil	3.0 ± 0.31 n = 7	11	1.9 ± 0.03 n = 10	7.3	2.9×10^{-3} $\pm 4.3 \times 10^{-5}$
0-3 cm Temperate Forest Soil	10 ± 0.92 n = 8	47	4.6 ± 0.28 n = 10	22	6.9×10^{-2} $\pm 4.0 \times 10^{-3}$

Table 2.1. "Before", "after", and calculated uptake values for selected dynamic incubations. b.d. = below detection limit; n.a. = not applicable

2.5.3. Field Sampling

In 1994, field sampling entailed taking samples with 60 mL polypropylene syringes. Syringes were loaded to the removable sample loop then attached to the GC-ECD for analysis. Syringe samples were analyzed within 2 hours of sampling to minimize leakage effects.

After August, 1998, air samples from the field were taken in 500 mL stainless steel sample canisters. Sample cans were cleaned with a vacuum/pressurization

technique. Blank cans were run during every sampling analysis day to determine if there was any background contamination of CH_3Br. Blanks ranged from between 0 and 6500 area counts with an average of 1665 for 52 sampling days. These detector responses yield background contamination of 0 to 1.0 pptv CH_3Br and an average of 0.54. The automation of the analytical system provided for a more consistent analysis with less operator error. The temperatures of the GC Cryotrap were held within $\pm 3°$ of their set values. The flow controller used for control of the sample/standard loading to the sample loop was set at 51.3 mL min^{-1}. This flow was consistently 53.9 ± 0.14 when compared to a Gilibrator-2, Primary Flow Controller (Gilian Instrument Corp.).

Replicate analyses of ambient air samples revealed an instrument analysis error of $\pm 6\%$ for 10 samples. Sample canisters were generally analyzed within 24 hours of sampling even though sample mixing ratios in the canister were determined to be consistent over a 6 day period.

2.6. Conclusions

The measurement techniques described in this chapter are consistent and precise methods for producing CH_3Br standards and for measuring CH_3Br at ambient mixing ratios. The "heart cutting" system and subsequent cryotrapping of CH_3Br produce clear chromatograms. The dynamic dilution system made it possible to produce many different mixing ratios of CH_3Br for soil uptake studies in a short period of time. Automation of analytical system has been responsible for making the analysis for CH_3Br more consistent, less labor intensive and less time consuming. It is now possible to sample

ambient CH_3Br exchange from three to four field sites in one week whereas before only two sites could be sampled per week and the fluxes began above ambient levels.

CHAPTER 3

UPLAND SOIL EXCHANGE OF ATMOSPHERIC METHYL BROMIDE

3.1. Introduction

In 1992, the parties of the Montreal Protocol listed CH_3Br as an ozone depleting substance because of its ozone depletion potential (ODP) of 0.7. This classification meant that there would be an eventual phasing out of the production and use of fumigant CH_3Br. At this point, the interest in the environmental fate of CH_3Br intensified. At that time, most published research had focused on the volatilization of CH_3Br during fumigation while few studies had been completed to determine the interactions between CH_3Br and soil [*Arvieu*, 1983; *Mignard and Benet*, 1989]. CH_3Br in soils has at least four potential loss mechanisms: 1. hydrolysis, 2. abiological reaction with soil organic matter, 3. microbial degradation and 4. direct volatilization to the atmosphere.

Hydrolysis of CH_3Br with pore water occurs by means of the following association:

$$\mathbf{CH_3Br + H_2O \rightarrow CH_3OH + H^+ + Br^-}$$

This reaction occurs at a relatively slow rate with $k = 1.04 \times 10^{-5}$ min^{-1} at 20°C [*Arvieu*, 1983]. Abiological reaction with organic matter occurs via adsorption of the methyl group to an active site on the organic matter:

$$\mathbf{CH_3Br + OM \rightarrow CH_3OM + Br^-}$$

Rates of this reaction are probably dependent on amount of organic matter present as well

as its condition in the soil.

Microbial degradation of fumigant CH_3Br is cited in many works but is hard to quantify because of the simultaneously occurring abiological degradation. *Miller et al.*, 1997 suggest that a microbial oxidation of CH_3Br proceeds as:

$$CH_3Br + 1.5O_2 \rightarrow HCO_3^- + 2H^+ + Br^-$$

After a facultative methylotroph from fumigated soils that consumes CH_3Br was isolated [*Connell Hancock et al.*, 1998], *Miller et al.*, 1997 determined that the partitioning of fumigant application of CH_3Br between the four pathways was: 50% to volatilization to the atmosphere, 20% to adsorption to soil organic matter, 25% to microbial consumption, and the remaining 5% to hydrolytic breakdown in pore water. As the concentration of the applied fumigant increased, adsorption and volatilization became the major measurable processes.

The rates of the soil uptake processes are also influenced by environmental factors such as temperature, moisture content, and organic matter content [*Gan et al.* 1994; *Rice et al.* 1996; *Yates et al.*, 1996; *Gan et al.* 1996; *Anderson et al.*, 1997; *Gan et al.* 1997; *Wang et al.*, 1997; *Dimitriou and Tsoukali*, 1998] as well as the presence and abundance of microorganisms that are responsible for its destruction [*Oremland et al.* 1994; *Ou et al.*, 1997; *Connell Hancock et al.*, 1998; *Miller et al.* 1997].

In 1995, we reported the first measurements of the uptake of near ambient concentrations of CH_3Br by soils [*Shorter et al.*, 1995]. We estimated that the global soil sink of atmospheric CH_3Br was 42 Gg yr^{-1}. Our findings significantly changed the global tropospheric budget of CH_3Br and had a direct effect on the ODP calculations bringing it

from 0.7 to 0.4. Moisture and temperature manipulations of soil incubations revealed a possible microbial sink mechanism. Through the use of antibiotics and sterilization techniques, we determined that the soil uptake of ambient CH_3Br is primarily completed through aerobic bacterial activity [*Hines et al.*, 1998].

In order to test if this process was a ubiquitous destruction mechanism occurring in all soils of the world, we expanded our sample data to include more soils from many different soil types as well as a range of climatic zones. After optimization of our analytical system, we were able to measure ambient levels of CH_3Br and ventured upon measuring ambient uptake at two sites through an entire growing season. We felt that this would give us some idea of the natural variability of CH_3Br exchange as well as some idea of the controls on the destruction of CH_3Br.

The research presented in this chapter includes measurements of the uptake of CH_3Br by soil from a variety of biomes from across the United States, Costa Rica, Brazil, Canada, Finland, Siberia, China and Germany. Soils were collected by colleagues. Field measurements of ambient and above ambient exchange of CH_3Br, CO_2 and CH_4 were also completed. In 1994, near ambient flux measurements were made from mid-July through the end of November at three sites: temperate forest (College Woods, Durham, NH), temperate grassy clearing (Crill backyard, Lee, NH), and a cultivated area (Moore Fields cornfield, Durham, NH). During the growing season of 1999, ambient CH_3Br exchange was monitored at two upland sites weekly from late May through mid-November: temperate forest (College Woods, Durham, NH) and a cultivated area (Kingman Farm cornfield, Madbury, NH). SF_6, an inert tracer, was used during some field flux

measurements to determine the non-biological loss of gasses from the chamber headspace.

3.2. Laboratory Soil Incubations

3.2.1. Methods

We determined that laboratory incubations of soils yield similar results as field flux measurements and since it was not economically or logistically feasible to conduct field experiments at locations around the world, laboratory incubations of soils collected around the world were completed. Soil samples for laboratory incubation from 0-5 cm, 5-10 cm and 10-15 cm depths were collected from over 90 sampling locations from across the continental United States, Alaska, Canada, Costa Rica, Brazil, Germany, China, Finland and Siberia. The sampling sites consisted of cultivated, forest, meadow, pasture and desert locations. Soil classifications for each sampling site were obtained either during sample collection or from soil maps. Soils were stored in doubled plastic bags at 0°C and were assayed within 4 weeks of sampling. Experiments completed to determine loss of activity in soils up to 6 months of storage after collection revealed that there was a loss of less than one third the original activity over the longest time period.

Static laboratory incubations entailed placing 5 to 20 grams of soil into twelve, 200 ml glass vials which were sealed and suspended in a 25°C water bath. The vials were injected with 3 ml of 270 parts per billion by volume (ppbv) CH_3Br to obtain an initial head space mixing ratio of approximately 4 ppbv. The vial head space was flushed with Ultra High Purity Nitrogen (UHP N_2) at specified time intervals onto a sample loop immersed in a dry ice/isopropanol bath (-70°C). The sample loop contained a 2cm long

plug of Poropak Q (Alltech) packing and quartz wool to allow the head space sample to be immobilized on the plug. The sample loop was immersed in boiling water and connected to an electron capture detector gas chromatograph (8A GC-ECD, Shimadzu). The oxygen (O_2) doped N_2 carrier gas flowed through the sample loop carrying the volatilized head space sample into the pre-column, through the analytical column and then to the detector. Details of the sampling and analytical procedures can be found in Chapter 2: Collection and analysis of samples for CH_3Br.

The resulting peak areas were compared to daily standard curves and concentrations calculated. The daily standard curves included replicates of the following 5 volumes of standard: 1.0, 0.5, 0.25, 0.1 and 0.05 ml of 270 ppbv CH_3Br. The average r^2 of the linear regression fit of peak area versus nmoles of CH_3Br for the 6 month period of sampling was 0.9998. Replicate head space samples for each of the six time segments were completed. A reaction rate constant, k, was determined as the slope of the regression fit of the natural log of nmoles of CH_3Br versus time. This k, in min^{-1}, was then normalized to the weight of dry soil (ds) in the vial resulting in a measured reaction rate constant with the units of $min^{-1}g^{-1}_{ds}$. More details on methodology can be found in Chapter 2: Collection and analysis of samples for CH_3Br.

Soil pH, water content, and organic matter were measured for all of the incubated soils. pH was measured using a combination electrode and 10 g of air dried soil in a 0.01 M $CaCl_2$ solution. Soil moisture content was determined by placing 5 to 20 g of soil in a drying oven at 70°C for 24 hours. Soil organic matter content was measured by ashing 3 to 7 g of oven dried soil in a muffle furnace at 450°C for 24 hours. Details of the

measurement procedures can be found in *Carter*, 1993.

3.2.2. Results

A total of 170 laboratory soil incubations were completed. The data were divided into biome type and by sampling depth and are presented in Table 3.1. Uptake is represented by k, the first order reaction rate constants. Temperate ecosystems sampled in our study showed the fastest uptake overall with decreasing uptake by boreal, cultivated, and tropical samples in that order. In all samples, the surface soils had the fastest measured reaction rate constants as compared to the samples at depth. Temperate grasslands were represented by the least number of sampling locations while the most samples were from cultivated areas and temperate forests.

The tropical samples had the highest field moisture content while cultivated areas had the lowest moisture. Temperate forest soils showed the highest average organic matter content and cultivated areas the lowest. The lowest pH values were found in the tropical samples as well as the boreal regions. The pH of temperate samples were higher but the highest pH's recorded were from the cultivated soils. In almost all the samples, moisture and organic matter content decreased with depth while pH generally increased.

The relationship between field moisture and organic matter content appeared to be linear over all the samples incubated (Figure 3.1). Therefore, when plotting reaction rate constant k versus organic matter and moisture content the relationships are consistent but are not independent (Figure 3.2 a and b).

Biome	Depth (cm)	k (min^{-1})	Moisture Content (%)	Organic Matter (%)	pH	n
Tropical Forest and Savanna	0-5 5-10 10-15	0.053±0.020 0.049 ±0.011 0.057 ±0.007	44.1 ± 2.2 47.6 ±1.7 41.6 ±2.0	23.6 ± 2.0 20.53 ± 1.5 20.3 ±1.2	4.0 ±0.4 4.3 ±0.6 4.4 ±0.7	9 2 4
Temperate Forest and woodland shrub	0-5 5-10 10-15	0.403±0.054 0.235±0.027 0.151±0.023	38.1±3.2 21.6±2.0 17.3±1.7	30.5±4.3 7.7±1.2 5.1±0.7	4.9±0.2 5.3±0.2 5.2±0.2	31 21 20
Temperate Grassland	0-5 5-10 10-15	0.524±0.229 0.136 ±0.053 0.059±0.011	31.3±13.3 22.3±7.319 16.8±2.4	17.9±12.0 6.5±3.0 3.6±0.3	5.4±0.3 5.3±0.3 5.3±0.3	2 2 2
Boreal Forest	0-5 5-10 10-15	0.205±0.072 0.271±0.203 0.128±0.030	20.8±5.1 26.0±21.0 21.4±7.8	13.5±6.0 12.1±8.9 8.25±3.4	4.9±0.2 4.37±0.1 4.6 ±0.5	6 2 4
Cultivated Land	0-5 10-15	0.164±0.023 0.091±0.012	18.0±1.7 18.6±1.7	8.4±1.4 6.8±1.1	6.0±0.1 5.9±0.2	37 28

Table 3.1. Averages and standard error of the mean of n samples for soil incubations of all soils measured. Biome classifications are from Matthews, 1983.

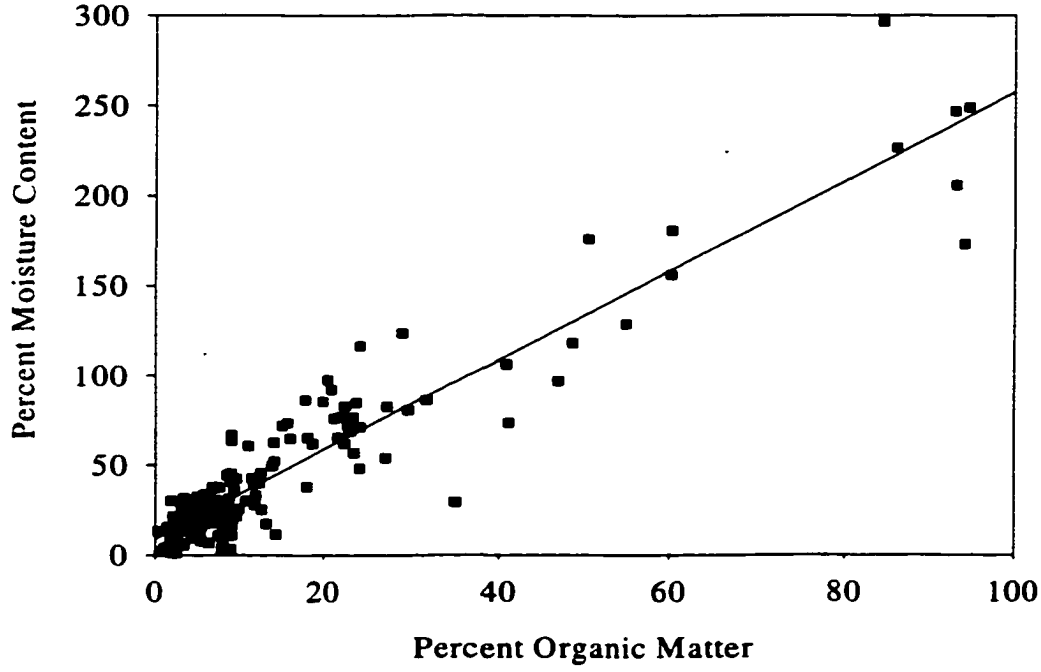

Figure 3.1. Relationship between soil organic matter and soil moisture content of all completed soil incubations. Equation of the linear regression is : MC = 2.5OM + 9.3, r^2 = 0.88.

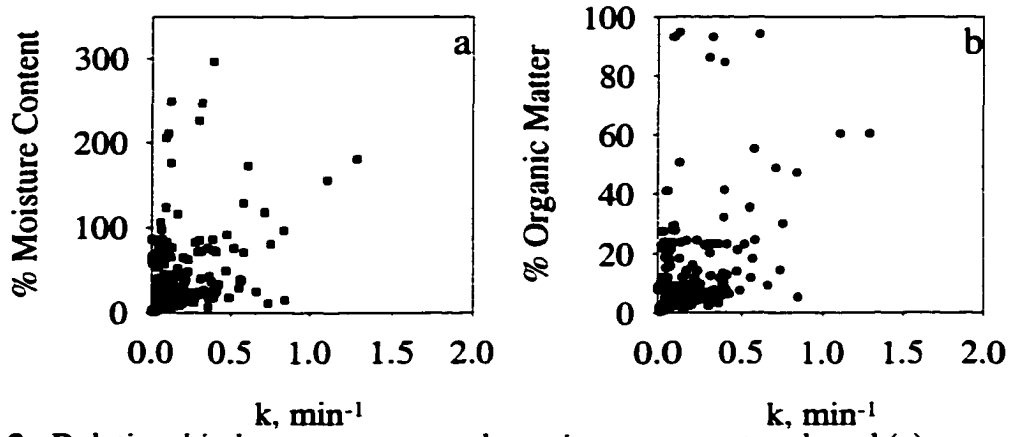

Figure 3.2. Relationship between measured reaction rate constant k and (a) percent moisture content (■) and (b) percent organic matter content (●) for all soil incubations.

When measured reaction rate constants of surface soils are normalized for moisture content by dividing by the grams of dry soil (ds) in the incubation vial, the relationship with organic matter and biome becomes more apparent (Figure 3.3 a, b and c).

Figure 3.4 shows the range of pH and reaction rate constant k in min^{-1} g_{ds}^{-1}. A broad range of soil pH was measured while most of the reaction rates were within a small range except for the low pH samples where there is a broad range of values.

Soil incubations during which soil moisture and temperature were manipulated, were completed on specific samples to determine effects of these environmental factors on the uptake of CH_3Br. Figure 3.5 a and b are plots of temperature response of soil incubations. Figure 3.6 is a plot of moisture manipulations completed on surface soils from College Woods and a NH cultivated site. The temperature manipulation studies revealed a significant relationship with a maximum uptake temperature specific to each soil sample. The moisture study revealed a similar relationship but the data were more variable.

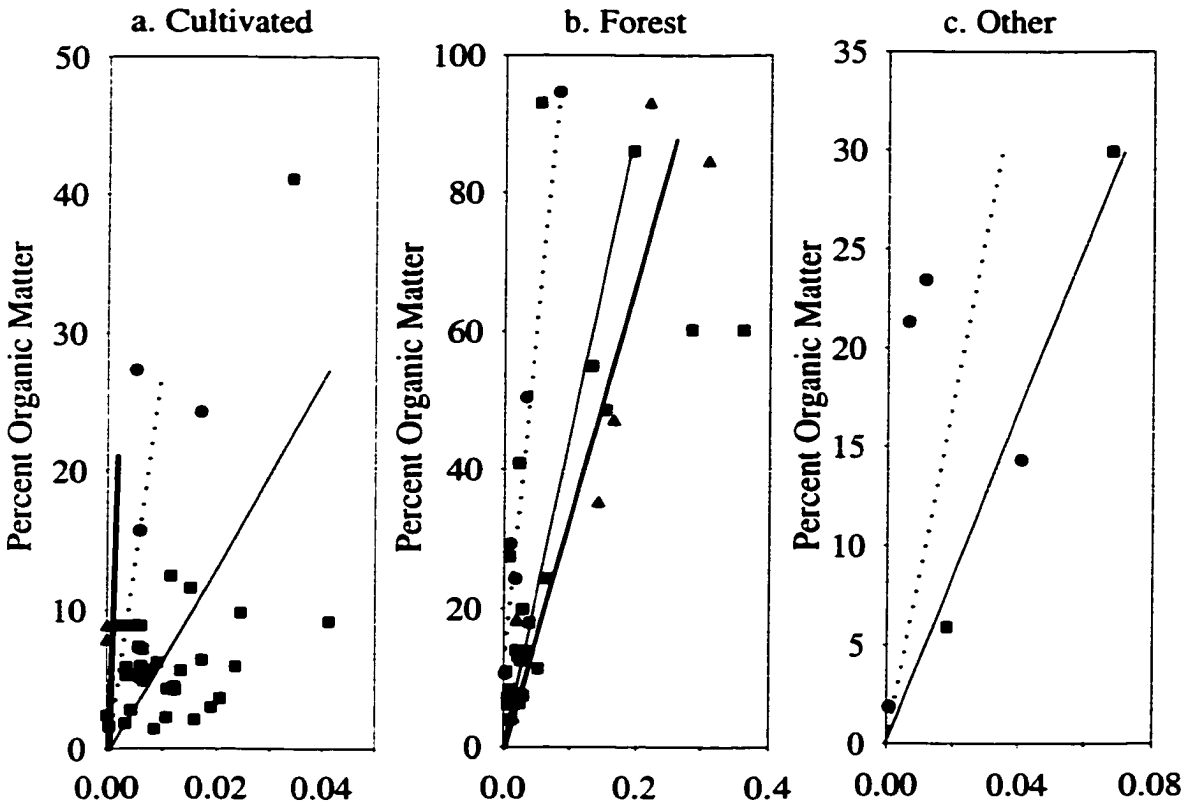

Figure 3.3. Relationship between reaction rate constant k and biome and land use type. (a) Cultivated land, (b) Forested land and (c) other biomes including pasture and grassland. Temperate (■), tropical (●) and , boreal(▲) with interpreted biome specific relationships: solid line = temperate, dotted line = tropical, and darker solid line = boreal.

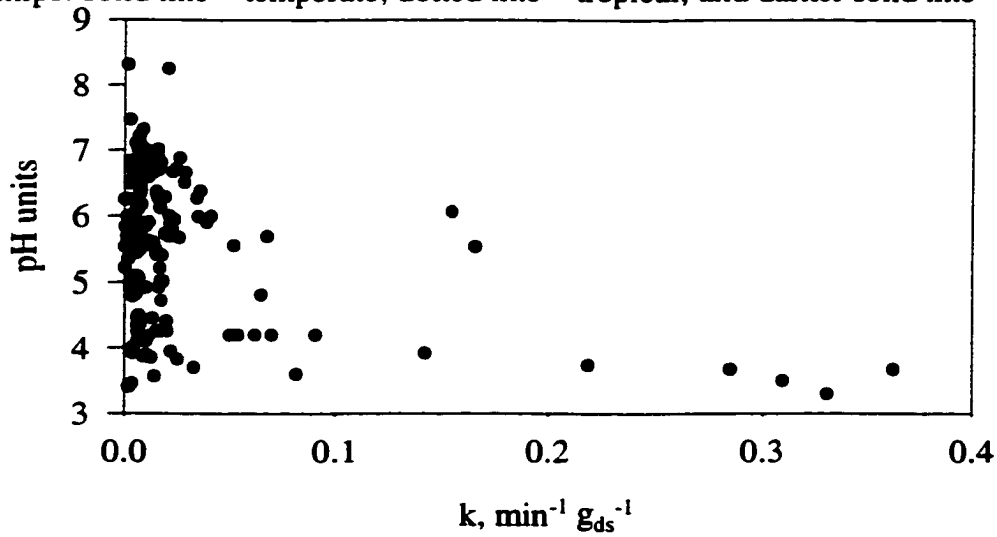

Figure 3.4. Relationship between reaction rate constant, k normalized to moisture and pH of all incubated soils.

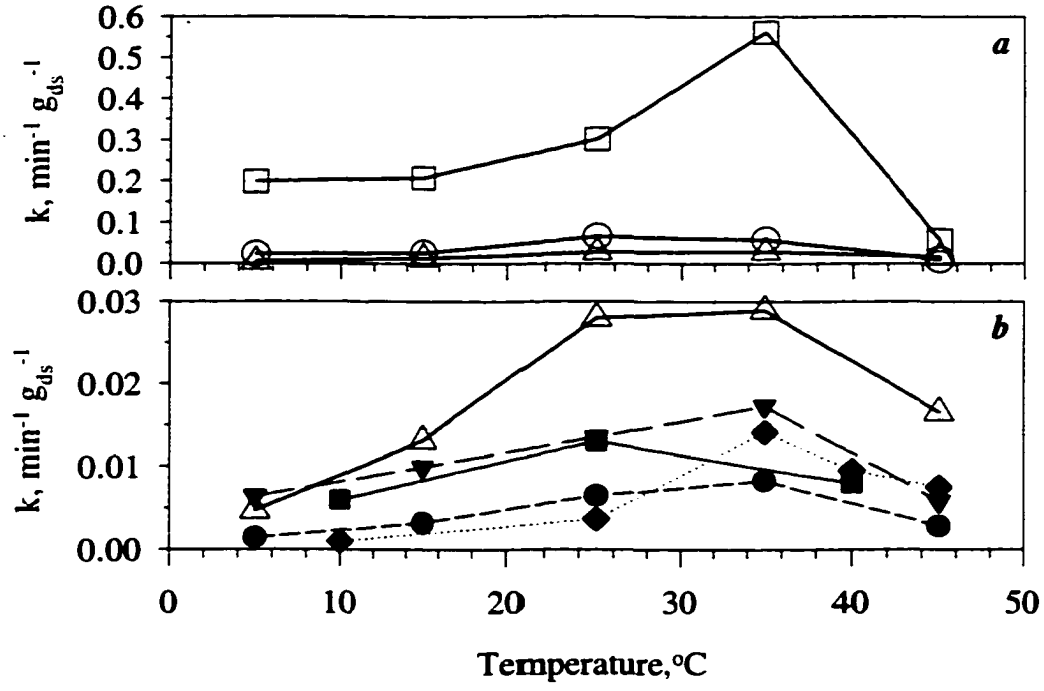

Figure 3.5 a and b. Temperature manipulation of selected soil samples. (a) College Woods samples from 0-5 cm (□), 5-10 cm (○) and 10-15 cm (Δ). (b) College Woods 10-15 cm (Δ), Boreal Forest 1-4 cm (■), cultivated sites in NH (◆), 0-3 cm, Iowa 0-5 cm (▼), and Illinois , 0-5 cm (●).

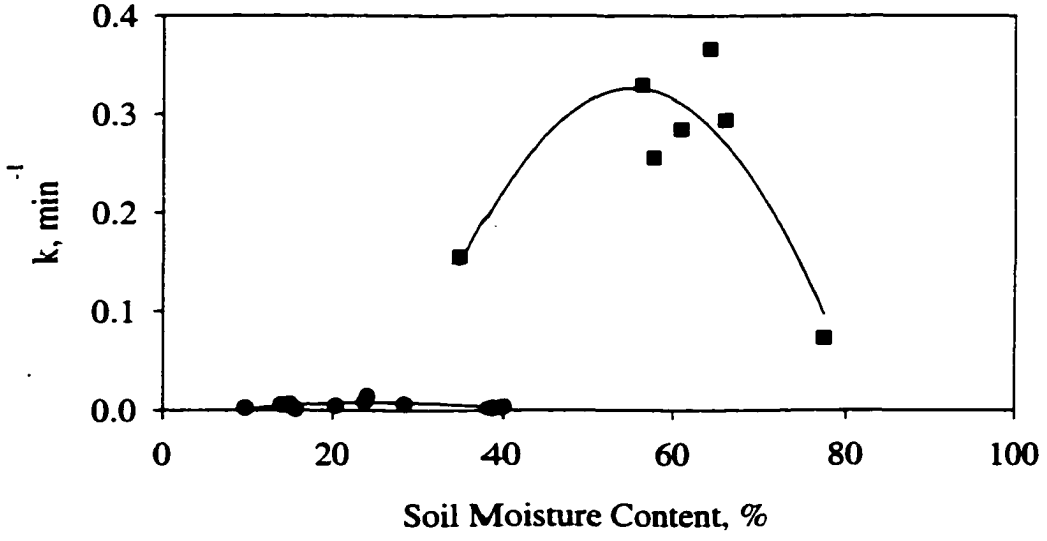

Figure 3.6. Results of moisture manipulation experiments on surface NH cultivated (●) and College Woods (■) soil.

To determine whether the temperature and moisture relationships were indicative of microbial destruction of CH_3Br in soils, experiments utilizing sterilization through autoclaving and antibiotics were completed (Figure 3.7). Sterilization by autoclaving showed almost complete loss of activity while addition of tetracycline and chloramphenicol inhibited uptake as well. Application of cyclohexamide had no noticeable effect on the uptake of CH_3Br in the soils.

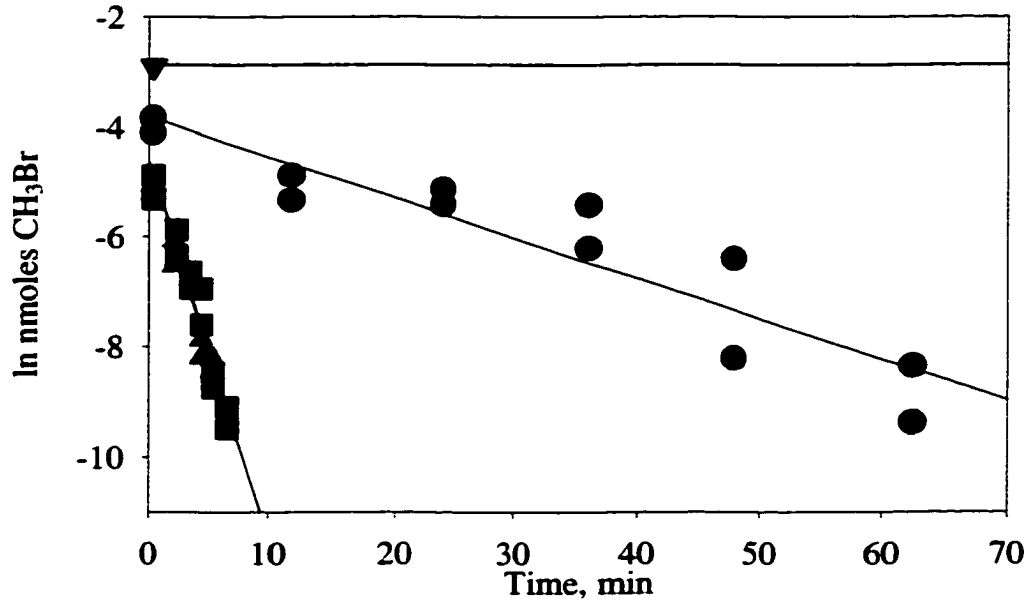

Figure 3.7. Manipulation experiments on College Woods 0-5 cm soils. Unaltered (▲), cyclohexamide addition (■), chloramphenicol and tetracycline addition (●), autoclaved sample(▼). All data shown are fit with linear regressions. Autoclaved data show only one sample because the rest of the samples were taken over a week period and do not fit on this graph.

UHP N_2 was added to the vial headspace to create an anaerobic environment and uptake was measured to determine the effects (Figure 3.8). The control vials showed rapid uptake of CH_3Br while the 100% N_2 environment showed considerably decreased

uptake rates. The effect of high CH_4 availability on the uptake rate of CH_3Br was also determined by adding CH_4 to the headspace of the vials. Uptake was not significantly affected by the addition of 3% CH_4 (Figure 3.8).

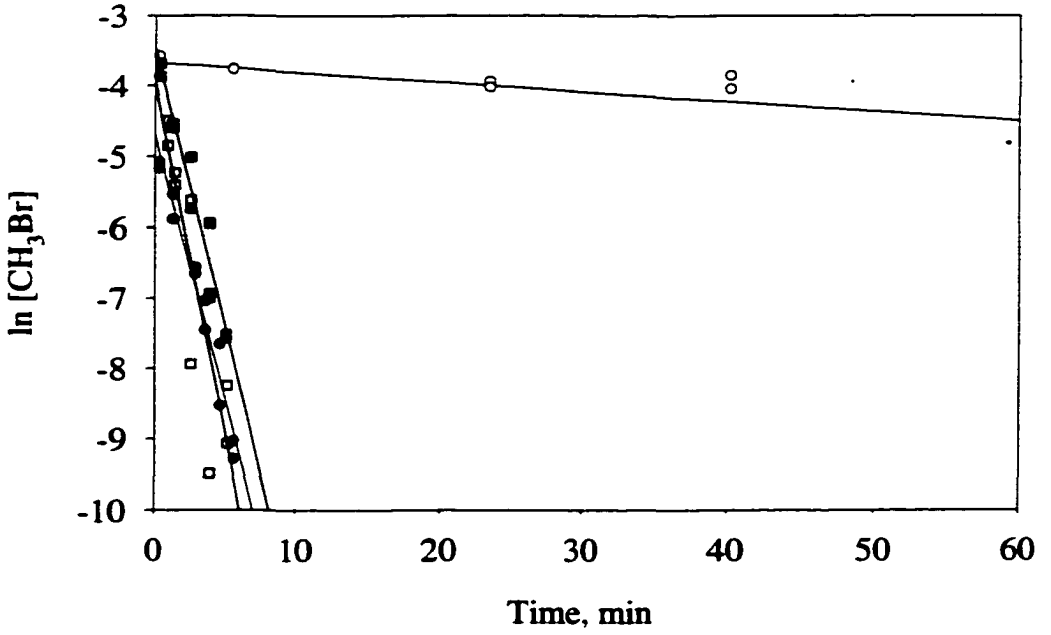

Figure 3.8. CH_4 and N_2 atmosphere experiments. ●and ■ - no manipulation, □ - 3% CH_4 and ○ - 100% N_2 environment.

3.2.3. Discussion

The highest uptake rates were measured in temperate zone soils (Table 3.1). This may be because all the soil incubations were performed at 25°C which is closer to the average ambient temperature for the temperate soils than it is for tropical and northern soils. There should be an optimum moisture and organic matter content where the microbes responsible for uptake reside [*Madigan et al.*, 1997], but because of the variation of soil properties the individual effects of these factors are difficult to isolate.

On average, surface soils tend to be wetter than the deeper soils in all samples,

except cultivated soils are slightly drier probably due to their greater exposure to evaporation. The largest amounts of organic matter were measured in the surface layers (0-5 cm) compared to the deeper layers (10-15 cm). The difference was consistent across biomes with about 14% less organic matter in the tropical soils, 83% less in the temperate forest soils, 80% less in the temperate grassland soils and 19% less in the cultivated soils. The boreal soils actually showed about 3% more organic matter at 10-15 cm than at 0-5 cm. The 5-10 cm organic matter reported as 12.1% appears anomalous (Table 3.1). This value is lower because the samples taken in Siberia and Finland were only sampled at the surface and at depth. These were peat soils with high organic matter contents that made the average for surface and deeper layer much higher.

pH varied considerably between climatic zones. The cultivated areas showed the highest pH probably due to liming processes to bring pH to optimum growing conditions for crops [*Foth*, 1990]. Lowest pH values were measured in the tropical soils as expected because the humid environment leads to the leached nature of the soils [*Foth*, 1990]. The boreal soils averaged lower pH's as well probably due to the mineralization of the organic matter content which is relatively high in these soils [*Foth*, 1990]. Temperate forest values were on average lower than temperate grassland values also primarily due to higher average organic matter contents.

There was no obvious relationship between either moisture content or organic matter content and reaction rate constant (Figure 3.2 a and b) even though there is an obvious relationship between organic matter content and moisture content (Figure 3.1). Normalizing the reaction rate constant k to grams of dry soil in the incubation chamber

and plotting it versus organic mater content helps to identify some general relationships within landuse types. Figure 3.3a shows tropical cultivated soils with generally a lower range of uptake than temperate soils even though they have a similar range in organic matter content. This relationship holds true in the forest soils as well (Figure 3.3 b). Boreal forest soils show a range of uptake between the tropical and temperate values. Other biomes including grassland and pasture show the same relation ship with brome as in cultivated and forest soils (Figure 3.3 c). These plots reveal biome as well as land use differences between soils sampled. Thus, they reveal more information than just presenting biome averages in Table 3.1.

Temperature manipulation studies reveal a specific response to temperature that is consistent with that of a microbial population (Figure 3.5) [*Madigan et al.*, 1997]. Optimum temperatures (i.e. greatest uptake rates measured) were found to be between 25 and 35 °C for temperate soils and closer to 25 °C for the boreal soils studied. This result may not be significant because on closer inspection of the data, there are only three temperatures measured for the boreal sample therefore there could be a maximum temperature somewhere between 25 and 40 °C.

Moisture manipulation studies also reveal a system sensitive to moisture content (Figure 3.6). If the soil is too dry, reaction rates decrease due to stress on the microbial population. As the moisture content increases, diffusion of CH_3Br is limited to the microenvironment therefore reaction rates drop again. Cultivated soils showed a similar relationship with moisture as the forest soil but the optimum moisture is much lower. This is probably because at ambient conditions, the cultivated soils tend to dry out rather

quickly due to exposure and they have much lower organic matter contents. This makes the cultivated soil less than an optimum place for microbial activity to flourish.

Sterilization and antibiotic application revealed that the mechanism for near ambient CH_3Br uptake is microbial (Figure 3.7). Sterilization of the soil essentially stopped uptake indicating that the uptake was microbial and not due to hydrolysis or reaction with organic matter. Chloramphenicol addition had no effect on the uptake rates indicating that soil fungi were not responsible for uptake of CH_3Br. Application of chloramphenicol and tetracycline did inhibit uptake by the soil system. This indicates that the consumption of CH_3Br is probably bacterial. Further experiments utilizing a N_2 environment and a high CH_4 environment (Figure 3.8) reveal that the consumption of CH_3Br in soils is an aerobic process and is not performed by methanotrophs like those presently in pure culture [*Hines et al.*, 1998].

The highest uptake rates and therefore microbial activity, in all soil profiles were in the 0-5 cm layer sample. Methane oxidation has been observed in the soil profile with maximum rates in the 3-6 cm zone [*Czepiel et al.*, 1995]. That study used soil samples from locations similar to the work in this dissertation. Their results are consistent with our earlier finding that the microorganisms responsible for the uptake of CH_4 may be different than those that take up CH_3Br.

The flux of tropospheric CH_3Br into the soil was calculated from the measured reaction rate constants obtained in the laboratory incubation experiments. I used the same approach as *Bender and Conrad*, 1993:

$$Flux = k * V * d * b.d. * [C_a] * \left(\frac{1440 min}{day}\right) * \left(\frac{94.9 g CH_3Br}{mole}\right) * \left(\frac{10^4 cm^2}{m^2}\right)$$

where Flux is in g m^{-2} day^{-1}, k is in min^{-1} g^{-1}_{ds} (average of all soil incubations performed), V is the vial head space of 200 cm^3 for the laboratory experiments, d is the depth of uptake in cm (assumed to be 1 cm because the uptake is the fastest in the surface soils), b.d. is the bulk density of the soil in g cm^{-3}, and $[C_a]$ is 4.1 x 10^{-16} moles cm^{-3} (ambient CH_3Br = 10 pptv [*Kurylo et al.*, 1999]).

Global Extrapolation. To estimate the global sink of tropospheric CH_3Br to upland soils we extrapolated to land areal extent using global estimates of land area by Matthews, 1983. Flux, in g m^{-2} day^{-1}, was multiplied by the areal extent of land and by the number of days in the growing season. It is assumed that since the uptake is a microbial process, this activity is insignificant when the soil is frozen. Table 3.2 contains the results of these calculations.

The total global uptake of ambient CH_3Br by soils is 75.0 ± 27.9 Gg yr^{-1}. This is an improved estimate compared to our previous one for the soil sink of 42 Gg yr^{-1} [*Shorter et al.*, 1995] because we include here more samples from a larger variety of soil types with different soil properties and from many biome types across a broad latitudinal range. Estimates of uptake for all biomes except the tropics increase but the most pronounced difference is in the boreal forest uptake measurements (Table 3.3). The original estimates were made only with sandy soils from Manitoba, Canada. The added boreal soils had higher organic matter contents and higher measured k values.

Biome	Area* (10^6 km^2)	Active season (d yr^{-1})	k (min^{-1})	Flux (μg m^{-2} d^{-1})	Gg yr^{-1}
Tropical forest and savanna	22.5	365	0.05	0.56	4.6 ± 1.7
Temperate forest and woodland shrub	20.0	240	0.40	6.20	29.8 ± 6.2
Temperate grassland	9.0	240	0.52	7.21	15.6 ± 9.0
Boreal forest	12.0	180	0.21	5.99	12.9 ±8.2
Cultivated land	14.0	240	0.16	1.76	5.9 ± 0.8
				Total	**75.0 ± 27.9**

* *Matthews*, 1983

Table 3.2. Global extrapolation of soil sink of atmospheric CH_3Br. Errors in yearly emissions are standard error of the mean from the measured reaction rate constant k. Yearly fluxes are reported as Gg yr^{-1} where Gg = 10^9 g

Biome	*Shorter et al.*, 1995	*Serça et al.* 1998	This study
Tropical Forest and savanna	6.5	5.8	**4.6 ± 1.7**
Temperate Forest and woodland shrub	21.7	26.8	**29.8 ± 6.2**
Temperate Grassland	9.7	8.9	**15.6 ± 9.0**
Boreal Forest	1.7	1.7	**12.9 ±8.2**
Cultivated Land	2.7	47.6	**5.9 ± 0.8**
Total	**42 ±32**	**91 ± 44**	**75 ± 28**

Table 3.3. Comparison of published global soil uptake values using Matthews, 1983 land area values. Fluxes are reported in Gg yr^{-1}.

The only other published research on the uptake of ambient CH_3Br by soils gives an estimate for global soil uptake of 91 ± 44 Gg yr^{-1} [*Serça et al.*, 1998]. The largest

discrepancy between the two studies appears to be in the cultivated and boreal estimates. *Serça et al.'s* observed deposition velocities for agricultural CH_3Br uptake were measured at an agricultural field site in Colorado (n=7). The discrepancy with our estimates are probably due to differences in measurement technique, sampling location and flux calculation method. Their field measurements were completed in a recently plowed agricultural field that had not received rainfall since plowing. Both studies reveal that microbially mediated uptake is common but that sampling in one location, as we did in 1995, will give an estimate that is restricted to sites with similar physical characteristics. Their boreal estimates are actually values from our estimates in 1995. *Serça et al.*, 1998 reported uptake by peat bog microcosms from Minnesota kept in Colorado and came up with a wetland uptake estimate of 2.1 Gg yr^{-1} but this does not account for the discrepancy in estimates.

3.3. Field measurements

3.3.1. Methods

Flux measurements were made from mid-July through the end of November, 1994 at three temperate sites: forest (College Woods, Durham, NH), grassy clearing (Crill backyard, Lee, NH), and cornfield (Moore Fields, Durham, NH). College Woods is a 28 ha woodlot given to the University of New Hampshire in 1893. It has never been clearcut and has not been logged since UNH received it. It is a mixed deciduous-conifer forest based in a drained upland inceptisol. Our research group has conducted biweekly flux measurements of CH_4 and CO_2 as well as maintained an automated temperature profile system since 1989. The Crill backyard site is a recently cut, grass covered site based in

an 80-120 year forest similar to College Woods but on a sandy spodosol. The cornfield site was a wooded area when UNH received it in 1941. It was logged extensively until it was converted to agriculture in the 1960's. The cornfield is located in a well drained, glacial till spodosol.

During the growing season of 1999, ambient CH_3Br exchange was monitored at two temperate upland sites every week from late May through mid-November: a forest (College Woods, Durham, NH) and a cornfield (Kingman Farm, Madbury, NH). The College Woods site is described briefly above. Kingman Farm was given to the University of New Hampshire in 1961. It has since served as a research facility. Soils are spodosols with marine and glacial till parent materials.

Field sampling of CH_3Br exchange entailed placing either a clear chamber made of Teflon film and Lexan or a dark chamber made of aluminum on an aluminum collar cut into the soil surface. Chamber volumes and collar areas for the 1994 and 1999 field sampling seasons were 0.0027 m^3 and 0.091m^2, and 0.1437 m^3 and 0.397 m^2, respectively. Since we had determined in the laboratory incubations that the uptake was first order and our analytical system had limitations, in the 1994 field experiments we added an aliquot of CH_3Br to the chamber headspace to bring concentrations to an initial concentration of 500 pptv. In 1999 this was not necessary due to improvements in the analytical system that allowed analysis at and below ambient concentrations of CH_3Br in smaller sample volumes. Samples of enclosed headspace were taken at specified time intervals. Field samples collected in 1994 were taken with 60 mL polypropylene syringes (Becton Dickinson). The syringes were loaded to the sample loop immersed in the

cryobath and analyzed by GC-ECD as described previously in Chapter 2.

Field samples taken after August, 1998 were taken with stainless steel 500 mL sample canisters using a Gast pump, pressurizing the canisters to 60 psig. 4 samples were taken at 5 minutes intervals from the chamber headspace. An ambient air sample was taken after every flux measurement. The chamber, air, surface, and -10 cm depth temperatures were measured during the flux period. Automated temperature measurements were made every minute and hourly averaged at the College Woods and Kingman Farm sites for the sampling periods.

During some of the field flux measurements, SF_6, an inert tracer, was introduced into the chamber headspace before sampling for an initial mixing ratio of 30 parts per billion (ppbv). SF_6 was used to determine non-biological diffusive loss of gas from the chamber headspace [*Dörr and Münnich*, 1990; *Rolston et al.*, 1991; *Trumbore*, 1995].

The syringes and sample canisters were analyzed for CH_3Br, CH_4, CO_2 and SF_6 within 24 hours. The CH_3Br mixing ratios were determined using a gas chromatograph equipped with an electron capture detector (GC-ECD) [*Kerwin et al.*, 1996]. Analysis techniques for CH_3Br in syringe and sample canisters is detailed in Chapter 2.

CH_4, CO_2 and SF_6 were measured using a portion of the syringe sample or the canister sample by extracting 60 mL with a polypropylene syringe. A gas chromatograph equipped with a flame ionization detector (GC-FID) was used to determine CH_4 and a thermal conductivity detector gas chromatograph (GC-TCD) was used for analysis of CO_2. Another GC-ECD equipped with a 12-port valve was used to analyze for SF_6 in the sample.

3.3.2. Results

CH_3Br flux measurements at College Woods were completed between 7/12/94 and 11/23/94 (Figure 3.9). Negative numbers denote flux of CH_3Br into the soil surface. CH_3Br uptake increases while soil moisture and chamber temperatures decrease throughout the sampling period with the exception of the last sampling day when the soil moisture increased and the CH_3Br flux decreased.

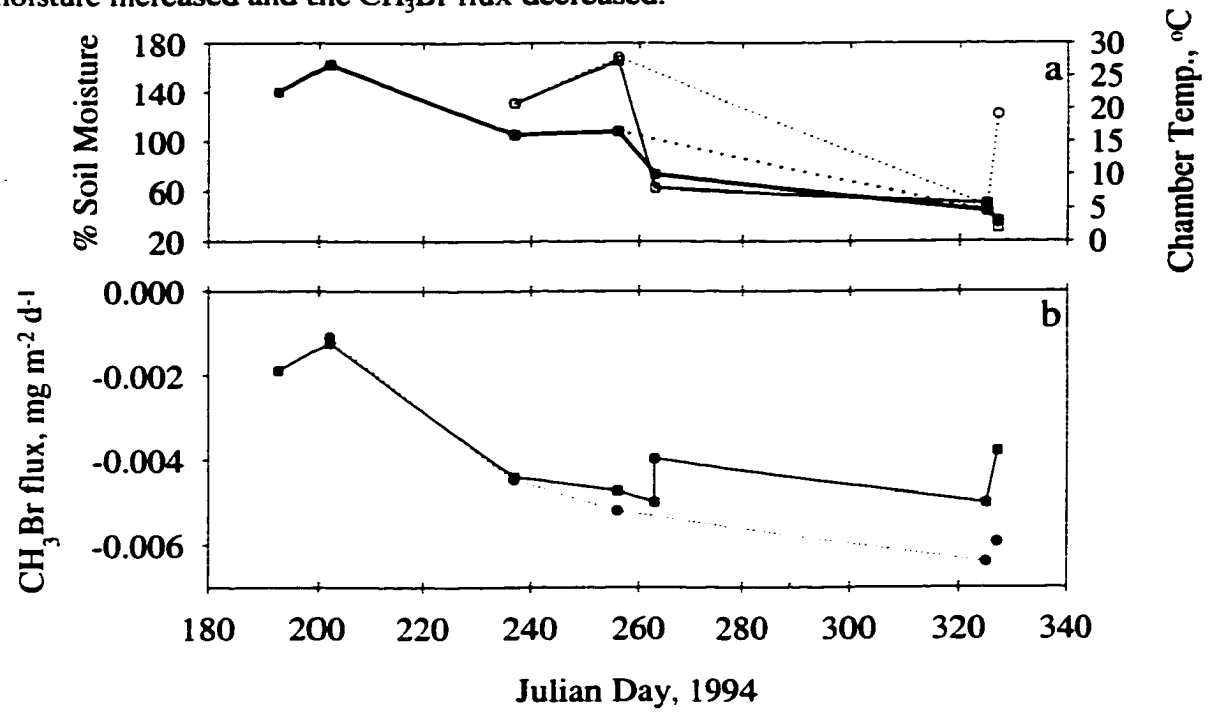

Figure 3.9.a and b. Field data from College Woods, 1994. (a) Surface soil moisture(open symbols)and chamber temperature (shaded symbols)for Collar 1 (■, □) and Collar 3 (●, ○). (b) CH_3Br fluxes for Collar 1 (■), Collar 2 (▲) and Collar 3 (●).

CH_3Br fluxes were measured at the Moore Fields cornfield six times between 8/10/94 and 9/19/94 (Figure 3.10). Collars were removed from the site for harvesting on 9/19/94 and were placed in the ground at the Crill grassy clearing site. Fluxes at the cornfield remained relatively constant over the sampling period except for increase in

uptake on day 255. The chamber temperature decreased over the sampling period and the 0-5 cm soil moisture was variable. Site 1 was measured consistently and was located between rows of corn. Site 2 was also located between rows of corn and was measured twice. The collar was then moved to Site 3, an open field of bare soil where measurements resumed.

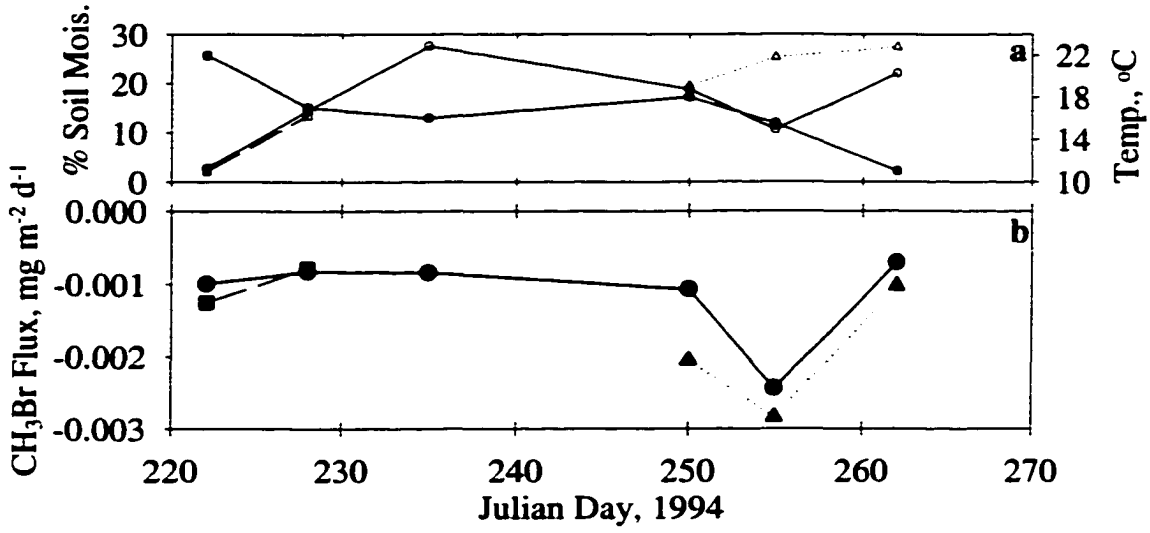

Figure 3.10. a and b. Field data from Moore Fields cornfield, 1994. (a) Surface soil moisture(open symbols)and chamber temperature (shaded symbols) for Site 1 (●, ○), Site 2 (■, □) and Site 3 (▲,△). (b) CH_3Br fluxes for Site 1 (●), Site 2 (■) and Site 3 (▲).

CH_3Br fluxes were measured at the grassy clearing from 10/7/94 and 11/17/94 (Figure 3.11). Fluxes at this site decreased over the sampling period. The chamber temperature and surface soil moisture varied only slightly over the same period.

Measurement of the non-biological diffusion of the inert tracer SF_6 out of the headspace of the chamber was completed at various sampling times throughout the 1994 sampling period. The measured loss rate of SF_6, k_{SF6}, was used to calculate a physical diffusi0ve loss constant for CH_3Br, k_{CH3Br}, using Graham's law.

$$k_{CH3Br} = k_{SF6} * \left(\sqrt{\frac{m_{CH3Br} + m_{air}}{m_{CH3Br} * m_{air}}}, \sqrt{\frac{m_{SF6} + m_{air}}{m_{SF6} * m_{air}}} \right)$$

where m_{CH3Br} is the molecular weight of CH_3Br (95 g $mole^{-1}$), m_{air} is the molecular weight of air (28 g $mole^{-1}$) and m_{SF6} is the molecular weight of SF_6 (146 g $mole^{-1}$). A comparison of the measured rate constant, k_{meas} from the field fluxes with the calculated diffusive loss of CH_3Br, k_{CH3Br} can help determine if uptake of CH_3Br is diffusionally controlled or possibly enhanced by biological processes. Figure 3.12 is the measured CH_3Br reaction rates versus the calculated diffusion from the SF_6 measurements for the 1994 sampling season.

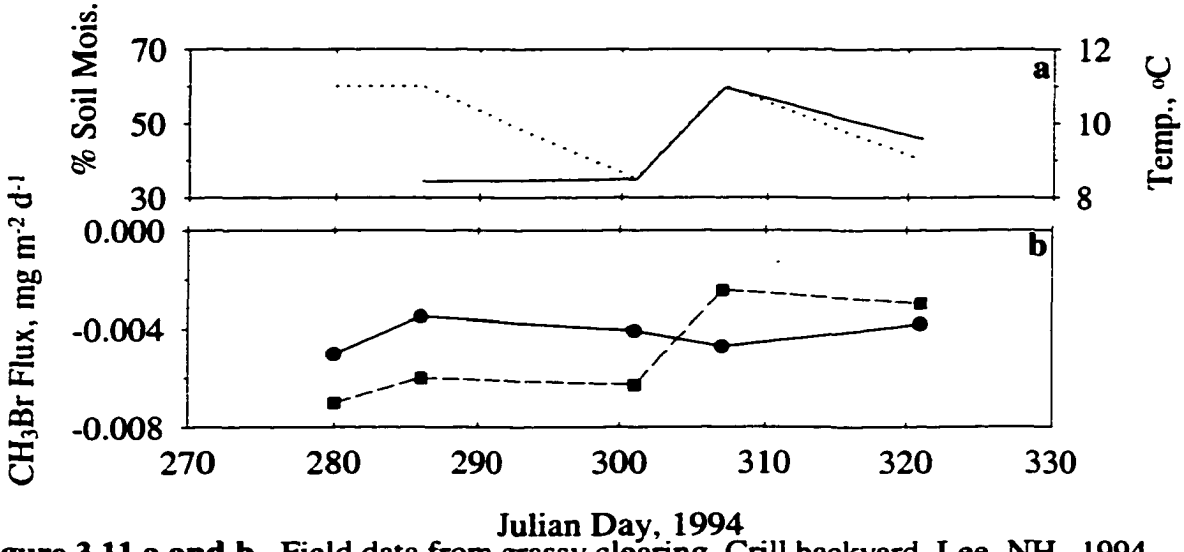

Figure 3.11 a and b. Field data from grassy clearing, Crill backyard, Lee, NH., 1994. (a) Surface soil moisture (—) and chamber temperature (···) were essentially the same for both sampling sites. (b) CH_3Br fluxes for Grass Site 1 (●) and Grass Site 2 (■).

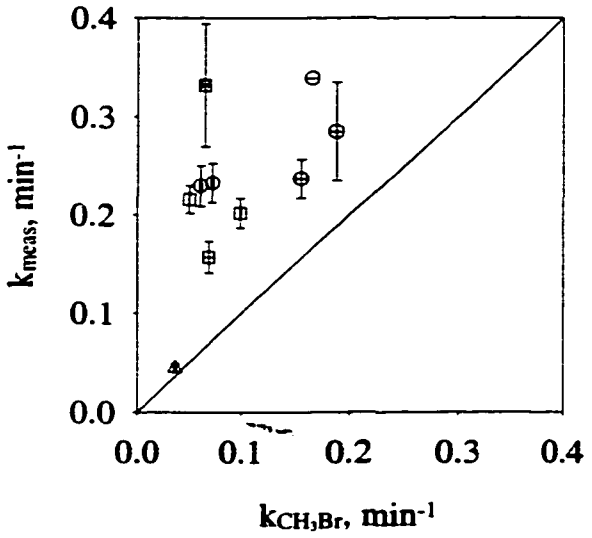

Figure 3.12. Diffusion measurements from 1994 field season from College Woods (●), cornfield (▲), and the grassy clearing(■). Error bars on the y-axis are the error of the slope fit of the linear regression of the ln[CH_3Br] versus time. Error bars on the x-axis are the error of the slope fit of the linear regression of the ln[SF_6] versus time adjusted for the weight of CH_3Br. The line plotted is the 1:1 line.

Field sampling in 1999 occurred with more frequency. Sampling took place approximately every week at both upland sites, College Woods and Kingman Farm. Figure 3.13 presents the seasonal sampling data from College Woods for 1999. Two collar sites were monitored throughout the sampling period. Both collars have been in the ground since 1989. The summer of 1999 was marked by a serious drought in the Northeast United States. This ended in early September when large amounts of rainfall were received during two hurricane events (Figure 3.13 a). The seasonal CH_3Br exchange at College Woods was dominated by periods of uptake; however four sampling days showed net emissions of CH_3Br.

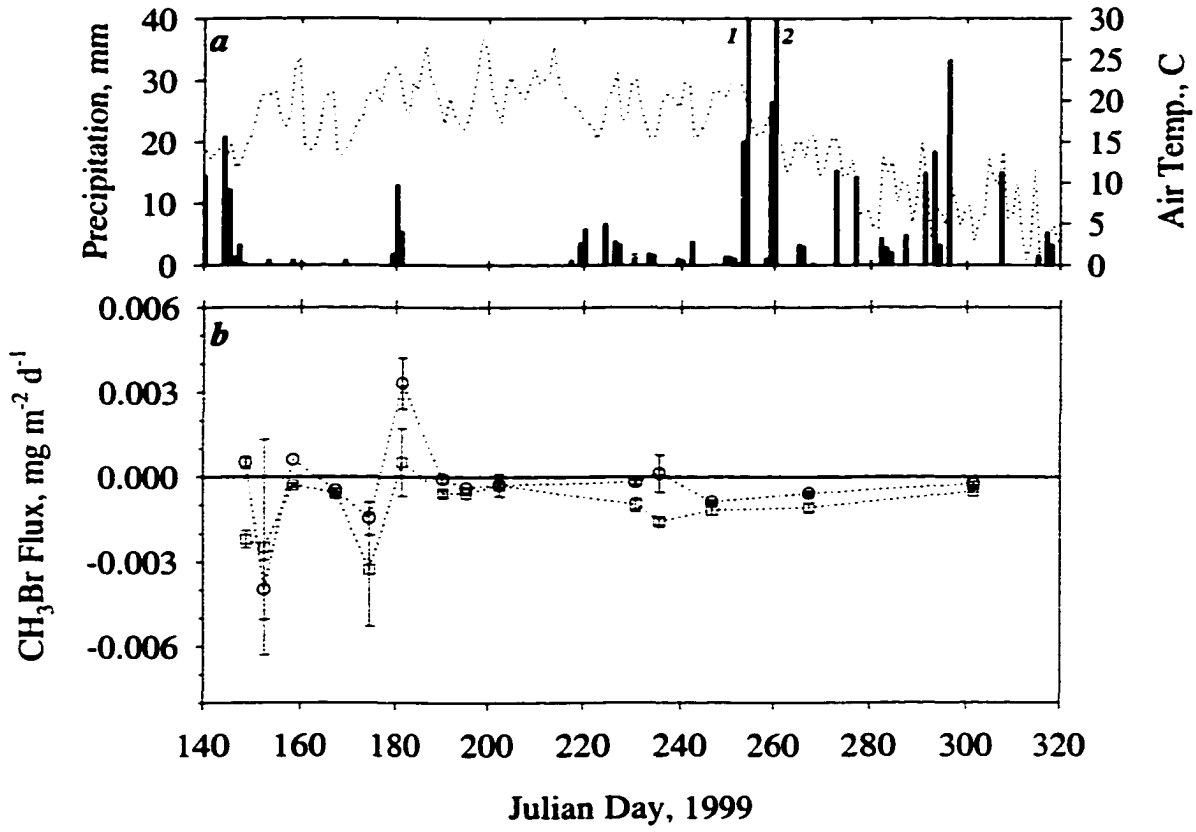

Figure 3.13 a and b. Seasonal field data from College Woods, 1999. (a) Daily average temperature (dotted line) and daily total precipitation (black bars). 1 and 2 are rainfall events equaling 87.6mm and 75.7mm, respectively. (b) Ambient CH_3Br exchange at Collar 1 (O) and Collar 2 (□). Error bars are standard error of the slope of the regression fit of the ln of CH_3Br versus time.

Kingman Farm showed the same drought conditions as the rest of the Northeast US in 1999. There were two significant rainfall events in September as well that brought soil moisture conditions back to predrought conditions. Figure 3.14 a and b are the plots of the seasonal data for Kingman Farm. The CH_3Br exchange appeared more variable than the College Woods site. Collars were taken out of the ground on day 117, 154, 167, and 272 for pre-planting tilling of the soil, planting of the seeds, placement between corn

rows, and post harvest tilling and planting of winter wheat.

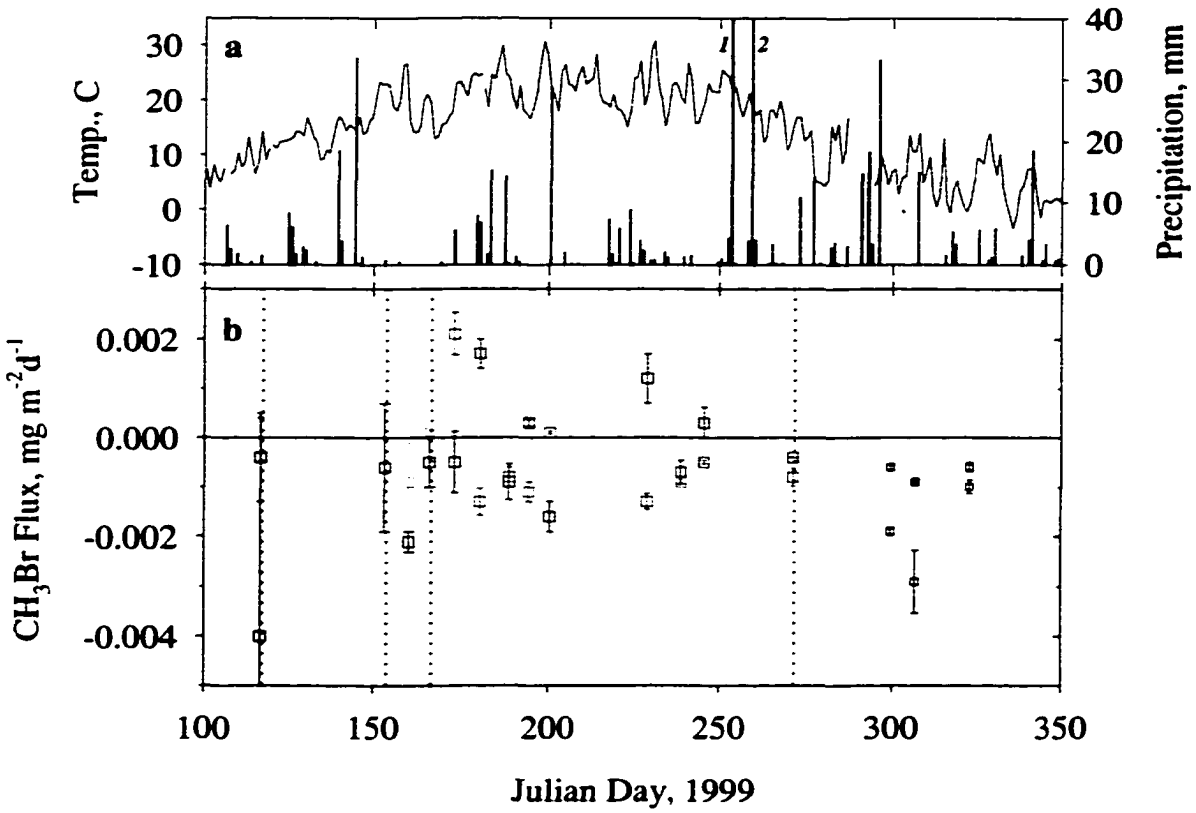

Figure 3.14 a and b. Seasonal field data from Kingman Farm, 1999.(a) Daily average temperature (solid line) and daily total precipitation (black bars). 1 and 2 are rainfall events equaling 100.6mm and 97.8mm, respectively. (b) Ambient CH_3Br exchange at many collars 2 (□). Error bars are standard error of the slope of the regression fit of the ln of CH_3Br versus time. Dotted vertical lines denote collar removal and new placement as described in text.

On 22 sampling occasions, non-biological diffusion was measured using the inert tracer, SF_6. As described in the methods section, the measured reaction rate of SF_6, k_{SF6}, was converted to the non-biological diffusion rate constant for CH_3Br, k_{CH3Br}. Figure 3.15 shows the measured uptake rate versus the calculated diffusion rate of CH_3Br for both College Woods (a) and Kingman Farm (b). The 1:1 line is plotted to show the

relationship between pure diffusion of a gas (falling on the 1:1 line), diffusion + biological uptake (above the 1:1 line) and diffusion + emission (below the 1:1 line).

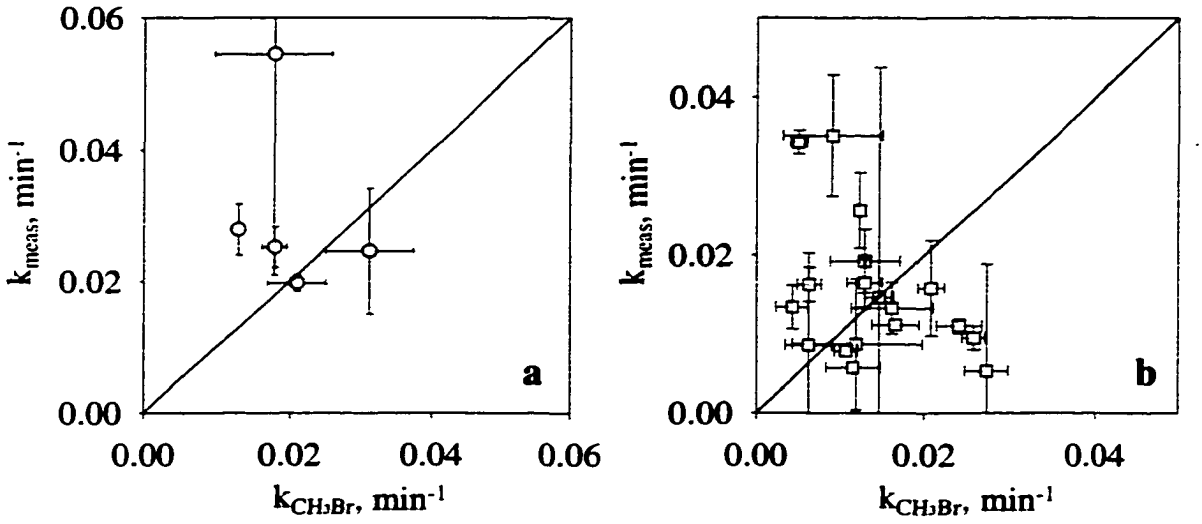

Figure 3.15 a and b. Measured CH_3Br uptake versus calculated non-biological diffusion for College Woods(a) and Kingman Farm (b) sampling in 1999. Solid line is 1:1 line. Error bars are standard error of the linear regression fit of the ln of CH_3Br versus time.

3.3.3. Discussion

The 1994 field measurements were made between 7/21 and 11/23 (Figures 3.9, 3.10 and 3.11). The College Woods and Moore Fields cornfield showed decreasing temperature over this period. Since the grassy site was only sampled 5 times in just over a month, there was little change in chamber temperature. Soil moisture at the College Woods site decreased over this period while the cultivated site showed marked changes in soil moisture from day to day. The grassy site soil moisture varied only slightly over the sampling period. All sites showed a net uptake of CH_3Br into the soil ranging from 0.007 mg m^{-2} d^{-1} at the grassy site to 0.0007 mg m^{-2} d^{-1} measured at the cornfield site. At all

sites, the uptake of CH_3Br decreased as the sampling period ended in November.

The relationship between moisture content and temperature that were seen in the laboratory incubation manipulation experiments is somewhat evident in the field data (Figure 3.16 a and b). The relationships were not as well defined probably due to the nature of field sampling. Laboratory experiments were completed by manipulating one component and holding everything else constant. When all the field moisture data from 1994 are plotted versus the rate as k, there appears to be increasing uptake with increasing temperature and moisture content. The moisture data might show a possible decrease in uptake as the moisture content increased above 55 % but the r^2 of the curve fit is only 0.43 with limited data above 55% moisture content. The chamber temperature versus rate as k show an apparently linear relationship, yet again the r^2 of the linear regression fit is only 0.41. The field data do not represent the full range of measurements made in the laboratory incubations. Therefore it was difficult to determine if the consumption decreases after a maximum temperature is reached. We assume this does occur because we have determined in laboratory incubations that the uptake is microbial, but the field data do not show this.

Measurements of the non-biological diffusion of CH_3Br using SF_6 as a tracer show that at the College Woods and grassy sites the uptake is due to both diffusion and biological consumption (Figure 3.12). That is, all the observations fall above the 1:1 line in Figure 3.12. Only one measurement of diffusion was made at the cornfield site. This data point falls on the 1:1 line indicating that at this location, uptake of CH_3Br is equal to diffusion. This can be interpreted to indicate that the uptake measurement made that day

was limited by the diffusion of CH_3Br to the surface.

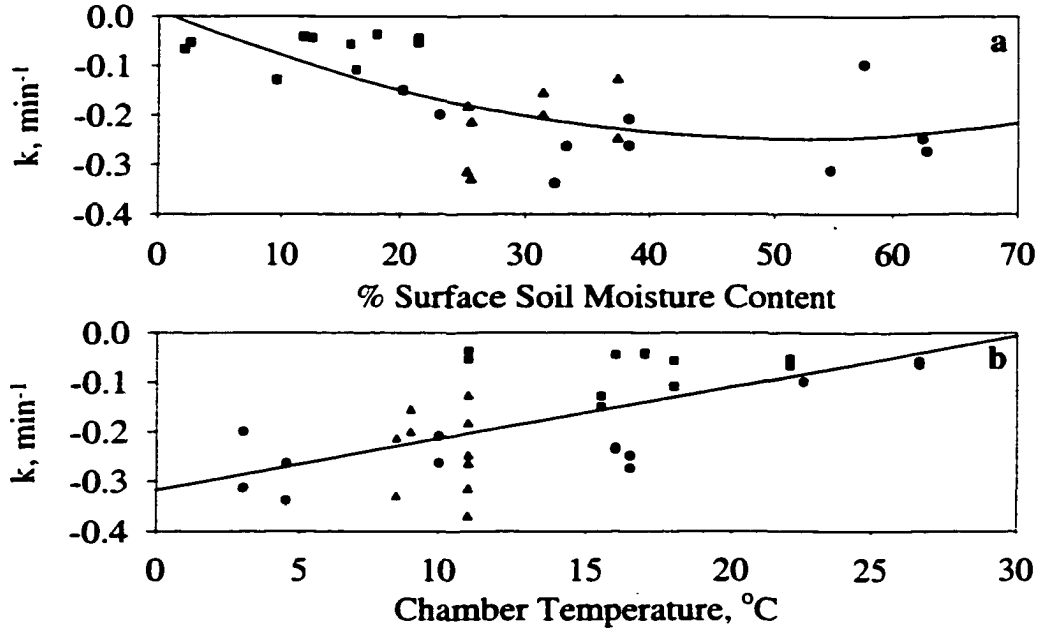

Figure 3.16 a and b. Relationship of reaction rate constant k to field soil moisture (a) and temperature of the chamber (b). College Woods (●), cornfield (▲), and the grassy clearing (■) are all plotted together.

The 1999 field data encompass a longer time period with a higher frequency of sampling than the 1994 sampling season. The 1999 flux measurements were made at ambient concentrations whereas in 1994, we added CH_3Br to the chamber headspace to achieve a measurable flux. The data from 1999 show periods of consumption of CH_3Br as well as periods of emission at both the College Woods and Kingman Farm sites (Figure 3.13b and 3.14b). The College Woods data show 4 specific sampling days when net emissions of CH_3Br were occurring. Each of these sampling days coincides with either a large rainfall event the previous day or a number of small rainfall events for a few days prior to sampling (Figure 3.13a). There are probably two processes occurring

simultaneously to produce this net efflux of CH_3Br from the system. First, the water from precipitation makes the soil micropore environment temporarily anaerobic. Since we have determined that consumption is completed by aerobic bacteria, these conditions should inhibit the microbial consumption of CH_3Br. Secondly, the presence of micropore water could inhibit gaseous diffusion of ambient CH_3Br to the microorganisms responsible for consumption. The soil moisture data did not show a significant relationship with the efflux measurements but since it is a bulk measurement, it may not be indicative of the moisture conditions at the site of activity or in microsites.

Production must also be occurring at the same time as the decreased consumption to produce a net efflux of CH_3Br from the site. The wetter conditions may provide a more favorable environment for the production of CH_3Br during the decomposition of litter. CO_2 production during dark chamber fluxes is a direct measurement of the decomposition of organic matter in aerobic upland soils. Though there are only eight measurements of both net emission of CH_3Br and respiration at the two sites, there appears to be a significant relationship between these parameters (Figure 3.17). Fungal production of CH_3Br during metabolic processes has been quantified in laboratory experiments [*Harper*, 1985; *Harper and Kennedy*, 1986] and globally extrapolated to a yearly production rate of 1.7 Gg [*Lee-Taylor and Holland*, 2000]. This production may also be enhanced because the rainfall is a source of Br ions due to our proximity to the ocean. *Harper and Kennedy* [1986] observed increased production of methyl halides by fungi when halide concentrations in growth media were increased. The two processes in concert constitute a net efflux from the system until the aerobic environment is

reestablished.

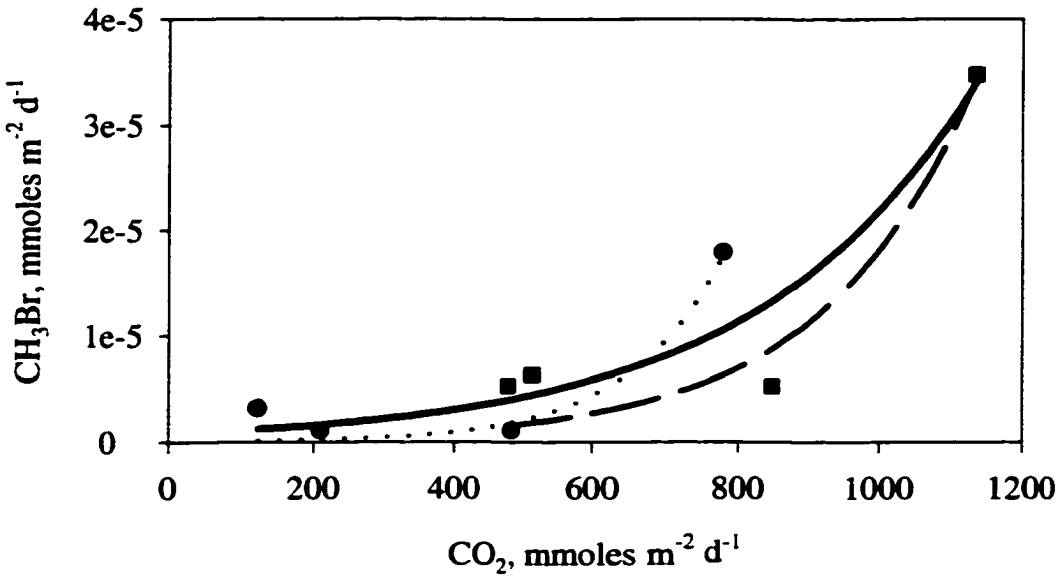

Figure 3.17. Net CH_3Br production versus respiration at College Woods (■) and Kingman Farm (●). College Woods data curve fit (dark dashed line): $CH_3Br = 8.1x10^{-7}exp(3.3x10^{-3}\ CO_2)$ with an $r^2 = 0.926$. Kingman Farm data curve fit (dark dotted line): $CH_3Br = 8.1x10^{-7}exp(3.3x10^{-3}\ CO_2)$ with an $r^2 = 0.946$. The curve fit for all data (dark solid line) is $CH_3Br = 8.1x10^{-7}exp(3.3x10^{-3}\ CO_2)$ with an $r^2 = 0.854$.

CH_3Br production does appear to occur concomitantly with net uptake as demonstrated by the diffusion data in Figure 3.14a and b. Significant quantities of CH_3Cl may be produced by fungi even when they are in a low Cl^- environment, similar to decaying litter, because of the high affinity of the fungal methylating system for halides [*Watling and Harper*, 1998].

The Kingman Farm data indicate greater variability of net consumption and production of CH_3Br than the College Woods data. The mean direction of flux for the season is into the soil but there were six measurements of net efflux from the system. After pre-planting tilling and post harvest tilling, net uptake of CH_3Br occurred (Figure 3.14b). During the growing season, there were periods when net production of CH_3Br

was noted. These emission events did not specifically coincide with the rainfall events as occurred at College Woods, but the field was periodically irrigated with sprinklers and the efflux might have coincided with these events. Similarly to College Woods, there appears to be a combination of consumption and production processes occurring. Figure 3.15b shows that when uptake was measured there were many cases when there was also production occurring (data falling below the 1:1 line). In some cases when uptake was occurring it was greater than pure diffusion of CH_3Br, therefore there does appear to be a significant microbial mechanism controlling the uptake of CH_3Br. The range of uptake measured at this site reveals the variability in measurements and shows that the one measurement of diffusion in 1994 at the cornfield site may not have been representative of the sum of the seasonal processes occurring.

Seasonal estimates of net CH_3Br exchange at College Woods and Kingman Farm were calculated from a 3-sampling-day running mean of the average of the two fluxes for that day. Calculated net uptake was 0.14 mg m^2 and 0.16 mg m^2 for temperate forest and cultivated areas respectively. Extrapolating this to global land areas from Matthews, 1983 gives us yearly uptake of CH_3Br of 2.8 and 2.3 Gg for temperate forest and cultivated areas. The cultivated estimate is about 3 times less than we estimated from our laboratory soil incubations (Table 3.2). The laboratory estimates were made with cultivated soils from many latitudes while the field measurements are from the temperate zone. Temperate cultivated soils would represent a shorter growing season than those cultivated soils in more tropical regions and would therefore result in a smaller uptake estimate.

The temperate forest flux estimate derived from direct chamber methods is about one tenth of the estimate from soil incubations. This discrepancy could be related to the potential for efflux of CH_3Br from the system. Depending on fungal characteristics as well as precipitation control of microenvironmental conditions, this total could increase or decrease. It is possible that because this was a particularly hot and dry year for the Northeast US that conditions for the aerobic bacterial growth were not optimal *[Madigan et al., 1997]*. These same conditions may have made it possible for fungal growth to occur at specific times when an influx of moisture occurred. The frequency and timing of sampling events (whether right after a rainfall event or during drier periods) will also have an effect upon the estimates for global consumption.

3.4. Conclusions

Our estimate of the global uptake rate for soils from soil incubations is almost twice that reported in 1995 [*Shorter et al.*, 1995] but 20% less than that reported by *Serça et al.* 1998. This is primarily due to the fact that our broadened database includes soils from 90 sampling sites from locations across the globe. By sampling at so many sites we believe that this is a more representative estimate for uptake by soils than our previous one.

The field measurements disagreed some what with our laboratory incubation results. Field measurements reveal periods of consumption as well as production of CH_3Br with a net influx to the soil surface. Cultivated soils seem to behave similarly in the field as in soil incubations probably because of similar soil characteristics between field and laboratory sampling. Temperate forest soils show efflux of CH_3Br not measured

in the laboratory. These periods seem to be related to precipitation events implying that possibly fungal production is occurring simultaneously with a decrease in aerobic uptake.

The uptake of ambient CH_3Br by soils is a ubiquitous process that varies with location. The rate of uptake is dependent on soil physical properties as well as sampling location with specific controls difficult to isolate. We have determined that the process is controlled by aerobic bacterial metabolism but that fungal production must also be taken into account. The geochemical cycling of CH_3Br in upland soils is a complex process. Further study is required to determine the conditions under which production or consumption of CH_3Br in the field becomes the dominant process. Field sampling of greater frequency over several growing seasons especially encompassing rainfall events might give us a better idea about the controls on net flux and allow us to better estimate a global flux.

CHAPTER 4

EXCHANGE OF METHYL BROMIDE IN WETLANDS

4.1. Introduction

Since CH_3Br became a target for prohibition, much research has been completed to determine the natural cycling of CH_3Br in the atmosphere and therefore the effect of anthropogenic CH_3Br use. The current understanding of the tropospheric CH_3Br budget reveals an imbalance in the budget with sinks equal to 210 Gg yr^{-1} and sources equal to 151 Gg yr^{-1}, a discrepancy of 59 Gg yr^{-1} [*Yvon-Lewis*, 2000]. This imbalance of the tropospheric budget can either be explained by an overestimate of the sinks of atmospheric CH_3Br or a significant missing source. During our search for the missing source of CH_3Br, we thought that wetlands might have the potential to produce and emit significant amounts of CH_3Br because flooded, organic rich soils were known to produce methyl halides [*Muramatsu and Yoshida*, 1995].

In the fall of 1998, we determined that wetlands were a source of atmospheric CH_3Br [*Varner et al.*, 1999b]. Extrapolation of these limited data led us to believe that this source was significant to the tropospheric budget of CH_3Br. We continued to measure fluxes over an entire growing season at the two sites studied in Varner et al., 1999b, located in the Northeast United States. The study took place over the 1999 growing season at two freshwater peatlands, Sallie's Fen and Angie's Bog, where we have made seasonal measurements of methane (CH_4) and carbon dioxide (CO_2) exchange

for close to ten years [*Frolking and Crill*, 1994]. Measurements of CH_3Br were made biweekly at the two sites from April 19th -December 2nd , 1999. The measurements revealed a net efflux of CH_3Br from both sites that when globally extrapolated has a significant impact on the atmospheric budget of CH_3Br. The measurements also revealed that though the net seasonal flux of CH_3Br is to the atmosphere, diffusion of CH_3Br to the wetland surface occurs under certain physical conditions.

4.2. Methods

Field sampling of CH_3Br, CH_4 and CO_2 fluxes took place from September through November, 1998 and May through December, 1999 at two temperate wetland sites. The first sampling site, Sallie's Fen, is a nutrient poor fen located in Barrington, New Hampshire (43°12.5'N, 71°03.5'W). It is dominated primarily by *Sphagnum* spp., *Carex* spp., and ericacious shrubs and has a surface area of 1.9×10^4 m^2. This wetland ranges from minerotrophic (high pH) wet edges to an ombotrophic (low pH) central area. The site has been studied for CH_4 and CO_2 exchange with the atmosphere since 1989 [*Frolking and Crill*, 1994]. Continuous, hourly averaged data for this site include water level, wind speed, temperature (air and a peat profile to 90 cm), relative humidity, net radiation, photosynthetically active radiation and barometric pressure. Daily total precipitation was also recorded.

Angie's Bog, the second sampling site, is a nutrient rich fen located adjacent to the Merrymeeting River in New Durham, New Hampshire (43°26.2'N, 71°10.4'W). It is dominated primarily by *Sphagnum* spp. Controlled water releases from Merrymeeting Lake as well as the site's hydrologic link to the river help to maintain a relatively uniform

wetness in the wetland throughout much of the year. Species composition, hydrology and pH indicate that Angie's Bog is more akin to a nutrient rich fen rather then an ombotrophic bog. CH_4 and CO_2 fluxes were measured semi-continuously at this site from 1989 through 1994. A water level monitoring well and a thermocouple profile (+25, peat surface, -5 and -10 cm) were installed at Angie's Bog in April of 1999. Automated data logging of hourly average temperatures and waterlevel began April 7, 1999 and continued throughout the sampling period.

Trace gas flux measurements of CH_3Br, CH_4, CO_2 and SF_6 were made using a transparent, climate controlled Lexan and Teflon chamber (100cm or 50cm, depending upon vegetation, height x 63cm x 63cm) placed on an aluminum collar imbedded in the wetland. The collars sampled at Sallie's Fen have been permanently placed in the peat surface from 3 to 10 years. The collars at Angie's Bog were inserted in August of 1998.

The chamber was placed on the collar and sealed with water. Four 2.5 L gas samples from the chamber headspace were taken at different times (t = 1,6,11, and 16 minutes). Samples were compressed into electropolished, stainless steel cylinders for analysis in the laboratory. An ambient methyl bromide sample was taken at each collar as well. The chamber, air, surface, and -10 cm depth temperatures and pH of the surface water were recorded during the measurements. On approximately one third of the sampling days, SF_6, an inert tracer, was introduced into the chamber headspace before sampling for an initial concentration of 30 parts per billion (ppbv). SF_6 has been used to determine non-biological diffusive loss of gas from the chamber headspace [*Dörr and Münnich*, 1990; *Rolston et al.*, 1991; *Trumbore*, 1995].

The sample canisters were analyzed for CH_3Br, CH_4, CO_2 and SF_6 within 24 hours. The CH_3Br mixing ratios were determined using a gas chromatograph equipped with an electron capture detector (GC-ECD). Details of CH_3Br analysis are in Chapter 2 - COLLECTION AND ANALYSIS OF SAMPLES FOR CH_3Br and *Kerwin et al.*, 1996.

CH_4, CO_2 and SF_6 were measured using a portion of the syringe sample or the canister sample by extracting 60 mL with a polypropylene syringe. A gas chromatograph equipped with a flame ionization detector (GC-FID) was used to determine CH_4 and a thermal conductivity detector gas chromatograph (GC-TCD) was used for analysis of CO_2. Another GC-ECD equipped with a 12-port valve was used to analyze for SF_6.

If the trace gas concentration versus time revealed a linear relationship or zero order, fluxes were calculated using the following equation:

$$\text{Flux} = \text{Slope} * \frac{P}{(R*T)} * \left(\frac{V_c}{A_c}\right) * \left(\frac{10^9 \text{ nmoles}}{\text{mole}}\right) * \left(\frac{1440 \text{ min}}{\text{day}}\right) * c$$

where Flux is in nmoles $m^{-2} d^{-1}$, Slope is equal to ppmv or pptv min^{-1}, P is air pressure of approximately 1 atm, R is the gas constant equal to 8.206×10^{-5} m^3 atm K^{-1} mol^{-1}, T is the chamber temperature in Kelvin, V_c is the chamber volume, A_c is the collar area, and c is a constant to convert from mixing ratios to molar volumes (10^{-6} for ppmv measurements and 10^{-12} for pptv measurements).

In some instances, CH_3Br uptake was observed and the behavior of the concentration versus time relationship revealed first order kinetics. The following equation was then used to calculate uptake of CH_3Br:

$$Flux = k_{meas} * [C_i] * \left(\frac{V_c}{A_c}\right) * \left(\frac{1440\,min}{day}\right)$$

where Flux is in nmoles $m^{-2}\,d^{-1}$, k_{meas} is the first order reaction rate constant in min^{-1}, C_i is the initial concentration of CH_3Br in the headspace or ambient CH_3Br in nmoles m^{-3}, V_c is the chamber volume and A_c is the collar area.

SF_6 uptake was used to measure diffusive loss of CH_3Br from the chamber. The measured diffusion reaction rate constant of SF_6, k_{SF6}, was used to calculate a physical diffusive loss constant for CH_3Br, k_{CH3Br}, using Graham's law.

$$k_{CH3Br} = k_{SF6} * \left(\sqrt{\frac{m_{CH3Br} + m_{air}}{m_{CH3Br} * m_{air}}}, \sqrt{\frac{m_{SF6} + m_{air}}{m_{SF6} * m_{air}}}\right)$$

where m_{CH3Br} is the molecular weight of CH_3Br (95 g $mole^{-1}$), m_{air} is the molecular weight of air (28 g $mole^{-1}$) and m_{SF6} is the molecular weight of SF_6 (146 g $mole^{-1}$). A comparison of the measured reaction rate constant, k_{meas} from the field fluxes with the calculated diffusive loss of CH_3Br, k_{CH3Br} can help determine if uptake of CH_3Br is diffusionally controlled or possibly enhanced by microbial processes.

4.3. Results

4.3.1. Sallie's Fen

The 1998 sampling season at Sallie's Fen began on September 1st and ended November 9th (Figure 4.1 a and b). Two flux measurements were made on each of 7

sampling days. Collar 9 was measured at every visit to the Fen while the other flux measurement was taken at a randomly selected collar. A net efflux of CH_3Br from the Fen was measured on every day except the final sampling day when Collar 6 showed a small net uptake of CH_3Br. Over the sampling period, the average daily temperature decreased from approximately 15 to almost 0 °C. The waterlevel over this period rose almost 25 cm.

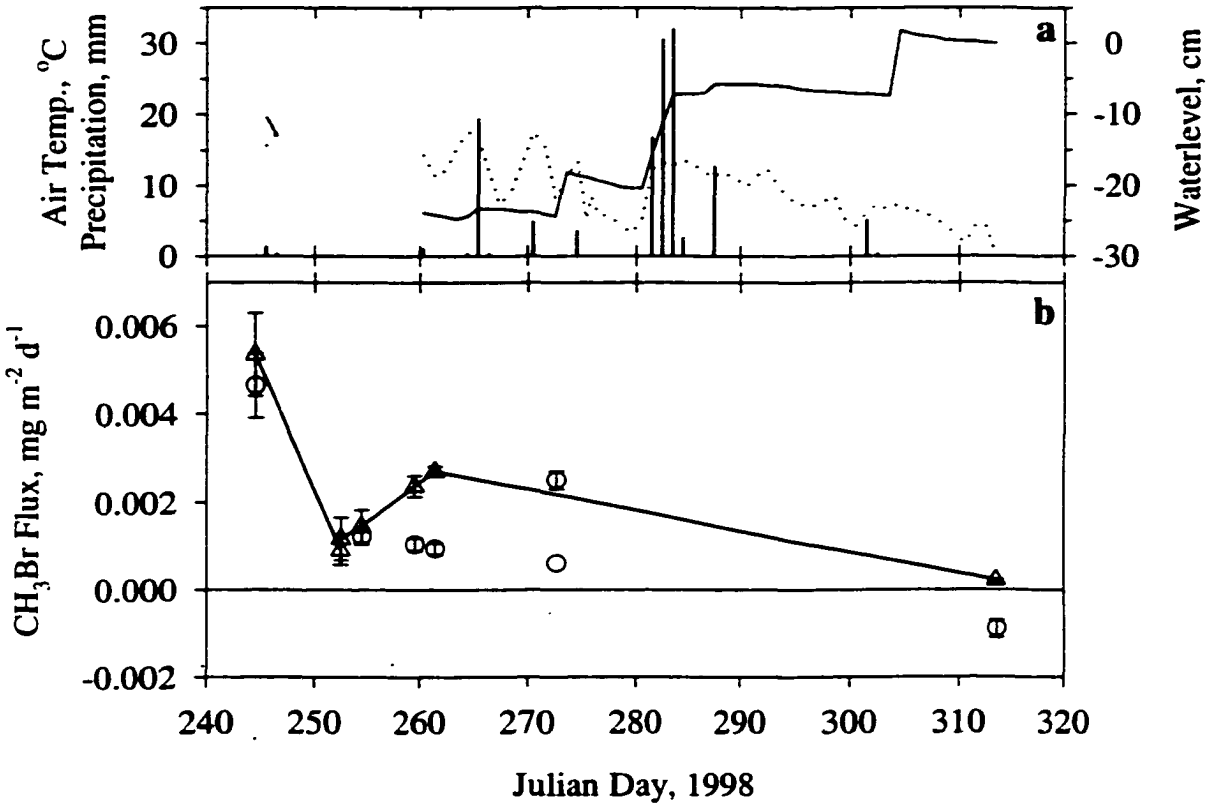

Figure 4.1 a and b. Data plotted are from Sallie's Fen during the 1998 season. (a) average daily temperature (···), daily total precipitation (bars) and average daily waterlevel (- -)(b) Collar 9 (Δ) and other collars (O) CH_3Br flux. Error bars represent the error of the slope of the linear regression fit of the chamber headspace measurements of [CH_3Br] versus time.

The daily averaged waterlevel, air temperature and daily total precipitation as well as the seasonal CH_3Br exchange at Sallie's Fen for 1999 are plotted in Figure 4.2a and b. The 1999 sampling season at Sallie's Fen was marked by a drought period in the Northeast U.S. This can clearly be seen in the waterlevel data in Figure 4.2a as a precipitous drop in waterlevel of almost 50 cm over the course of 100 days. The second part of the sampling season is marked by two, very large rainfall events associated with hurricanes in September (4.2 *1* and *2*). The waterlevel actually regains its pre-drought level by the end of the sampling season (Figure 4.2a).

The magnitude of CH_3Br fluxes varies from net emissions to net uptake at different times throughout the sampling period. Collar 4 which was sampled at every visit to the Fen shows a discernable pattern in flux. The mid-season shows net emissions while on either end of the season net uptake occurs. The other collars that were sampled reveal the spatial variability in flux measurements at Sallie's Fen.

The relationships between waterlevel, air temperature and -20 cm peat temperature to CH_3Br exchange for Sallie's Fen are shown in Figure 4.3a, b and c. There were definitive relationships found between measured CH_3Br exchange rates and these parameters measured at the Fen. Using a multiple linear regression with waterlevel, air temperature and -20 cm temperature to predict CH_3Br flux, a seasonal model was calculated (Figure 4.4). Summing the flux over the entire growing season reveals a net efflux from Sallie's Fen of 0.21 mg of CH_3Br m^{-2} for 1999.

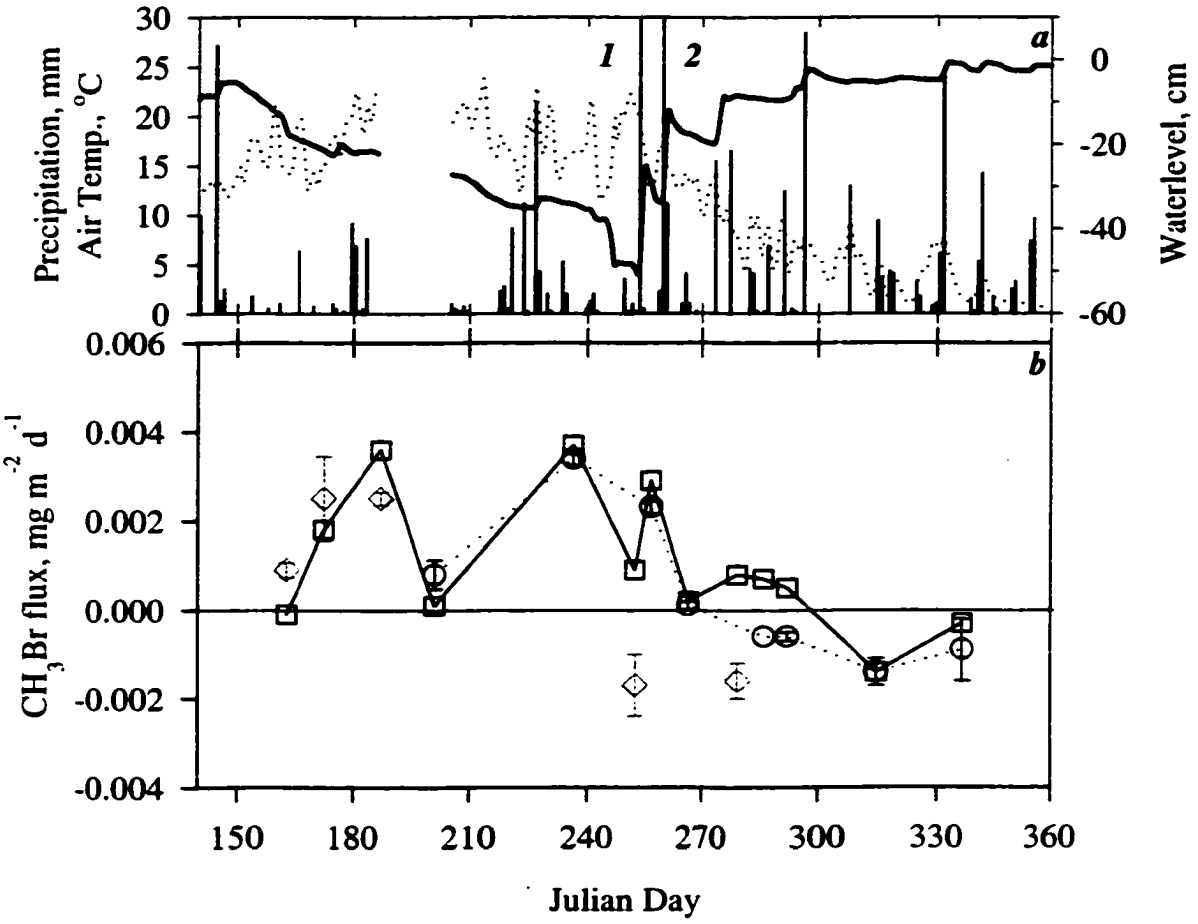

Figure 4.2 a and b. 1999 seasonal CH_3Br flux and meteorological characteristics from Sallie's Fen. a. Daily averaged +10 cm temperature and waterlevel and daily total precipitation versus day of year. Measurements are taken every minute with thermistors, mounted potentiometer, and a tipping bucket precipitation gage and averaged every hour. Daily averages are for 12 noon local time. Dotted line is temperature, solid line is waterlevel, and bars are total precipitation. *1* and *2* represent large rainfall events of 100 and 90 mm, respectively. b. CH_3Br fluxes are plotted versus the day of year. The data are shown with error bars calculated from standard error of the regression fit of flux for that day. The solid line connects data from Collar 4 (□) sampled at each visit. The dotted line connects data from Collar 2 (○) sampled at some visits. The final data (◇) are measurements from collars randomly sampled throughout the Fen.

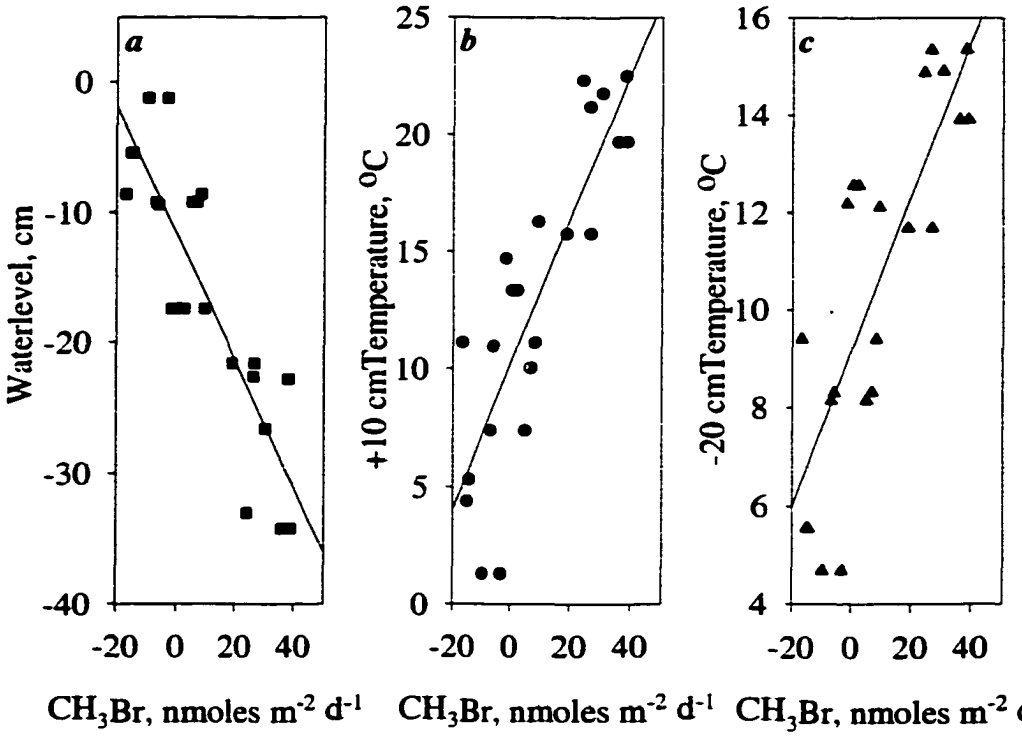

Figure 4.3 a, b and c. Relationship between measured meteorological parameters and CH_3Br flux at Sallie's Fen. a. Waterlevel (WL) versus CH_3Br flux (F) shows the linear relationship: WL = -0.49 F - 11.6 with an $r^2 = 0.75$. b. Air temperature (AT) versus CH_3Br flux (F) shows the linear relationship: AT = 0.31 F + 10.2 with an $r^2 = 0.71$. c. -20 cm peat temperature (PT) versus CH_3Br flux (F) shows the linear relationship: PT = 0.16 F + 9.16 with an $r^2 = 0.71$.

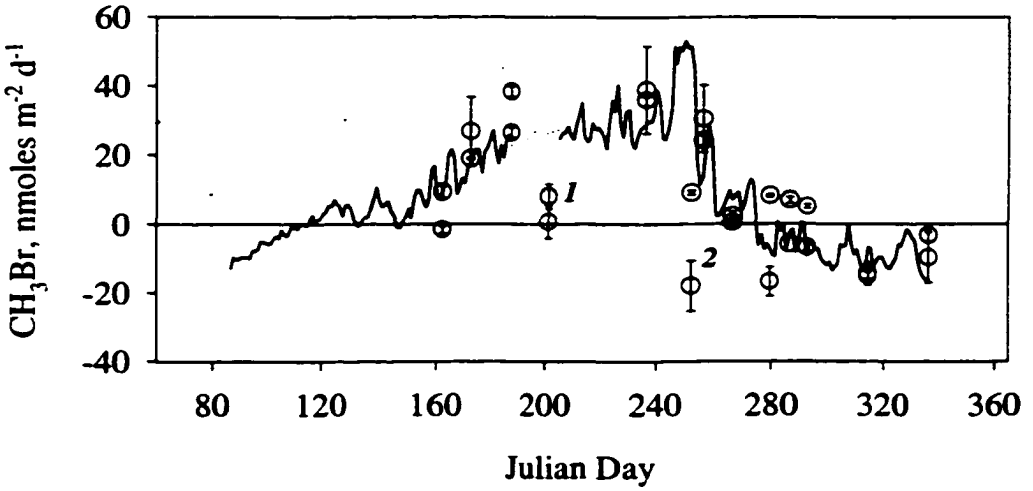

Figure 4.4. Measured (O) and modeled (—) CH_3Br flux in nmoles m^{-2} d^{-1} versus the day of year for 1999 at Sallie's Fen. Data are shown with error bars calculated from standard error of slope of linear regression of measured concentration versus time. Model

calculated from a multiple linear regression of CH_3Br flux (F) versus waterlevel (WL), air temperature (AT), and -20 cm peat temperature (PT) where F = -1.1WL + 1.8AT - 2.0PT - 10.53, $r^2 = 0.77$. Daily averaged waterlevel. Air temperature and peat temperature were used to calculate seasonal CH_3Br flux. The dotted portion of the modeled data is when the meteorological station was down therefore data were inferred. *1* and *2* represent data referred to later in the text.

Studies of diffusion of CH_3Br from the chamber headspace using the previously described SF_6 tracer method show that upon comparison, the calculated k_{CH3Br} is always faster (or falls below the 1:1 line) than the k_{meas} (Figure 4.5). Figure 4.5 also shows that the physical diffusion of CH_3Br to the surface of the fen (k_{CH3Br}) decreased as the season ended while concurrently, k_{meas} increased.

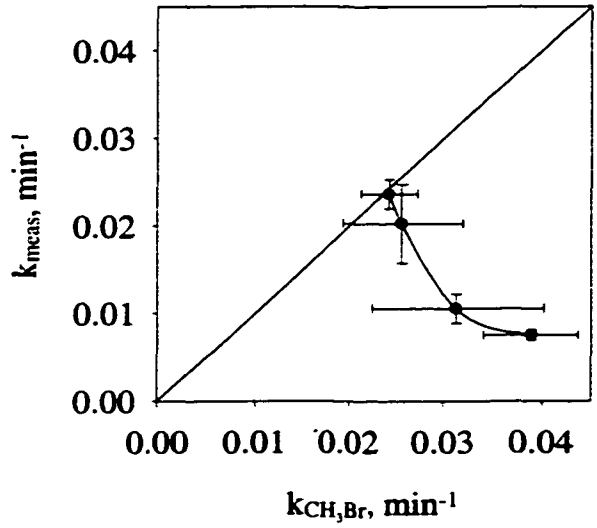

Figure 4.5. Measured uptake of CH_3Br, k_{meas}, versus calculated diffusional uptake of CH_3Br, k_{CH3Br}, at Sallie's Fen. Error bars are standard error of the slope of the regression fit of ln[CH_3Br] versus time. A 1:1 line is plotted for reference.

4.3.2. Angie's Bog

The 1998 sampling season at Angie's Bog ran from October 7th through November 5th. Collars 1 and 2 were emplaced 10 years ago for CH_4 and CO_2 sampling.

They were sampled only once because they were smaller than the clear chambers we use presently. Collars 5 and 6 were placed in the wetland on October 7th and were sampled 4 times later in the season. The main difference between collars 5 and 6 is the proximity of the peat surface to the waterlevel. Collar 5, a hummock, was microtopographically higher than Collar 6, a hollow. This means that the surface of the peat was further above the water surface at Collar 5 than at Collar 6.

The 1998 sampling season was rather short but it did reveal some patterns in flux (Figure 4.6 a and b). Collars 1 and 2 showed almost exactly the same net emissions of CH_3Br. Collar 5 showed net uptake of emissions with a slight increase as the season ended. Collar 6 showed net efflux of CH_3Br through the sampling season with a leveling off as the season ended. Chamber temperature decreased as the sampling season ended.

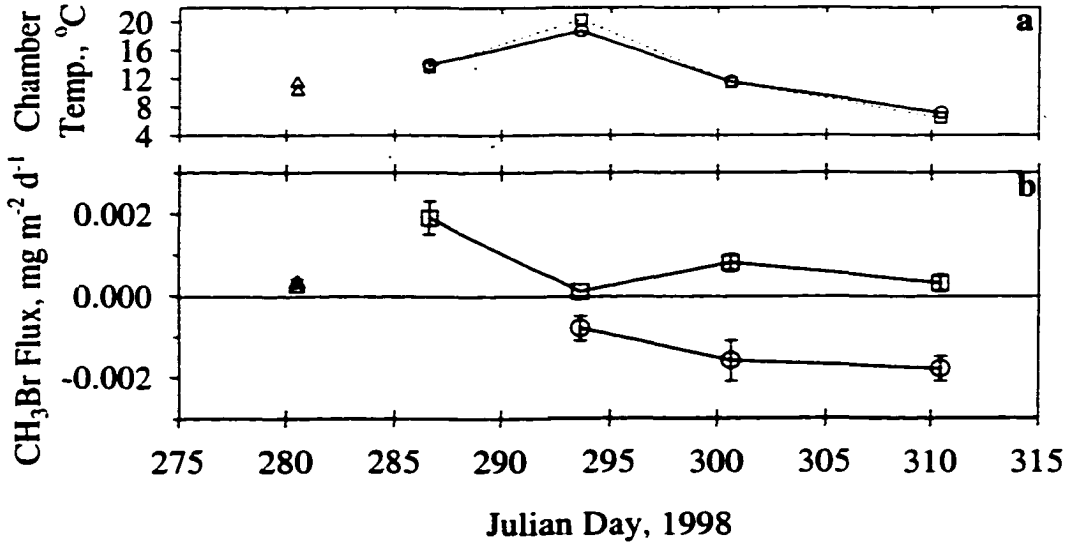

Figure 4.6 a and b. Data plotted are from Angie's Bog during the 1998 season. (a) chamber temperature for each collar (b) CH_3Br flux measurements for collars 1 and 2 (Δ), collar 5 (○) and collar 6 (□) . Error bars represent the error of the slope of the linear regression fit of the chamber headspace measurements of [CH_3Br] versus time.

An automated data system was placed at Angie's Bog in early 1999 to monitor waterlevel and a temperature profile. The daily averaged waterlevel, air temperature and daily total precipitation as well as the seasonal CH_3Br exchange at Angie's Bog for 1999 are shown in Figure 4.7a and b. Again, a drop in waterlevel is apparent over the growing season primarily due to the drought experienced in much of the Northeast United States in the summer of 1999.

The seasonal exchange of CH_3Br at Angie's Bog has a different signature than Sallie's Fen (Figure 4.7b.). Collar 5 and 6 as described previously were sampled at each visit to Angie's Bog. Collar 5 showed uptake of methyl bromide throughout the entire season of sampling except on day 300 when a small efflux of CH_3Br was observed. Collar 6 showed efflux of CH_3Br throughout the entire sampling season.

There was no apparent relationship between temperature and waterlevel with CH_3Br exchange at Angie's Bog as was found at Sallie's Fen. Therefore, a more traditional approach to estimating the seasonal exchange of CH_3Br with Angie's Bog was taken. A 3-sampling-day running mean of flux for each collar (Figure 4.8) was used to extrapolate between measurements. The season was presumed to begin upon thaw and end at freeze up. Assuming that half the of the Bog (total area of 2×10^5 m^2) is hummock (similar to Collar 5) and half is hollow (similar to Collar 6), we calculated a seasonal net efflux of 0.043 mg of CH_3Br m^{-2} from Angie's Bog in 1999.

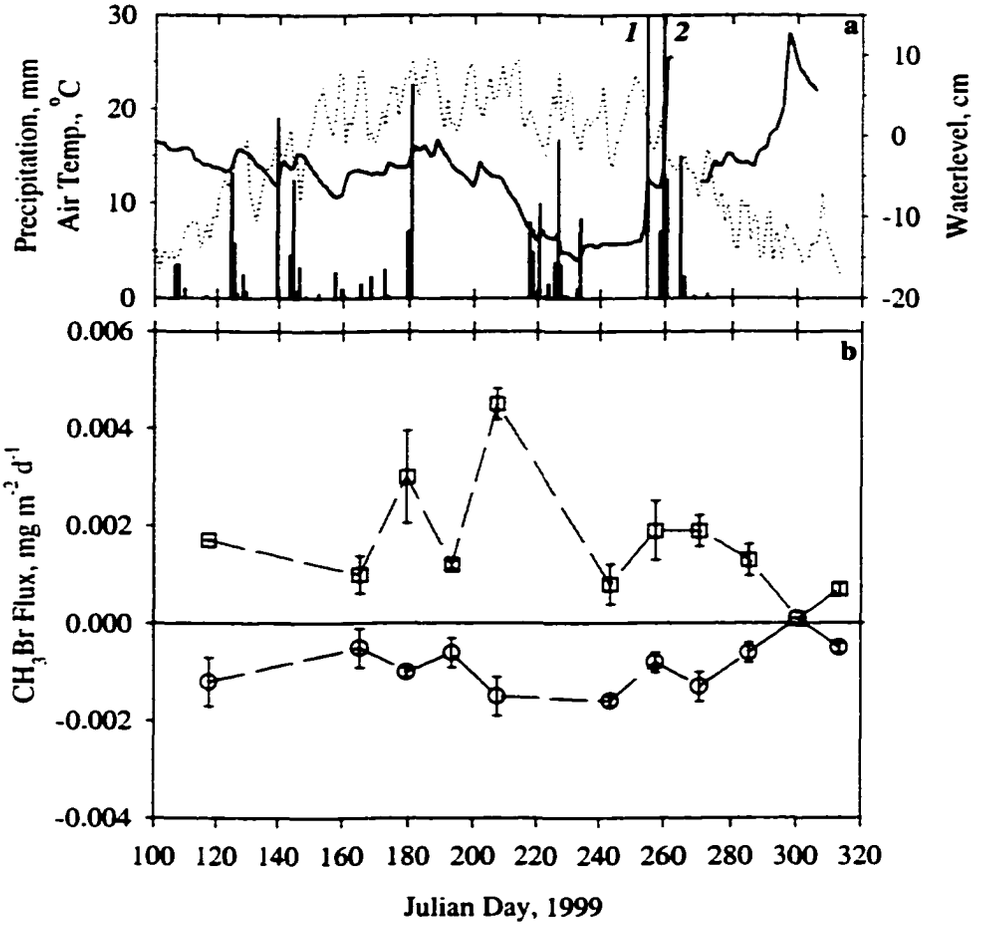

Figure 4.7 a and b. 1999 seasonal CH_3Br flux and meteorological characteristics fromAngie's Bog. a. Daily averaged +25 cm temperature and waterlevel and daily total precipitation versus day of year. Measurements for temperature and waterlevel were taken every minute with Type T thermocouples and a mounted potentiometer and were averaged every hour. Daily averages are for 12 noon local time. Precipitation data is from the New Hampshire State Climatologist, Barry Keim. Dotted line is temperature, solid line is waterlevel, and bars are total precipitation.. *1* and *2* represent large rainfall events of 81 and 98 mm, respectively. b. CH_3Br fluxes are plotted versus the day of year. The data are shown with error bars calculated from standard error of the regression fit of flux for that day. A solid line connects data from Collar 5 (○) and Collar 6 (□) sampled at every visit to the site.

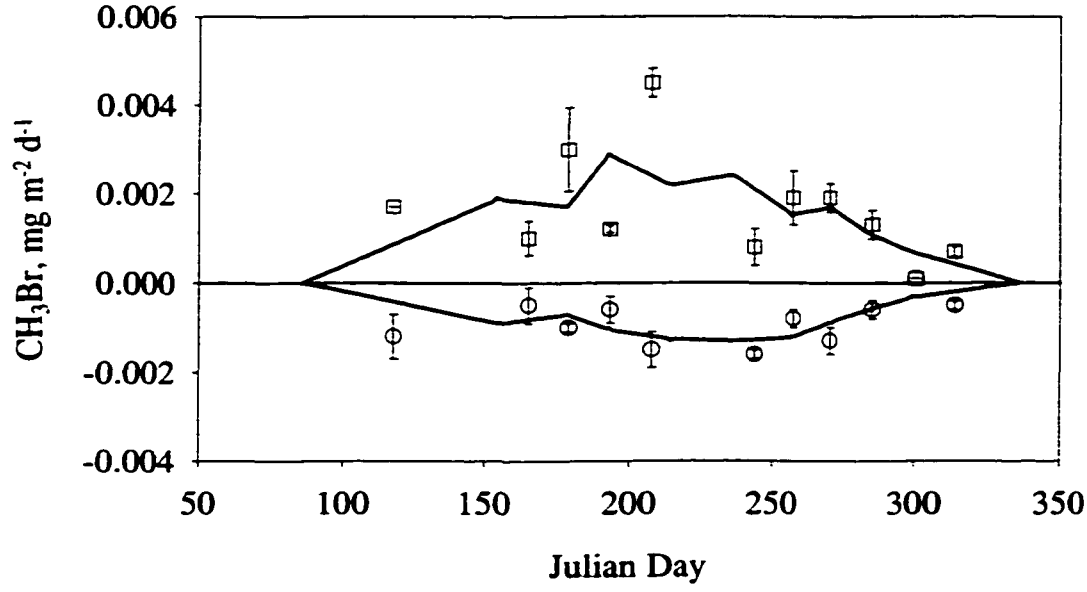

Figure 4.8. Measured (Collar 5(O) and Collar 6(□)) and modeled (—) CH_3Br flux in nmoles m^{-2} d^{-1} versus the day of year for 1999 at Angie's Bog. Data are shown with error bars calculated from standard error of slope of linear regression of measured concentration versus time. Model calculated a 3-sampling-day running mean of measured CH_3Br flux.

4.3.3. Global Extrapolation

To estimate a global flux of CH_3Br by wetlands we took a similar approach as Bartlett and Harriss, 1993 for global methane emissions from wetlands. Land areas of wetlands from specific climatic zones were determined from Matthews and Fung, 1987 (Table 4.1). Since it is difficult to obtain average waterlevel data for wetlands throughout the world, we chose to extrapolate using just the air temperature and CH_3Br flux relationship found at Sallie's Fen. The linear relationship between CH_3Br flux and air temperature was determined to be:

$$\text{Flux} = 2.3 * T - 18.3$$

The average daily temperature of the growing season was then used to determine the flux

in nmoles $m^{-2}d^{-1}$. This was then multiplied by the areal estimates of wetlands for that climatic zone and the days of the growing season. The results yield an estimate of 2.2 Gg yr^{-1} of CH_3Br emitted by wetlands each year (Table 4.1).

BIOME	Latitude	Wetland Area* (m^2)	Length of Growing Season (days)	Average Temperature of Growing Season (°C)	Flux of CH_3Br (Gg yr^{-1})
Arctic	80-60N	1.47E+12	100	10	.06
Boreal	60-45N	1.50E+12	150	15	.34
Temperate	45-30N; 30-50S	1.38E+11	150	20	.05
Subtropical	30-20N	1.38E+11	180	25	.09
Tropical	20 N– 30S	1.89E+12	180	30	1.6
				TOTAL	**2.2**

* Matthews and Fung, 1987

Table 4.1. Estimate of the global flux of CH_3Br to the atmosphere by wetlands.

4.4. Discussion

4.4.1. Sallie's Fen

The 1998 and 1999 sampling seasons show similar results at Sallie's Fen where overlap occurs. There is considerable spatial variability throughout the entire sampling season in 1999 (Figure 4.2b). Nevertheless, there is a consistent relationship between flux and air temperature, waterlevel and peat temperature (Figure 4.3 a, b and c). Since these relationships are linear, a multiple linear regression and daily averaged meteorological data provide a model to estimate the exchange of CH_3Br for the entire 1999 growing season (Figure 4.4). We feel that this model approximates the seasonal

signature of the fluxes well though there are times where there is a significant discrepancy in modeled versus measured data. These locations marked on Figure 4.4 with the numbers 1 and 2, may be explained in two ways. The automated meteorological system was without power when measurements were made on day 201 (a) therefore those data were not used in the original model calculation. A rain gage we operated only 15 miles from the sampling site showed a daily total precipitation for day 200 equal to 30 mm. Those measurements made on day 252 (b) were made when the waterlevel in the Fen was the lowest it had been the entire summer. For three days prior to the measurement, small rain events were measured. In both cases, these rain events could have caused an influx of water to the Fen that would have essentially altered the micro-environment along the watertable. It is possible that this alteration would manifest itself in a temporary lowering of CH_3Br fluxes either because the CH_3Br production zone needed to be reestablished or the CH_3Br produced could not diffuse through the new level of water.

On the occasions when uptake was measured at Sallie's Fen, k_{meas}, it was always slower than the measured rate of diffusion, k_{CH3Br} (Figure 4.5). This implies that production of CH_3Br was occurring even though the net flux was into the peat surface. The diffusion measurements made with the SF_6 tracer method were only implemented during the latter part of the sampling season. The resulting measurements showed a decrease over time in physical diffusion to the peat surface. The decrease in physical diffusion, k_{CH3Br}, was probably due to in part to temperatures decreasing and the water level increasing (diffusion to a water surface is slower than to a peat surface).

An increase in k_{meas} towards the 1:1 line was observed over the measurement

period (Figure 4.5). This is most probably due to a decrease in production of CH_3Br occurring due to a decrease in temperature. Since the measured uptake, k_{meas}, approaches equality with the diffusion rate, there does not appear to be a biological sink. If there was a sink, the data should fall above the 1:1 line indicating that measured uptake was greater than uptake expected purely from physical diffusion. Some have suggested that methyl halides can be consumed in freshwater anaerobic environments by methanotrophic bacteria [*Oremland et al.*, 1994; *Goodwin et al.*, 1998]. There is no evidence from this data set that consumption of CH_3Br is occurring at a greater rate than pure diffusion.

Methanogenic bacteria, present in freshwater anaerobic environments such as these, have been known to use methylated compounds to produce CH_4 [*Conrad*, 1996]. If this is occurring, there could be a relationship between uptake of CH_3Br and CH_4 production. Since we only measured net CH_4 flux from the Fen which is a sum of production as well as consumption we do not know if there is a relationship. Since this system is a complex combination of potential production and consumption pathways, the determination of controlling factors on production, consumption and release needs a more focused study than just the measurement of net fluxes.

4.4.2. Angie's Bog

The 1998 data for Angie's Bog seem to follow similar trend as the measurements made in 1999 (Figure 4.6 and 4.7). Since Angie's Bog is only approximately 40 miles North of Sallie's Fen their precipitation and average air temperatures for the 1999 sampling season are similar. The largest difference between the two wetlands is revealed in the waterlevel record at Angie's Bog (Figure 4.7a). As was mentioned previously, this

was a very dry period for the Northeast U.S. but you do not see the precipitous drop in water level at the Bog that you see at the Fen. The magnitude of drop in waterlevel is actually less than half that at the Fen, about 15 cm. This is primarily due to the fact that Angie's Bog is actually hydrologically connected to the Merrymeeting River, downstream from the Merrymeeting Lake and seems to remain at a relatively constant water level through almost all of the sampling season until the large precipitation events in early September. The last large rise in waterlevel was due to a large release of water from the Merrymeeting Lake that occurs in the fall to prepare for the spring influx.

The linear relationships between CH_3Br flux and temperature and waterlevel as seen with the Sallie's Fen data is not present in the data for Angie's Bog. This could be due to the fact that the waterlevel was maintained at a more constant level throughout the season thereby negating water level effects over the season.

4.4.3. Global Extrapolation

We estimate the global emissions of CH_3Br by freshwater wetlands to be 2.2 Gg yr^{-1} (Table 4.1). We feel that this is a better estimate than our previous one of 4.6 Gg yr^{-1} from Varner et al., 1999b because here we measured CH_3Br exchange during an entire growing season. Our global estimates show that though the Boreal and Arctic regions have vast areas of wetlands, they have the smallest total emissions because their growing season is shorter and their average temperature is lower. The Tropical regions appear to be the greatest source of CH_3Br from freshwater wetlands due to their longer growing season and wetter and warmer climate. If water level could be integrated into the global estimate, it may more accurately represent the actual global contribution to atmospheric

CH_3Br by wetlands.

Though we are confident that the relationships we have measured between CH_3Br flux and temperature and waterlevel are valid, we feel that this global extrapolation is a conservative estimate. There could be potential for greater fluxes from the Arctic and Boreal regions than we have calculated. Acidic (pH , 4.6) and cool (<15°C) wetland environments have shown high rates of production of methylated sulfur compounds [*Kiene and Hines*, 1995]. In these environments studied, methanogens, potential consumers of methylated compounds, were not capable of consuming dimethylsulfide (DMS) or other methylated compounds. Therefore, flux out of the peat surface approximated actual production rates [*Hines*, personal communication].

Recently, Keppler et al., 2000 measured abiotic production of CH_3Br from suspended organic matter from peat water. These measurements were made under controlled laboratory conditions and CH_3Br was produced during the oxidation of organic matter. The production increased when more Br^- and Fe(III) were present.

Both the biotic and abiotic factors affecting production of CH_3Br could cause our global estimates to increase or decrease depending on the specific environmental conditions. Tropical wetland regions are less acidic than our study area whereas Arctic and Boreal regions generally have lower pH's. Tropical wetland soils are leached therefore may have less available Br- whereas just the opposite may be true in northern areas. The amount of Fe(III) in soils varies greatly in each climatic zone.

These data are the only available seasonal estimates of wetland flux of CH_3Br. Dimmer et al., 1999 show emissions from peatland ecosystems in Ireland. Their

measurements were completed during the month of September in 1998. Their average measured efflux of CH_3Br was 1.1 mg m^{-2} from marshes and peatland bogs, approximately 5 times greater than our estimate for Sallie's Fen. The differences are most likely due to the site characteristics (microtopography and plant species), sampling period (one month versus seasonal) and sampling techniques.

Serça et al., 1998 reported uptake of ambient CH_3Br by peat microcosms at NCAR, Boulder, Colorado. Their measurements revealed a net uptake of CH_3Br of 0.84 mg m^{-2} each year by bogs, swamps and marshes. This value is 3 times the maximum uptake measured during the entire season at our sampling locations. It is difficult to determine the cause of such a discrepancy only to say that temperature and waterlevel information were not reported so it is impossible to compare our results with theirs. Their sampling techniques differed greatly because they added CH_3Br to the chamber headspace and we began the experiments at local ambient concentrations.

4.5. Conclusions

In 1998, we measured and published the first estimates for the global production of CH_3Br from wetlands. The data presented in this chapter are the first seasonal data for CH_3Br exchange from wetland ecosystems. These data reveal that the cycling of CH_3Br in terrestrial ecosystems is a rather complex process. The measurements indicate that Sallie's Fen and Angie's Bog are net sources of CH_3Br to the atmosphere although observations over the season reveal periods of uptake and efflux of CH_3Br. Diffusion studies imply that any uptake that is observed appears to be due to the physical diffusion of CH_3Br to the wetland surface that probably is not microbially driven. Sallie's Fen

CH_3Br flux measurements correlated well with air temperature, water level and peat temperature. This relationship was not observed at Angie's Bog.

Measurements indicate a net efflux from both Sallie's Fen and Angie's Bog of 0.21 and 0.43 mg of CH_3Br m^{-2} in 1999, respectively. An extrapolation of these net flux rates to a global estimate, using measured relationships to air temperature, reveals a net flux of 2.2 Gg yr^{-1} of CH_3Br from wetlands. This source is 8% of the terrestrial source contributions to the tropospheric budget of CH_3Br. We plan to complete latitudinal studies of wetlands to show the ubiquity and magnitude of the wetland source. We will also continue our seasonal studies at these sites in an effort to pinpoint controlling factors on efflux as well as uptake. All of this information is critical in the determination of the tropospheric budget of CH_3Br and to the calculation of its ODP.

CHAPTER 5

IMPLICATIONS AND THE FUTURE OF CH_3Br RESEARCH

The research presented in this thesis has had a significant impact on our understanding of the tropospheric budget of CH_3Br. The discovery of the soil sink of CH_3Br significantly changed the estimate of the lifetime as well as the ozone depletion potential (ODP) of CH_3Br. The consumption of CH_3Br in soils is conducted by aerobic bacteria and appears to be a ubiquitous process. Extrapolation of the soil sink yields a global uptake estimate of 75 Gg yr^{-1}. These are the first field measurements of ambient exchange of CH_3Br by soils over an entire season. They reveal that though consumption is the predominant process, production of CH_3Br is also occurring. Previous to this, production of CH_3Br by soil fungi was measured only in the laboratory setting. Further study is required to determine the conditions under which production or consumption of CH_3Br in the field becomes the dominant process. Field sampling of greater frequency over several growing seasons, especially encompassing rainfall events, should give us a better idea about the controls on net flux and allow us to better estimate a global flux.

The discovery of wetlands as a net source of CH_3Br has also changed our understanding of the cycling of halocarbons in natural environments. These compounds, though low in concentration in the atmosphere, are significantly exchanged within the biosphere. There appears to be a microbial mechanism for production and no indication that microbial consumption is occurring. The magnitude of the global efflux of CH_3Br

from wetlands is approximately 8% of the known terrestrial sources of CH_3Br. Its importance may increase as the anthropogenic input of CH_3Br to the atmosphere decreases once the ban on use is in effect.

The biogeochemical cycling of CH_3Br in soils, both upland and wetland, is a complex process that we have only begun to understand. There are potential research endeavors in many areas associated with this topic. Seasonal monitoring of fluxes at upland sites could give us a better idea of variability within and between years as well as controlling factors on fluxes. Since our study was completed during an anomalously dry year, it would be interesting to see how an average and wet year behave. Research into the production mechanisms in cultivated and forested soils is also something that should be studied in greater detail. There appears to be a fine line between net consumption and production in these environments. The apparent sensitivity of the system to water and temperature implies that global climate change may have an effect on the net flux magnitude as well as direction.

Wetland ecosystems are famous for their ability to process compounds and are sources of important trace gases to the atmosphere. The discovery of the source of CH_3Br is just another indication that these systems are capable of transformation of organic matter to many forms. Further research to determine the ubiquity of this source is necessary to give us a better idea of the global distribution of this source. Continuing seasonal monitoring of the exchange of CH_3Br in wetlands is important so that controlling factors can be determined and extrapolations can be based in sound relationships. Microbiological research should also be completed to determine which

microbes are responsible for production. The determination of the effect of vegetation on emissions is also a high priority.

A thorough understanding of the biogeochemical cycling of atmospheric CH_3Br in the terrestrial environment is important because as the ban on anthropogenic use occurs, natural sources and sinks will become more important in controlling the concentration of CH_3Br in the atmosphere. Understanding the controlling mechanisms of natural sources and sinks will help us to predict possible changes in the cycling due to future climate change.

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APPENDIX A

Table A.1. Soil sample inventory.

Site	Latitude	Longitude	Description	Site name	Date Collected	Soil Order	Soil Suborder	Soil Descriptio	Land Use	Cover/Crop	Biome
Costa Rica	10.20	83.53	Residual Forest		09/29/95				Forest		Tropical
Costa Rica	10.20	83.53	2 year old pasture		09/29/95				Pasture		Tropical
Costa Rica	10.20	83.53	5 year old pasture		09/29/95				Pasture		Tropical
Costa Rica	10.20	83.53	6 year old pasture		09/29/95				Pasture		Tropical
Costa Rica	10.20	83.53	8 year old pasture		09/29/95				Pasture		Tropical
Costa Rica	10.20	83.53	13 year old pasture		09/29/95				Pasture		Tropical
Costa Rica	10.20	83.53	21 year old pasture		09/29/95				Pasture		Tropical
Costa Rica	10.43	84	KCC +		09/29/95				Agricultural	Corn	Tropical
Costa Rica	10.43	84	KCC -		09/29/95				Agricultural	Corn	Tropical
Costa Rica	10.43	84	KCP +		09/29/95				Agricultural	Corn	Tropical
Costa Rica	10.43	84	KCP -		09/29/95				Agricultural	Corn	Tropical
Costa Rica	10.43	84	KDC +		09/29/95				Agricultural		Tropical
Costa Rica	10.43	84	KDC -		09/29/95				Agricultural		Tropical
Costa Rica	10.43	84	KDP +		09/29/95				Agricultural		Tropical
Costa Rica	10.43	84	KDP -		09/29/95				Agricultural		Tropical
Costa Rica	10.43	84	KD1 High Terrace, 0-3 cm		04/24/94				Agricultural		Tropical
Costa Rica	10.43	84	KD2 High Terrace, 3-6 cm		04/24/94				Agricultural		Tropical
Costa Rica	10.43	84	KD3 High terrace, 8-10 cm		04/24/94				Agricultural		Tropical
Costa Rica	10.43	84	KD4 High terrace, 20-22		04/24/94				Agricultural		Tropical
Costa Rica	10.43	84	KD5 High terrace, 0-3 cm		04/24/94				Agricultural		Tropical
Costa Rica	10.43	84	KD6 High terrace, 3-6 cm		04/24/94				Agricultural		Tropical
Costa Rica	10.43	84	KD7 High Terrace 8-10 cm		04/24/94				Agricultural		Tropical
Costa Rica	10.43	84	KD8 High terrace, 20-22 c		04/24/94				Agricultural		Tropical
College Woods	43.13	70.93	3-7 cm		04/11/94	Inceptisols	Eutrochrepts	Aquic	Forest		Temperate
College Woods	43.13	70.93	10-15 cm		04/11/94	Inceptisols	Eutrochrepts	Aquic	Forest		Temperate
College Woods	43.13	70.93	0-3 cm		10/20/94	Inceptisols	Eutrochrepts	Aquic	Forest		Temperate
College Woods	43.13	70.93	3-7 cm		10/20/94	Inceptisols	Eutrochrepts	Aquic	Forest		Temperate
College Woods	43.13	70.93	0-3 cm		12/19/94	Inceptisols	Eutrochrepts	Aquic	Forest		Temperate
College Woods	43.13	70.93	3-7 cm		12/19/94	Inceptisols	Eutrochrepts	Aquic	Forest		Temperate
College Woods	43.13	70.93	0-3 cm		10/15/96	Inceptisols	Eutrochrepts	Aquic	Forest		Temperate
College Woods	43.13	70.93	3-7 cm		10/15/96	Inceptisols	Eutrochrepts	Aquic	Forest		Temperate
College Woods	43.13	70.93	10-15 cm		10/15/96	Inceptisols	Eutrochrepts	Aquic	Forest		Temperate
UNH Cornfield	43.12	71.01	0-3 cm		07/08/94	Inceptisols	Haplaquepts	Aeric	Agricultural	Corn	Temperate
Manitoba			OJP, Alder, surface cover		06/16/94				Forest	Jack pine	Boreal

Site	Latitude	Longitude	Description	Site name	Date Collected	Soil Order	Soil Suborder	Soil Descriptio	Land Use	Cover/Crop	Biome
Manitoba			OJP, Alder, 1-3 cm		06/16/94				Forest	Jack pine	Boreal
Manitoba			OJP, Alder, 5-10 cm		06/16/94				Forest	Jack pine	Boreal
Manitoba			OJP, Alder, 20-25 cm		06/16/94				Forest	Jack pine	Boreal
Manitoba			OJP, Lichen, 0-1 cm		06/16/94				Forest	Jack pine	Boreal
Manitoba			OJP, Lichen, 1-4 cm		06/16/94				Forest	Jack pine	Boreal
Manitoba			OJP, Lichen, 5-10 cm		06/16/94				Forest	Jack pine	Boreal
Manitoba			OBS, Lichen		09/10/95				Forest	Black Spruce	Boreal
Manitoba			OBS, Sphagnum		09/10/95				Forest	Black Spruce	Boreal
Manitoba			OBS, Feather Moss		09/10/95				Forest	Black Spruce	Boreal
IOWA	41.36	91.13	0-5 cm	Site 1	4/26/97	Mollisols	Hapludolls	Entic	Agricultural		Temperate
IOWA	41.36	91.13	11-15 cm	Site 1	4/26/97	Mollisols	Hapludolls	Entic	Agricultural		Temperate
IOWA	41.52	91.23	0-3 cm	Site 2	4/26/97	Alfisols	Ochraqualfs	Mollic	Agricultural		Temperate
IOWA	41.52	91.23	10-12 cm	Site 2	4/26/97	Alfisols	Ochraqualfs	Mollic	Agricultural		Temperate
IOWA	41.51	90.98	0-3 cm	Site 3	4/26/97	Alfisols	Ochraqualfs	Mollic	Agricultural		Temperate
IOWA	41.51	90.98	10-12 cm	Site 3	4/26/97	Alfisols	Ochraqualfs	Mollic	Agricultural		Temperate
IOWA	41.50	90.90	0-3 cm	Site 4	4/26/97	Alfisols	Hapludalphs	Typic	Agricultural		Temperate
IOWA	41.50	90.90	10-13 cm	Site 4	4/26/97	Alfisols	Hapludalphs	Typic	Agricultural		Temperate
IOWA	41.47	90.88	0-3 cm	Site 5	4/26/97	Alfisols	Hapludalphs	Typic	Forest		Temperate
IOWA	41.47	90.88	3-6 cm	Site 5	4/26/97	Alfisols	Hapludalphs	Typic	Forest		Temperate
IOWA	41.47	90.88	20-25 cm	Site 5	4/26/97	Alfisols	Hapludalphs	Typic	Forest		Temperate
MICHIGAN	42.28	85.38	0-5 cm	MIF01	6/3/97	Alfisols	Hapludalphs	Typic	Forest		Temperate
MICHIGAN	42.28	85.38	5-10 cm	MIF01	6/3/97	Alfisols	Hapludalphs	Typic	Forest		Temperate
MICHIGAN	42.28	85.38	10-20 cm	MIF01	6/3/97	Alfisols	Hapludalphs	Typic	Forest		Temperate
MICHIGAN	42.07	86.45	0-5 cm	MIF02	6/3/97	Alfisols	Hapludalphs	Typic	Forest		Temperate
MICHIGAN	42.07	86.45	5-10 cm	MIF02	6/3/97	Alfisols	Hapludalphs	Typic	Forest		Temperate
MICHIGAN	42.07	86.45	10-15 cm	MIF02	6/3/97	Alfisols	Hapludalphs	Typic	Forest		Temperate
MICHIGAN	41.83	86.69	0-5 cm	MIF03	6/3/97	Entisols	Udipsamments	Aquic	Forest		Temperate
MICHIGAN	41.83	86.69	5-10 cm	MIF03	6/3/97	Entisols	Udipsamments	Aquic	Forest		Temperate
MICHIGAN	41.83	86.69	10-15 cm	MIF03	6/3/97	Entisols	Udipsamments	Aquic	Forest		Temperate
MICHIGAN	42.28	85.40	0-5 cm	MIA01	6/3/97	Alfisols	Hapludalphs	Typic	Agricultural		Temperate
MICHIGAN	42.28	85.40	10-15 cm	MIA01	6/3/97	Alfisols	Hapludalphs	Typic	Agricultural		Temperate
MICHIGAN	42.36	85.74	0-5 cm	MIA02	6/3/97	Alfisols	Haplaquolls	Typic	Agricultural		Temperate
MICHIGAN	42.36	85.74	10-15 cm	MIA02	6/3/97	Alfisols	Haplaquolls	Typic	Agricultural		Temperate
MICHIGAN	42.06	86.45	0-5 cm	MIA03	6/3/97	Alfisols	Hapludalphs	Typic	Agricultural		Temperate

Site	Latitude	Longitude	Description	Site name	Date Collected	Soil Order	Soil Suborder	Soil Descriptio	Land Use	Cover/Crop	Biome
MICHIGAN	42.06	86.45	10-15 cm	MIA03	6/3/97	Alfisols	Hapludalphs	Typic	Agricultural		Temperate
ILLINOIS	41.40	89.58	0-5 cm	ILF01	6/4/97	Alfisols	Hapludalphs	Typic	Forest		Temperate
ILLINOIS	41.40	89.58	5-10 cm	ILF01	6/4/97	Alfisols	Hapludalphs	Typic	Forest		Temperate
ILLINOIS	41.40	89.58	10-15 cm	ILF01	6/4/97	Alfisols	Hapludalphs	Typic	Forest		Temperate
ILLINOIS	41.45	89.91	0-5 cm	ILF02	6/4/97	Alfisols	Hapludolls	Typic	Forest		Temperate
ILLINOIS	41.45	89.91	5-10 cm	ILF02	6/4/97	Alfisols	Hapludolls	Typic	Forest		Temperate
ILLINOIS	41.45	89.91	10-15 cm	ILF02	6/4/97	Alfisols	Hapludolls	Typic	Forest		Temperate
ILLINOIS	41.42	90.13	0-5 cm	ILF03	6/4/97	Alfisols	Hapludalphs	Typic	Forest		Temperate
ILLINOIS	41.42	90.13	5-10 cm	ILF03	6/4/97	Alfisols	Hapludalphs	Typic	Forest		Temperate
ILLINOIS	41.42	90.13	10-15 cm	ILF03	6/4/97	Alfisols	Hapludalphs	Typic	Forest		Temperate
ILLINOIS	41.39	89.57	0-5 cm	ILA01	6/4/97	Alfisols	Hapludalphs	Typic	Agricultural		Temperate
ILLINOIS	41.39	89.57	10-15 cm	ILA01	6/4/97	Alfisols	Hapludalphs	Typic	Agricultural		Temperate
ILLINOIS	41.41	89.83	0-5 cm	ILA02	6/4/97	Alfisols	Haplaquolls	Typic	Agricultural		Temperate
ILLINOIS	41.41	89.83	10-15 cm	ILA02	6/4/97	Alfisols	Haplaquolls	Typic	Agricultural		Temperate
ILLINOIS	41.45	89.91	0-5 cm	ILA03	6/4/97	Alfisols	Hapludolls	Typic	Agricultural		Temperate
ILLINOIS	41.45	89.91	10-15 cm	ILA03	6/4/97	Alfisols	Hapludolls	Typic	Agricultural		Temperate
ILLINOIS	41.42	90.13	0-5 cm	ILA04	6/4/97	Alfisols	Hapludalphs	Typic	Agricultural		Temperate
ILLINOIS	41.42	90.13	10-15 cm	ILA04	6/4/97	Alfisols	Hapludalphs	Typic	Agricultural		Temperate
IOWA	41.68	93.10	0-5 cm	IWA01	6/4/97	Mollisols	Argiudolls	Typic	Agricultural		Temperate
IOWA	41.68	93.10	10-15 cm	IWA01	6/4/97	Mollisols	Argiudolls	Typic	Agricultural		Temperate
IOWA	41.70	93.21	0-5 cm	IWA02	6/4/97	Mollisols	Udifluvents	Mollic	Agricultural		Temperate
IOWA	41.70	93.21	10-15 cm	IWA02	6/4/97	Mollisols	Udifluvents	Mollic	Agricultural		Temperate
IOWA	41.50	93.45	0-5 cm	IWA03	6/4/97	Mollisols	Argiudolls	Typic	Agricultural		Temperate
IOWA	41.50	93.45	10-15 cm	IWA03	6/4/97	Mollisols	Argiudolls	Typic	Agricultural		Temperate
IOWA	41.49	93.67	0-5 cm	IWA04	6/4/97	Mollisols	Argiudolls	Typic	Agricultural		Temperate
IOWA	41.49	93.67	10-15 cm	IWA04	6/4/97	Mollisols	Argiudolls	Typic	Agricultural		Temperate
NEBRASKA	40.60	99.08	0-5 cm	NBF01	6/5/97	Entisols	Ustipsamment	Typic	Forest		Temperate
NEBRASKA	40.60	99.08	5-10 cm	NBF01	6/5/97	Entisols	Ustipsamment	Typic	Forest		Temperate
NEBRASKA	40.60	99.08	10-15 cm	NBF01	6/5/97	Entisols	Ustipsamment	Typic	Forest		Temperate
NEBRASKA	40.57	99.09	0-5 cm	NBF02	6/5/97	Mollisols	Haplustolls	Typic	Forest		Temperate
NEBRASKA	40.57	99.09	5-10 cm	NBF02	6/5/97	Mollisols	Haplustolls	Typic	Forest		Temperate
NEBRASKA	40.57	99.09	10-15 cm	NBF02	6/5/97	Mollisols	Haplustolls	Typic	Forest		Temperate
NEBRASKA	41.02	100.57	0-5 cm	NBF03	6/5/97	Entisols	Ustorthents	Typic	Forest		Temperate
NEBRASKA	41.02	100.57	5-10 cm	NBF03	6/5/97	Entisols	Ustorthents	Typic	Forest		Temperate

Site	Latitude	Longitude	Description	Site name	Date Collected	Soil Order	Soil Suborder	Soil Descriptio	Land Use	Cover/Crop	Biome
NEBRASKA	41.02	100.57	10-15 cm	NBF03	6/5/97	Entisols	Ustorthents	Typic	Forest		Temperate
NEBRASKA	40.59	99.09	0-5 cm	NBA01	6/5/97	Entisols	Ustipsamments	Typic	Agricultural		Temperate
NEBRASKA	40.59	99.09	10-15 cm	NBA01	6/5/97	Entisols	Ustipsamments	Typic	Agricultural		Temperate
NEBRASKA	40.57	99.08	0-5 cm	NBA02	6/5/97	Mollisols	Haplustolls	Typic	Agricultural		Temperate
NEBRASKA	40.57	99.08	10-15 cm	NBA02	6/5/97	Mollisols	Haplustolls	Typic	Agricultural		Temperate
NEBRASKA	41.02	100.57	0-5 cm	NBA03	6/5/97	Entisols	Ustorthents	Typic	Agricultural		Temperate
NEBRASKA	41.02	100.57	10-15 cm	NBA03	6/5/97	Entisols	Ustorthents	Typic	Agricultural		Temperate
NEBRASKA	40.99	100.75	0-5 cm	NBA04	6/5/97	Entisols	Ustipsamments	Typic	Agricultural		Temperate
NEBRASKA	40.99	100.75	10-15 cm	NBA04	6/5/97	Entisols	Ustipsamments	Typic	Agricultural		Temperate
COLORADO	40.69	105.26	0-5 cm	COF01	6/16/97	Alfisols	Eutroboralfs	Lithic	Forest		Temperate
COLORADO	40.69	105.26	5-10 cm	COF01	6/16/97	Alfisols	Eutroboralfs	Lithic	Forest		Temperate
COLORADO	40.69	105.26	10-15 cm	COF01	6/16/97	Alfisols	Eutroboralfs	Lithic	Forest		Temperate
COLORADO	40.70	105.02	0-5 cm	COA01	6/16/97	Mollisols	Cryaquolls	Typic	Agricultural		Temperate
COLORADO	40.70	105.02	10-15 cm	COA01	6/16/97	Mollisols	Cryaquolls	Typic	Agricultural		Temperate
COLORADO	40.90	104.80	0-5 cm	COA02	6/16/97	Mollisols	Argiustolls	Aridic	Agricultural		Temperate
COLORADO	40.90	104.80	10-15 cm	COA02	6/16/97	Mollisols	Argiustolls	Aridic	Agricultural		Temperate
COLORADO	40.90	104.83	0-5 cm	COA03	6/16/97	Aridisols	Haplargids	Ustollic	Agricultural		Temperate
COLORADO	40.90	104.83	10-15 cm	COA03	6/16/97	Aridisols	Haplargids	Ustollic	Agricultural		Temperate
WYOMING	42.83	105.31	0-5 cm	WYA01	6/16/97	Aridisols	Haplargids	Ustollic	Agricultural		Temperate
WYOMING	42.83	105.31	10-15 cm	WYA01	6/16/97	Aridisols	Haplargids	Ustollic	Agricultural		Temperate
WYOMING	44.29	106.95	0-5 cm	WYF01	6/17/97	Alfisols	Cryoboralfs	Typic	Forest		Temperate
WYOMING	44.29	106.95	5-10 cm	WYF01	6/17/97	Alfisols	Cryoboralfs	Typic	Forest		Temperate
WYOMING	44.29	106.95	10-15 cm	WYF01	6/17/97	Alfisols	Cryoboralfs	Typic	Forest		Temperate
WYOMING	44.83	107.33	0-5 cm	WYF02	6/17/97	Alfisols	Cryoboralfs	Typic	Forest		Temperate
WYOMING	44.83	107.33	5-10 cm	WYF02	6/17/97	Alfisols	Cryoboralfs	Typic	Forest		Temperate
WYOMING	44.83	107.33	10-15 cm	WYF02	6/17/97	Alfisols	Cryoboralfs	Typic	Forest		Temperate
WYOMING	44.29	106.95	0-5 cm	WYM01	6/17/97	Alfisols	Cryoboralfs	Typic			Temperate
WYOMING	44.29	106.95	5-10 cm	WYM01	6/17/97	Alfisols	Cryoboralfs	Typic			Temperate
WYOMING	44.29	106.95	10-15 cm	WYM01	6/17/97	Alfisols	Cryoboralfs	Typic			Temperate
MONTANA	45.77	111.76	0-5 cm	MTA01	6/19/97	Mollisols	Argiborolls	Aridic	Agricultural		Temperate
MONTANA	45.77	111.76	10-15 cm	MTA01	6/19/97	Mollisols	Argiborolls	Aridic	Agricultural		Temperate
MONTANA	45.77	111.76	0-5 cm	MTA02	6/19/97	Inceptisols	Cryochrepts	Typic	Agricultural		Temperate
MONTANA	45.77	111.76	10-15 cm	MTA02	6/19/97	Inceptisols	Cryochrepts	Typic	Agricultural		Temperate
IDAHO	47.64	116.86	0-5 cm	IDF01	6/19/97	Alfisols	Haploxeralfs	Ultic	Forest		Temperate

Site	Latitude	Longitude	Description	Site name	Date Collected	Soil Order	Soil Suborder	Soil Descriptio	Land Use	Cover/Crop	Biome
IDAHO	47.64	116.86	5-10 cm	IDF01	6/19/97	Alfisols	Haploxeralfs	Ultic	Forest		Temperate
IDAHO	47.64	116.86	10-15 cm	IDF01	6/19/97	Alfisols	Haploxeralfs	Ultic	Forest		Temperate
IDAHO	47.69	116.80	0-5 cm	IDF02	6/19/97	Inceptisols	Xerumbrepts	Andic	Forest		Temperate
IDAHO	47.69	116.80	5-10 cm	IDF02	6/19/97	Inceptisols	Xerumbrepts	Andic	Forest		Temperate
IDAHO	47.69	116.80	10-15 cm	IDF02	6/19/97	Inceptisols	Xerumbrepts	Andic	Forest		Temperate
OHIO	40.10	82.61	0-5 cm	OHA01	7/6/97	Alfisols	Hapludalphs	Aquic	Agricultural		Temperate
OHIO	40.10	82.61	5-10 cm	OHA01	7/6/97	Alfisols	Hapludalphs	Aquic	Agricultural		Temperate
OHIO	40.10	82.61	10-15 cm	OHA01	7/6/97	Alfisols	Hapludalphs	Aquic	Agricultural		Temperate
OHIO	40.09	82.51	0-5 cm	OHF02	7/6/97	Alfisols	Hapludalphs	Ultic	Forest		Temperate
OHIO	40.09	82.51	5-10 cm	OHF02	7/6/97	Alfisols	Hapludalphs	Ultic	Forest		Temperate
OHIO	40.09	82.51	10-15 cm	OHF02	7/6/97	Alfisols	Hapludalphs	Ultic	Forest		Temperate
OHIO	40.06	82.47	0-5 cm	OHM03	7/6/97	Alfisols	Hapludalphs	Typic			Temperate
OHIO	40.06	82.47	5-10 cm	OHM03	7/6/97	Alfisols	Hapludalphs	Typic			Temperate
OHIO	40.06	82.47	10-15 cm	OHM03	7/6/97	Alfisols	Hapludalphs	Typic			Temperate
ALASKA	61.22	149.90	0-5 cm	AKF01	7/14/97	Spodosols	Cryorthods	Typic	Forest		Boreal
ALASKA	61.22	149.90	7.5 cm	AKF01	7/14/97	Spodosols	Cryorthods	Typic	Forest		Boreal
ALASKA	61.22	149.90	40 cm	AKF01	7/14/97	Spodosols	Cryorthods	Typic	Forest		Boreal
ALASKA	61.60	149.10	0-5 cm	AKA01	7/14/97	Entisols	Cryorthents	Typic	Agricultural		Boreal
ALASKA	61.60	149.10	10-15 cm	AKA01	7/14/97	Entisols	Cryorthents	Typic	Agricultural		Boreal
ALASKA	61.60	149.10	0-5 cm	AKA02	7/14/97	Entisols	Cryorthents	Typic	Agricultural		Boreal
ALASKA	61.60	149.10	10-15 cm	AKA02	7/14/97	Entisols	Cryorthents	Typic	Agricultural		Boreal
GERMANY	53.78	-10.62	0-5 cm	GERF01	7/18/97				Forest	Beech, maple	Temperate
GERMANY	53.78	-10.62	5-10 cm	GERF01	7/18/97				Forest	Beech, maple	Temperate
GERMANY	53.78	-10.62	10-15 cm	GERF01	7/18/97				Forest	Beech, maple	Temperate
GERMANY	53.78	-10.62	0-5 cm	GERA01	7/18/97				Agricultural	Rye	Temperate
GERMANY	53.78	-10.62	10-15 cm	GERA01	7/18/97				Agricultural	Rye	Temperate
GERMANY	51.06	-11.32	0-5 cm	GERA02	7/20/97				Agricultural	Rye	Temperate
GERMANY	51.06	-11.32	10-15 cm	GERA02	7/20/97				Agricultural	Rye	Temperate
GERMANY	51.84	-7.51	Litter	GERF03	7/23/97				Forest	Beech, oak	Temperate
GERMANY	51.84	-7.51	Organic layer	GERF03	7/23/97				Forest	Beech, oak	Temperate
GERMANY	51.84	-7.51	0-5 cm	GERF03	7/23/97				Forest	Beech, oak	Temperate
GERMANY	51.84	-7.51	5-10 cm	GERF03	7/23/97				Forest	Beech, oak	Temperate
GERMANY	51.84	-7.51	10-15 cm	GERF03	7/23/97				Forest	Beech, oak	Temperate
GERMANY	51.84	-7.51	0-5 cm	GERA03	7/23/97				Agricultural		Temperate

Site	Latitude	Longitude	Description	Site name	Date Collected	Soil Order	Soil Suborder	Soil Descriptio	Land Use	Cover/Crop	Biome
GERMANY	51.84	-7.51	10-15 cm	GERA03	7/23/97				Agricultural		Temperate
GERMANY	52.15	-7.76	Litter	GERF04	7/23/97				Forest		Temperate
GERMANY	52.15	-7.76	Organic layer	GERF04	7/23/97				Forest		Temperate
GERMANY	52.15	-7.76	0-5 cm	GERF04	7/23/97				Forest		Temperate
GERMANY	52.15	-7.76	5-10 cm	GERF04	7/23/97				Forest		Temperate
GERMANY	52.15	-7.76	10-15 cm	GERF04	7/23/97				Forest		Temperate
GERMANY	52.15	-7.76	0-5 cm	GERA04	7/23/97				Agricultural		Temperate
GERMANY	52.15	-7.76	10-15 cm	GERA04	7/23/97				Agricultural		Temperate
OREGON	45.99	123.92	Litter	ORF01	8/7/97				Forest	Sitka Spruce	Temperate
OREGON	45.99	123.92	0-5 cm	ORF01	8/7/97				Forest	Sitka Spruce	Temperate
OREGON	45.99	123.92	5-10 cm	ORF01	8/7/97				Forest	Sitka Spruce	Temperate
OREGON	45.99	123.92	10-15 cm	ORF01	8/7/97				Forest	Sitka Spruce	Temperate
OREGON	45.52	123.11	0-5 cm	ORA01	8/7/97				Agricultural	Tomatoes	Temperate
OREGON	45.52	123.11	10-15 cm	ORA01	8/7/97				Agricultural	Tomatoes	Temperate
NEW MEXICO	35.08	106.65	Litter	NMR01	8/13/97	Entisols	Torrifluvents	Typic	River		Temperate
NEW MEXICO	35.08	106.65	0-5 cm	NMR01	8/13/97	Entisols	Torrifluvents	Typic	River		Temperate
NEW MEXICO	35.08	106.65	5-10 cm	NMR01	8/13/97	Entisols	Torrifluvents	Typic	River		Temperate
NEW MEXICO	35.08	106.65	10-15 cm	NMR01	8/13/97	Entisols	Torrifluvents	Typic	River		Temperate
NEW MEXICO	35.08	106.65	15-20 cm	NMR01	8/13/97	Entisols	Torrifluvents	Typic	River		Temperate
NEW MEXICO	34.33	107.58	Litter	NMD01	8/13/97	Mollisols	Argiborolls	Typic	Desert		Temperate
NEW MEXICO	34.33	107.58	0-5 cm	NMD01	8/13/97	Mollisols	Argiborolls	Typic	Desert		Temperate
NEW MEXICO	34.33	107.58	5-10 cm	NMD01	8/13/97	Mollisols	Argiborolls	Typic	Desert		Temperate
NEW MEXICO	34.33	107.58	10-15 cm	NMD01	8/13/97	Mollisols	Argiborolls	Typic	Desert		Temperate
Brazil	-22.96	43.28	litter	RJF01	12/05/97				Forest		Tropical
Brazil	-22.96	43.28	root mat	RJF01	12/05/97				Forest		Tropical
Brazil	-22.96	43.28	0-5 cm	RJF01	12/05/97				Forest		Tropical
Brazil	-22.96	43.28	5-10 cm	RJF01	12/05/97				Forest		Tropical
Brazil	-22.96	43.28	10-15 cm	RJF01	12/05/97				Forest		Tropical
Finland	66.55	25.75	0-5 cm	FDF01	09/20/97				Forest		Boreal
Finland	66.55	25.75	10-15 cm	FDF01	09/20/97				Forest		Boreal
Finland	66.55	25.75	0-5 cm	FDB01	09/20/97				Bog		Boreal
Finland	66.55	25.75	10-15 cm	FDB01	09/20/97				Bog		Boreal
Finland	66.33	25.92	0-5 cm	FDF02	09/20/97				Forest	Birch	Boreal
Finland	66.33	25.92	10-15 cm	FDF02	09/20/97				Forest	Birch	Boreal

Site	Latitude	Longitude	Description	Site name	Date Collected	Soil Order	Soil Suborder	Soil Descriptio	Land Use	Cover/Crop	Biome
Finland	66.08	26.33	0-5 cm	FDF03	09/20/97				Forest		Boreal
Finland	66.08	26.33	10-15 cm	FDF03	09/20/97				Forest		Boreal
Siberia			0-5 cm	SIF01	09/02/97						Boreal
Siberia			0-5 cm	SIF02	09/02/97					Spruce/fir	Boreal
Siberia			10-15 cm	SIF02	09/02/97					Spruce/fir	Boreal
Siberia			0-5 cm	SIF03	09/02/97					Aspen	Boreal
Siberia			10-15 cm	SIF03	09/02/97					Aspen	Boreal
Siberia			0-5 cm	SIF04	09/02/97					Pinus Siberia	Boreal
Siberia			10-15 cm	SIF04	09/02/97					Pinus Siberia	Boreal
Costa Rica	10.42	84.03	0-5 cm	CRF01	11/21/97	Andisol			Forest	laSelva	Tropical
Costa Rica	10.42	84.03	5-10 cm	CRF01	11/21/97	Andisol			Forest	laSelva	Tropical
Costa Rica	10.42	84.03	10-15 cm	CRF01	11/21/97	Andisol			Forest	laSelva	Tropical
Costa Rica	10.42	84.03	0-5 cm	CRF02	11/21/97	Inceptisols	Humitropept		Forest	laSelva	Tropical
Costa Rica	10.42	84.03	5-10 cm	CRF02	11/21/97	Inceptisols	Humitropept		Forest	laSelva	Tropical
Costa Rica	10.42	84.03	10-15 cm	CRF02	11/21/97	Inceptisols	Humitropept		Forest	laSelva	Tropical
Costa Rica	10.37	83.95	0-5 cm	CRA01	11/21/97	Andisol			Agricultural	Palmheart	Tropical
Costa Rica	10.37	83.95	10-15 cm	CRA01	11/21/97	Andisol			Agricultural	Palmheart	Tropical
Costa Rica	10.37	83.95	0-5 cm	CRA02	11/21/97	Inceptisols	Humitropept	Oxic	Agricultural	Palmheart	Tropical
Costa Rica	10.37	83.95	10-15 cm	CRA02	11/21/97	Inceptisols	Humitropept	Oxic	Agricultural	Palmheart	Tropical
Costa Rica	10.35	83.97	0-5 cm	CRP01	11/21/97	Inceptisols	Humitropept		Pasture		Tropical
Costa Rica	10.35	83.97	10-15 cm	CRP01	11/21/97	Inceptisols	Humitropept		Pasture		Tropical
Costa Rica	10.45	84.00	0-5 cm	CRP02	11/21/97	Andisol			Pasture		Tropical
Costa Rica	10.45	84.00	10-15 cm	CRP02	11/21/97	Andisol			Pasture		Tropical

APPENDIX B

Table B.1. Soil incubation summary.

Date	Site	Sampling Depth	Moisture Content (%dry)	Temp (C)	k (min^-1)	Normalized k (k/gds)	r2	pH (units)	Organic matter (%)
8/11/94	CW	0-3 cm	103.0	45	0.144	0.057		3.67	60.3
7/11/94	CW	0-3 cm	57.1	25	0.503	0.155		3.67	60.3
7/13/94	CW	0-3 cm	26.3	25	0.004	0.001		3.67	60.3
7/14/94	CW	0-3 cm	128.5	25	0.721	0.329		3.67	60.3
7/15/94	CW	0-3 cm	195.5	25	0.261	0.155		3.67	60.3
7/18/94	CW	0-3 cm	344.1	25	0.159	0.142		3.67	60.3
7/27/94	CW	0-3 cm	110.0	35	1.242	0.521		3.67	60.3
8/09/94	CW	0-3 cm	110.1	15	0.493	0.207		3.67	60.3
5/24/94	CW	0-3 cm	136.1	25	0.918	0.217		3.67	60.3
4/21/94	CW	0-3 cm	180.9	25	1.290	0.362		3.67	60.3
5/23/94	CW	0-3 cm	156.1	25	1.110	0.285		3.67	60.3
6/02/94	CW	3-7cm	74.7	35	0.281	0.049		4.20	22.9
5/12/94	CW	3-7cm	72.7	25	0.314	0.054		4.20	22.9
5/11/94	CW	3-7cm	71.8	25	0.290	0.050		4.20	22.9
5/05/94	CW	3-7cm	71.8	25	0.408	0.070		4.20	22.9
6/03/94	CW	3-7cm	73.3	45	0.055	0.010		4.20	22.9
4/20/94	CW	3-7cm	76.3	25	0.516	0.091		4.20	22.9
4/14/94	CW	3-7cm	76.3	25	0.353	0.062		4.20	22.9
6/17/94	CW	3-7cm	73.5	5	0.089	0.015		4.20	22.9
6/08/94	CW	3-7cm	70.5	15	0.151	0.026		4.20	22.9
6/17/94	CW	10-15cm	44.4	5	0.025	0.004		4.26	8.7
4/21/94	CW	10-15cm	43.1	25	0.104	0.015		4.26	8.7
6/03/94	CW	10-15cm	45.6	45	0.113	0.016		4.26	8.7
6/02/94	CW	10-15cm	42.8	35	0.144	0.206		4.26	8.7
6/01/94	CW	10-15cm	42.6	15	0.031	0.004		4.26	8.7
5/20/94	CW	10-15cm	44.9	25	0.135	0.020		4.26	8.7
5/17/94	CW	10-15cm	43.1	25	0.120	0.017		4.26	8.7
5/17/94	CW	10-15cm	43.1	25	0.115	0.016		4.26	8.7
5/16/94	CW	10-15cm	43.7	25	0.103	0.015		4.26	8.7
5/03/94	CR	3-6cm	68.9	25	0.035	0.006		4.46	23.1
5/02/94	CR	0-3cm	53.9	25	0.034	0.005		4.82	27.3
4/28/94	CR	8-10cm	65.4	25	0.034	0.006		4.47	21.7
4/27/94	CR	3-6cm	68.9	25	0.040	0.007		4.46	23.1
4/25/94	CR	0-3cm	53.9	25	0.033	0.005		4.82	27.3
8/11/94	UNH Corn	0-3cm	31.3	45	0.057	0.008		5.85	8.9
7/27/94	UNH Corn	0-3cm	32.0	35	0.107	0.014		5.85	8.9
7/18/94	UNH Corn	0-3cm	66.7	25	0.017	0.003		5.85	8.9
7/15/94	UNH Corn	0-3cm	63.3	25	0.011	0.002		5.85	8.9

Date	Site	Sampling Depth	Moisture Content (%dry)	Temp (C)	k (min^-1)	Normalized k (k/gds)	r2	pH (units)	Organic matter (%)
7/14/94	UNH Corn	0-3cm	40.4	25	0.040	0.006		5.85	8.9
7/13/94	UNH Corn	0-3cm	25.5	25	0.029	0.004		5.85	8.9
7/11/94	UNH Corn	0-3cm	17.5	25	0.049	0.006		5.85	8.9
6/30/94	UNH Corn	0-3cm	18.4	10	0.005	0.001		5.85	8.9
6/29/94	UNH Corn	0-3cm	17.7	40	0.034	0.004		5.85	8.9
6/28/94	UNH Corn	0-3cm	16.2	25	0.044	0.005		5.85	8.9
6/26/94	UNH Corn	0-3cm	10.8	25	0.020	0.002		5.85	8.9
6/30/94	Manitoba	1-4cm	14.2	10	0.048	0.006		4.92	5.2
6/26/94	Manitoba	1-4cm	10.8	25	0.142	0.016		4.92	5.2
6/28/94	Manitoba	1-4cm	18.7	25	0.085	0.010		4.92	5.2
6/29/94	Manitoba	1-4cm	12.2	40	0.075	0.008		4.92	5.2
3/26/97	CR	0-3cm	86.6	25	0.002	0.000	0.987		
3/26/97	CR - 2yr.	0-3cm	58.8	25	0.005	0.001	0.972		
3/28/97	CR - 5yr.	0-3cm	67.0	25	0.005	0.001	0.972		
3/28/97	CR - 6yr.	0-3cm	63.9	25	0.018	0.003	0.848		
3/28/97	CR - 8yr.	0-3cm	63.2	25	0.002	0.000	0.930		
5/7/97	IA: Site 5	0-3 cm	42.6	25	0.363	0.052	0.977	5.55	11.4
5/7/97	IA: Site 1	0-5 cm	2.0	25	0.008	0.000	0.920	5.84	1.6
5/14/97	IA: Site 2	0-3 cm	13.8	25	0.213	0.012	0.950	5.58	4.5
5/14/97	IA: Site 3	0-5 cm	14.3	25	0.076	0.004	0.953	6.61	2.8
5/15/97	IA: Site 4	0-3 cm	17.4	25	0.227	0.013	0.989	6.66	5.7
5/15/97	IA: Site 5	4-10 cm	30.3	25	0.092	0.006	0.955	4.25	3.8
5/16/97	IA: Site 1	11-15 cm	5.7	25	0.025	0.001	0.969	5.99	2.3
5/16/97	IA: Site 2	10-12 cm	19.1	25	0.062	0.004	0.961	6.73	3.6
5/19/97	IA: Site 3	10-12 cm	16.0	25	0.058	0.003	0.971	6.50	3.4
5/19/97	IA: Site 4	10-13 cm	24.8	25	0.122	0.008	0.986	6.38	4.9
6/18/97	MIF01	0-5 cm	24.1	25	0.180	0.011	0.972	5.90	4.0
6/18/97	MIF01	5-10 cm	18.9	25	0.094	0.006	0.930	6.17	4.1
6/19/97	MIF01	10-20 cm	15.7	25	0.045	0.003	0.965	6.49	2.2
6/19/97	MIF02	0-5 cm	62.6	25	0.230	0.019	0.984	5.73	14.0
6/20/97	MIF02	5-10 cm	45.2	25	0.076	0.006	0.966	5.44	8.8
6/20/97	MIF02	10-15 cm	36.8	25	0.053	0.004	0.953		6.7
6/23/97	MIF03	0-5 cm	6.6	25	0.091	0.006	0.971	6.56	6.2
6/24/97	MIF03	5-10 cm	22.4	25	0.101	0.006	0.958	7.00	4.1
6/24/97	MIF03	10-15 cm	19.8	25	0.084	0.005	0.964	7.11	3.1
6/26/97	MIA01	0-5 cm	23.1	25	0.279	0.017	0.991	6.81	6.4
6/26/97	MIA01	10-15 cm	13.1	25	0.123	0.007	0.981	7.10	2.3
6/30/97	MIA02	0-5 cm	11.3	25	0.193	0.011	0.953	6.80	2.3

Date	Site	Sampling Depth	Moisture Content (%dry)	Temp (C)	k (min^-1)	Normalized k (k/gds)	r2	pH (units)	Organic matter (%)
6/30/97	MIA02	10-15 cm	10.1	25	0.130	0.007	0.938	6.34	1.8
7/01/97	MIA03	0-5 cm	7.6	25	0.061	0.003	0.966	6.50	1.8
7/01/97	MIA03	10-15 cm	9.7	25	0.030	0.002	0.955	6.26	1.9
7/02/97	ILF01	0-5 cm	17.8	25	0.387	0.023	0.971	6.67	6.4
7/02/97	ILF01	5-10 cm	20.1	25	0.268	0.016	0.963	6.70	5.9
7/03/97	ILF01	10-15 cm	17.7	25	0.235	0.014	0.967		4.4
7/03/97	ILF02	0-5 cm	17.8	25	0.489	0.029	0.980	6.66	7.5
7/07/97	ILF02	5-10 cm	12.5	25	0.264	0.015	0.939	6.37	4.9
7/07/97	ILF02	10-15 cm	9.4	25	0.053	0.003	0.951	6.84	4.3
7/08/97	ILF03	0-5 cm	17.3	25	0.380	0.022	0.953	5.80	13.1
7/08/97	ILF03	5-10 cm	21.5	25	0.245	0.015	0.941	5.41	9.5
7/09/97	ILF03	10-15 cm	19.3	25	0.218	0.013	0.970	4.45	9.0
7/09/97	ILA01	0-5 cm	14.5	25	0.191	0.011	0.957	6.98	4.3
7/10/97	ILA01	10-15 cm	16.4	25	0.129	0.007	0.969	6.56	4.2
7/10/97	ILA02	0-5 cm	10.9	25	0.103	0.006	0.954	6.79	7.3
7/14/97	ILA02	10-15 cm	22.4	25	0.088	0.005	0.971	6.59	7.1
7/14/97	ILA03	0-5 cm	1.0	25	-0.001	-0.000	0.484	6.25	2.4
7/16/97	ILA03	10-15 cm	4.3	25	0.023	0.001	0.948	5.68	1.4
7/16/97	ILA04	0-5 cm	45.4	25	0.157	0.011	0.943	5.57	12.5
7/17/97	ILA04	10-15 cm	31.2	25	0.145	0.009	0.947	5.56	8.6
7/17/97	IWA01	0-5 cm	25.5	25	0.389	0.024	0.991	6.72	9.8
7/18/97	IWA01	10-15 cm	17.7	25	0.114	0.007	0.981	6.77	4.1
7/18/97	IWA02	0-5 cm	27.1	25	0.099	0.006	0.971	6.51	7.2
7/21/97	IWA02	10-15 cm	29.6	25	0.040	0.003	0.938	6.51	7.6
7/21/97	IWA03	0-5 cm	40.2	25	0.215	0.015	0.985	6.34	11.6
7/22/97	IWA03	10-15 cm	28.8	25	0.121	0.008	0.960	6.17	7.5
7/22/97	IWA04	0-5 cm	25.0	25	0.660	0.041	0.966	6.00	9.2
7/23/97	IWA04	10-15 cm	26.8	25	0.329	0.021	0.979	5.69	7.4
7/23/97	NBF01	0-5 cm	60.6	25	0.048	0.004	0.704	6.71	10.9
7/24/97	NBF02	0-5 cm	44.2	25	0.155	0.011	0.887	6.59	8.4
7/24/97	NBF02	5-10 cm	37.7	25	0.106	0.007	0.959	6.49	6.7
7/25/97	NBF02	10-15 cm	33.2	25	0.423	0.028	0.973	6.51	6.2
7/25/97	NBF03	0-5 cm	30.4	25	0.089	0.006	0.956	7.08	7.1
7/28/97	NBF03	5-10 cm	22.4	25	0.257	0.016	0.956	7.01	5.7
7/28/97	NBF03	10-15 cm	17.2	25	0.247	0.014	0.926	6.74	4.5
7/29/97	NBA01	0-5 cm	33.1	25	0.090	0.006	0.901	6.53	6.0
7/29/97	NBA01	10-15 cm	26.4	25	0.041	0.003	0.938	6.82	3.1
7/30/97	NBA03	0-5 cm	22.7	25	0.200	0.012	0.917	6.73	4.3

Date	Site	Sampling Depth	Moisture Content (%dry)	Temp (C)	k (min^-1)	Normalized k (k/gds)	r2	pH (units)	Organic matter (%)
7/30/97	NBA03	10-15 cm	22.1	25	0.127	0.008	0.904	6.80	3.7
7/31/97	NBA04	0-5 cm	19.0	25	0.393	0.023	0.965	5.94	6.0
7/31/97	NBA04	10-15 cm	12.0	25	0.073	0.004	0.905	6.03	2.1
8/01/97	NBA02	0-5 cm	33.7	25	0.112	0.007	0.961	5.89	5.7
8/01/97	NBA02	10-15 cm	32.3	25	0.089	0.006	0.955	6.09	4.9
8/04/97	COA01	0-5 cm	18.8	25	0.111	0.007	0.950	7.10	4.9
8/04/97	COA01	10-15 cm	15.1	25	0.119	0.007	0.975	7.22	4.3
8/05/97	COA02	0-5 cm	6.6	25	0.356	0.019	0.924	6.28	3.0
8/05/97	COA02	10-15 cm	14.9	25	0.088	0.005	0.858	6.69	2.7
8/06/97	COA03	0-5 cm	15.7	25	0.090	0.005	0.976	5.52	5.3
8/06/97	COA03	10-15 cm	6.4	25	0.058	0.003	0.974	5.46	3.4
8/07/97	COF01	0-5 cm	49.5	25	0.468	0.035	0.873	5.99	13.8
8/07/97	COF01	5-10 cm	40.0	25	0.308	0.022	0.846	5.88	12.2
8/08/97	COF01	10-15 cm	8.0	25	0.174	0.009	0.985	5.83	5.3
8/08/97	WYA01	0-5 cm	21.3	25	0.292	0.016	0.974	6.27	2.1
8/11/97	WYA01	10-15 cm	12.1	25	0.070	0.004	0.975	6.51	2.5
8/11/97	WYF01	0-5 cm	71.1	25	0.580	0.065	0.977	4.81	24.3
8/12/97	WYF01	5-10 cm	21.8	25	0.281	0.017	0.976	4.72	6.5
8/12/97	WYF01	10-15 cm	30.0	25	0.075	0.004	0.979	4.95	1.9
8/13/97	WYM01	0-5 cm	80.8	25	0.753	0.068	0.966	5.69	29.9
8/13/97	WYM01	5-10 cm	42.3	25	0.189	0.013	0.930	5.59	9.5
8/14/97	WYM01	10-15 cm	31.6	25	0.049	0.003	0.982	5.56	3.3
8/14/97	WYF02	5-10 cm	23.8	25	0.240	0.016	0.936	6.88	8.1
8/15/97	WYF02	0-5 cm	117.9	25	0.712	0.154	0.953	6.06	48.5
8/15/97	WYF02	10-15 cm	26.2	25	0.135	0.009	0.971	7.03	6.0
8/18/97	MTA01	0-5 cm	24.9	25	0.328	0.020	0.974	8.25	3.6
8/18/97	MTA01	10-15 cm	20.3	25	0.043	0.003	0.968	7.47	2.5
8/19/97	MTA02	0-5 cm	15.6	25	0.147	0.008	0.967	7.32	1.4
8/19/97	MTA02	10-15 cm	13.2	25	0.024	0.001	0.924	8.31	0.4
8/20/97	IDF01	0-5 cm	25.2	25	0.410	0.026	0.958	5.67	12.6
8/20/97	IDF01	5-10 cm	21.5	25	0.275	0.017	0.978	6.12	5.5
8/21/97	IDF01	10-15 cm	17.2	25	0.180	0.011	0.932	5.62	4.5
8/21/97	IDF02	0-5 cm	37.9	25	0.565	0.039	0.938	5.90	18.0
8/22/97	IDF02	5-10 cm	17.5	25	0.358	0.021	0.940	6.00	5.0
8/22/97	IDF02	10-15 cm	9.0	25	0.126	0.007	0.944	5.49	1.8
8/25/97	OHA01	0-5 cm	23.7	25	0.145	0.009	0.961	5.57	6.2
8/25/97	OHA01	5-10 cm	22.9	25	0.110	0.007	0.971	5.67	4.8
8/26/97	OHA01	10-15 cm	23.7	25	0.112	0.007	0.982	5.67	4.6

Date	Site	Sampling Depth	Moisture Content (%dry)	Temp (C)	k (min^-1)	Normalized k (k/gds)	r2	pH (units)	Organic matter (%)
8/26/97	OHM03	5-10 cm	17.7	25	0.082	0.005	0.981	4.95	3.5
8/27/97	OHF02	0-5 cm	37.2	25	0.209	0.014	0.985	5.50	7.5
8/27/97	OHF02	5-10 cm	28.0	25	0.098	0.006	0.943	5.05	4.1
8/28/97	OHF02	10-15 cm	22.0	25	0.044	0.003	0.921	4.93	3.1
8/28/97	OHM03	0-5 cm	24.5	25	0.295	0.018	0.971	5.01	5.9
9/03/97	OHM03	10-15 cm	16.8	25	0.070	0.004	0.976	5.00	3.9
9/03/97	AKF01	0-5 cm	29.2	25	0.548	0.141	0.934	3.92	35.2
9/04/97	AKA01	0-5 cm	2.6	25	0.000	0.000	0.004	5.53	7.8
9/04/97	AKF01	40 cm	6.1	25	0.120	0.006	0.941	4.50	3.3
9/05/97	AKF01	7.5 cm	5.2	25	0.068	0.007	0.951	4.37	3.2
9/05/97	AKA01	10-15 cm	14.1	25	0.031	0.002	0.820	5.35	7.9
9/10/97	AKA02	0-5 cm	3.1	25	0.000	0.000	0.023	5.21	8.8
9/10/97	AKA02	10-15 cm	6.9	25	0.053	0.003	0.922	5.46	7.9
9/10/97	ORF01	Litter	106.3	25	0.053	0.022	0.981	3.95	40.9
9/11/97	ORF01	0-5 cm	82.8	25	0.094	0.009	0.981	3.87	27.5
9/11/97	ORF01	5-10 cm	82.9	25	0.274	0.025	0.957	3.83	22.5
9/16/97	ORA01	0-5 cm	73.6	25	0.392	0.034	0.975	6.27	41.1
9/16/97	ORA01	5-10 cm	86.3	25	0.387	0.036	0.982	6.38	31.9
9/17/97	ORF01	10-15 cm	52.1	25	0.162	0.012	0.985	3.85	14.1
9/17/97	GEF01	0-5 cm	85.5	25	0.302	0.028	0.994		19.9
10/09/97	GEF01	5-10 cm	39.4	25	0.555	0.039	0.866		11.6
10/09/97	GEF01	10-15 cm	36.4	25	0.379	0.026	0.888		9.2
10/14/97	GEA01	0-5 cm	28.2	25	0.052	0.003	0.952		5.9
10/14/97	GEA01	10-15 cm	25.8	25	0.066	0.004	0.988		5.5
10/15/97	GEA02	0-5 cm	27.0	25	0.054	0.003	0.991		5.3
10/15/97	GEA02	10-15 cm	25.3	25	0.047	0.003	0.978		5.0
10/16/97	GEA03	0-5 cm	24.8	25	0.098	0.006	0.968		5.1
10/16/97	GEA03	10-15 cm	22.6	25	0.095	0.006	0.923		4.5
10/17/97	GEF03	litter	226.5	25	0.298	0.194	0.955		86.0
10/17/97	GEF03	10-15 cm	13.2	25	0.085	0.005	0.897		3.4
10/21/97	GEF03	organic	128.6	25	0.577	0.132	0.911		55.0
10/21/97	GEF03	5-10 cm	15.7	25	0.222	0.013	0.842		4.1
10/22/97	GEF03	0-5 cm	24.1	25	0.400	0.025	0.942		7.7
10/22/97	GEF04	5-10 cm	8.8	25	0.039	0.002	0.959		1.8
10/24/97	GEF04	0-5 cm	23.2	25	0.316	0.019	0.930		7.3
10/24/97	GEF04	10-15 cm	7.9	25	0.031	0.002	0.951		1.8
10/28/97	GEF04	litter	205.8	25	0.087	0.053	0.927		93.0
10/28/97	GEA04	0-5 cm	15.8	25	0.096	0.006	0.975		5.3

Date	Site	Sampling Depth	Moisture Content (%dry)	Temp (C)	k (min^-1)	Normalized k (k/gds)	r2	pH (units)	Organic matter (%)
10/29/97	GEA04	10-15 cm	16.1	25	0.076	0.004	0.925		5.1
10/29/97	NMR01	0-5 cm	11.3	25	0.737	0.041	0.988		14.3
10/30/97	NMR01	10-15 cm	16.3	25	0.119	0.007	0.939		3.9
10/30/97	NMR01	15-20 cm	1.9	25	0.012	0.001	0.622		0.7
10/30/97	NMR01	5-10 cm	15.2	25	0.845	0.049	0.949		5.1
10/30/97	NMD01	0-5 cm	1.3	25	0.024	0.001	0.947		1.9
11/04/97	NMD01	5-10 cm	4.1	25	0.030	0.002	0.857		1.3
11/04/97	NMD01	10-15 cm	3.6	25	0.016	0.001	0.872		1.0
11/05/97	SIF03	10-15 cm	64.8	25	0.200	0.016	0.908	5.20	16.0
11/05/97	SIF03	5-10 cm	92.1	25	0.474	0.045	0.975		21.0
11/06/97	SIF02	0-5 cm	65.4	25	0.120	0.020	0.961	4.41	18.1
11/06/97	SIF02	10-15 cm	41.4	25	0.139	0.010	0.977	4.10	11.7
11/12/97	FDF03	0-5 cm	20.0	25	0.233	0.014	0.975	3.57	4.1
11/12/97	FDF03	10-15 cm	13.0	25	0.054	0.006	0.909		2.0
11/13/97	FDF02	0-5 cm	296.4	25	0.391	0.309	0.931	3.50	84.4
11/13/97	FDF02	10-15 cm	442.1	25	0.042	0.023	0.972	3.38	91.6
12/04/97	FDF01	0-5 cm	246.9	25	0.316	0.219	0.887	3.74	92.9
12/04/97	FDF01	10-15 cm	173.0	25	0.606	0.331	0.948	3.30	94.0
12/05/97	FDB01	0-5 cm	348.9	25	0.699	0.313	0.862	n/a	90.5
12/05/97	FDB01	10-15 cm	656.6	25	0.350	0.264	0.725		94.2
12/08/97	SIF01	0-5 cm	96.8	25	0.839	0.165	0.862	5.53	46.9
12/08/97	CRA01	10-15 cm	71.9	25	0.049	0.004	0.957	5.08	15.0
12/09/97	CRA02	0-5 cm	48.2	25	0.228	0.017	0.973	5.01	24.2
12/09/97	CRA02	10-15 cm	56.7	25	0.077	0.006	0.895	4.35	23.6
12/16/97	CRP01	0-5 cm	76.7	25	0.127	0.011	0.908	4.18	23.4
12/16/97	CRA01	0-5 cm	73.6	25	0.066	0.006	0.919	5.08	15.7
12/17/97	CRF01	0-5 cm	116.4	25	0.161	0.017	0.967	5.40	24.3
12/17/97	CRF02	0-5 cm	123.5	25	0.089	0.010	0.942	3.90	29.2
01/06/98	CRF01	5-10 cm	97.6	25	0.060	0.006	0.940	5.48	20.5
01/06/98	CRF02	10-15 cm	77.0	25	0.044	0.004	0.984	4.01	22.1
01/13/98	CRF01	10-15 cm	86.6	25	0.064	0.006	0.959	5.65	17.8
01/13/98	CRP02	0-5 cm	76.1	25	0.071	0.006	0.985	4.88	21.3
01/15/98	CRP01	10-15 cm	62.1	25	0.074	0.006	0.982	4.10	22.5
01/15/98	CRP02	10-15 cm	61.9	25	0.046	0.004	0.906	4.79	18.7
01/21/98	CRF02	5-10 cm	84.9	25	0.038	0.003	0.973	3.92	23.8
01/21/98	RJF01	0-5 cm	30.1	25	0.034	0.002	0.946	3.41	10.6
01/23/98	SIF04	0-5 cm	211.1	25	0.102	0.105	0.836	n/a	n/a
01/23/98	SIF04	10-15 cm	30.8	25	0.201	0.026	0.923	6.88	n/a

Date	Site	Sampling Depth	Moisture Content (%dry)	Temp (C)	k (min^-1)	Normalized k (k/gds)	r2	pH (units)	Organic matter (%)
01/28/98	RJF01	root mat	176.0	25	0.119	0.033	0.974	3.70	50.4
01/28/98	RJF01	5-10 cm	33.0	25	0.049	0.003	0.906	3.46	11.9
01/30/98	RJF01	10-15 cm	27.7	25	0.027	0.002	0.959	3.41	11.7
01/30/98	RJF01	litter	249.1	25	0.118	0.082	0.905	3.60	94.6

Table B.2. Summary of soil incubation manipulations.

Autoclaved Date	Soil type/Site	Moisture Content (% wet)	k (min^-1)	Rate (k/gds)	Organic matter (%)	NOTES:
8/17-8/22/94	UNHCornfield 0-3cm	23.7	0	0		Autoclaved
8/17-8/22/94	Manitoba 1-4cm	12.3	0	0		Autoclaved
5/11-5/17/94	3-7cm College Woods	41.8	0	0		Autoclaved
5/23-5/26/94	0-3cm College Woods	60.9	0	0		Autoclaved
5/16-5/20/94	10-15cm College Woods	30.4	0	0		Autoclaved
Nitrogen inhibition: Anaerobic						
12/14/94	0-3 cm College Woods	42.5	0.8050	0.2800	78.0	
12/14/94	0-3 cm College Woods	42.5	1.0890	0.3780	78.0	Nitrogen environment
1/11/95	0-3 cm College Woods	70.2	0.5760	0.3870	79.7	
1/11/95	0-3 cm College Woods	70.2	0.6470	0.4350	79.7	Nitrogen environment
1/17/95	0-3 cm College Woods	68.8	0.7310	0.4670	82.4	
1/17/95	0-3 cm College Woods	68.8	0.5210	0.3340	82.4	Nitrogen environ.: longer flushing with N2
1/24/95	0-3 cm College Woods	68.7	0.7230	0.4620	80.6	
1/24/95	0-3 cm College Woods	68.7	0.5310	0.3390	80.6	Nitrogen environ.: longer flushing with N2
2/14/95	0-3 cm College Woods	69.7	0.7700	0.5083	78.2	
2/14/95	0-3 cm College Woods	67.4	0.0140	0.0085	75.7	Nitrogen environ.: longer flushing with N2 Let sit overnight in N2 env.
Nitrogen inhibition						
Ambient CH4 uptake:Anaerobic and aerobic						
2/6/95	0-3 cm College Woods	69.8	0.0009	0.0006	79.5	Aerobic
2/6/95	3-7 cm College Woods	29.2	0.1290	0.0018	12.5	Aerobic
2/6/95	0-3 cm College Woods	69.8	-0.0125	-0.0084	79.5	Nitrogen environment
2/6/95	3-7 cm College Woods	29.2	-0.0070	-0.0010	12.5	Nitrogen environment
2/8/95	0-3 cm College Woods	68.7	0.0009	0.0006	80.1	Aerobic
2/8/95	3-7 cm College Woods	28.9	0.1590	0.0022	13.1	Aerobic
2/8/95	0-3 cm College Woods	68.7	-0.0010	-0.0006	80.1	Nitrogen environment
2/8/95	3-7 cm College Woods	28.9	0.0100	0.0016	13.1	Nitrogen environment
2/14/95	0-3 cm College Woods	69.7	0.0008	0.0005	78.2	Aerobic
2/14/95	0-3 cm College Woods	69.7	0.0013	0.0009	78.2	Aerobic
2/14/95	0-3 cm College Woods	67.4	0.0004	0.0003	75.7	Nitrogen environment: left overnight
2/14/95	0-3 cm College Woods	67.4	-0.0022	-0.0014	75.7	Nitrogen environment: left overnight
Ambient CH4 uptake: With and without CH3Br						
12/12/94	0-3 cm College Woods	44.4	0.0013	0.0005	81.7	Ambient
12/12/94	0-3 cm College Woods	44.4	0.0007	0.0003	81.7	With CH3Br in headspace
12/12/94	0-3 cm College Woods	44.4	0.0008	0.0003	81.7	Same soil after airing out
12/12/94	3-7 cm College Woods	27.4	0.0096	0.0013	17.7	Ambient
12/12/94	3-7 cm College Woods	27.4	0.0086	0.0012	17.7	With CH3Br in headspace
12/12/94	3-7 cm College Woods	27.4	0.0094	0.0013	17.7	Same soil after airing out
Methane Inhibition						
11/01/94	3-7 cm College Woods	26.54	0.7300	0.0990	16.6	With 3% methane
11/01/94	3-7 cm College Woods	26.54	0.6560	0.0890	16.6	
10/31/94	0-3 cm College Woods	44.7	0.7330	0.2650	84.7	With 3% methane
10/31/94	0-3 cm College Woods	44.7	0.8400	0.3040	84.7	
10/27/94	3-7 cm College Woods	24.33	0.8400	0.1110	18.0	With 3% methane
10/27/94	3-7 cm College Woods	24.33	0.7330	0.0970	18.0	
10/26/94	0-3 cm College Woods	44.54	0.8520	0.3070	84.8	
10/26/94	0-3 cm College Woods	44.54	1.3700	0.4940	84.8	With 3% methane
10/25/94	3-7 cm College Woods	24.5	0.6320	0.0840	18.1	
10/25/94	3-7 cm College Woods	24.5	0.9280	0.1230	18.1	With 3% methane
10/24/94	0-3 cm College Woods	44.8	0.8100	0.2930	•	
10/24/94	0-3 cm College Woods	44.8	0.9300	0.3360	•	With 3% methane
12/08/94	0-3 cm College Woods	44.33	0.9330	0.3350	84.9	
12/08/94	0-3 cm College Woods	44.33	0.9370	0.3370	84.9	With 5% methane

Date	Soil type/Site	Moisture Content (% wet)	k (min^-1)	Rate (k/gds)	Organic matter (%)	NOTES:
Antibiotic Inhibition						
1/13/95	0-3 cm College Woods	70.1	0.5210	0.3490	81.4	Ethanol control
1/13/95	0-3 cm College Woods	70.1	0.3500	0.2330	81.4	.22ml/5g soil of tetracycline/chloramphenicol mixture
1/23/95	0-3 cm College Woods	70.3	0.4750	0.3300	81.6	.22ml/5g soil of tetracycline/chloramphenicol mixture
1/23/95	0-3 cm College Woods	71.2	0.2980	0.2070	80.6	.44ml/5g soil of tetracycline/chloramphenicol mixture
1/26/95	0-3 cm College Woods	71.7	0.3710	0.2623	86.7	.22ml/5g soil of tetracycline/chloramphenicol mixture
1/26/95	0-3 cm College Woods	71.7	0.0740	0.0521	80.0	.44ml/5g soil of tetracycline/chloramphenicol mixture
						Let sit overnight
12/13/94	0-3 cm College Woods	40.3	0.678	0.227	82.2	Let sit for 2hrs.
12/13/94	0-3 cm College Woods	40.3	0.635	0.212	82.2	With Cyclohexamide added:Let sit for 2hrs.
1/27/95	0-3 cm College Woods	70.7	0.61	0.413	81.4	Let sit for 4 hrs.
1/27/95	0-3 cm College Woods	70.7	0.625	0.426	81.4	With Cyclohexamide added:Let sit for 4 hrs.
2/15/95	0-3 cm College Woods	70.5	0.65	0.444	79.8	Left overnight
2/15/95	0-3 cm College Woods	67.6	0.68	0.421	73.7	With Cyclohexamide added: Left Overnight

APPENDIX C

Table C.1. Summary of field flux measurements of CH3Br uptake for the 1994 sampling season.

Date	Julian Day	Sampling Site	Moisture (% dry) Surface:	Below:	Temp (C)	k (/min)	Flux (mg/m2d)	Rate (k/gds)	pH (units)	Bulk Density (g/cm3)	Organic matter (%)	NOTES:
07/12/94	193	CWSite 1			22.5	0.100	0.0019	0.00038				
07/21/94	202	CWSite 1			26.7	0.065	0.0012	0.00026				
08/25/94	237	CWSite 1	130.9		16.0	0.233	0.0044	0.00094		0.67		SF6 : k = .069min^-1
09/13/94	256	CWSite 1	165.7		16.5	0.250	0.0047	0.00107				
09/20/94	263	CWSite 1	62.7		10.0	0.264	0.0050	0.00069		0.67		
09/20/94	263	CWSite 1	62.7		10.0	0.210	0.0040	0.00055		1.03		Fresh Leaves in chamber
11/21/94	325	CWSite 1	50.0	153.5	4.5	0.265	0.0050	0.00064				SF6 : k = .058min^-1
11/23/94	327	CWSite 1	30.4	95.6	3.0	0.201	0.0038	0.00042		0.48		
07/21/94	202	CWSite 2			26.7	0.058	0.0011	0.00023				
07/21/94	202	CWSite 3			26.7	0.060	0.0011	0.00026				
08/25/94	237	CWSite 3	130.9		16.0	0.237	0.0045	0.00103				SF6 : k = .149min^-1
09/13/94	256	CWSite 3	168.2		16.5	0.275	0.0052	0.00119				
11/21/94	325	CWSite 3	47.8	204.4	4.5	0.339	0.0064	0.00081				SF6 : k = .159min^-1
11/23/94	327	CWSite 3	121.4	210.7	3.0	0.314	0.0059	0.00112		0.48		SF6 : k = .18min^-
08/10/94	222	UNH Cornfield Site	2.7		22	0.053	0.0010	0.00005	5.95			In cornfield
08/16/94	228	UNH Cornfield Site	14.41		17	0.044	0.0008	0.00004	5.75		5.55	In cornfield
08/23/94	235	UNH Cornfield Site	27.57		16	0.045	0.0008	0.00005	5.93	1.30		SF6 : k = .035min^-1
09/07/94	250	UNH Cornfield Site	18.79		18	0.057	0.0011	0.00006	6.12		6.05	In barefield
09/12/94	255	UNH Cornfield Site	10.55		15.5	0.129	0.0024	0.00012			5.95	In barefield
09/19/94	262	UNH Cornfield Site	22.06		11	0.037	0.0007	0.00004			6.00	In barefield
08/10/94	222	UNH Cornfield Site 2	2.18		22	0.066	0.0012	0.00006	5.95			In barefield
08/16/94	228	UNH Cornfield Site 2	13.4		17	0.041	0.0008	0.00004	6.01		5.45	In barefield
09/07/94	250	UNH Cornfield Site 2	19.46		18	0.108	0.0021	0.00011			10.90	In barefield
09/12/94	255	UNH Cornfield Site 2	25.32		15.5	0.150	0.0028	0.00016			3.75	In barefield
09/19/94	262	UNH Cornfield Site 2	27.41		11	0.054	0.0010	0.00006			3.30	In barefield
10/07/94	280	Grass Site 1			11	0.266	0.0050	0.00022				
10/13/94	286	Grass Site 1	34.2	29.4	11	0.185	0.0035	0.00014				
10/28/94	301	Grass Site 1	34.9	30.2	8.5	0.216	0.0041	0.00017		1.59	9.52	SF6 : k = .048min^-1
11/03/94	307	Grass Site 1	59.7	35.7	11	0.250	0.0047	0.00023		2.01	16.34	
11/17/94	321	Grass Site 1	45.8	35.1	9	0.202	0.0038	0.00017		2.024	12.4	SF6 : k = .095min^-1
10/07/94	280	Grass Site 2			11	0.371	0.0070	0.00028				
10/13/94	286	Grass Site 2	34.2	29.4	11	0.317	0.0060	0.00023				
10/28/94	301	Grass Site 2	34.9	30.2	8.5	0.332	0.0063	0.00024		2.31	7.41	SF6 : k = .062min^-1
11/03/94	307	Grass Site 2	59.7	35.7	11	0.129	0.0024	0.00011		1.89	8.95	
11/17/94	321	Grass Site 2	45.8	35.1	9	0.157	0.0030	0.00012		1.782	7.75	SF6 : k = .066min^-1

APPENDIX D

Table D.1. Summary of field flux measurements from all sites for 1998 and 1999 sampling seasons.

Date	Time	Julian Day	Collar #	Tempe air Tcmbr	surface	-5 cm	-10 cm	Cz cm	Vc m3	CH3Br mg/m2 d	CH3Br mg/m2 d error	CH4 mg/m2 d	CH4 mg/m2 d err	CO2 mg/m2 d	CO2 mg/m2 d err	kSF6 (min-1)	kSF6 (min-1) error	kdiff min-1 calc.	kdiff min-1 error	kCH3Br (min-1) meas.	kCH3Br (min-1) error	pH units
09/01/98	10:22 AM	244.4	SF9	28.2	23.0		17.3			0.00535	0.00094	506.75	121.67	-7016.74	1408.80							
09/09/98	10:06 AM	252.4	SF9	20.1	17.6		15.3			0.00091	0.00033	299.68	116.46	-5381.53	301.19							4.5
09/09/98	10:46 AM	252.4	SF9	19.9	17.6		15.3			0.00116	0.00049	579.16	48.61	6702.74	646.35							4.5
09/11/98	10:06 AM	254.4	SF9	25.8	24.8		15.5			0.00145	0.00037	227.00	95.95	-3160.33	1069.82							4.3
09/16/98	12:32 PM	259.5	SF9	33.0	28.6		22.4			0.00237	0.00024	945.12	95.95	-4277.45	1324.66							5.6
09/18/98	10:24 AM	261.4	SF9	25.8	21.3		13.8			0.00271	0.00011	554.99	186.97	-3513.81	361.08							5.7
11/09/98	10:43 AM	313.4	SF9	8.1	3.4		1.4			0.00021	0.00003	38.72	6.05	2571.28	325.31							6.0
09/01/98	11:07 AM	244.5	SF5	27.8	25.7		18.6			0.00464	0.00073	214.58	38.81	-9064.73	2118.57							
09/11/98	10:59 AM	254.5	SF4	24.3	24.3		14.4			0.00121	0.00017	179.45	3.88	-8200.50	1588.08							5.0
09/16/98	01:16 PM	259.6	SF11	28.8	29.4		21.9			0.00104	0.00015	1270.46	86.36	-3180.26	554.37							none
09/18/98	11:11 AM	261.5	SF7	26.9	20.3		12.5			0.00094	0.00013	719.89	86.36	-8977.98	1989.74							3.9
09/29/98	02:05 PM	272.6	SF2	26.9	22.0		16.1			0.00251	0.00020	355.58	230.03	-12389.41	657.71							5.0
09/29/98	02:34 PM	272.6	SF2	23.5	21.0		14.9			0.00060	0.00003	115.24	154.48	-9919.97	1774.13							5.0
11/09/98	12:00 PM	313.5	SF6	7.9	3.0		1.5			-0.00085	0.00022	32.45	4.58	-129.38	37.10							5.0
10/07/98	12:16 PM	280.5	AB1	11.3	9.1		4.6	4	0.076	0.00024		15.13	0.25	2791.58	507.10							6.6
10/07/98	12:44 PM	280.5	AB2	10.2	11.0		5.4	8	0.086	0.00031	0.00010	9.08	0.24	600.17	20.46							5.6
10/13/98	02:27 PM	286.6	AB5	13.9	13.8		13.8	-15	0.138			26.64	2.24	-1057.18	338.23							5.4
10/20/98	03:24 PM	293.6	AB5	18.7	11.4		10.0	8	0.230	-0.00079	0.00025	8.72	2.75	-3163.14	741.42							4.7
10/27/98	03:02 PM	300.6	AB5	11.5	9.8		9.6	8	0.230	-0.00160	0.00049	27.16	2.32	-3729.23	799.75							4.8
11/06/98	10:21 AM	310.4	AB5	7.1	5.9		1.8	8	0.230	-0.00184	0.00028	43.82	1.11	-2057.93	212.53							none
10/13/98	02:53 PM	286.6	AB6	13.6	13.0		13.0	8	0.230	0.00194	0.00036	86.69	2.01	-5987.86	420.92							5.1
10/20/98	02:57 PM	293.6	AB6	20.3	10.7		10.1	-15	0.138	0.00008		23.64	4.90	-2666.30	470.38							4.6
10/27/98	02:32 PM	300.6	AB6	11.4	10.5		6.8	-15	0.138	0.00080	0.00019	18.12	2.62	-2705.69	419.04							5.4
11/06/98	09:55 AM	310.4	AB6	6.4	3.7		2.0	-15	0.138	0.00029	0.00018	33.53	2.89	-7304.31	369.04							none
06/11/99	10:00 AM	162.4	SF4	39.4			15.1	-33	0.127	-0.00015	0.00008	92.07	16.27	-3001.26	796.63					0.018	0.010	none
06/11/99	10:30 AM	162.4	SF1	16.5			14.6	-7	0.170	0.00089	0.00016	214.10	14.81	3883.30	411.34							none
06/21/99	09:45 AM	172.4	SF4	23.7	19.5		16.5	-33	0.127	0.00180	0.00002	74.76	12.98	-3900.33	882.40							none
06/21/99	10:15 AM	172.4	SF3	22.8	21.3		15.6	-10	0.238	0.00254	0.00095			-8326.09	1865.24							none
07/06/99	09:09 AM	187.4	SF10	32.2	21.4		18.9	-33	0.266	0.00251	0.00015	400.72	43.55	-5264.03	616.78							5.4
07/06/99	09:34 AM	187.4	SF4	26.8	24.1		19.8	-33	0.326	0.00364	0.00015			-9020.93	1544.00							none
07/20/99	09:30 AM	201.4	SF4	28.5	24.7		17.9	-33	0.326	0.00007	0.00046	161.74	63.72	-12959.82	3218.80							none
07/20/99	10:00 AM	201.4	SF2	27.4	24.7		17.9	-25	0.298	0.00076	0.00032	274.41	41.70	-8266.78	813.12							none
08/24/99	10:43 AM	236.4	SF4	34.0	20.4		16.1	-33	0.326	0.00370	0.00120											none
08/24/99	11:17 AM	236.5	SF2	35.1	22.4		16.4	-25	0.298	0.00341	0.00016											none
09/09/99	11:00 AM	252.5	SF4	30.8	26.9		19.5	-33	0.266	0.00087	0.00005	2712.95	95.74	7866.85	2164.25							
09/09/99	11:25 AM	252.5	SF3	29.3	26.2		19.4	-12	0.349	-0.00170	0.00068	117.59	18.34	-14029.11	749.84					0.014	0.005	
09/13/99	02:09 PM	256.6	SF4	37.3	20.1		16.3	-33	0.266	0.00289	0.00092	16.70	2.19	-7543.02	1079.82							none
09/13/99	02:54 PM	256.6	SF2	32.4	21.6		14.9	-25	0.298	0.00229	0.00014	31.30	4.84	-6501.70	1415.13							none
09/23/99	10:49 AM	266.5	SF4	22.3	18.5		14.3	-33	0.266	0.00023	0.00011	34.39	6.17	-9140.62	2623.41	0.149	0.003	0.155	0.003			4.7
09/23/99	11:24 AM	266.5	SF2	19.1	18.0		13.8	-25	0.298	0.00005	0.00009	5.32	18.86	-9599.66	1331.69	0.080	0.004	0.084	0.004			5.9
10/06/99	12:32 PM	279.5	SF4	21.8	19.0		9.3	-33	0.266	0.00078	0.00003	44.12	4.45	-6223.97	369.80	0.084	0.005	0.088	0.005			4.9

Date	Time	Julian Day	Collar #	Temp air Tcmbr	surface	-5 cm	-10 cm	Cz cm	Vc m3	CH3Br mg/m2 d	CH3Br mg/m2 d error	CH4 mg/m2 d	CH4 mg/m2 d err	CO2 mg/m2 d	CO2 mg/m2 d err	kSF6 (min-1)	kSF6 (min-1) error	kdiff min-1 calc.	kdiff min-1 error	kCH3Br (min-1) meas.	kCH3Br (min-1) error	pH units
-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
10/06/99	12:56 PM	279.5	SF3	19.0	9.9		8.8	-12	0.349	-0.00159	0.00040	35.44	5.40	-8268.84	198.45	0.086	0.008	0.090	0.008	0.018	0.005	4.6
10/13/99	12:16 PM	286.5	SF4	22.9	15.1		8.6	-33	0.266	0.00066	0.00009	46.58	6.41	-4670.29	540.67	0.065	0.005	0.068	0.005			4.9
10/13/99	12:46 PM	286.5	SF2	19.0	15.8		10.6	-25	0.298	-0.00055	0.00004	34.79	1.76	-4699.66	290.26	0.037	0.005	0.039	0.005	0.007	0.001	4.6
10/19/99	01:05 PM	292.5	SF4	20.6	10.1		8.5	-33	0.266	0.00049	0.00005	84.40	17.50	-2788.86	598.55	0.028	0.005	0.029	0.006			5.4
10/19/99	01:28 PM	292.6	SF2	15.4	6.9		7.2	-25	0.298	-0.00064	0.00010	29.43	4.83	-3823.84	3607.96	0.030	0.008	0.031	0.009	0.011	0.002	4.4
11/10/99	11:14 AM	314.5	SF4	19.8	15.6		7.9	-33	0.266	-0.00142	0.00010	71.43	4.06	-986.72	289.06	0.023	0.003	0.024	0.003	0.024	0.002	5.2
11/10/99	11:39 AM	314.5	SF2	18.6	15.3		4.9	-25	0.298	-0.00136	0.00030	19.99	0.50	-851.25	350.98	0.025	0.006	0.026	0.006	0.020	0.005	4.2
12/02/99	12:30 PM	336.5	SF4	10.2	1.7		0.8	-33	0.266	-0.00030	0.00019	27.27	5.19			0.114	0.004	0.119	0.005			frozen
12/02/99	01:02 PM	336.5	SF2	6.0	-0.1		-0.4	-25	0.298	-0.00091	0.00075	16.97	1.02			0.090	0.001	0.094	0.001	0.015	0.012	frozen
04/27/99	01:35 PM	117.6	AB5	13.3	12.0	10.6	8.0	-15	0.138	-0.00122	0.00055	12.67	5.15	-1705.75	569.71					0.055	0.024	5.3
06/14/99	11:00 AM	165.5	AB5	32.0	0.0	0.0	23.8	-15	0.138	-0.00052	0.00037	20.28	0.69	-2643.74	922.35					0.017	0.012	4.9
06/28/99	10:30 AM	179.4	AB5	25.0	24.0	0.0	19.0	-15	0.138	-0.00099	0.00011	138.55	40.52	1938.26	534.45					0.023	0.003	none
07/12/99	11:10 AM	193.5	AB5	31.3	30.1	0.0	19.8	-15	0.138	-0.00063	0.00027	147.39	15.93	-1528.70	449.96					0.025	0.011	5.7
07/26/99	10:20 AM	207.4	AB5	25.0	0.0	0.0		-15	0.138	-0.00154	0.00043	85.28	45.98	-3609.85	424.07					0.033	0.009	5.7
08/31/99	10:52 AM	243.5	AB5	29.4	23.0	0.0	15.8	-15	0.138	-0.00162	0.00014	24.08	2.70	-5355.38	421.46					0.039	0.003	5.6
09/14/99	12:42 PM	257.5	AB5	24.3	20.4	0.0	16.8	-15	0.138	-0.00076	0.00018	44.61	5.00	316.81	140.18	0.074	0.003	0.077	0.003	0.020	0.005	none
09/27/99	12:53 PM	270.5	AB5	20.3	19.7	0.0	15.2	-15	0.138	-0.00129	0.00030	47.07	13.30	-4221.44	839.72	0.217	0.008	0.227	0.008	0.045	0.010	5.3
10/12/99	12:17 PM	285.5	AB5	13.8	9.7	0.0	9.7	-15	0.138	-0.00056	0.00020	13.16	4.02	536.11	502.06	0.281	0.008	0.293	0.008	0.012	0.004	4.4
10/27/99	01:05 PM	300.5	AB5	12.5	8.3	0.0	6.4	-15	0.138	0.00011	0.00001	4.32	0.54	-1510.08	439.56	0.103	0.006	0.107	0.007			5.1
11/09/99	11:48 AM	313.5	AB5	6.1	2.0	0.0	4.0	-15	0.138	-0.00053	0.00010	9.62	1.42	-312.67	69.03					0.011	0.002	5.1
04/27/99	12:58 PM	117.5	AB6	14.0	9.7	7.1	6.2	8	0.230	0.00172	0.00001	28.84	2.54	-4243.96	568.35							5.4
06/14/99	10:30 AM	165.4	AB6	28.9	0.0	0.0	20.3	8	0.230	0.00096	0.00038	175.09	3.36	-14684.91	2014.24							4.8
06/28/99	10:10 AM	179.4	AB6	25.0	23.0	0.0	19.0	8	0.230	0.00296	0.00095	498.95	12.73	-6255.23	428.08							none
07/12/99	10:49 AM	193.5	AB6	29.4	22.0	0.0	15.2	8	0.230	0.00118	0.00008	513.18	16.33	-22704.40	4550.87							5.3
07/26/99	09:57 AM	207.4	AB6	25.0	0.0	0.0		8	0.230	0.00450	0.00032	490.43	15.66	-11165.31	1259.01							5.8
08/31/99	10:30 AM	243.4	AB6	28.5	30.7	0.0	13.2	8	0.230	0.00083	0.00041	306.73	0.96	-15352.20	2052.36							4.7
09/14/99	12:09 PM	257.5	AB6	26.5	19.1	0.0	16.8	8	0.230	0.00189	0.00060	225.64	61.50	-12473.25	1751.39	0.015	0.003	0.015	0.003			none
09/27/99	12:27 PM	270.5	AB6	20.8	20.6	0.0	11.9	8	0.230	0.00186	0.00032	139.27	8.19	-12619.58	1058.42	0.013	0.003	0.014	0.003			4.7
10/12/99	11:52 AM	285.5	AB6	11.7	7.8	0.0	7.8	8	0.230	0.00132	0.00032	47.01	2.16	-1540.29	983.18	0.015	0.002	0.016	0.002			5.3
10/27/99	12:34 PM	300.5	AB6	9.6	9.0	0.0	5.8	8	0.230	0.00005	0.00000	21.38	0.95	-2795.95	2.62	0.005	0.001	0.005	0.001			4.8
11/09/99	11:22 AM	313.5	AB6	6.7	1.0	0.0	2.4	8	0.230	0.00070	0.00012	28.89	0.61	1381.96	301.55							5.2
05/28/99	03:24 PM	148.6	CW1	21.6			18.6	10	0.183	0.00051	0.00016	-2.83	0.30	21085.21	1239.54							
06/01/99	09:35 AM	152.4	CW1	20.0			19.0	10	0.183	-0.00398	0.00106	-3.73	0.03	19317.09	2727.95					0.099	0.026	
06/07/99	10:26 AM	158.4	CW1	23.7			12.8	10	0.183	0.00061	0.00004	-9.42	2.48	22612.80	2700.73							
06/16/99	09:30 AM	167.4	CW1	16.7			12.7	10	0.183	-0.00052	0.00006	-5.98	0.93	14764.97	422.25					0.018	0.002	
06/23/99	09:30 AM	174.4	CW1	22.3			12.8	10	0.183	-0.00147	0.00057	-7.61	0.48	25055.88	764.88	0.030	0.006	0.031	0.006	0.025	0.010	
06/30/99	09:18 AM	181.4	CW1	20.0	19.0		18.0	10	0.183	0.00330	0.00091	-4.96	2.19	49908.74	1226.07							
07/09/99	09:31 AM	190.4	CW1	19.0	19.2		16.2	10	0.183	-0.00011	0.00014	-6.13	0.70	22061.26	5439.92					0.003	0.003	
07/14/99	10:01 AM	195.4	CW1	18.6	18.2		14.4	10	0.183	-0.00044	0.00002	-5.37	0.40	16196.19	2822.04					0.012	0.001	
07/21/99	09:49 AM	202.4	CW1	21.0	21.0			10	0.183	-0.00034	0.00040	-8.80	2.14	25248.53	1387.62					0.008	0.009	
08/18/99	02:45 PM	230.6	CW1	23.0	23.0			10	0.183	-0.00017	0.00010									0.003	0.002	
08/23/99	01:19 PM	235.6	CW1	25.4	25.7		15.3	10	0.183	0.00013	0.00066											
09/03/99	11:47 AM	246.5	CW1	27.2	27.6		15.4	10	0.183	-0.00088	0.00005	-2.53	0.70	11754.82	3626.95	0.020	0.004	0.021	0.004	0.020	0.001	

Date	Time	Julian Day	Collar #	Temp air Tcmbr	surface	-5 cm	-10 cm	Cz cm	Vc m3	CH3Br mg/m2 d	CH3Br mg/m2 d error	CH4 mg/m2 d	CH4 mg/m2 d err	CO2 mg/m2 d	CO2 mg/m2 d err	kSF6 (min-1)	kSF6 (min-1) error	kdiff min-1 calc.	kdiff min-1 error	kCH3Br (min-1) meas.	kCH3Br (min-1) error	pH units
09/24/99	12:07 PM	267.5	CW1	20.0	19.8		13.5	10	0.183	-0.00061	0.00007	-1.84	0.40	16599.28	1532.24	0.058	0.002	0.060	0.002	0.014	0.002	
10/28/99	11:06 AM	301.5	CW1	6.2	6.2		8.7	10	0.183	-0.00026	0.00007	-2.69	0.58	7055.13	226.99	0.048	0.003	0.050	0.003	0.008	0.002	
05/28/99	03:50 PM	148.7	CW2	21.6			18.6	10	0.183	-0.00220	0.00031	-3.72	0.13	20518.03	8215.47					0.101	0.014	
06/01/99	09:55 AM	152.4	CW2	21.6			19.3	10	0.183	-0.00246	0.00381	-3.12	0.70	11868.37	814.41					0.061	0.095	
06/07/99	10:47 AM	158.4	CW2	26.3			14.3	10	0.183	-0.00029	0.00007	-5.65	1.59	26142.73	5111.31					0.010	0.002	
06/16/99	10:00 AM	167.4	CW2	17.0	16.9		14.0	10	0.183	-0.00065	0.00017	-4.98	0.73	12144.12	1956.67					0.022	0.006	
06/23/99	10:00 AM	174.4	CW2	22.8				10	0.183	-0.00326	0.00201	-9.62	1.00	16053.85	2992.29	0.017	0.008	0.018	0.008	0.054	0.033	
06/30/99	09:40 AM	181.4	CW2	18.0	21.0		18.0	10	0.183	0.00052	0.00116	-6.90	1.72	37306.71	11238.47							
07/09/99	09:50 AM	190.4	CW2	19.1	19.0		16.5	10	0.183	-0.00061	0.00012	-7.53	0.19	23673.48	1274.99					0.014	0.003	
07/14/99	10:19 AM	195.4	CW2	19.9	20.5		15.2	10	0.183	-0.00064	0.00002	-7.55	0.65	11391.87	532.64					0.017	0.000	
07/21/99	10:07 AM	202.4	CW2	21.0	21.0			10	0.183	-0.00026	0.00009	-5.48	0.10	18306.52	1480.48					0.006	0.002	
08/18/99	03:05 PM	230.6	CW2	23.0	23.0			10	0.183	-0.00103	0.00024									0.017	0.004	
08/23/99	01:38 PM	235.6	CW2	25.0	25.8		16.0	10	0.183	-0.00160	0.00013									0.024	0.002	
09/03/99	11:25 AM	246.5	CW2	26.5	27.0		16.1	10	0.183	-0.00124	0.00017	-7.26	0.01	5948.85	3405.12	0.012	0.001	0.013	0.001	0.028	0.004	
09/24/99	11:40 AM	267.5	CW2	19.3	19.6		13.7	10	0.183	-0.00113	0.00014	-6.46	0.06	13996.21	1263.02	0.017	0.002	0.018	0.002	0.025	0.003	
10/28/99	10:46 AM	301.4	CW2	5.0	5.4		7.0	10	0.183	-0.00052	0.00005	-5.84	1.12	5005.62	679.22	0.049	0.003	0.051	0.003	0.015	0.001	
04/26/99	09:12 AM	116.4	KF1	12.0	12.7	8.4	8.3	10	0.183	-0.00036	0.00093	-0.50	0.17	7017.20	643.20	0.026	0.002	0.027	0.002	0.005	0.014	
04/26/99	09:37 AM	116.4	KF2	12.1	12.3	8.6	8.2	10	0.183	-0.00401	0.00441	-0.42	0.06	5719.09	582.12	0.130	0.011	0.135	0.012	0.059	0.064	
06/02/99	09:40 AM	153.4	KF1	38.8			20.9	22	0.231	-0.00063	0.00126	-0.42	0.09	13658.41	790.99	0.014	0.002	0.015	0.002	0.015	0.029	
06/09/99	11:03 AM	160.5	KF1	14.5			19.7	22	0.183	-0.00209	0.00023	-1.70	0.74	11762.93	1204.24					0.060	0.007	
06/09/99	11:23 AM	160.5	KF2	14.5			20.6	22	0.183	-0.00092	0.00080	0.23	0.22	7530.87	838.51					0.026	0.023	
06/15/99	10:00 AM	166.4	KF1	29.0			24.1	22	0.183	-0.00049	0.00047	-2.93	1.21	14559.18	1055.52	0.012	0.007	0.012	0.008	0.009	0.008	
06/15/99	10:30 AM	166.4	KF2	29.8			23.0	22	0.183	0.00012	0.00007	-0.49	0.09	9218.19	829.87	0.026	0.020	0.027	0.021			
06/22/99	09:30 AM	173.4	KF2	31.5			21.6	22	0.231	-0.00045	0.00062	-0.53	0.30	14009.96	1523.55	0.006	0.003	0.006	0.003	0.009	0.012	
06/22/99	09:49 AM	173.4	KF1	33.6	33.8		21.6	22	0.231	0.00205	0.00042	0.77	0.74	10109.64	530.75	0.031	0.014	0.032	0.015			
06/29/99	09:15 AM	180.4	KF2	27.0	27.0		24.0	22	0.231	0.00173	0.00030	-2.10	0.38	34239.19	2845.70	0.011	0.008	0.012	0.008			
06/29/99	09:45 AM	180.4	KF1	27.0	27.0		23.0	22	0.231	-0.00130	0.00027	-1.20	0.11	38891.95	2740.74	0.012	0.004	0.013	0.004	0.019	0.004	
07/07/99	01:52 PM	188.6	KF1	35.0	27.0		23.5	22	0.231	-0.00079	0.00020	-20.17	6.49	48699.90	3557.81	0.016	0.005	0.016	0.005	0.013	0.003	
07/07/99	02:12 PM	188.6	KF2	35.7	29.0		27.2	22	0.231	-0.00095	0.00036	-0.03	0.05	27928.67	46.55	0.020	0.001	0.021	0.002	0.016	0.006	
07/13/99	09:26 AM	194.4	KF2	18.9			20.3	22	0.231	0.00025	0.00008	-9.10	5.17	8352.01	457.62	0.016	0.003	0.017	0.004			
07/13/99	09:46 AM	194.4	KF1	20.1	19.7		19.5	22	0.231	-0.00106	0.00020	-3.38	0.54	16830.21	1390.17	0.012	0.002	0.013	0.002	0.016	0.003	
07/19/99	09:30 AM	200.4	KF1	40.2	34.7		23.7	22	0.231	0.00007	0.00003	-1.37	0.69	21317.15	505.23	0.007	0.002	0.007	0.002			
07/19/99	09:50 AM	200.4	KF2	36.2	28.9		23.4	22	0.231	-0.00165	0.00031	-1.17	0.47	10239.30	2022.95	0.012	0.000	0.012	0.000	0.026	0.005	
08/16/99	02:10 PM	228.6	KF2	26.0	26.0		22.0	22	0.231	0.00123	0.00048											
08/16/99	02:32 PM	228.6	KF1	26.0	26.0		22.0	22	0.231	-0.00134	0.00016									0.016	0.002	
08/26/99	01:24 PM	238.6	KF2	29.4	27.2		23.4	22	0.231	-0.00067	0.00023									0.009	0.003	
08/26/99	01:45 PM	238.6	KF1	27.4	28.2		20.8	22	0.231	-0.00093	0.00005									0.012	0.001	
09/02/99	10:41 AM	245.4	KF2	32.9	30.9		19.9	22	0.231	0.00028	0.00032	0.98	2.33	5378.75	1092.19	0.073	0.031	0.076	0.033			
09/02/99	11:02 AM	245.5	KF1	32.2	31.8		18.6	22	0.231	-0.00046	0.00004	-1.53	1.08	7636.65	900.14	0.010	0.001	0.011	0.001	0.008	0.001	
09/28/99	12:27 PM	271.5	KF2	26.5	25.2		18.0	22	0.231	-0.00036	0.00000	-5.17	0.92	5784.07	850.33	0.011	0.003	0.012	0.003	0.006	0.000	
09/28/99	12:53 PM	271.5	KF1	26.3	27.7		20.8	22	0.231	-0.00085	0.00018	-3.95	1.29	13190.00	1866.85	0.004	0.002	0.004	0.002	0.013	0.003	
10/26/99	10:25 AM	299.4	KF1	8.8	9.4		4.1	22	0.231	-0.00062	0.00005	-2.42	0.28	3554.57	455.51	0.023	0.002	0.024	0.003	0.011	0.001	
10/26/99	10:44 AM	299.4	KF2	9.1	11.5		5.5	22	0.231	-0.00193	0.00008	-0.97	1.51	5602.48	2217.03	0.005	0.001	0.005	0.001	0.034	0.001	

Date	Time	Julian Day	Collar #	Tempc air Tcmbr	surface	-5 cm	-10 cm	Cz	Vc	CH3Br	CH3Br	CH4	CH4	CO2	CO2	kSF6	kSF6	kdiff	kdiff	kCH3Br	kCH3Br	pH
11/02/99	10:04 AM	306.4	KF1	15.6	17.5		9.6	22	0.231	-0.00092	0.00002	-0.32	0.58	4037.08	441.90	0.016	0.003	0.017	0.003	0.011	0.000	
11/02/99	10:30 AM	306.4	KF2	16.3	16.1		10.0	22	0.231	-0.00292	0.00063	-3.12	0.04	5750.99	1996.84	0.009	0.006	0.009	0.006	0.035	0.008	
11/18/99	09:38 AM	322.4	KF1	1.6	2.0		1.3	22	0.231	-0.00058	0.00009	-0.27	1.58	2864.30	80.04	0.024	0.001	0.026	0.001	0.009	0.001	
11/18/99	10:02 AM	322.4	KF2	1.9	3.0		1.0	22	0.231	-0.00099	0.00013	-0.48	0.46	2385.45	300.06	0.006	0.001	0.006	0.001	0.016	0.002	